BCM Environmental
& Land Law, PLLC
Solutions for Northern New England

November 15, 2024

Via email
Representative Carol McGuire, Chair
Joint Legislative Committee on Administrative Rules
adminrules@leg.state.nh.us

Re: Request for Objection
Public Testimony in Opposition to NHDES Rulemaking: Env-Sw 800 – Landfill Requirements (OLS Notice Number 2024-74)

Dear Representative McGuire and Esteemed Members of the Joint Legislative Committee on Administrative Rules:

I write to you in representation of North Country Alliance for Balanced Change ("NCABC") to offer testimony in opposition to the Env-Sw 800 Final Proposed Rules provided by the New Hampshire Department of Environmental Services (the "Department"). Pursuant to Rule 301.02(d)(2) of the Joint Legislative Committee on Administrative Rules (the "Committee"), NCABC respectfully requests the Committee object to the Env-Sw 800 Final Proposed Rules on the below grounds. Please make this letter and its supporting attachments a part of your record on this matter.

In sum, the Env-Sw 800 Final Proposed Rules: (1) exceed the statutory authority of the Department; (2) are contrary to the intent of the legislature; and (3) are not in the public interest because they ignore public comment without any countervailing, credible evidence. As such, the Coalition respectfully urges the Committee to object to the Final Proposed Rules on these grounds.

Procedural History of the Rulemaking

This section recounts and documents the rulemaking process to date. Overall, the rulemaking process involved: (1) inappropriately disproportionate influence of the waste industry, via private meetings with the Department and unbalanced membership on the Waste Management Council; (2) the Department failing to address concerns and requests from the Department Rules Update Subcommittee of the House Environment and Agriculture Committee; (3) lack of supporting evidence; and (4) a steady weakening of the rules over several iterations.

The process to date suggests the Department may be rewriting the rules to specifically favor permitting certain pending or anticipated landfill proposals.

In anticipation of the current rules expiring on July 1, 2024, the Department began working on updating them in early 2023. With respect to the Env-Sw 800 portion of the rules, the Department held a Public Input Session on July 19, 2023, focusing exclusively on Env-Sw 804 landfill siting requirements.

On October 18, 2023, the Department issued a draft of proposed Chapter Env-Sw 800 followed by a three-week informal comment period that closed on November 7, 2023. The Department adjusted the draft rules based on comments received during this time, particularly from members of the regulated industry that had met privately with the Department. Shortly thereafter, on October 24, 2023, the Department presented the draft rules to the Department Rules Update Subcommittee (the "Subcommittee") of the House Environment and Agriculture Committee. At this initial meeting, members of the Subcommittee introduced concerns about leachate management and noted that the rules were lacking in certain areas, e.g., hydrogeological conditions, prohibited areas for landfills, etc. The Department met again with the Subcommittee on December 5, 2023, at which time the Subcommittee continued to express its general thoughts on the rules, particularly with respect to the surface water setback, leachate management, and PFAS management.

The Department had its first meeting with the Waste Management Council (the "Council") on January 18, 2024, at which it presented a new draft of the proposed rules.[1] In the weeks immediately following this presentation to the Council, the Department met privately with several members of the regulated industry, including the Androscoggin Valley Regional Refuse Disposal District (Mt. Carberry Landfill), Waste Management of New Hampshire (Turnkey Landfill), Casella (NCES Landfill and a pending applicant for a new landfill, through its subsidiary Granite State Landfill), and Resource Waste Services.

The Subcommittee held another hearing on January 31, 2024 to discuss the proposed rules. At this meeting, Subcommittee members shared their concerns about the progressive weakening of the proposed rules from the October draft to the January draft. Director Wimsatt explained that the rules had been changed in response to members of the regulated industry claiming without any evidence that "none of the facilities [they] are operating right now would ever be sited if these rules were in place . . . and if these rules were in place, none of [their] facilities would be able to be expanded." Director Wimsatt has presented no evidence to support this statement.

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[1] RSA 21-O:9, VI sets forth the procedure required for Department rulemaking with respect to the Waste Management Council. The Director of Waste Management must meet with the Waste Management Council to present all waste management rules proposed before filing a notice of the proposed rules. The Council must present any objections to the proposed rules to the Director and to the Commissioner of the Department. The Waste Management Council is statutorily composed of thirteen members intended to represent a balance of business and industry, municipalities, public health, academia, and conservation commissions. However, the following five seats on the Council have been vacant during the rulemaking through to last month: Public Interest (which also serves as Chair of the Council), Public Health Expert, Municipal Official, one of the two Elected Officials, and a representative of the Business or Financial Community. The seats that have been filled during the rulemaking are dominated by the waste industry: one representative of Licensed Sanitary or Environmental Engineer or Sanitary Engineering, one of the two Elected Officials, Community that Recycles or Recovers Solid Waste, Associate Professor Environmental Sciences or Sanitary Engineering, Municipal Public Works Field, Private Solid Waste Management Industry, Local Conservation Commission Member, and Private Industries that Generate Hazardous Waste. Such an imbalance results in biased consideration of proposed rules and denies the general public the representation the law requires in these deliberations.

Relatedly, the Subcommittee communicated concerns with the regulated industry having privileged access to the rulemaking process and having an inappropriately disproportionate influence on the outcome of the rules. The Subcommittee also worried the new proposed rules would make New Hampshire's solid waste rules the weakest in New England. For the next meeting, the Subcommittee asked the Department to provide evidence for the regulated industry's claim that no landfills would be able to be sited or expanded under the prior and a stronger iteration of the draft rules from October, but the Department has not provided these.

The Department next met with the Council on February 15, 2024 to present a revised version of the draft proposed rules which the Department had updated in response to the meetings it had had with members of the regulated industry. Industry representatives made further comments at the Council's meeting. The Council held a special meeting shortly thereafter on February 21, 2024 to further discuss the revised rules. This was followed by a letter dated February 23, 2024 in which the Council provided its written comments and concerns to the Department, including its position that the current version of the rules simply be readopted without any revisions to them.

The Department met with the Subcommittee again on March 6, 2024. Here, the Subcommittee indicated that it was dissatisfied at so many of the Council seats sitting vacant, especially because the empty seats were largely those meant to represent the concerns of the public. Director Wimsatt reiterated that "the industry has expressed concerns that the proposed siting criteria are so stringent as to effectively eliminate most potential future landfill sites and potential areas of expansion of existing landfill sites from eligibility." However, the Department was not able to provide the Subcommittee with any evidence, and the regulated industry was not willing to disclose any data or reports supporting the claim. Director Wimsatt explained that the Department had "overshot the runway" with its original draft of the rules, and the latest version reflected a course correction. The Subcommittee repeated its concerns over the rules being increasingly weakened with each iteration and the regulated industry having an inappropriately disproportionate impact on the rulemaking process.

A few days later, on March 8, 2024, the Department published the Env-Sw 800 Initial Proposed Rules. On March 21, 2024, the Department met with the Council for a third time, this time submitting the Initial Proposed Rules the Department intended to use for the formal rulemaking process.

The Subcommittee held another hearing to discuss the proposed rules on April 2, 2024. The Subcommittee again highlighted that the rules had been weakened more and more with each draft. In response, Director Wimsatt explained that "[w]hen you look at all [the] criteria that need to come together in order to identify a location where you can site a landfill, what we had originally been proposing was likely too stringent to really make that practicable or cost effective." The Subcommittee also opined that none of its comments from previous hearings had been incorporated into the draft rules. Simultaneously with this hearing, the Department requested a Fiscal Impact Statement from the Legislative Budget Assistant. The Fiscal Impact Statement was completed by the Legislative Budget Assistant on April 15, 2024, and assigned FIS number 24:072.

The Department met with the Subcommittee again on April 23, 2024. The Subcommittee reemphasized that the rules had been increasingly weakened with each iteration and that it seemed like the regulated industry was driving the rulemaking process. Specifically, the Subcommittee could point to several instances in the draft rules where industry feedback had been directly incorporated, but it could not do the same for feedback that the Subcommittee had given across its various meetings with the Department. In other words, the Subcommittee did not feel that its feedback to the Department had played any role in shaping the rules.

The Department filed the formal Rulemaking Notice for Env-Sw 800 with the Office of Legislative Services on April 18, 2024. This notice was published on April 26, 2024, and assigned OLS Notice Number 2024-74. The Department held a public hearing on May 20, 2024, at 1:00 p.m., at which it presented the proposed rules and received oral public input, including from NCABC. The Department then accepted approximately seventy-one sets of written comments through June 5, 2024, at 4:00 p.m. NCABC received copies of the comments from the Department only after NCABC commenced with the Right-to-Know Ombudsman an action against the Department for violation of the right-to-law statute for not providing them upon repeated requests. Attached to this letter as **Exhibit A** is a summary of the public comments NCABC prepared. Attached to this letter as **Exhibit B** is the robust package NCABC provided on June 5, 2024, which included legal analysis, expert analysis, evaluation of the proposed rules, recommended rules, a multi-state survey of landfill siting laws, and citation to the peer-reviewed science supporting it all.

Between June 5, 2024 and when it published the Final Proposed Rules, the Department purportedly reevaluated the proposed rules based on the approximately seventy-one sets of public comments and any other public input it receives, including NCABC's June 5, 2024 input, as it was required to do. However, the public comments overwhelmingly urged the rules be strengthened in favor of human health and environmental protection. Instead, the Final Proposed Rules were, once again, significantly weaker than the prior version, in favor of siting and expanding landfills.

The Department's Summary of Comments on Initial Proposal with NHDES Responses, dated October 16, 2024, attached as **Exhibit C**, buckets all the public and Office of Legislative Services input it received into ninety-seven comments. Of those, the Department made no change whatsoever in response to about twenty-six of the comments and made only non-substantive, clarifying changes in response to about twenty-seven other comments. Many of the substantive responses resulted in weakening the rules. *See infra* Section 1. Other "responses" did not actually respond to the comment, and therefore are tantamount to declining the proposed change. For example, Comment 10 makes the very specific request that "siting of a landfill should require measuring the hydraulic conductivity at the bedrock level," but the Department response addresses only the general characterization of bedrock through hydrogeologic investigation," which may or may not include determination of hydraulic conductivity.

The Joint Legislative Committee on Administrative Rules is scheduled to hold a public hearing about the Final Proposed Rules on November 21, 2024.

The Committee Should Object to the Env-Sw 800 Final Proposed Rules

The Committee has ample grounds upon which to object to the Env-Sw 800 Final Proposed Rules. The rules are beyond the authority of the Department, contrary to legislative intent, and contrary to the public interest.

1. ***The Env-Sw 800 Final Proposed Rules Exceed the Authority of the Department***

The Env-Sw 800 rules implement RSA 149-M, the purpose of which is "to protect human health, to preserve the natural environment, and to conserve precious and dwindling natural resources through the proper and integrated management of solid waste." RSA 149-M:1.

Though the legislature may empower an administrative agency to promulgate rules and regulations, the agency is limited to filling in details to effectuate the purpose of the statute. *Kimball v. New Hampshire Bd. of Accountancy*, 118 N.H. 567, 568 (1978). An agency exceeds its authority when it promulgates rules that contradict the terms of the governing statute. *Genworth Life Ins. Co. v. N.H. Dep't of Ins.*, 174 N.H. 78, 83 (2021). "[A]dministrative rules may not add to, detract from, or modify the statute which they are intended to implement." *Id.* (quoting *Appeal of Wilson*, 161 N.H. 659, 662 (2011)).

In this case, the Final Proposed Rules exceed the Department's authority from RSA 149-M, and in particular the purpose identified in section 1.

For example, in Final Proposed Rule Env-Sw 804.02(b), the Department excluded "pipelines carrying leachate or decomposition gas offsite for processing or treatment" from the requirement that a landfill and all associated infrastructure be located only in areas where groundwater monitoring for release detection can be conducted prior to a release having an adverse impact on groundwater quality at the property line. The Department also excluded adverse impacts to a water supply from consideration under this rule. Consequently, this Final Proposed Rule heightens threats to the assets the Department is bound to protect: human health, the natural environment, and New Hampshire's precious and dwindling natural resources.

Another example is Final Proposed Rule Env-Sw 804.02(d), which states, "Undisturbed in-situ soils for 5 feet immediately beneath the footprint shall have a representative saturated hydraulic conductivity of 1×10^{-3} centimeters per second (cm/sec) or less, unless the landfill design meets the requirement in Env-Sw 805.03(e)." Though this hydraulic conductivity standard is an improvement from the April 2024 initial proposed rule, it is still woefully insufficient to protect groundwater quality for two reasons. First, material with this level of conductivity is utterly unsuitable as a barrier that is meant to impede the flow of leachate that might be released from the landfill in the likely event of a leak. NCABC's June 5 package included expert evidence from Dr. Anirban De, P.E. which explained the hydraulic conductivity of the undisturbed in-situ soil at a landfill site should be no greater than 1 x 10^{-4} cm/s for the composite liner system to be effective in protecting the environment from leachate incursion. The Department's proposed hydraulic conductivity is ten times less protective than Dr. De's recommendation and runs counter to regional and global standards, also provided in NCABC's June 5 package.

Moreover, based on the Final Proposed Rules, the hydraulic conductivity standard is applied only to soils directly beneath the landfilling footprint, and not the entire landfill facility, e.g., the locations where leachate is stored and transported. The hydraulic conductivity standard is meant to prevent the rapid travel of contaminants to nearby groundwater and surface water supplies so the release can be detected and stopped before the contaminant hits a water resource. However, if it is not applied to the landfill facility outside of the landfilling area, such as leachate storage and transportation areas, then the public health and natural environment are not being protected from potential leaks of leachate which will contain harmful contaminants such as PFAS.

Finally, the Final Proposed Rules add a loophole that entirely undermines any hydraulic conductivity standard. Proposed landfill locations whose in situ soils do not meet the hydraulic conductivity standard can simply import and install a two-foot deep base material that does meet it. *See* Final Proposed Rules Env-Sw 804.02(d); 805.03(d) and (e). So, while the Final Proposed Rules do state a hydraulic conductivity standard, the loophole effectively swallows the rule such that there really is no requirement to meet any hydraulic conductivity standard. This means landfills could be located anywhere, no matter what the in-situ soil (assuming satisfaction of all other requirements).

Interestingly, the concept of a 2-foot layer of imported base material does not appear in any version of the rules until the very last version, the Final Proposed Rules, and no comment suggested a 2-foot layer. Upon information and belief, the Department met with waste industry representatives after June 5, 2024 and before the Final Proposed Rules were published, suggesting the possibility of another example of disproportionate influence of the waste industry in the rulemaking process.

NCABC submitted four scientific studies which support the siting of landfills over soil of low hydraulic conductivity. NCABC's comment package also included several scientific studies which show that landfill liners are unreliable at preventing the migration of contaminants in leachate from entering the subsurface and, eventually, groundwater. Liners exhumed from the ground after many years in the field exhibit deterioration in some cases. The combination of an engineered composite liner over a natural clay deposit (in situ soils with hydraulic conductivity greater than 1 x 10^{-4} cm/s) is the best protection against contaminants because of the ability of clay minerals to attenuate the contaminants to some extent.

In addition to the above, liners are only as reliable as the operators. For example, North Country Environmental Services, a Casella subsidiary operating a landfill in Bethlehem, recently realized and disclosed that over ten years ago its consultants mistakenly drilled numerous holes through its overliner, and those holes have existed and been allowing penetration through the overliner for those ten years without anyone realizing. *See* attached as **Exhibit D** Incident Report from Kim Crosby, Director of Compliance, North Country Environmental Services, Inc to N.H. Dep't of Env't Serv. (Sep. 6, 2024). While the operator is working the Department to address this situation, it illustrates that relying solely on liners or two-foot bases of material disregards the public health purposes of the enabling statue.

The Department has disregarded this overwhelming credible evidence and, instead, proposed rules which do not protect human health, preserve the natural environment, or conserve precious and dwindling natural resources. Instead, the Final Proposed Rules expose human health, the natural environment, and dwindling natural resources (i.e., drinking water sources) to unacceptable and avoidable risk of contamination from leachate.

In shocking disregard for the law, Director Wimsatt testified before the Subcommittee that the Department weakened the rules because members of the regulated industries had expressed that "none of the facilities [they] are operating right now would ever be sited if these rules were in place … and if these rules were in place, none of [their] facilities would be able to be expanded." However, the purpose of the rules is not to ease the siting or expansion of landfill facilities; the purpose of the rules is "to protect human health, to preserve the natural environment, and to conserve precious and dwindling natural resources through the proper and integrated management of solid waste." RSA 149-M:1.

Consequently, the Committee should object to the Final Proposed Rules because they exceed the authority of the Department. RSA 541-A:13, IV(a).

2. *The Env-Sw 800 Final Proposed Rules are Contrary to the Legislative Intent of Its Enabling Statute RSA 149-M*

The Committee should also object to the Final Proposed Rules because they are contrary to legislative intent. RSA 541-A:13, IV(b). Pursuant to Committee Rule 402.01(b) and (c), a proposed rule shall be considered contrary to legislative intent if the Committee determines that the rule violates a statutory purpose clause or the rule violates the overall purpose of the statute. To reiterate, the Env-Sw 800 rules implement RSA 149-M, the purpose of which is "to protect human health, to preserve the natural environment, and to conserve precious and dwindling natural resources through the proper and integrated management of solid waste." RSA 149-M:1.

As documented in the procedural history of rulemaking above, the Department iteratively weakened its rules about landfill siting requirements—despite concerns repeatedly expressed by the Subcommittee about the weakening of the rules—particularly with respect to surface water setbacks, leachate management, and PFAS management.

As detailed in the NCABC June 5 submission, PFAS, an emergent contaminant of increasing concern, has been shown to adversely affect human health, including increased rates of prostate, kidney, and testicular cancers; decreased fertility; developmental delays in children; immune system dysfunction; and liver damage. Recent scientific studies indicate that even minimal levels of PFAS contamination can lead to these adverse health effects. Consequently, the U.S. Environmental Protection Agency and the state of New Hampshire have identified PFAS as a threat to public health, safety, and welfare.

NCABC included in its public comments about the Env-Sw 800 Final Proposed Rules, submitted on June 5, 2024, several scientific studies which show the likelihood of landfills leaking leachate, the proliferation of PFAS, and the adverse health effects of PFAS. Given the proliferation of PFAS in modern products, any leak of leachate will contain PFAS compounds which may contaminate sources of drinking water and the environment generally. Because of this, and the issues discussed in the prior sections, the Env-Sw 800 Final Proposed Rules do not serve the purpose of RSA 149-M to "protect human health, to preserve the natural environment, and to conserve precious and dwindling natural resources" and, therefore, are beyond the authority of the Department and are contrary to the legislative intent of RSA 149-M.

3. *The Env-Sw 800 Final Proposed Rules are Contrary to the Public Interest*

Pursuant to RSA 541-A:11 and JLCAR Rule 403.01, the Committee should also object to the Final Proposed Rules because they are contrary to the public interest. A proposed rule shall be considered contrary to the public interest if the Committee determines that the agency failed to consider fully all public comments pursuant to RSA 541-A:11 because the agency did not provide the Committee with sufficient evidence that the public comment was overruled on the merits. *See* JLCAR Rule 403.01(a)(2).

The rulemaking record demonstrates the Department placed undue weight upon the unsubstantiated comments and input of representatives of the regulated industry. In contrast, the Department appears to have disregarded the substantiated NCABC comments, which include several scientific studies that show the Env-Sw 800 Final Proposed Rules are insufficient to effectuate the purpose of RSA 149-M. Moreover, the final Env-Sw 800 Final Proposed Rules threaten human health and the natural environment and directly contradict the purpose of RSA 149-M with insufficient substantiation from the Department.

As discussed in previous sections, NCABC submitted extensive evidence, including peer-reviewed science, that the Env-Sw 800 Final Proposed Rules are insufficient to protect human health, the natural environment, and the vital drinking water resources in New Hampshire. *See*

Exhibits A, B. The overwhelming, credible evidence submitted in NCABC's comments remains uncontested because the Department has not provided or cited any evidence that supports the Final Proposed Rules or that shows NCABC's comments were overruled on the merits.

Furthermore, the Department received many dozens of public comments which also opposed the initial proposed Env-Sw 800 rules, yet the Department has provided no evidentiary rebuttal to these comments either. The Department has stated multiple times that they relied only on existing, internal Department knowledge and ex parte conversations with members of the regulated industry when crafting the landfill siting rules.

"An agency 'must respond in a reasoned manner to those [comments] that raise significant problems.'" *In re Section 301 Cases*, 570 F. Supp. 3d 1306, 1338 (2022) (quoting *City of Waukesha v. EPA*, 320 F.3d 228, 257 (D.C. Cir. 2003)). The Court of International Trade further opined:

> Significant comments are those which, if true, raise points relevant to the agency's decision and which, if adopted, would require a change in an agency's proposed rule. Failure to respond to comments is significant only insofar as it demonstrates that the agency's decision was not based on a consideration of the relevant factors.

Id. (quotations and citations omitted). NCABC's comments raise significant problems with the Final Proposed Rules and require changes to the Department's Final Proposed Rules. The Department has not responded to NCABC's comments in a reasoned manner which demonstrates why it overruled NCABC's comments, or otherwise provided any countervailing evidence. Therefore, the Department cannot have overruled NCABC's comments on the merits.

When the National Highway Traffic Safety Administration ("NHTSA") rescinded via rulemaking its requirement for passive restraint systems in new vehicles, the U.S. Supreme Court ruled the agency had failed to present an adequate basis and explanation for the rescission. *Motor Vehicle Mfrs. Ass'n v. State Farm Mut. Auto. Ins. Co.*, 463 U.S. 29 (1983). The Court quoted itself from a previous decision to explain the NHTSA's failure to fully consider relevant factors: "There are no findings and no analysis here to justify the choice made, no indication of the basis on which the [agency] exercised its expert discretion." *Id.* at 48 (quoting *Burlington Truck Lines, Inc. v. United States*, 371 U.S. 156, 167 (1962)).

Here, the Department has similarly failed to justify its choices in the Env-Sw 800 Final Proposed Rules by providing no bases for its exercise of discretion and to show it overruled NCABC's comments on the merits.

"The object of notice and rulemaking is fairness; '[n]otice of a proposed rule is sufficient if it affords interested parties a reasonable opportunity to participate in the rulemaking process, and if the parties have not been deprived of the opportunity to present relevant information by lack of notice that the issue was there.'" *Plymouth Vill. Water & Sewer Dist. v. Scott*, 2019 N.H.

Super. LEXIS 18, *13 (2019) (quoting James T. O'Reilley, *Administrative Rulemaking* § 5.8 (2019 ed.)). "Among the information that must be revealed for public evaluation are the 'technical studies and data' upon which the agency relies in its rulemaking." *Id.* at *14 (quoting James T. O'Reilly). The Department has not provided any such technical studies or data upon which it relied, and instead ignored the technical studies and data contained in its rulemaking record. By relying on only unsubstantiated influence from the waste industry, the Department has effectively rendered meaningless the public's opportunity to be heard.

Though the Department iteratively weakened the draft rules, it provided no scientific, credible evidence either to the Subcommittee or to the public which supported the changes. Director Wimsatt claimed the draft rules presented in October 2023 would prohibit the development of future landfill sites and expansion of existing landfill sites based on private discussions with representatives of the regulated industry. The Department did not respond to requests by the Subcommittee to provide evidence to support these claims. The Department has once again weakened the Env-Sw 800 rules in its Final Proposed Rules while providing rationale but no evidence to support its changes. The Department is obligated to disclose all the information it considers during its rulemaking so that the public may have adequate notice to meaningfully participate. "By requiring the 'most critical factual material' used by the agency be subjected to informed comment, the [Administrative Procedure Act] provides a procedural device to ensure that agency regulations are tested through exposure to public comment, to afford affected parties an opportunity to present comment and evidence to support their positions, and thereby to enhance the quality of judicial review." *Plymouth Vill. Water & Sewer Dist.*, 2019 N.H. Super. LEXIS at *13–14 (quotation omitted). The Department failed to meet this obligation and denied the public the opportunity to rebut the studies and data from the regulated industry upon which the Department relied, if indeed it has any.

A proposed rule shall also be considered contrary to the public interest if the Committee determines it is designed to benefit the administrative convenience of the agency to the detriment of the public. JLCAR Rule 403.01(g). Director Wimsatt claimed in multiple hearings before the Subcommittee that the original draft of the proposed rules from October 2023 would prohibit the development of future landfill sites or expansion of existing landfill sites. Director Wimsatt made these claims based on discussions with representatives of the regulated industry but no supporting evidence. Director Wimsatt expressly stated the subsequent drafts of the proposed rules were crafted in response to those discussions, which shows that the Final Proposed Rules have been designed, at least in part, to benefit the administrative convenience of the agency to approve future landfill permits. Therefore, the Final Proposed Rules are contrary to the public interest and the Committee has grounds to object to them.

Conclusion

The Env-Sw 800 Final Proposed Rules are beyond the statutory authority of the Department, contrary to the intent of the legislature, and not in the public interest. As such, the Committee should object to the rules on these grounds.

Thank you for your time and attention to NCABC’s input. Please reach out to me with any questions. I can be reached via phone at (603) 225-2585 or via email at manzelli@nhlandlaw.com.

Very truly yours,

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EXHIBIT A

Attachment A: Public Comments on Env-Sw 800 Rulemaking (OLS Notice 2024-74)

Date (2024)	Commenter Organization	Commenter Name	Position on Proposed Rules	Length	Description
1/17	Business & Industry Association of New Hampshire	Skelton, Michael (President & CEO)	Objects to proposed rules from Oct. 16, 2023	One page	Proposed changes will prevent any further siting of disposal capacity, resulting in shortage of in-state disposal facilities which would increase costs for business in every NH industry
2/21	McLane Middleton obo Waste Management of New Hampshire, Inc.	Rouvalis, Mark C.	Objects to proposed rules from Feb. 15, 2024	Couple pages	Proposed rule changes would impose expensive, unnecessary, and redundant regulatory requirements
2/23	New Hampshire Waste Management Council	Sweet, Daniel (Acting Chair)	Objects to proposed rules from Feb. 15, 2024	Couple pages	Strongly urges DES to readopt current Env-Sw rules; proposed rules will increase construction costs for landfills, unreasonably limit future expansion potential of state's few remaining facilities, may decrease stability of state's landfills, and fails to adequate address review process for pending permit applications
2/27	McLane Middleton obo Waste Management of New Hampshire, Inc.	Rouvalis, Mark C.	Recommends some revisions	Several pages	Leachate testing requirements should be eliminated; revise odor control evaluation requirement; remove reduction of threshold for reporting secondary leachate flow rates; amend proposed definition of "diversion"; remove bedrock requirement for bottom liner system; remove change to setback requirement; amend vegetated buffer requirement; remove geosynthetic clay liner requirement; add clarifications; allow more time to install intermediate cover
3/1	National Waste & Recycling Association	Dubuque, Lewis A. (Northeast Region Vice President)	Objects to proposed rules	Couple pages	Supports position of New Hampshire Waste Management Council to readopt current Env-Sw 800 rules
5/1	Androscoggin Valley Regional Refuse Disposal District	Riendeau, Lisa G. (Executive Director)	Recommends some revisions	Couple pages	Clarifications to which undisturbed in-situ soils beneath footprint; highlights typo; clarify frequency of intermediate cover
5/21	Self	Webb, Rebecca	Wants more regulation	One para	Casual, frustrated
5/22	North Country Alliance for Balanced Change	Tower, Tom	Proposed rules are inadequate	Several para	Copy of comments presented at hearing, general overview of comprehensive comment package submitted later
5/22	Self	Geil, Leon H.	Standards should be stricter	Couple para	Plenty of sites available in NH meet stricter criteria; skeptical that landfill operators care about public health and welfare

Attachment A: Public Comments on Env-Sw 800 Rulemaking (OLS Notice 2024-74)

Date (2024)	Commenter Organization	Commenter Name	Position on Proposed Rules	Length	Description
5/22	Self	Morrison, Nancy Carbonneau	Soil conductivity criteria should be strengthened	Couple para	NH regulations are much weaker than neighboring states, should be strengthened
5/22	Self	Riege-Blackman, Virginia	Propose safer rules	Short	Propose safer rules after gathering evidence from experts and neighboring states
5/23	Self	Francoeur, Dennis	Against new landfills and expansions, want stricter regulations	Couple para	Past history of contamination and DES's lack of enforcement, new regulations needed to protect NH
5/23	Self	Ghioto, Gary	Wants stricter standards for hydraulic conductivity of pollutants		Proposed rules should at least match Maine standards; protect NH citizens from MA and CT waste
5/24	Self	Etter, Bruce	Wants stricter standards	One para	Opposed to currently proposed revisions, current Bethlehem resident
5/24	Self	French, Elaine	Wants stricter standards	Short	Opposed to currently proposed revisions
5/24	Self	Haring-Smith, Tori	Wants stricter standards	One para	Opposed to currently proposed revisions; NH is dumping ground for NE
5/25	Self	Wessler, Eliot	Wants stricter hydraulic conductivity standard	Several pages	Some proposed revisions are significant improvements, but changes to hydraulic conductivity standard are arbitrary and capricious and supported by zero evidence
5/27	Self	Thorne, Sarah	Wants stricter standards	Short	Opposed to currently proposed revisions
5/28	Self	Bryant, Andrea	Wants stricter standards	One page	Opposed to currently proposed revisions; DES should protect environment and NH residents; should learn from neighboring state regulators
5/28	Self	Doucette, Sarah	Wants stricter standards	Couple pages	Opposed to currently proposed revisions; DES should protect NH environment and public health
5/29	Self	Cote, Lois	Wants stricter standards	Couple para	Opposed to currently proposed revisions; DES needs to strengthen environmental and public health protections
5/29	Self	Laramie, Michael	Wants stricter standards	One para	Opposed to currently proposed revisions
5/29	Self	Shepardson, Marge	Wants stricter standards	Short	Opposed to currently proposed revisions
5/30	Self	Brown, Paula	Wants stricter standards	Short	Opposed to currently proposed revisions
5/30	Self	Kellogg, Pat	Opposed to rule changes	Short	Opposed to currently proposed revisions

Attachment A: Public Comments on Env-Sw 800 Rulemaking (OLS Notice 2024-74)

Date (2024)	Commenter Organization	Commenter Name	Position on Proposed Rules	Length	Description
5/30	Self	Swan, Jon	Opposed to rule changes		Opposed to currently proposed revisions; copy/pasted Sarah Doucette's op-ed in Concord Monitor
5/30	Self	Wright, Michael	Wants stricter standards	Several pages	Opposed to currently proposed revisions; hydraulic conductivity changes are extremely weak; should manage buffer zone of at least 1000 feet from any surface water body; increase setbacks from property lines and public roads; mandate double-liner systems; require immediate leachate removal; design stormwater management systems for 100-year storm event; require advanced erosion control materials and methods; measure hydraulic conductivity at bedrock level
5/31	Self	Rand, Cindy	Opposed to rule changes	Short	Opposed to currently proposed revisions
6/2	Self	Pastoriza, Kris	Wants stricter standards	Short	Supports more stringent landfill regulations
6/3	Self	Hunt, Patricia	Wants stricter standards	Couple para	Should strengthen rules that are already too weak to protect water quality from leachate
6/3	Self	Ross, Duncan	Wants stricter standards	Several para	Properly balance business interests with needs of state's flora, fauna, its waters, and its citizens; should establish science-based regulations
6/3	Self	Ross, Ralph	Wants stricter standards	Short	Opposed to currently proposed revisions
6/4	City of Nashua Solid Waste Department	Santos, Darrin (Environmental Engineer) and Jeff Lafleur	Requests clarifications and grandfathering of existing infrastructure	Multiple pages	Add grandfathering of existing infrastructure; clarify requirements; odor reporting requirement is redundant
6/4	Self	Dudley, Jo Beth	Wants stricter standards	Multiple pages	Requirements are too lax and should be updated
6/4	Self	Evankow, Abby	Wants stricter standards	One para	Opposed to currently proposed revisions
6/4	Self	Knowles, Andrea	Wants stricter standards	Couple para	Big business threatens clean water; NH is dumping ground for NE
6/4	Self	Richman, Susan	Wants stricter standards	Couple para	Proposed revisions are too lax
6/5	BCM obo NCABC	Manzelli, Amy	Wants stricter standards	Hundreds of pages	Proposed rules do not meet statutory purposes or reflect balanced input; includes suggested changes to proposed rules and scientific, peer-reviewed evidence

Attachment A: Public Comments on Env-Sw 800 Rulemaking (OLS Notice 2024-74)

Date (2024)	Commenter Organization	Commenter Name	Position on Proposed Rules	Length	Description
6/5	Casella Waste Systems, Inc.	Nicolai, Samuel C. (Vice President of Engineering & Compliance)	Requests some revisions	Several para	Allow variances from proposed rule; allow more exceptions for maximum slope
6/5	CMA Engineers obo Androscoggin Valley Regional Refuse Disposal District	Schmidt, Paul D., P.E. (President)	Recommends some revisions	Couple pages	Clarifications to which undisturbed in-situ soils beneath footprint; highlights typo; clarify frequency of intermediate cover
6/5	Sanborn Head & Associates, Inc.	Steinhauser, Eric S. (Senior Vice President)	Recommends some revisions	Several pages	Remove reference to specific ASTM standards; revise groundwater protection standards; odor control evaluation requirement is overly burdensome; remove decrease in reporting threshold for secondary leachate flow rates; simplify and streamline landfill reclamation process
6/5	Sugar Hill Select Board	Connors, Margaret	Wants stricter standards	Short	Opposed to currently proposed revisions; DES should prioritize environment
6/5	Waste Management of New Hampshire, Inc.	Reichert, Anne, P.E. (Construction Project Manager) and Steven Poggi, P.E. (Area Director of Disposal Operations)	Recommends some revisions	Several pages	Grandfather existing permits; prohibition of penetration of liner systems should be limited to base liner at bottom of landfill; highlights typos; remove reduction of threshold for reporting secondary leachate flow rate
6/5	Self	Allgire, Austin	Wants stricter standards	Couple para	Landfills are environmental disaster; should encourage incinerators
6/5	Self	Barrett, Cynthia	Wants stricter standards	One para	Opposed to currently proposed revisions; should follow success of neighboring states; DES should preserve and protect natural environment
6/5	Self	Bartlett, Kevin	Wants system change	Several para	Include Transportation, Economic Development, and Energy Departments; create task force to create new model for solid waste management as resource recovery and utilization
6/5	Self	Beffa-Negrini, Patricia	Wants stricter standards	Couple para	Rules should protect human health and environment; DES should rewrite proposed rules
6/5	Self	Blaney, Joanne	Wants stricter standards	Couple para	Opposed to currently proposed revisions

Attachment A: Public Comments on Env-Sw 800 Rulemaking (OLS Notice 2024-74)

Date (2024)	Commenter Organization	Commenter Name	Position on Proposed Rules	Length	Description
6/5	Self	Boswell, Laurie	Wants stricter standards	One para	Opposed to currently proposed revisions; DES should protect NH environment and human health
6/5	Self	Casey, Carol	Wants stricter standards	Short	Opposed to currently proposed revisions
6/5	Self	Davis, Peggy	Wants stricter standard	One para	Wants NHDES to protect environment and NH residents
6/5	Self	Duguay, Jay	Wants stricter standards	Several para	Hydraulic conductivity changes are terrible; need safeguards and regulations to protect environment and natural resources
6/5	Self	Finkel, Adam	Wants stricter standards	Several pages	DES has created the weakest locational criteria in the world which allow leachate to reach aquifer/groundwater within hours
6/5	Self	Gold, Gerald	Wants stricter standards	Short	Opposed to currently proposed revisions
6/5	Self	Harlan, Frances	Wants further refinement of hydraulic conductivity standards	Couple para	Very amiable, encouraging comment to further refine regulations to protect groundwater
6/5	Self	Harris, Cynthia and Richard	Want stricter standards	Couple para	Opposed to currently proposed revisions
6/5	Self	Lajoie, Katie	Wants stricter standards	Couple pages	Draft rules not sufficiently protective of public health and environment; should plan for zero waste
6/5	Self	MacAllister, Lisa	Wants stricter standards	Couple para	Concerned about PFAS, leachate, and toxic waste; cites Bethlehem landfill as disaster
6/5	Self	McConnell, Bruce	Wants stricter standard	One para	Disappointed by DES
6/5	Self	Mittleman, Nancy and William Stiffler	Want stricter standards	Couple para	Opposed to currently proposed revisions
6/5	Self	Odell, Gregory	Wants stricter standards	Short	Opposed to currently proposed revisions; DES should protect NH environment, wildlife, people, and future of tourism industry
6/5	Self	Orzech, Joseph M.	Opposed to GSL site in Dalton	Couple para	Opposed to currently proposed revisions; skeptical that landfill liner will leak and pollute water of Forest Lake
6/5	Self	Payne, Walter	Wants stricter standards	One para	Opposed to currently proposed revisions; DES should protect environment and human health; NH is dump for NE
6/5	Self	Pinsonneault	Wants stricter standards	Several para	Opposed to currently proposed revisions; NH is dumping ground for NE

Attachment A: Public Comments on Env-Sw 800 Rulemaking (OLS Notice 2024-74)

Date (2024)	Commenter Organization	Commenter Name	Position on Proposed Rules	Length	Description
6/5	Self	Smith, Kathleen J., MD	Wants stricter standards	One para	Opposed to currently proposed revisions; DES should protect health of North Country residents, particularly children and developing fetuses, from potential pollution from landfills
6/5	Self	Sweet, Lisa	Wants stricter standards	One para	Opposed to currently proposed revisions
6/5	Self	Tuthill, John	Opposed to proposed revisions	One para	Fundamental issues of policy and intent must be more fully explored within legislative and executive branches of State government
6/5	Self	Warner, Dr. Deborah	Wants stricter standards	Couple para	Opposed to currently proposed revisions; DES should protect environment and human health; NH is dump for NE
6/5	Self	Wright, Rick	Wants stricter standards	Short	Wants environmentally friendly rules
6/6	Self	Friedrichs, Emily	Wants stricter standards	One para	Opposed to currently proposed revisions; DES should protect public health and natural resources

EXHIBIT B

BCM Environmental
& Land Law, PLLC
Solutions for Northern New England

June 5, 2024

Via Email
Emily Jones, Compliance Assurance Section Supervisor
Solid Waste Management Bureau
New Hampshire Department of Environmental Services
emily.m.jones@des.nh.gov
swmbrules@des.nh.gov

Re: Rulemaking: Env-Sw 800 – Landfill Requirements (OLS Notice Number 2024-74)

Dear Ms. Jones:

Pursuant to the Rulemaking Notice published by the New Hampshire Department of Environmental Services (the "Department") on April 26, 2024, I submit this package of written materials related to the Department's proposed changes to Chapter Env-Sw 800 on behalf of my client, the North Country Alliance for Balanced Change (NCABC). Included in this package are:

1. A side-by-side comparison of the existing rules to the proposed rules with expert evaluation (**EXHIBIT A**);
2. NCABC's requested changes to the proposed rules based on NCABC's experts and with supporting references of peer-reviewed, scientific evidence (**EXHIBIT B**);
3. Copies of the peer-reviewed scientific evidence supporting NCABC'S changes to the proposed rules (**EXHIBIT E**);
4. A state-by-state comparison showing that New Hampshire's solid waste siting rules are already the weakest in New England (**EXHIBIT C**); and
5. Curriculum Vitae of Experts Anirban De, Ph.D., P.E., and Muriel Robinette, P.G. (**EXHIBIT D**).

Please make this letter and the supporting exhibits part of the Department's record in this matter.

Summary

The Department has not yet accomplished revised rules that meet the statutory purposes or reflect balanced input. The Department has proffered objectives including practicability and cost effectiveness as bases for the currently proposed revised rules, but those bases lack legal merit. Accordingly, NCABC respectfully requests the Department accept the rule revisions proposed and amply explained and justified through copious scientific and legal evidence throughout this submission.

Purpose of the Rules

As a threshold matter, it is critically important to note the Env-Sw 800 rules implement RSA 149-M. As a consequence, the Env-Sw 800 rules—by law—must implement the statutory purpose of RSA 149-M, which is "to protect human health, to preserve the natural environment, and to conserve precious and dwindling natural resources through the proper and integrated management of solid waste." RSA 149-M:1.

Procedural History of the Rulemaking

This section recounts and documents the rulemaking process to date.

In anticipation of the current rules expiring on July 1, 2024, the Department began soliciting public comment in 2023 in advance of drafting proposed rule amendments to Chapter Env-Sw 800. On March 13, 2023, the Department held a Public Input Session on Env-Sw 800 landfill requirements (as well as Env-Sw financial assurance). However, this session did not include rules related to landfill siting because of pending bills in the legislature. After these bills did not pass, the Department held another Public Input Session on July 19, 2023, focusing exclusively on Env-Sw 804 landfill siting requirements.

On October 18, 2023, the Department issued a draft of proposed Chapter Env-Sw 800 for informal comment, followed by a three-week informal comment period that closed on November 7, 2023. The Department adjusted the draft rules based on comments received during this time, particularly from members of the regulated industry that had met privately with the Department. Shortly thereafter, on October 24, 2023, the Department presented the draft rules to the DES Rules Update Subcommittee (the "Subcommittee") of the House Environment and Agriculture Committee (the "Committee"). At this initial meeting, members of the Subcommittee introduced concerns about leachate management and noted that the rules were lacking in certain areas (e.g., hydrogeological conditions, prohibited areas for landfills, etc.). The Department met again with the Subcommittee on December 5, 2023, at which time the Subcommittee continued to express its general thoughts on the rules, particularly with respect to the surface water setback, leachate management, and PFAS management.

The Department had its first meeting with the Waste Management Council[1] (the "Council") on January 18, 2024, at which it presented a draft of the proposed rules. In the weeks immediately following this presentation to the Council, the Department met privately with several members of the regulated industry, including the Androscoggin Valley Regional Refuse Disposal District (Mt. Carberry Landfill), Waste Management of New Hampshire (Turnkey

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[1] The Waste Management Council is statutorily composed of thirteen members intended to represent a balance of business and industry, municipalities, public health, academia, and conservation commissions. However, the following five seats on the Council have been vacant during the rulemaking: Public Interest (which also serves as Chair of the Council), Public Health Expert, Municipal Official, one of the two Elected Officials, and a representative of the Business or Financial Community. The seats that have been filled are dominated by the waste industry: one representative of Licensed Sanitary or Environmental Engineer or Sanitary Engineering, one of the two Elected Officials, Community that Recycles or Recovers Solid Waste, Associate Professor Environmental Sciences or Sanitary Engineering, Municipal Public Works Field, Private Solid Waste Management Industry, Local Conservation Commission Member, and Private Industries that Generate Hazardous Waste.

Landfill), Casella (NCES Landfill and a pending applicant for a new landfill, through its subsidiary Granite State Landfill), and Resource Waste Services.

The Subcommittee held another hearing at which the proposed rules were discussed on January 31, 2024. At this meeting, members of the Subcommittee shared that they were concerned about the weakening of the proposed rules from the October draft to the January draft. Director Wimsatt explained that the rules had been changed in response to the Department's conversations with the regulated industry, with members of the regulated industry claiming that "none of the facilities [they] are operating right now would ever be sited if these rules were in place . . . and if these rules were in place, none of [their] facilities would be able to be expanded." Director Wimsatt has presented no evidence to support this statement. Relatedly, the Subcommittee communicated concerns with the regulated industry having privileged access to the rulemaking process and having disproportionate influence on the outcome of the rules. The Subcommittee also worried the new proposed rules would make New Hampshire's solid waste rules the weakest in New England. For the next meeting, the Subcommittee asked the Department to provide evidence for the regulated industry's claim that no landfills would be able to be sited or expanded under the prior, stronger iteration of the draft rules from October, but the Department has not provided any.

The Department next met with the Council on February 15, 2024, to present a revised version of the draft proposed rules. The Department had updated the draft rules in response to the meetings it had had with members of the regulated industry. Industry representatives made further comments at the Council's meeting. The Council held a special meeting shortly thereafter on February 21, 2024, to further discuss the revised rules. This was followed by a letter dated February 23, 2024, in which the Council provided its written comments and concerns to the Department, including its position that the current version of the rules simply be readopted without any revisions.

The Department met with the Subcommittee again on March 6, 2024. Here, the Subcommittee indicated that it was dissatisfied at so many of the Council seats sitting vacant, especially because the empty seats were largely those meant to represent the concerns of the public. Director Wimsatt reiterated that "the industry has expressed concerns that the proposed siting criteria are so stringent as to effectively eliminate most potential future landfill sites and potential areas of expansion of existing landfill sites from eligibility." However, the Department was not able to provide the Subcommittee with any evidence, and the regulated industry was not willing to disclose its data and reports supporting the claim. Director Wimsatt explained that the Department had "overshot the runway" with its original draft of the rules, and the latest version reflected a course correction. The Subcommittee repeated its concerns over the rules being weakened with each iteration and the regulated industry having disproportionate impact on the rulemaking process.

A few days later, on March 8, 2024, the Department published the Initial Proposal for Env-Sw 800 rule changes. On March 21, 2024, the Department met with the Council for a third time, this time submitting the proposed draft rules that it intended to use for the formal rulemaking process.

The Subcommittee held another hearing to discuss the proposed rules on April 2, 2024. The Subcommittee again highlighted that the rules had been weakened with each draft. In response, Director Wimsatt explained that "[w]hen you look at all [the] criteria that need to come together in order to identify a location where you can site a landfill, what we had originally been proposing was likely too stringent to really make that practicable or cost effective." The Subcommittee also opined that none of its comments from previous hearings had been incorporated into the draft rules. Simultaneously with this hearing, the Department requested a Fiscal Impact Statement from the Legislative Budget Assistant. The Fiscal Impact Statement was completed by the Legislative Budget Assistant on April 15, 2024, and assigned FIS number 24:072.

The Department met with the Subcommittee again on April 23, 2024. The Subcommittee reemphasized that the rules had been weakened with each iteration and that it seemed like the regulated industry was driving the rulemaking process. Specifically, the Subcommittee could point to several instances in the draft rules where industry feedback had been directly incorporated, but it could not do the same for feedback that the Subcommittee had given across its various meetings with the Department. In other words, the Subcommittee did not feel that its feedback to the Department had played a role in shaping the rules.

The Department filed the formal Rulemaking Notice for Env-Sw 800 with the Office of Legislative Services on April 18, 2024. This notice was published on April 26, 2024, and assigned OLS Notice Number 2024-74. The Department held a public hearing on May 20, 2024, at 1:00 p.m., at which it presented the proposed rules and received oral public input, including from NCABC. The Department is accepting written comments through June 5, 2024, at 4:00 p.m. The Department must reevaluate the proposed rules based on the public input it receives.

Evaluation of Current vs. Proposed Rules

Attached as **EXHIBIT A** is a matrix comparing the existing (2014 through present) rules to the most recent version of the proposed rules with annotations by Anirban De, Ph.D., P.E., and Muriel Robinette, P.G. According to these experts, the proposed rules in red are less protective of public health and the environment, the rules in green are more protective of public health and the environment, and the rules in yellow are equally protective of public health and the environment. While the Department has claimed that "the proposed rules will benefit the environment, public health, and welfare" in its Rulemaking Notice, the comparison shows that several of the Env-800 rules will become *less* protective of public health and the environment.

Additionally, while the comparison does show that certain rules will become more protective, many of these improvements are qualitatively minor (i.e., they are only slightly more protective). Conversely, many of the rules that will become less protective do so to a marked degree (i.e., they become significantly less protective). Therefore, the quantity of green and red on the matrix does not tell the complete story of the overall protectiveness of the proposed rules; while there may be more green rules on the chart, the magnitude of change to the red rules is much more severe.

Overall, the evaluation contained in **EXHIBIT A** shows that most changes would make no difference or would be significantly less effective at accomplishing the statutory purposes of protecting human health, preserving the natural environment, and conserving precious and dwindling natural resources through the proper and integrated management of solid waste.

Requested Rule Changes

NCABC, by its experts Dr. De and Ms. Robinette, revised the Department's proposed rules to make them more protective of public health and the environment, accordant with the statutory purpose, based on peer-reviewed, scientific evidence. These requested rules are attached as **EXHIBIT B**. Along with being prepared with the expert assistance of Dr. De and Ms. Robinette, the proposed changes are supported by peer-reviewed scientific studies, which are attached as **EXHIBIT D** (except for those references which are textbooks).

NCABC respectfully requests the Department revise its proposed rules to incorporate NCABC's requested changes, which are supported by peer-reviewed science and help to achieve the Department's statutory mandate to protect human health and the environment in siting solid waste facilities.

State-by-State Regulatory Comparison

It is also important for the Department to consider New Hampshire's solid waste rules in the context of other New England states, especially because solid waste is typically viewed at the northeastern regional level. Attached as **EXHIBIT C** is a matrix comparing New Hampshire's landfill siting requirements with those of its New England neighbors—Maine, Vermont, Massachusetts, and Rhode Island. This comparison shows that **New Hampshire's siting requirements are already the weakest in the region**; they are already the least protective of public health and the environment.

As described above, the Department's proposed rule changes will further weaken standards, putting New Hampshire even farther behind its neighbors and contravening the statutory purpose of RSA 149-M. If the Department allows New Hampshire to continue to lag behind other states in the region, it will incentivize landfill developers to further concentrate waste disposal in the Granite State. At the very least, New Hampshire's landfill siting requirements should be on par with other New England states. The Department should not allow New Hampshire to be the dumping ground of the region, especially when the state's natural environment and livability are some of its best assets, ecologically and economically.

Thank you for your time and attention to NCABC's input. Please reach out to me with any questions. I can be reached via phone at (603) 225-2585 or via email at manzelli@nhlandlaw.com.

Very truly yours,

Amy Manzelli

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Exhibit A

NCABC Evaluation of Env-Sw 800 Solid Waste Rules

Criteria	**Current Rules 2014 – 2024**	**3/8/24 NHDES Draft**	**More Protective; Neutral; Less Protective**
Siting Requirements: Env-Sw 804.01	(a) The siting requirements in this part shall apply to all landfills except: (1) Facilities that hold and continue to operate under a permit issued pursuant to RSA 149-M prior to the 2005 readoption of the solid waste rules and any facilities scheduled to close; (2) Permit-exempt facilities identified in Env-Sw 302.03 or Env-Sw 810; (3) Permit-by-notification facilities having an active life of 90 days or less; (4) Research and development permit facilities, as provided by Env-Sw 312.02(b); and (5) Emergency permit facilities, as provided by Env-Sw 313.02(b).	(a) The siting requirements in this part shall apply to all landfills **except**: (1) Facilities that hold and continue to operate under a permit issued pursuant to RSA 149-M prior to the ~~2005~~***2024*** readoption of the solid waste rules and any facilities scheduled to close. ***Landfill footprints and associated infrastructure permitted pursuant to a standard permit in accordance with Env-Sw 314 or a type I-A permit modification in accordance with Env-Sw 315 for which a permit or permit modification was issued prior to the 2024 readoption of the solid waste rules***	**Neutral**
Groundwater Protection Standards: Env-Sw 804.02 (a) – (d)	(a) A landfill shall not be sited within the well head protection area of a community or noncommunity, non-transient water supply well system as delineated in the department's source water protection area inventory. (b) A landfill and all associated leachate storage units shall be located only in areas where groundwater monitoring for release detection, characterization and remediation can be conducted prior to a release having an adverse affect on a water supply.	(a) A landfill shall not be sited within the well head protection area of a community or non-community, non-transient water supply well system as delineated in the department's source water protection area inventory. (b) A landfill and all associated ***stormwater,*** leachate storage units, ***and decomposition gas infrastructure*** shall be located only in areas where groundwater monitoring for release detection, characterization and remediation can be conducted prior to a release having an adverse ~~affect~~ ***impact***	**Less Protective**

Exhibit A

Criteria	**Current Rules 2014 – 2024**	**3/8/24 NHDES Draft**	**More Protective; Neutral; Less Protective**
	(c) Identification of the areas cited in (b) above shall be based upon a hydrogeologic investigation which provides all site-specific information required to model the pre-construction and post-construction groundwater and surface water regimen. (d) The base of the bottom liner system, or the base of the facility if unlined, shall be a minimum of 6 feet above the seasonal high groundwater table and the confirmed bedrock surface.	on ***groundwater quality at the property line or*** a water supply. ***(c) Undisturbed in-situ soils for 5 feet immediately beneath the footprint shall have an average saturated hydraulic conductivity of ~~1~~5 x 10-3 centimeters per second (cm/sec) or less.*** ***(d) The base of the bottom most liner system, or the base of the facility if unlined, shall be a minimum of 6 feet above the seasonal high groundwater table and the confirmed bedrock surface.*** (~~c~~***e***) Identification of the areas cited in (b) ***through (d)*** above shall be based upon a hydrogeologic investigation which provides all site-specific information required to model the pre-construction and post-construction groundwater and surface water regimen***, and other information as necessary to demonstrate compliance with the siting criteria***.	🟥
Surface Water Protection Standards: Env-Sw 804.03 (b)	(b) A landfill and all associated leachate storage units shall be located only in areas where potential adverse effects to surface water quality, due to erosion, sedimentation, siltation, flood, or discharge of contaminants, can be prevented or minimized and mitigated by facility design.	(b) A landfill and all associated ***stormwater,*** leachate storage units***, and decomposition gas infrastructure*** shall be located only in areas where potential adverse ~~effects~~***impacts*** to surface water quality, due to erosion, sedimentation, siltation, flood, or discharge of contaminants, can be prevented or minimized and mitigated by facility design.	Contaminant handling areas ARE commonly where releases occur and with a SAND hydraulic conductivity standard, this is NOT more protective

Exhibit A

Criteria	**Current Rules 2014 – 2024**	**3/8/24 NHDES Draft**	**More Protective; Neutral; Less Protective**
Env-Sw 804.03 (c)	(c) Identification of the areas cited in (b) above shall be based on a thorough hydrogeological investigation to demonstrate the following: (1) Compliance with Env-Sw 804.02; (2) That engineering design measures can be incorporated to control erosion, sedimentation and siltation; and (3) The potential release of contaminants to surface waters can be prevented, attenuated or otherwise remediated.	(c) A landfill and associated stormwater, leachate, and decomposition gas infrastructure shall be located such that a discharge, spill, leachate release or other failure of the waste containment system or associated infrastructure will be detected and assessed, and remediation initiated **prior to** contamination reaching any perennial water body.	Without a site-specific TRAVEL TIME determination, this language is meaningless
Env-Sw 804.03(d)	The footprint of a landfill shall not be located within 200 feet of any perennial surface water body, measured from the closest bank of a stream and closest shore of a lake, as applicable.	(d) The footprint of a landfill shall not be located within***:*** ***(1)*** 200~~***500***~~ feet of any ***first or second order*** perennial ***stream; and*** ***(2) 500 feet of any other perennial*** surface water body, measured from the closest bank of a stream and closest shore of a ***pond or*** lake, as applicable.	Neutral
Env-Sw 804.03 (e)-(f)	(e) Footprint of a landfill shall not be located within 200 feet upgradient and 100 feet downgradient of a wetland within jurisdiction of RSA 482-A, excluding any drainage appurtenances related to the site that is n to allowed to be filled under the authority of RSA 482-A. (f) The footprint of a landfill shall not be located within 1,000 feet upgradient of a surface water reservoir or intake used for a community drinking water supply.	(e) The footprint of a landfill shall not be located within 200 feet ~~upgradient and 100 feet downgradient~~ of a wetland within the jurisdiction of RSA 482-A, excluding any drainage appurtenances related to the site, that is not allowed to be filled under the authority of RSA 482-A. (f) The footprint of a landfill shall not be located within 1,000 feet ~~upgradient~~ of a surface water reservoir or intake used for a community drinking water supply.	Neutral
Env-Sw-804.03 (g)	(g) The footprint of a landfill shall not be located within the 100-year flood hazard zone.	(g) The footprint of a landfill shall not be located within the ~~100~~***500***-year flood***plain*** hazard zone.	More Protective

Exhibit A

Criteria	**Current Rules 2014 – 2024**	**3/8/24 NHDES Draft**	**More Protective; Neutral; Less Protective**
Env-Sw 804.03 (h)		***(h) Identification of the areas cited in (a) through (g) above shall be based on a thorough hydrogeological investigation to demonstrate the following:*** ***(1) Compliance with the siting requirements of Env-Sw 804.02 and Env-Sw 804.03;*** ***(2) That engineering design measures can be incorporated to control erosion, sedimentation, and siltation; and*** ***(3) Any potential release of contaminants to surface waters can be prevented or, in the case of a release, detected and remediated.***	Neutral
Set Back: Env-Sw 804.04	(a) There shall be a minimum 100-foot buffer strip between the property line and the footprint of the landfill.	There shall be a minimum 100-foot ~~buffer strip~~ ***setback*** between the property line and the footprint of the landfill***, of which the 50 feet nearest the property line shall be vegetated for purposes of shielding the waste storage and handling areas and controlling the off-site transport of dust and windblown litter***.	Neutral
Env-Sw 804.04 (c)-(d)	(c) For landfills sited on a parcel of land on which a landfill which is subject to a standard permit exists on the 2014 effective date of this chapter, a minimum distance of 500 feet shall be maintained between the footprint of the landfill and all existing residences not owned by the applicant. (d) For facilities approved after the 2014 effective date of this chapter and sited on a parcel of land on which no landfill having a standard permit exists, a minimum 500-foot vegetated buffer shall be established and maintained as provided in Env-Sw 805.11 between the footprint of the landfill and all properties not	~~(c) For landfills sited on a parcel of land on which a landfill which is subject to a standard permit exists on the 2014 effective date of this chapter, a minimum distance of 500 feet shall be maintained between the footprint of the landfill and all existing residences not owned by the applicant.~~ (~~d~~***c***) ~~For facilities approved after the 2014 effective date of this chapter and sited on a parcel of land on which no landfill having a standard permit exists,~~ ***There shall be*** a minimum 500-foot ~~vegetated buffer shall be established and maintained as provided in Env-Sw 805.11~~***setback*** between the footprint of the landfill and all properties not owned by the applicant or its affiliates that either contain residences,	

Exhibit A

Criteria	**Current Rules 2014 – 2024**	**3/8/24 NHDES Draft**	**More Protective; Neutral; Less Protective**
	owned by the applicant or its affiliates that either contain residences or are zoned for residential use.	***residential care facilities, nursing homes, prisons***, or ***that*** are zoned for residential use.	🟨
		(d) There shall be a minimum 1,000-foot setback between ~~the property line and~~ the footprint of the landfill,~~ of which the 500 feet nearest the property line shall be vegetated,~~ and all properties containing public schools, licensed day care facilities, and hospitals.	More Protective
Env-Sw 804.04 (e)	(e) The footprint of a landfill receiving putrescible wastes shall not be located within 10,000 feet of any airport runway used by turbojet aircraft or 5,000 feet of any airport runway used by only piston-type aircraft.	(e) The footprint of a landfill ***or landfill expansion*** receiving putrescible wastes shall not be located within 10,000 feet of any airport runway used by turbojet aircraft or 5,000 feet of any airport runway used by only piston-type aircraft.	Neutral
Geologic Siting Limitations: Env-Sw 804.05	(b) No landfill footprint or associated leachate storage units shall overlie an area underlain by karstified dolomite or limestone or an area susceptible to mass movements of earth material such as landslides, rockfalls, mudslides, slumps, earth flows, or subsidence.	(b) No landfill footprint or associated ***stormwater,*** leachate ~~storage units,~~ ***or decomposition gas, infrastructure*** shall overlie an area underlain by karstified dolomite or limestone or an area susceptible to mass movements of earth material such as landslides, rockfalls, mudslides, slumps, earth flows, or subsidence.	Neutral
Other Siting Limitations: Env-Sw 804.06	A new landfill shall be sited only on property which is owned by the permittee.	~~Other Siting Limitations~~***Property Ownership***. A ~~new~~ landfill ***or landfill expansion*** shall be sited only on property which is owned by the permittee.	Neutral
Design and Construction Requirements: Env-Sw 805.01 (a)	(1) Portions of existing permitted facilities which were constructed or approved for construction as of October 29, 1997;	(1)Portions of existing permitted facilities which were constructed or approved for construction as of ***the 2024 effective date of this chapter*** ~~October 29, 1997;~~	Neutral
General Landfill Design Requirements: Env-Sw 805.02	(4) A groundwater and surface water monitoring system, if required pursuant to RSA 485-C and Env-Or 700 or predecessor rules Env-Wm 1403;	(4) A groundwater and surface water monitoring system, if required pursuant to RSA 485-C and Env-Or 700 ~~or predecessor rules Env-Wm 1403;~~	Neutral

Criteria	**Current Rules 2014 – 2024**	**3/8/24 NHDES Draft**	**More Protective; Neutral; Less Protective**
	(5) A stormwater management system pursuant to Env-Sw 805.09;	(5) A stormwater management system pursuant to Env-Sw 805.09;	🟨
Env-Sw 805.02(6)	(6) A decomposition gas control system pursuant to Env-Sw 806.07;	(6) A decomposition gas control ***and migration monitoring*** system pursuant to Env-Sw ***805.18*** ~~806.07~~	More Protective
Env-Sw 805.02 (b)	(3) A final capping system pursuant to Env-Sw 805.10;	***(3) A decomposition gas control and migration monitoring system pursuant to Env-Sw 805.18;***	More Protective
Landfill Subgrade and Base Grade: Env-Sw 805.03 (a)	(a) The landfill subgrade shall be graded and prepared for landfill construction. (b) Subgrade materials shall have a saturated hydraulic conductivity of 1 x 10-4 centimeters per second (cm/sec) or less. (c) The subgrade shall have sufficient structural integrity to support the facility under all anticipated loading conditions during all phases of construction, operation and closure.	***(1)*** Be ~~***the in-situ earth surface***~~ graded and prepared for landfill construction.***; and*** ~~(b) Subgrade materials shall have a saturated hydraulic conductivity of 1 x 10-4 centimeters per second (cm/sec) or less.~~ (~~c~~***2***) ~~The subgrade shall have~~ ***Have*** sufficient structural integrity to support the facility under all anticipated loading conditions during all phases of construction, operation, and closure.	Neutral
Env-Sw 805.03 (f)	(f) For geomembrane lined facilities, the subgrade below the liner shall: (1) Be prepared to a depth which provides a uniform and consistent bedding layer which shall be stable under loading;	(f***d***) For geomembrane lined facilities, the ~~subgrade~~***base*** below the liner ***and above the subgrade*** shall: (1) Be prepared to a depth ***of not less than 12 inches, except as provided in (e) below, and*** which provides a uniform and consistent bedding layer which shall be stable under loading;	More Protective
Env-Sw 805.03(d)(4)	Env-Sw 805-03(b) subgrade materials shall have a saturated hydraulic conductivity of 1X10^{-4} cm/sec or less	(4) Consist of a soil with a saturated hydraulic conductivity of 1X10^{-4} cm/sec or less.	Neutral
Env-Sw 805.03 (e)		(~~g~~***e***) ***Where undisturbed in-situ soils are not present, the base shall be prepared in accordance with (d) above and prepared to a depth of 24 inches.***	More Protective
Liner Material and Construction Requirements:	Env-Sw 805.05 (f)(2) Contain no stones greater than one inch in diameter, and no sharp or angular materials;	***(2) The liner shall be free from stones greater than one inch in diameter and stones having a sharp or angular surface;***	Neutral

Criteria	Current Rules 2014 – 2024	3/8/24 NHDES Draft	More Protective; Neutral; Less Protective
Env-Sw 805.04			
Env-Sw 805.04 (c) (1)(2)	(c) Composite liners shall consist of: (1) A geomembrane liner, as specified by (b) above; and (2) A soil component as specified by (a) above or a manufactured geosynthetic clay liner.	(c) Composite liners shall consist of: (1) A geomembrane liner, as specified by (b) above; and (2) A soil component as specified by (a) above or a manufactured geosynthetic clay liner ***(GCL)*** ~~***with a hydraulic conductivity of not more than 5 x 10-9 cm/sec***~~.	Neutral
Liner System Design Standards: Env-Sw 805.05(f)	(f) Except as provided by (g) below, each liner within a liner system shall be covered in the base area by an overlying layer of select granular soil materials 12 inches in depth or more as required to:	(f) Except as provided by (g) below, each ~~***geomembrane***~~ liner within a liner system shall be covered ~~in the base area~~ by ***a drainage geocomposite and, in the base area,*** an overlying layer of select granular soil ***drainage*** materials 12 inches in depth or more as required to:	Neutral
Env-Sw 805.05(g)	(g) For multi-liner systems, geosynthetics may be used to separate the liners in areas of extended side slopes where placement and maintenance of granular materials is not possible or practical for reasons of stability.	(g) For multi-liner systems, geosynthetics may be used to separate the liners in areas of extended side slopes where placement and maintenance of granular ***soil drainage*** materials is not possible or practical for reasons of stability	Neutral
Env-Sw 805.05 (k)(l)		***(k) For multi-liner systems required to include a composite liner and using a GCL to fulfill the requirement, the GCL shall extend across the base area and 10 feet up sideslopes, as measured in vertical feet.*** ***(l) Each liner system in a multi-liner system shall be hydraulically separate***	More Protective
Leachate Collection and removal System Design Standards: Env-Sw 805.06		***(c) Leachate collection and removal systems located outside the waste deposition area shall be leak tight and accessible for leak testing, inspection and repair.***	More Protective

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Env Sw 805.06 (d)	(d) Leachate collection and removal systems shall be designed to function effectively during both the active life of the landfill and the landfill closure and post-closure period. Therefore, for the purpose of sizing the system(s) components and specifying materials with an appropriate design life expectancy, the leachate generation rates and volumes for the above specified time period shall be considered.	(~~d~~***e***) Leachate collection and removal systems shall be designed to function effectively during both the active life of the landfill and the landfill closure and post-closure ***care*** period. Therefore, for the purpose of sizing the system(s) components and specifying materials with an appropriate design life expectancy, the leachate generation rates***,*** and volumes***, and chemical composition*** for the above specified time period shall be considered.	Neutral
Env Sw 805.06 (e)	(e) Leachate collection and removal systems shall be designed to maintain one foot or less of hydraulic head on all portions of the liner, excluding the leachate collection sumps if any, during routine operations including the 25-year storm event with a duration equivalent to the time of concentration of the drainage area of the component being sized.	(~~e~~***f***) Leachate collection and removal systems shall be designed to maintain one foot or less of hydraulic head on all portions of the liner, excluding the leachate collection sumps if any, during routine operations ~~including~~ ~~***plus snow melt infiltration,***~~ ***plus*** the 25-year storm event with a duration equivalent to the time of concentration of the drainage area of the component being sized***, plus 20 percent***.	More Protective
Env Sw 805.06 (j)	(j) Pipes which require solvent welding shall not be used.	(~~j~~***k***) Pipes which require solvent welding ~~shall not~~ ***may only*** be used ***in leachate vaults*** ~~***that provide secondary containment and are***~~ ***equipped with a high-water alarm, a backup high-water alarm, and automatic dialers in accordance with (q) below***. (~~k~~***l***) The ***granular soil*** drainage blanket ***materials in the liner system***	Less Protective
Env Sw 805.06 (p)(q)	(o) Pump stations located outside the waste deposition area shall be designed to provide the following: (1) Backup pumping capacity; (2) Backup power supply; (3) High-water alarm; and (4) Efficient operation during both average and peak flows.	(~~o~~***p***) Pump stations located outside the waste deposition area shall be designed to provide the following: (1) Backup pumping capacity; (2) Backup power supply; (3) High-water alarm; and ***(4) Backup high-water alarm;*** ***(5) Alarms to automatic dialer; and***	Neutral

Criteria	Current Rules 2014 – 2024	3/8/24 NHDES Draft	More Protective; Neutral; Less Protective
	(p) Tanks, sumps or other storage units associated with leachate collection and removal systems shall be equipped with high-water alarms.	(4***6***) Efficient operation during both average and peak flows. (~~p~~***q***) Tanks, sumps, ~~or~~***and*** other storage units associated with leachate collection and removal systems shall be equipped with high-water alarms***, backup high-water alarms, and automatic dialers***.	
Env Sw 805.06		***(r) Pipes, tanks, sumps, and other conveyance or storage units associated with leachate collection and removal systems outside the waste deposition area shall have secondary containment or be double-walled except for underground pipes, manholes and other buried leachate systems existing prior to the 2024 readoption of this chapter.***	More Protective
Leak Detection and Location System Design Standards: Env-Sw 805.07(a)	(a) A leak detection and location system designed to detect and isolate the location of leaks through a liner shall be required beneath each liner installed at a lined landfill, unless the potential for leakage through the bottom most liner is reduced by one or both of the following design features: (1) Geonet is incorporated throughout the leachate collection and removal system for the bottom most liner, in order to rapidly convey leachate off the liner and thereby limit the potential for hydraulic head to develop on the liner; or (2) The bottom most liner is a composite liner which meets the requirements of Env-Sw 805.04(c).	~~(a) A leak detection and location system designed to detect and isolate the location of leaks through a liner shall be required beneath each liner installed at a lined landfill, unless the potential for leakage through the bottom most liner is reduced by one or both of the following design features:~~ ~~(1) Geonet is incorporated throughout the leachate collection and removal system for the bottom most liner, in order to rapidly convey leachate off the liner and thereby limit the potential for hydraulic head to develop on the liner; or~~ ~~(2) The bottom most liner is a composite liner which meets the requirements of Env-Sw 805.04(c).~~ (~~b~~***a***) ***In multi-liner systems, the bottom most liner system shall also be the*** ~~L~~***l***eak detection and location systems ~~shall be~~	Neutral
Env-Sw 805.07		***(b) In single-liner systems, a leak detection and location system shall be installed beneath the bottom most liner, unless the potential for leakage is reduced by installing a composite liner that meets the requirements of Env-Sw 805.03(c).***	More Protective

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Criteria	Current Rules 2014 – 2024	3/8/24 NHDES Draft	More Protective; Neutral; Less Protective
		(c) A leak detection and location system shall *be* designed to:	
Groundwater and Surface Water Monitoring System Design Standards: Env-Sw 805.08	(a) At least one groundwater monitoring well shall be installed hydraulically upgradient from the landfill and at least 3 monitoring wells shall be installed in each down-gradient direction.	(a) ***The location of groundwater monitoring wells and surface water sampling points shall be based on site-specific hydrogeology, but in no case shall be less than*** ~~At least~~ one groundwater monitoring well ~~shall be~~ installed hydraulically upgradient from the landfill and at least 3 monitoring wells ~~shall be~~ installed in each down-gradient direction.	Neutral
Storm Water Management System Design Standards: Env Sw 805.09	(b) Stormwater management systems shall be designed to accommodate the 25-year storm event of a duration equivalent to the time of concentration of the drainage area being served.	(b) Stormwater management systems shall be designed to accommodate the ~~25~~***50***-year storm event of a duration equivalent to the time of concentration of the drainage area being served.	More Protective
Env Sw 805.09 (f)(g)	(f) Permanent sedimentation ponds and detention ponds shall be sized to handle the 25-year/24-hour storm event with no less than one foot of freeboard below the emergency spillway invert. (g) Peak surface run-off from the landfill site during the 25-year storm event shall be controlled and maintained at the pre-development discharge rate, in accordance with RSA 485-A.	(f) Permanent sedimentation ponds and detention ponds shall be sized to handle the ~~25~~***50***-year/24-hour storm event with no less than one foot of freeboard below the emergency spillway invert. (g) Peak surface run-off from the landfill site during the ~~25~~***50***-year storm event shall be controlled and maintained at the pre-development discharge rate, in accordance with RSA 485-A.	More Protective
Landfill Capping System Design Standards: Env-Sw 805.10	(d) For unlined landfills, the type of capping system required pursuant to (e) or (f) below shall be based on which system type will meet the performance standards in Env-Sw 807.04, using the following factors to make the determination (6) Proximity to drinking water supplies	(d) For unlined landfills, the type of capping system required pursuant to (e) or (f***g***) below shall be based on which system type will meet the performance standards in Env-Sw 807.04, using the following factors to make the determination 6) Proximity to drinking water supplies***, surface waters, and floodplains***;	More Protective
Env. Sw 805.10	(Layer 2) c. Consist of 12 inches of sand with 100% passing the one inch sieve and with no more than 12% passing the	(Layer 2) c. Consist of ***at least*** 12 inches of sand with 100% passing the one inch sieve and with no more than 12%	Neutral

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	number 200 sieve on a weight basis if for a facility without an active gas extraction system or 6 inches of soil with 100% passing the one inch sieve if for a facility with an active gas extraction system; and d. Be constructed in accordance with a quality assurance/quality control plan established pursuant to Env-Sw 805.16;	passing the number 200 sieve on a weight basis if for a facility without an active gas extraction system or ***at least*** 6 inches of soil with 100% passing the one inch sieve if for a facility with an active gas extraction system; and ~~***soil meeting the requirements of (1) through (3) below, or at least 6 inches of soil meeting the requirement of (3) below and a manufactured GCL meeting the requirement of (4) below.***~~ ~~***1. Soil shall be a recompacted natural soil with uniform and consistent characteristics, or a uniform and consistent natural soil blended with an admixture, such as bentonite;***~~ ~~***2. Soil shall have a compacted hydraulic conductivity of 1 x 10 -7 cm/sec or less;***~~ ~~***3. Soil shall pass on a weight basis 100% through a one-inch sieve;***~~ ~~***4. GCL shall have a hydraulic conductivity of not more than 5 x 10 -9 cm/sec; and***~~ ~~d~~***c***. ~~Be constructed in accordance with a quality assurance/quality control plan established pursuant to Env-Sw 805.16~~ ~~***protected from damage due to frost, desiccation, and differential movement***~~;	
Env Sw 805.10	(Layer 3) b. Consist of a geomembrane with a minimum thickness of 40 mils or an impermeable soil, or admixture; and c. Be constructed in accordance with a quality assurance/quality control plan established pursuant to Env-Sw 805.16;	(Layer 3) b. Consist of a geomembrane with a minimum thickness of 40 mils ~~or an impermeable soil, or admixture~~; and ~~c. Be constructed in accordance with a quality assurance/quality control plan established pursuant to Env-Sw 805.16~~;	Neutral
Env Sw 805.10	(Layer 4) 2. Geonet and no less than 12 inches of drainage sand, specified based on the results of a hydraulic	(Layer 4) 2. ~~Geonet~~***Drainage geocomposite*** and no less than 12 inches of drainage sand, specified based on the results of a	Neutral

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Criteria	**Current Rules 2014 – 2024**	**3/8/24 NHDES Draft**	**More Protective; Neutral; Less Protective**
	calculation supporting the design and containing no more than 15% calcium carbonate; d. Be constructed in accordance with a quality assurance/quality control plan established pursuant to Env-Sw 805.16; and	hydraulic calculation supporting the design and containing no more than 15% calcium carbonate; ***and*** ~~d. Be constructed in accordance with a quality assurance/quality control plan established pursuant to Env-Sw 805.16; and~~	
Env-Sw 805.10		***(h) Landfill capping systems shall be constructed in accordance with a quality assurance/quality control plan established pursuant to Env-Sw 805.16.***	Neutral
Env-Sw 805.10	c. Limits, to the extent practicable, surface water from infiltrating into the waste.	c. Limits, ~~to the extent practicable~~, surface water from infiltrating into the waste.	Less Protective
Env-Sw 805.10	p) Except in areas where berms, swales, or other structures are constructed to control storm water, the average slope of capping systems shall not exceed 2.5 horizontal to 1 vertical.	***~~p~~q***) Except in areas where berms, swales, or other structures are constructed to control storm water, the ~~average~~ ***maximum*** slope of capping systems shall not exceed 2.5 horizontal to 1 vertical.	More Protective
Other Landfill Design Requirements: Env-Sw 805.11		(l)The v***V***egetated buffer zone***(s)*** ~~required by Env-Sw 804.04(c)~~ shall be ***designed,***: ~~(1) E~~***e***stablished***,*** and maintained to minimize impacts to abutting properties***, including by shielding waste storage, handling and disposal areas and controlling the off-site transport of dust and windblown litter, as follows:***; ~~and~~ ***(1) In the setback required by Env-Sw 804.04(a), the 50 feet nearest the property line;*** (2) ***In the setback required by Env-Sw 804.04(c), the 400 feet nearest the property line; and*** ***(3) In the setback required by Env-Sw 804.04(d), the 500 feet nearest the property line***	Neutral Neutral

Criteria	Current Rules 2014 – 2024	3/8/24 NHDES Draft	More Protective; Neutral; Less Protective
		m) A vegetated buffer zone shall be ~~D~~designed***, established and maintained*** to minimize the impact of ingress and egress access roads on abutting properties. ***(~~m~~n) An odor control plan shall be prepared and implemented as part of the technical specifications when excavation of putrescible waste is required during landfill construction.*** ***(~~n~~o) A landfill shall be designed such that all waste containment and structural components, including but not limited to, liner and leachate collection systems and cap systems, are constructed to resist the maximum horizontal acceleration in lithified earth materials within a seismic impact zone as defined in 40 CFR 258.14.*** ***(~~o~~p) A stability assessment of the landfill leachate management systems, and other structures such as mechanically stabilized earth berms, shall be performed and shall:*** ***(1) Include an analysis of potential failure planes for both static and seismic conditions.*** ***(2) Be supported by corroborative field and laboratory data that defines the site geology and hydrogeology, geotechnical characteristics, waste mass characteristics, and geosynthetic characteristics.*** ***(~~p~~q) All walls, berms, or other structures used to retain waste shall be:*** ***(1) Located on a stable foundation as demonstrated by geotechnical investigation and calculations;*** ***(2) Designed with a static factor of safety of at least 1.5 against overturning and sliding; and***	🟨

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Criteria	Current Rules 2014 – 2024	3/8/24 NHDES Draft	More Protective; Neutral; Less Protective
		(3) Designed to prevent the lateral movement of the waste mass. ***(~~q~~r) A settlement assessment shall be performed to predict total and differential settlement of landfill systems, and shall include:*** ***(1) a demonstration that systems will maintain their integrity and performance at maximum predicted settlements; and*** ***(2) A plan view showing settlement contours when predicted landfill settlements exceed two feet.*** ***(~~r~~s) Design features shall include the means to control and extinguish fires which might occur within the landfill and to otherwise limit the potential for liner damage due to fire.*** ***(t) No permit or permit modification shall be granted for a landfill or landfill expansion unless groundwater monitoring can be accomplished, when required, in accordance with this chapter and pursuant to RSA 485-C.***	🟨
Env-Sw 805.14	(c) Design features shall include the means to control and extinguish fires which might occur within the landfill and to otherwise limit the potential for liner damage due to fire.	~~(c) Design features shall include the means to control and extinguish fires which might occur within the landfill and to otherwise limit the potential for liner damage due to fire.~~	Less Protective
Env-Sw 805.15	(a) Landfills for any waste type(s) not specifically identified in Env-Sw 805.12 through Env-Sw 805.14 shall be designed as double lined facilities, except as provided by (b) below and subject to the landfilling prohibitions in Env-Sw 806.12. (b) Landfills which receive only stumps and brush or only asbestos or only inert demolition debris, as assured through the provisions of the facility's operating plan, may be designed as unlined landfills pursuant	(a) Landfills for any waste type(s) not specifically identified in Env-Sw 805.12 through Env-Sw 805.14 shall be designed as double lined facilities ***pursuant to Env-Sw 805.05 and one of the liners shall be a composite liner pursuant to Env-Sw 805.04(c)***, except as provided by (b) below and subject to the landfilling prohibitions in Env-Sw 806.12. (b) Landfills which receive only stumps and brush~~ or only asbestos~~ ~~***waste***~~ ~~or only inert demolition debris~~, as assured	More Protective

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Criteria	**Current Rules 2014 – 2024**	**3/8/24 NHDES Draft**	**More Protective; Neutral; Less Protective**
	to Env-Sw 805.02(b).	through the provisions of the facility's operating plan, may be designed as unlined landfills pursuant to Env-Sw 805.02(b).	🟩
Env-Sw 805.17	(a) No permit shall be granted for vertical expansion of a landfill, as defined in Env-Sw 104.61 unless: (1) The existing landfill is equipped with a double liner system meeting the requirements of Env-Sw 805.05; or (2) The vertical expansion incorporates a double liner system meeting the requirements of Env-Sw 805.05 over the existing landfill. (b) All mechanically-stabilized earth berms used to retain waste within the vertical expansion of a landfill shall be: (1) Designed with a static factor of safety of at least 1.5 against overturning and sliding; (2) Constructed on a stable foundation as demonstrated by calculations and geotechnical investigation; and (3) Separated from stored waste by a double liner system meeting the requirements of Env-Sw 805.05.	(a) No permit ***or permit modification*** shall be granted for vertical expansion of a landfill, as defined in Env-Sw 104.61 unless: (1) The existing landfill is equipped with a double liner system meeting the requirements of Env-Sw 805.05;***,*** or (2) T***t***he ***proposed*** vertical expansion incorporates a double liner system meeting the requirements of Env-Sw 805.05 over the existing landfill***; or*** ***(3) For landfills receiving MSW, the existing landfill is equipped with a double liner system permitted prior to the 2024 readoption of this chapter, and there is no evidence of release(s) of contaminants through the liner system(s) to the environment or other damage to the liner system(s).*** ***(2b) Stability and settlement assessments required pursuant to Env-Sw 805.11(n) shall be performed, at a minimum, for the existing landfill prior to vertical expansion; for the combined existing landfill and vertical expansion during construction and operation; and for the combined existing landfill and vertical expansion at full capacity.;*** ***(3) Settlement calculations are performed pursuant to Env-Sw 805.11(q) for the combined existing landfill and vertical expansion at full capacity; and*** ***(4) Groundwater monitoring can be accomplished as required in accordance with this chapter and pursuant to RSA 485-C*** ~~(b) All mechanically-stabilized earth berms used to retain waste within the vertical expansion of a landfill shall be:~~	Neutral

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Criteria	**Current Rules 2014 – 2024**	**3/8/24 NHDES Draft**	**More Protective; Neutral; Less Protective**
		~~(1) Designed with a static factor of safety of at least 1.5 against overturning and sliding;~~ ~~(2) Constructed on a stable foundation as demonstrated by calculations and geotechnical investigation ; and~~ ~~(3) Separated from stored waste by a double liner system meeting the requirements of Env-Sw 805.05.~~	🟨
Env-Sw 806.05	(1) Routine facility operations, including operations during the 25-year storm event, shall not result in more than one foot of hydraulic head on the liner system(s);	(1) Routine facility operations, including operations during the 25-year storm event ***and snow melt infiltration plus 20 percent***, shall not result in more than one foot of hydraulic head on the liner system(s);	More Protective
Env-Sw 806.08	(k)(3) Except for flow which the department agrees is the result of the dewatering of the drainage layer following construction, rates which exceed 100 gallons per tributary acre per day shall require the permittee to file an investigation report with the department in accordance with Env-Sw 806.09.	(l)(3) ~~Except for flow which the department agrees is the result of the dewatering of the drainage layer following construction,~~ r***R***ates which exceed ~~100~~***50*** gallons per tributary acre per day shall ~~require the permittee to file an investigation report with the department in accordance with Env-Sw 806.09~~.***:*** ***a. Be reported to the department in accordance with Env-Sw 1005.09; and*** ***b. Require the permittee to submit to the department a response action plan within 30 days of submitting the report required by a. above.*** ***(m) The response action plan required by (l)(3) above:*** ***(1) Shall include:*** ***a. Confirmation of the source and cause(s) of the increase in flow;*** b. Response actions to address the cause(s); and ***c. A schedule for implementing the response action plan; and*** ***(2) May include but is not limited to the following actions:***	More Protective

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Criteria	Current Rules 2014 – 2024	3/8/24 NHDES Draft	More Protective; Neutral; Less Protective
		a. Increasing monitoring and reporting;	🟩

Exhibit B

Env-Sw 800 NHDES DRAFT Solid Waste Rules with Recommended Language, Supporting References & Notes

Criteria	3/8/24 NHDES DRAFT	NCABC Recommended Language
Groundwater Protection Standards: Env-Sw 804.02 (a) – (d)	(b) A landfill and all associated ***stormwater,*** leachate storage units, ***and decomposition gas infrastructure*** shall be located only in areas where groundwater monitoring for release detection, characterization and remediation can be conducted prior to a release having an adverse ~~affect~~ ***impact*** on ***groundwater quality at the property line or*** a water supply. ***(c) Undisturbed in-situ soils for 5 feet immediately beneath the footprint shall have an average saturated hydraulic conductivity of ~~1~~5 x*** 10^{-3} ***centimeters per second (cm/sec) or less.*** ***(d) The base of the bottom most liner system, or the base of the facility if unlined, shall be a minimum of 6 feet above the seasonal high groundwater table and the confirmed bedrock surface.*** (~~c~~***e***) Identification of the areas cited in (b) ***through (d)*** above shall be based upon a hydrogeologic investigation which provides all site-specific information required to model the pre-construction and post-construction groundwater and surface water regimen***, and other information as necessary to demonstrate compliance with the siting criteria***.	(b) A landfill and all associated ***stormwater,*** leachate storage units, ***and decomposition gas infrastructure*** shall be located only in areas where groundwater monitoring for release detection, characterization and remediation can be conducted prior to a release having an adverse ~~affect~~ ***impact*** on ***groundwater quality at the property line or*** a water supply. ***(c) The minimum in-situ groundwater travel time between a release and the closest surface water receptor for any landfill site is 5 years, measured between the edge of waste or leachate handling area and closest surface water receptor, whichever is closest. Travel time is determined from groundwater flow based on the geometric mean of representative in-situ hydraulic conductivity field tests with, conservatively, no attenuation.*** ***~~(c)~~ (d) Undisturbed in-situ soils for 5 feet immediately beneath the footprint and infrastructure area shall have an average saturated hydraulic conductivity of ~~15 x 10-3~~ 1 x*** 10^{-4}***centimeters per second (cm/sec) or less.*** ***~~(d)~~ (e) The base of the bottom most liner system, or the base of the facility if unlined, shall be a minimum of ~~6~~ 8 feet above the seasonal high groundwater table and the confirmed bedrock surface.*** ~~(c~~***e***) (f) Identification of the areas cited in (b) ***through (~~d~~e)*** above shall be based upon a ***comprehensive*** hydrogeologic investigation which provides all site-specific information required to model the pre-construction and post-construction groundwater and surface water regimen***, including nearby bedrock water supplies, and other sensitive receptors as applicable to demonstrate compliance with the siting criteria***.
Surface Water Protection Standards: Env-Sw 804.03 (b)	(b) A landfill and all associated ***stormwater,*** leachate storage units***, and decomposition gas infrastructure*** shall be located only in areas where potential adverse ~~effects~~***impacts*** to surface water quality, due to erosion, sedimentation, siltation, flood, or discharge of contaminants, can be prevented or minimized and mitigated by facility design.	(b) A landfill and all associated ***stormwater,*** leachate storage units***, and decomposition gas infrastructure*** shall be located only in areas where potential adverse ~~effects~~***impacts*** to surface water quality, due to erosion, sedimentation, siltation, flood, or discharge of contaminants, can be prevented or minimized and mitigated by facility design, ***including the requirement that leachate storage and handling areas be constructed in areas underlain by the same liner system required for waste disposal described in Env-Sw 805.***
Env-Sw 804.03 (c)	(c) A landfill and associated stormwater, leachate, and decomposition gas infrastructure shall be located such that a discharge, spill, leachate release or other failure of the waste containment system or associated infrastructure will be detected and assessed, and	(c) A landfill and associated stormwater, leachate, and decomposition gas infrastructure shall be located such that a discharge, spill, leachate release or other failure of the waste containment system or associated infrastructure will be detected and assessed, and remediation initiated **prior to** contamination reaching any perennial water body, ***as determined by a minimum 5-year travel time***

Criteria	3/8/24 NHDES DRAFT	NCABC Recommended Language
	remediation initiated **prior to** contamination reaching any perennial water body.	***between the spillage and the closest perennial water body, as determined in Env-Sw 804.***
Env-Sw 804.03(d)	(d) The footprint of a landfill shall not be located within***:*** ***(1)*** 200~~***500***~~ feet of any ***first or second order*** perennial ***stream; and*** ***(2) 500 feet of any other perennial*** surface water body, measured from the closest bank of a stream and closest shore of a ***pond or*** lake, as applicable.	(d) The footprint of a landfill, ***including the location of its leachate storage and handling infrastructure, shall not be located within a 5-year travel time of any*** ~~***(1)*** 200***500*** feet of any ***first or second order*** perennial ***stream; and***~~ ~~***(2) 500 feet of any other***~~ ***perennial*** surface water body, measured from the closest bank of a stream and closest shore of a ***pond or*** lake, as applicable. ***Travel time is determined as described in Env Sw 804.***
Env-Sw 804.03 (e)- (f)	(e) The footprint of a landfill shall not be located within 200 feet ~~upgradient and 100 feet downgradient~~ of a wetland within the jurisdiction of RSA 482-A, excluding any drainage appurtenances related to the site, that is not allowed to be filled under the authority of RSA 482-A. (f) The footprint of a landfill shall not be located within 1,000 feet ~~upgradient~~ of a surface water reservoir or intake used for a community drinking water supply.	(f) The footprint of a landfill shall not be located within ~~1,000 feet upgradient~~ ***5-year travel time*** of a surface water reservoir or intake used for a community drinking water supply. ***The travel time is determined as described in Env Sw 804.***
Env-Sw 804.03 (h)	***(h) Identification of the areas cited in (a) through (g) above shall be based on a thorough hydrogeological investigation to demonstrate the following:*** ***(1) Compliance with the siting requirements of Env-Sw 804.02 and Env-Sw 804.03;*** ***(2) That engineering design measures can be incorporated to control erosion, sedimentation, and siltation; and*** ***(3) Any potential release of contaminants to surface waters can be prevented or, in the case of a release, detected and remediated.***	***(3) Any potential release of contaminants to surface waters can be prevented or, in the case of a release, detected and remediated prior to reaching a surface water resource.***
Env Sw 805.06 (j)	(~~j~~***k***) Pipes which require solvent welding ~~shall not~~ ***may only*** be used ***in leachate vaults*** ~~***that provide secondary containment and are***~~ ***equipped with a high-water alarm, a backup high-water alarm, and automatic dialers in accordance with (q) below***. (~~k~~***l***) The ***granular soil*** drainage blanket ***materials in the liner system***	(~~j~~***k***) Pipes which require solvent welding ~~shall not~~ ***may only*** be used ***in leachate vaults that provide secondary containment and are equipped with a high-water alarm, a backup high-water alarm, and automatic dialers in accordance with (q) below***.
Env Sw 805.06 (p)(q)	(~~o~~***p***) Pump stations located outside the waste deposition area shall be designed to provide the following: (1) Backup pumping capacity; (2) Backup power supply; (3) High-water alarm; and	(~~p~~***q***) Tanks, sumps, ~~or~~***and*** other storage units associated with leachate collection and removal systems shall be ***co-located with the same leak detection liner system as required for waste disposal as specified in Env Sw 805 and be*** equipped with high-water alarms***, backup high-water alarms, and automatic dialers***.

Criteria	3/8/24 NHDES DRAFT	NCABC Recommended Language
	(4) Backup high-water alarm; ***(5) Alarms to automatic dialer; and*** (~~4~~***6***) Efficient operation during both average and peak flows. (~~p~~***q***) Tanks, sumps, ~~or~~***and*** other storage units associated with leachate collection and removal systems shall be equipped with high-water alarms***, backup high-water alarms, and automatic dialers***.	
Env Sw 805.06	***(r) Pipes, tanks, sumps, and other conveyance or storage units associated with leachate collection and removal systems outside the waste deposition area shall have secondary containment or be double-walled except for underground pipes, manholes and other buried leachate systems existing prior to the 2024 readoption of this chapter.***	***(r) Pipes, tanks, sumps, and other conveyance or storage units associated with leachate collection and removal systems located outside the waste deposition area shall be co-located with the same leak detection liner system as required for waste disposal and have secondary containment or be double-walled except for underground pipes, manholes, and other buried leachate systems existing prior to the 2024 readoption of this chapter.***

Notes:

The proposed language for Env-Sw 804.02 (c) states that "*Undisturbed in-situ soils for 5 feet immediately beneath the footprint shall have an average saturated hydraulic conductivity of 5 x 10^{-3} centimeters per second (cm/sec) or less*". A hydraulic conductivity of 5 x 10^{-3} cm/s is more than 14 feet per day or about one mile per year. This amount of conductivity is typical of sands, which are used to drain water. Specifically, the design standards for the landfill capping system [Env-Sw 805.10(e)(4)c] refers to a "free-draining sand layer with saturated hydraulic conductivity of no less than 1 x 10^{-3} cm/sec" which will drain the water that infiltrates through the topsoil on the landfill cover. The conductivity specified for the in-situ soil beneath the landfill is five times more permeable than the infiltration layer on the top. This kind of material is <u>not suitable</u> for acting as a barrier that is supposed to impede the flow of leachate that might flow out of the landfill in the event of a leak.

For reference, the regulations in the states neighboring NH have requirements which are more stringent, and they apply to subsurface geohydrologic conditions that are generally similar to those found in NH. Maine: Chapter 401 (1)(C)(3b)] requires "The in-situ soils must have an undisturbed hydraulic conductivity less than or equal to 1 x 10^{-5} cm/sec." The new proposed NHDES Rules language would make a site in NH 500 times more permeable than a site in Maine. Vermont: Subchapter 7, Section 6-703(b)(4) "Minimum criteria for a landfill facility are based on underlying soils with a maximum permeability of 1 x 10^{-4} cm/sec. Landfill sites with more permeable soils will be evaluated on a case by case basis, but are generally not acceptable."

In my professional opinion (Dr. Anirban De, P.E.), the hydraulic conductivity of the undisturbed in-situ soil at the landfill site should be no more than 1 x 10^{-4} cm/sec for the composite liner system to be effective in protecting environment from leachate incursion.

Authoritative sources in technical literature recommend siting landfills over soil with low hydraulic conductivity because "[s]*trata with low hydraulic conductivity limit rate of downward and lateral movement of escaped leachate and possible contamination of underlying aquifer (if present)*" – Qian et al. (2002). Other technical experts have made similar recommendations, e.g., Sharma and Reddy (2004), Sharma and Lewis (1994), and Oweis and Khera (1998). An average hydraulic conductivity of 5 x 10^{-3} cm/sec, as recommended by the NHDES proposed language, is considered a medium to high hydraulic conductivity relative to landfills. Similarly, a low hydraulic conductivity relative to landfills would be 1 x 10^{-4} cm/sec or smaller.

References Generally Supportive of NCABC Proposed Language:

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2) Madon, I., D. Drev, and J. Likar (2019). “Long-Term Risk Assessments Comparing Environmental Performance of Different Types of Sanitary Landfills.” *Waste Management,* 96: 96-107.

3) Regadio, M., J.A. Black, and S.F. Thornton (2020). “The Role of Natural Clays in the Sustainability of Landfill Liners.” *Detritus: Multidisciplinary Journal for Waste Resources and Residues,* available at (doi.org) 10.31025/2611-4135/2020.13946.

4) Rowe, R.K., H. Sangam, and C. Lake (2003). “Evaluation of an HDPE Geomembrane after 14 Years as a Leachate Lagoon Liner.” *Canadian Geotechnical Journal,* 40(3): 536-550.

5) Staley, Brian, Ph.D., P.E., “Per- and Polyfluoroalkyl Substances (PFAS) in Solid Waste,” Environmental Research & Education Foundation/US Composting Council, 2019.

6) Melvin, R.L., De Lima, V, and Stone, B. D. (1992). “The Stratigraphy and Hydraulic Properties of Tills in Southern New England.” US Geological Survey Open-File Report 91-481.

7) Moore, Richard Bridge, (2004). Quality of Water in the Fractured Bedrock Aquifer of NH, Scientific Investigations Report 2004-5093, US Geological Survey, 30p.

8) Migration behavior of landfill leachate contaminants through alternative composite liners": https://www.sciencedirect.com/science/article/pii/S0048969711004323 Varank, et al (2011), Science of the Total Environment, Science Direct.

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10) Keros Cartwright, Robert A. Griffin, and Robert H. Gilkeson (1977) Migration of Landfill Leachate Through Glacial Tills; Groundwater Vol 15, No 4.

11) Griffin, R.A. and Shimp, N.F, 1976, Attenuation of Pollutants in Municipal Landfill Leachate by Clay Minerals, EPA 68-03-0211.

12) Hinton, MJ, Schiff, SL, English, MC (1993) Physical Properties Governing Groundwater Flow in a Glacial Till Catchment, Journal of Hydrology, vol 142, Feb 1993.

13) "Fractured Bedrock Aquifer Hydrogeologic Characterization for a Bioaugmentation Pilot Study," P. Jeffers and V. Wittig, GeoSyntec Consultants, Contaminated Site Clean-Up Information, Environmental Protection Agency, Technology Innovation Program, http://www.cluin.org/products/siteprof/2004fracrockconf/cdr_pdfs/indexed/group1/148.pdf.

14) Danthurebandara, M et al, 2012 Environmental and Socio-Economic Impacts of Landfills, ECO-TECH November, 2012.

References Specifically Supporting Siting Landfills Over Soil of Low Hydraulic Conductivity:

15) Sharma, H. D. and Lewis, S., P. (1994). "Waste Containment Systems, Waste Stabilization, and Landfills: Design and Evaluation": published by John Wiley, ISBN 0-471-21599-6.

16) Sharma, H.D. and Reddy, K. R. (2004). Geoenvironmental Engineering: Site Remediation, Waste Containment, and Emerging Waste Management Technologies, published by John Wiley, ISBN 978-0471575368.

17) Oweis, I. S. and Khera, R. P. (1998) "Geotechnology of Waste Management," by I.S. Oweis and R.P. Khera, published by PWS, ISBN 0534945244.

18) Qian, X., Koerner, R. M., and Gray, D. H. (2002) "Geotechnical Aspects of Landfill Design and Construction," published by Prentice Hall, ISBN 0130125067.

Major Takeaways From Technical Literature:

Landfill liners have limitations preventing the migration of contaminants in leachate from entering the subsurface and, eventually, groundwater. Liners exhumed from the ground after many years in the field have exhibited deteriorations in some cases. [Rowe, et al. (2003); Reference 4]

Though engineered composite liners (combination of geomembrane and clay or geosynthetic clay liner) are more protective of groundwater than a clay liner alone, a landfill with composite liner that is located over a natural clay deposit can better protect the environment because of the ability of the clay minerals to attenuate the contaminants to some extent. [Regadio, et al (2020), Rowe, et al. (2003); References 3 and 4]

Exhibit B

The NH proposed rules change would permit landfills to be built over natural deposits that may have hydraulic conductivity values as high as $5x10^{-3}$ cm/sec, which is typical of sand. Sand does not have any capacity to attenuate contaminants the way clay can. In some states (e.g., neighboring Maine), the maximum hydraulic conductivity of the in-situ soil at a landfill site must be less than 1×10^{-5} cm/sec, which is typical of clay. As has been extensively reported in technical literature, clay has a capacity to naturally attenuate contaminants and thus be protective of surrounding water resources from migrating leachate.

Exhibit C

Multi-State Comparison of Landfill Siting Requirements

Siting Requirement	New Hampshire (current rules 2014 - 2024)	Maine	Vermont	Massachusetts	Rhode Island
Groundwater Buffer	6′ (Seasonal high groundwater table) (Env-Sw 804.02(d))	May not lie over or be within 300′ of a significant sand and gravel aquifer (CMR 06-096-401(1)(C)(2)(b))	Prohibited (Class I & II Groundwater Areas) (CVR 12-036-003 § 6-702(a)(1)) 6′ (High Seasonal Water Table) (CVR 12-036-003 § 6-703, Table B) 10′ (Bedrock) (CVR 12-036-003 § 6-703, Table B)	Prohibited (Potentially Productive Aquifers; Threat of an adverse impact to groundwater through discharge of leachate) (310 CMR 16.40(3)(a)(10), (16)) 4′ (Maximum high groundwater table) (310 CMR 16.40(3)(a)(12))	Prohibited (If likely to cause pollution of groundwater; Where solid waste may be in direct contact with groundwaters) (250 RICR 140-05-2.3.5(A)(1), (C)(1)) 5′ (Highest water table level) (250 RICR 140-05-2.3.5(C)(1))
Wetland Buffer	200′ upgradient, 100′ downgradient (Env-Sw 804.03(e))	Prohibited (Coastal wetland) (CMR 06-096-401(1)(C)(2)(d))	Prohibited (Class I-III wetlands & buffer zones) (CVR 12-036-003 § 6-702(a)(2)-(4))	Prohibited (Resource area protected by the Wetlands Protection Act) (310 CMR 16.40(3)(a)(13))	Prohibited (250 RICR 140-05-2.3.14(B))
Surface Water Buffer	1,000′ upgradient (Env-Sw 804.03(f))	100′ (Classified Surface Water) (CMR 06-096-401(1)(C)(3)(a)(v)) 1,000′ (Water Supply Spring) (CMR 06-096-401(1)(C)(3)(a)(vi))	Prohibited (River Corridors, Watershed for Class A Waters) (CVR 12-036-003 § 6-702(a)(9)-(10)) 500′ (Outstanding Resource Water)	400′ upgradient (Perennial water course that drains to a surface drinking water supply) (310 CMR 16.40(3)(a)(9)) 400′ to a lake, 200′ to a Riverfront Area (310 CMR 16.40(3)(a)(14))	Prohibited (If likely to cause pollution of surface waters) (250 RICR 140-05-2.3.5(A)((1)) 200′ (Any surface water) (250 RICR 140-05-2.3.5(B)(1))

Siting Requirement	New Hampshire (current rules 2014 - 2024)	Maine	Vermont	Massachusetts	Rhode Island
		1,000′ (Class AA or Class SA waters) (CMR 06-096-401(1)(C)(2)(a))	(CVR 12-036-003 § 6-702(a)(11)) 300′ (Minimum Distance to Waters) (CVR 12-036-003 § 6-703, Table B)		1,200′ (Any river) (250 RICR 140-05-2.3.5(B)(1))
Flood Hazard	Not within 100-year flood hazard zone (Env-Sw 804.03(g))	Not within 100-year floodplain (CMR 06-096-401(1)(C)(3)(d))	Prohibited (Floodways, Special Flood Hazard Areas, Mapped Fluvial Erosion Hazard Zones, 100-year floodplain) (CVR 12-036-003 §§ 6-702(a)(8); 6-1003(3)(B))	Prohibited (100-year floodplain) (310 CMR 16.40(3)(a)(13))	Prohibited (100-year floodplain) (250 RICR 140-05-2.3.14(A))
Property Line Buffer	100′ (Env-Sw 804.04(a))	300′ (CMR 06-096-401(1)(C)(3)(a)(ii))	300′ (CVR 12-036-003 § 6-703, Table B)	100′ (310 CMR 16.40(4)(h))	600′ (250 RICR 140-05-2.3.12)
Road Buffer	Class I & II = 300′ Class III-VI = 100′ (Env-Sw 804.04(b))	300′ (All Public Roads) (CMR 06-096-401(1)(C)(3)(a)(i))	300′ (Public Highways) (CVR 12-036-003 § 6-1003(a)(2)) Must be accessible from a state or federal highway or Class III or better town highway (CVR 12-036-003 § 6-703(b)(6))	Prohibited (If traffic impacts would constitute a danger to the public health, safety, or the environment) (310 CMR 16.40(4)(b))	N/A
Residential Buffer	500′ vegetated (Env-Sw 804.04(d))	1,000′ (CMR 06-096-401(1)(C)(3)(a)(iii))	1,000′ (CVR 12-036-003 § 6-703, Table B)	1,000′ (310 CMR 16.40(3)(a)(15))	Must maintain an undeveloped, vegetated buffer

Siting Requirement	New Hampshire (current rules 2014 - 2024)	Maine	Vermont	Massachusetts	Rhode Island
				Prohibited (Certain agricultural lands) (310 CMR 16.40(4)(a))	zone area that serves to mitigate nuisance impacts such as dust, litter, odor, and noise from the facility to human activities (250 RICR 140-05-1.9(P))
Airport Buffer	Turbojet = 10,000' Piston = 5,000' (Env-Sw 804.04(e))	Landfill must not pose a bird hazard to aircraft (10,000' for turbojet, 5,000' for piston) (CMR 06-096-401(1)(C)(1)(b))	Landfill must not pose a bird hazard to aircraft (10,000' for turbojet, 5,000' for piston) (CVR 12-036-003 § 6-1006(b)(12))	Prohibited (Where bird hazards to air traffic would pose a danger to public health and safety) (310 CMR 16.40(4)(g))	Landfill must not pose a bird hazard to aircraft (10,000' for turbojet, 5,000' for piston) (250 RICR 140-05-2.3.19)
Geologic Buffer	200' (From faults that have displaced in Holocene time) (Env-Sw 804.05(a))	200' (From faults that have displaced in Holocene time) (CMR 06-096-401(1)(C)(2)(c))	Seismic Impact Analysis OR demonstration that landfill is outside of a seismic impact zone (CVR 12-036-003 § 6-1006(b)(5))	200' (From faults that have displaced in Holocene time) (310 CMR 19.038(2)(d)(4)) Prohibited (Seismic impact zones) (310 CMR 19.038(2)(d)(2)) Landfills in unstable areas must incorporate engineering measures that ensure the integrity	200' (From faults that have displaced in Holocene time) (250 RICR 140-05-2.3.20) Prohibited (Seismic impact zones) (250 RICR 140-05-2.3.21) Landfills in unstable areas must incorporate engineering measures that ensure the integrity

Siting Requirement	New Hampshire (current rules 2014 - 2024)	Maine	Vermont	Massachusetts	Rhode Island
				of structural components (310 CMR 19.038(2)(d)(3))	of structural components (250 RICR 140-05-2.3.22)
Property Ownership Required?	Yes, but can be a lease, easement, or other legal right (Env-Sw 804.06; 1003.03(a))	N/A	Yes (Fee simple title or a lease agreement) (CVR 12-036-003 § 6-504(c)(5))	No (But fee simple owner must sign application) (310 CMR 16.08(5)(e))	No, but the real property owner must certify that he allows the operation and is the guarantor of proper closure (250 RICR 140-05-1.7(E)(3))
Distance to Other Solid Waste Facility	"Shall not physically interfere" (Env-Sw 1003.01)	N/A	N/A	Preferential consideration given to sites located in municipalities in which no existing landfill is located and in municipalities not already participating in a regional disposal facility (310 CMR 16.40(4)(j), (l))	N/A
Easements and Rights-of-Way Allowed?	Yes, but must not adversely affect facility's ability to meet all requirements (Env-Sw 1003.03(b))	N/A	N/A	N/A	N/A
Other Activities Allowed?	Yes, as long as the activity does not interfere with the facility operating in compliance	N/A	N/A	N/A	N/A

Exhibit C

Siting Requirement	New Hampshire (current rules 2014 - 2024)	Maine	Vermont	Massachusetts	Rhode Island
	(Env-Sw 1102.02)				
Sand Dune Buffer	N/A	Prohibited (Coastal sand dune) (CMR 06-096-401(1)(C)(2)(d))	N/A	N/A	N/A
Mountain Buffer	N/A	Prohibited (Fragile mountain areas) (CMR 06-096-401(1)(C)(2)(d))	Prohibited (Areas with highly erodible soils or steep slopes) (CVR 12-036-003 § 6-703(b)(5))	N/A	Sedimentation and erosion control plan must identify all areas of disturbed, erodible, non-vegetated, non-stable soils (250 RICR 140-05-2.1.4(A)(1))
Time of Travel to Sensitive Receptors	N/A	Landfill = >6 years; Leachate Storage = >3 years (CMR 06-096-401(1)(C)(1)(c))	N/A	N/A	N/A
Sand/Gravel Deposit Buffer	N/A	100’ (CMR 06-096-401(1)(C)(3)(a)(iv))	N/A	N/A	N/A
Well/Drinking Water Buffer	Prohibited (Well head protection area of a community or non-community, non-transient water supply well system; Sanitary protective area of a public water system well) (Env-Sw 804.02(a), 1003.04(c)) 1,000’ upgradient	1,000’ (CMR 06-096-401(1)(C)(3)(a)(vii))	1,000’ (CVR 12-036-003 § 6-703, Table B) Prohibited (Source Protection Areas) (CVR 12-036-003 § 6-1003(a)(3)(C))	15,000’ upgradient (Existing public water source well or proposed drinking water source area) (310 CMR 16.40(3)(a)(4)) 1,000’ upgradient, 500’ otherwise (Private water supply well) (310 CMR 16.40(3)(a)(11)) Prohibited	Prohibited (Watershed of any surface public water supply; Drainage areas of surface public water supplies; Ground overlying groundwater reservoirs or recharge areas) (250 RICR 140-05-2.3.5(B), (D)(1)) 400’

Exhibit C

Siting Requirement	New Hampshire (current rules 2014 - 2024)	Maine	Vermont	Massachusetts	Rhode Island
	(Surface water reservoir or intake for a community drinking water supply) (Env-Sw 804.03(f))			(Zone II area or Interim Wellhead Protection Area of an existing public water supply or a proposed drinking water source area; If any discharge from the facility would pose a danger to an existing or proposed water source area; Recharge area of a Sole Source Aquifer; Zone of contribution of an existing public water supply or proposed drinking water source area, or recharge area of a surface drinking water supply; Zone A or B of a surface drinking water supply) (310 CMR 16.40(3)(a)(1)–(3), (5)–(8))	(Existing public water supply well) (250 RICR 140-05-2.3.5(C)(2))
In-Situ Soil Hydraulic Conductivity	May not be sited in area of karstified dolomite or limestone (Env-Sw 804.05(b))	≤ 1x10^{-5} cm/sec (CMR 06-096-401(1)(C)(3)(b))	≤ 1x10^{-4} cm/sec (CVR 12-036-003 § 6-703, Table B)	≤ 1x10^{-4} cm/sec[i] (310 CMR 16.40(3)(a)(10))	N/A

Exhibit C

Siting Requirement	New Hampshire (current rules 2014 - 2024)	Maine	Vermont	Massachusetts	Rhode Island
Wildlife	The facility may not "appreciably jeopardize" the continued existence of threatened and endangered species (Env-Sw 1002.03)	Prohibited (Significant wildlife habitat) (CMR 06-096-401(1)(C)(3)(f))	Prohibited in National Wildlife Refuge, wildlife management area, and/or threatened or endangered species habitat (CVR 12-036-003 § 6-702(a)(5)-(7)) Prohibited in Green Mountain National Forest (CVR 12-036-003 § 6-1003(a)(3)(A))	Prohibited if it would have an adverse impact on Endangered, Threatened, or Special Concern species; an Ecologically Significant Natural Community; a Wildlife Management Area; state forests; state or municipal parklands or conservation land; MDC reservations; lands with conservation, preservation, agricultural, or watershed protection restrictions; conservation land owned by a private non-profit land conservation organization and open to the public (310 CMR 16.40(4)(c), (e))	Prohibited if it would cause or contribute to the taking of any endangered or threatened species or if it would cause or contribute to the destruction or adverse modification of critical habitat (250 RICR 140-05-1.9(J))

Siting Requirement	New Hampshire (current rules 2014 - 2024)	Maine	Vermont	Massachusetts	Rhode Island
Miscellaneous			"Least possible reasonable impact on the environment" (CVR 12-036-003 § 6-703(a))	Prohibited (Areas of Critical Environmental Concern) (310 CMR 16.40(4)(d))	

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[i] A landfill may not be sited over a Restricted Area (310 CMR 16.02), including a Potentially Productive Aquifer (310 CMR 16.40(3)(a)(10)), which, by definition, is hydraulic conductivities of sand (≥ $1x10^{-3}$). Therefore, by default, sites with a soil hydraulic conductivity ≤ $1x10^{-4}$ would not constitute a Restricted Area due to a Potentially Productive Aquifer. This means that Massachusetts has a functional in-situ soil hydraulic conductivity requirement of ≤ $1x10^{-4}$.

Exhibit D

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M.S.	Civil Engineering, Illinois Institute of Technology, Chicago, IL (1991)
B.C.E.(Hons.)	Civil Engineering, Jadavpur University, Calcutta, India (1989)

REGISTRATION:

Registered Professional Civil Engineer (P.E.)

California:	License Number C58889
New York:	License Number 080871

APPOINTMENTS:

School of Engineering, Manhattan College, Bronx, New York:
Interim Dean since July 2023

Civil & Environmental Engineering Department, Manhattan College, Bronx, New York:
Assistant Professor 2002-2008, Associate Professor 2008 to 2017, Professor since 2017
Associate Chairperson 2010 to 2015, Chairperson 2015-2023

The University of Sydney, Australia: Visiting Faculty Scholar at the School of Civil Engineering:
July through November 2009

Rensselaer Polytechnic Institute, Troy, New York: Visiting Assistant Professor of Civil & Environmental Engineering: June through August 2004

GeoSyntec Consultants, Walnut Creek, California: Senior Staff Engineer: 1996-1999, Assistant Project Engineer: 1999-2001, Project Engineer: 2001-2002

PROFESSIONAL EXPERIENCE:

Dr. Anirban De has thirty years of experience performing analyses and design in the field of geotechnical and geoenvironmental engineering. His current research interests include design of geosynthetic systems, site characterization, geotechnical centrifuge modeling, and settlement of landfills. Additional areas of research include physical and numerical modeling of high strain rate loading, such as effects of blasts and penetrations. His professional specialty is the design of geotechnical and geosynthetic components for a variety of geotechnical and geoenvironmental applications, as well as behavior of geotechnical systems under seismic, blasts, and other types of dynamic loading..

RESEARCH AREAS:

- Shear strength of geosynthetic components in landfill liner and cover systems
- Study of long term performance of landfill cover
- Effects of explosions on earth dams and underground structures
- High strain-rate loading of geomaterials
- Installation and pullout capacity of deep sea anchors
- Experimental modeling of geosynthetic anchor trench
- Contaminant transport through soil through centrifuge modeling
- Geotechnical site characterization and field instrumentation
- Undergraduate civil engineering curriculum development

PEER REVIEWER:

Served as reviewer for the following journals:

Journal of Geotechnical and Geoenvironmental Engineering
Journal of Performance of Constructed Facilities
Journal of Hazardous, Toxic, and Radioactive Waste
Journal of Testing and Evaluation
Journal of Earthquake Technology
Journal of Applied Clay Science
Geotechnical Testing Journal
International Journal of Rock Mechanics and Mining Sciences
Advances in Civil Engineering
Geosynthetics International
Geotextiles and Geomembranes
Environmental Geotechnics
Natural Hazards
Shock and Vibration
Waste Management

PROFESSIONAL AFFILIATIONS:

American Society of Civil Engineers / Geo-Institute
Committees: Body of Knowledge (2nd Edition), Body of Knowledge Educational Fulfillment, Geoenvironmental, Geotechnical Committee of Metropolitan (NY) Section
International Society of Soil Mechanics and Geotechnical Engineering
Accreditation Board of Engineering and Technology (ABET): Civil Engineering Program Evaluator

REPRESENTATIVE CONSULTING PROJECTS:

Engineering analyses and design

1. Annual settlement monitoring of superfund landfills: Santa Barbara County, California
2. Annual settlement monitoring of superfund landfill: Los Angeles County, California
3. Slope stability analyses for superfund landfills: Santa Barbara County, California
4. Slope stability analyses for superfund landfill: Los Angeles County, California
5. Expert consulting for design of commercial development on top of a superfund landfill site: Los Angeles County, California

Litigation support

1. Permit review for wind farm in three counties in western New York State
2. Review of engineering design for municipal solid waste landfill: Pierce County, Washington
3. Permit review for municipal solid waste landfill: Cattaraugus County, New York (including participation in public comment hearing)
4. Closure review for superfund landfill: Delaware County, New York

5. Permit review for municipal solid waste landfill: Sullivan County, New York (including expert witness testimony before Administrative Law Judge)
6. Permit review for expansion of a hazardous waste landfill: Niagara County, New York (including testifying at adjudicatory hearing)
7. Review of stability issues at landfill: Allegany County, New York
8. Permit review for landfill expansion: Chemung County, New York
9. Review of insurance claim for damage to residential property allegedly due to construction: Bronx County, New York

RESEARCH GRANTS:

1. "Manhattan College Engineering Scholarship Initiative (MCESI)", *National Science Foundation*, Award No.: 1458294 , Principal Investigator: Dr. Zahra Shahbazi, Co-Principal Investigators: Dr. Anirban De and Dr. Walter Saukin. Duration: 2015-2020.

2. "RUI: Understanding the Role of Flexible and Rigid Barriers in Mitigating Surface Blast Effects on Underground Structures", *National Science Foundation*, Award No.: 0928537, Principal Investigator: Dr. Anirban De. Duration 2009-2014.

3. Collaborative proposal with Rensselaer Polytechnic Institute (RPI): "NEESR-II: Advanced Site Monitoring and Effective Characterization of Site Nonlinear Dynamic Properties and Model Calibration", *National Science Foundation*, Award No.: 0830325, Principal Investigator: Dr. Mourad Zeghal, Co-Principal Investigator: Dr. Tarek Abdoun and Dr. Anirban De. Duration: 2008-2014.

4. "Developing a Curriculum Incorporating the Civil Engineering Body of Knowledge and Sustainable Design through an Active Urban Laboratory", *National Science Foundation*, Award No.: 0530606, Principal Investigator: Dr. Moujalli Hourani, Co-Principal Investigator: Dr. Anirban De. Duration: 2005-2009.

5. Collaborative proposal with Rensselaer Polytechnic Institute (RPI): "Surface Blast Effects on Tunnels and Pipelines", received Research Opportunity Award from the *National Science Foundation* for research in collaboration with RPI. Principal Investigator: Dr. T. F. Zimmie (RPI). Dr. Anirban De – Visiting Assistant Professor at RPI. Duration: Summer 2004.

PUBLICATIONS: (* Indicates undergraduate student co-author, $^+$ indicates graduate student co-author)

Book (authored)

"*Geotechnical Site Characterization*", Momentum Press, New York, 217 pages, 2016.

Book (edited)

"Geoenvironmental Practices and Sustainability: Linkages and Directions" Springer, 290 pages, ISBN: 978-981-10-4076-4, pages, 2017. (with G.L.S. Babu, K.R. Reddy, and M. Datta)

Book Chapter

"Site Characterization of Landfills Through In Situ Testing" in *Geoenvironmental Practices and Sustainability: Linkages and Directions* (Springer), pages 99-106, 2017.

Articles in Peer-reviewed Journals

"Effects of aging and temperature on milling-induced stresses and cracks in Hot Mix Asphalt (HMA) pavements", in Construction and Building Materials, (Elsevier), Vol. 313, DOI: https://doi.org/10.1016/j.conbuildmat. 2021.125493, 2021. (with K. Diouri+, E.V. Dave, J. Sias, and R. B. Mallick)

"Pore-pressure development near tunnel due to underwater explosion from centrifuge tests", by Anirban De, Anthony Niemiec, and Thomas F. Zimmie, in International Journal of Physical Modelling in Geotechnics, ICE, Vol. 21, No. 5, doi: DOI: 10.1680/jphmg.19.00037. 2021. (with A. Niemiec* and T. F. Zimmie)

"Physical and Numerical Modeling to Study Effects of an Underwater Explosion on a Buried Tunnel", *Journal of Geotechnical and Geoenvironmental Engineering*, ASCE, Vol. 143, No. 5, 2017. (with A. Niemiec* and T. F. Zimmie)

"Effects of surface explosion on underground tunnel and potential mitigation measures", *Transportation Infrastructure Geotechnology*, (Springer), Vol. 3, No. 2, pp. 74-90. 2016. (with Thomas F. Zimmie)

"Numerical and physical modeling of geofoam barriers as protection against effects of surface blast on underground tunnels", *Geotextiles and Geomembranes*, (Elsevier), Vol. 44, pp. 1-12. 2016. (with Alberto N. Morgante* and Thomas F. Zimmie)

"Numerical simulation of surface explosions over dry, cohesionless soil", *Computers and Geotechnics* (Elsevier), Vol. 43, pp. 72-79, 2012.

"Municipal Solid Waste Landfill Settlement: Postclosure Perspectives", *Journal of Geotechnical and Geoenvironmental Engineering*, ASCE, Vol. 133, No. 6, June 2007 (with H. D. Sharma)

"Centrifuge Modeling of Surface Blast Effects on Underground Structures", *Geotechnical Testing Journal*, ASTM, Vol. 30, No. 5, September 2007 (with T. F. Zimmie)

"CPT-based seismic stability assessment of a hazardous waste site", *Soil Dynamics and Earthquake Engineering*, Special Issue, (Elsevier), Vol. 26, No. 2-4, February-April 2006, pp. 201-208 (with N. Matasovic, E. Kavazanjian, and R. J. Dunn)

"Estimation of Dynamic Interfacial Properties of Geosynthetics", *Geosynthetics International*, Earthquake Engineering Special Issue, 1998, Vol. 5, Nos. 1-2, pp. 17–39 (with Thomas F. Zimmie).

"Application of Geotechnical Centrifuge Testing to Evaluate Unconventional Highway Materials", *Transportation Research Record*, National Research Council, Washington D.C., No. 1577, pp. 96-100, 1997 (with T. F. Zimmie).

"Accelerated Groundwater Transport Studies Using a Geotechnical Centrifuge", *Transportation Research Record*, No. 1434, Washington, D.C. 1994, pp. 47-54, (with T. F. Zimmie and M. B. Mahmud).

"Accelerated Physical Modelling of Radioactive Waste Migration in Soil", *Canadian Geotechnical Journal*, October 1994, Vol. 31, No. 5, pp. 683-691, (with T. F. Zimmie and M. B. Mahmud).

Articles in Peer-reviewed Conference Proceedings

"A Study on the Effect of Milling on Stress Distributions in Asphalt Pavements" in Proceedings of the 9th International Conference on Maintenance and Rehabilitation of Pavements—Mairepav9, Zurich, Switzerland, 2020. (With K. Diouri, R. Bousselham, A. Hera, T. El-Korchi, and R. Mallick).

"Study of the effects of explosion on a buried tunnel through centrifuge model tests", published in *Physical Modelling in Geotechnics*, edited by McNamara et al. pp. 779-784, London, U.K. 2018 (with Thomas F. Zimmie)

"Response of Tunnel in Saturated Soil to an Underwater Explosion", published in Poromechanics VI, *Proceedings of the Sixth Biot Conference on Poromechanics*, pp. 1507-1515. ASCE, Paris, France. 2017 (with Thomas F. Zimmie)

"Pull-Out Capacity Analysis of Offshore Torpedo Anchors Using Finite-Element Analysis", published in *Proceedings of the Twenty-fifth (2015) International Ocean and Polar Engineering Conference*, pp. 1042-1047, Kona, Hawaii. 2015 (with David Pecorini^{+})

“Installation and Load Capacity of Torpedo Anchors in Offshore Applications”, published in *GeoCongress 2015, Geotechnical Special Publication*, ASCE, pp. 792-801, San Antonio, Texas. 2015 (with David Pecorini+ and Alberto Morgante*)

“Modeling the effects of surface blast on underground structures with or without protective barriers” session titled “Performance of Transportation Geosystems Under Service and Extreme Loading Conditions”, *Compendium of the 93rd Annual Meeting of Transportation Research Board* in Washington D. C. 2014 (with Alberto N. Morgante* and Thomas F. Zimmie)

“Mitigation of blast effects on underground structure using compressible porous foam barriers”, published in Poromechanics V, *Proceedings of the Fifth Biot Conference on Poromechanics*, ASCE, Vienna, Austria. 2013 (with Alberto N. Morgante* and Thomas F. Zimmie)

“Effects of Surface Explosions on Top of Earth Embankment Dams”, published in *GeoCongress 2013, Geotechnical Special Publication*, ASCE, pp. 444-447, San Diego, California. 2013 (with Sean Butler*)

“Undergraduate Geotechnical Lesson Modules Based on New Orleans Levee Failures”, published in *GeoCongress 2012, Geotechnical Special Publication*, ASCE, Oakland, California. pp. 1273-1282, 2012

“Modeling of Surface Blast Effects on Underground Structures”, *Proceedings of GeoFrontiers 2011,* ASCE, Dallas, Texas, page 1534-1543 (with R. Conry*)

“Physical Modeling of Explosive Effects on Tunnels”, *Proceedings of the Fourth International Symposium on Tunnel Safety and Security*, Frankfurt, Germany, pages 159-167. 2010 (with T. F. Zimmie, T. Abdoun, and A. Tessari)

“Centrifuge Modeling of Explosion Craters Formed Over Underground Structures”, *GeoCongress 2008: Geosustainability and Geohazard Mitigation*, New Orleans, Lousiana. Geotechnical Special Publication 178, ASCE, pp. 311-318, 2008.

“Modeling of Surface Blast Effects on Underground Structures”, *Proceedings of GeoCongress 2006*, ASCE, Atlanta, Georgia (with T. F. Zimmie)

“Centrifuge Experiments to Study Surface Blast Effects on Underground Pipelines”, *Proceedings of Pipelines 2005*, ASCE, Houston, Texas, August 2005. (with T. F. Zimmie and K. E. Vamos*)

“Experimental and Numerical Modeling of Geosynthetic Anchor Trench”, *Proceedings of GeoFrontiers 2005*, ASCE, Austin, Texas, January 2005. (with D. A. Vellone+)

“Undergraduate Geotechnical Education, 2004", *Proceedings of GeoFrontiers 2005*, ASCE, Austin, Texas, January 2005. (with G. Mullen, A. K. Ashmawy, P. J. Culligan, M. Mauldon, F. C. Townsend, and A. Welker).

"Site Characterization of Five Hazardous Waste Landfills", *Proceedings of the International Site Characterization Conference, ISC’2,* Porto, Protugal, September, 2004 (with N. Matasovic and R. J. Dunn).

“Site Characterization, Design, and Construction for Closure of Four Hazardous Waste Landfills at a Superfund Site”, *Proceedings of the Fifth International Conference on Case Histories in Geotechnical Engineering*, New York, New York, April 2004. (with R. J. Dunn and N. Matasovic)

“Slope Stability at a Hazardous Waste Site – Evaluation of the CPT Cone Factor Nk Using Dynamic Property Correlations”, *Proceedings of the 11th International Conference on Soil Dynamics and Earthquake Engineering,* Berkeley, California, January 2004, Vol. 2, pp. 478-484. (with N. Matazovic, R. J. Dunn, and E. Kavazanjian, Jr.)

“A New MSW Landfill Well Below Groundwater in a Highly Seismic Region”, Sardinia Landfill Symposium 2003. (with R. J. Dunn)

“Optimization of a Geocomposite Drainage Layer for Closure of Four Hazardous Waste Landfills”, Proceedings of the Seventh International Conference on Geosynthetics, Nice, France , pp. 545-548. 2002. (with R. J. Dunn)

“An Innovative Geosynthetic Cover for a Deep Hazardous Waste Landfill in a Seismic Environment”, *Proceedings of Geosynthetics 2001*, Portland, Oregon, Volume 1, pp. 77-90, 2001 (with R. J. Dunn).

“Estimation of Dynamic Frictional Properties of Geonet Interfaces”, *Proceedings of Geosynthetics 99*, Boston, Massachusetts, Volume 1, pp. 545-558, 1999 (with T. F. Zimmie).

“A Study of Slip Displacements Caused by Dynamic Loading at Geosynthetic Interfaces”, *Geotechnical Earthquake Engineering and Soil Dynamics III*, Geotechnical Special Publication No. 75, Panos Dakoulas, Mishac Yegian and Robert Holtz (editors), ASCE, Vol. 2, August 1998, pp. 997-1007 (with T. F. Zimmie).

“Frictional Behavior of Landfill Liner Interfaces with Geonets”, *Proceedings of the Sixth International Conference on Geosynthetics*, Atlanta, Georgia, Vol. 1, 1998, pp. 443-446 (with T. F. Zimmie).

“Landfill Stability: Static and Dynamic Geosynthetic Interface Friction Values”, *Proceedings of Geosynthetics Asia ‘97*, Bangalore, India 1997, (with T. F. Zimmie).

“Estimation of Slip Displacement Caused by Dynamic Loading at Geosynthetic Interfaces”, *Proceedings of the Eighth International Conference on Soil Dynamics and Earthquake Engineering*, Istanbul, Turkey, 1997, (with T. F. Zimmie).

“Dynamic Shear Behavior of Geosynthetic Interfaces”, *Proceedings of International Conference on Soil Mechanics and Foundation Engineering*, Hamburg, Germany, 1997, Vol. 3, pp. 1737-1740, (with T. F. Zimmie).

“Factors Influencing Dynamic Frictional Behavior of Geosynthetic Interfaces”, *Proceedings of Geosynthetics 97*, Long Beach, CA, Volume 2, pp. 837-849, 1997 (with T. F. Zimmie).

“Centrifuge Modeling to Study Stability of Dams”, *Proceedings of the Annual Conference of the Association of State Dam Safety Officials*, Seattle, WA, 1996 (with T. F. Zimmie).

“Seismic Analysis of Landfills”, *Environmental Geotechnology with Geosynthetics*, (Rao and Banerjee, editors), pp. 266-274, 1996 (with R. Gunturi).

"Geosynthetic Research Using the Centrifuge", *Geotechnical News*, September 1995, Vol. 13, No. 3, pp. 30-33, (with T. F. Zimmie).

"Study of Geosynthetic Interface Friction", *Centrifuge '94 Conference*, Singapore, August 1994, pp. 301-306, (with T. F. Zimmie and M. B. Mahmud).

"Centrifuge Modelling to Study Dynamic Friction at Geosynthetic Interfaces", *Proceedings of the Fifth International Conference on Geotextiles, Geomembranes and Related Products*, Singapore, September 1994, pp. 415-418, (with T. F. Zimmie and M. B. Mahmud).

"Use of a Geotechnical Centrifuge to Simulate Long Term Landfill Cover Performance", Proceedings of the *Eighth International Conference on Computer Methods and Advances in Geomechanics*, Morgantown, WV, May 1994, pp. 1809-1814, (with T. F. Zimmie and M. B. Mahmud).

"Simulation of long term performance of landfill covers", *Centrifuge '94 Conference*, Singapore, August, 1994. pp. 375-380, (with T. F. Zimmie and M. B. Mahmud).

"Application of Centrifuge Modeling to Contaminant Migration in Seabed Waste Disposal", Proceedings of the *Fourth Canadian Conference on Marine Geotechnical Engineering*, St. John's, Newfoundland, June, 1993, Vol. II, pp. 610-624, (with T. F. Zimmie and M. B. Mahmud).

Theses and Reports

“*Study of Interfacial Friction of Landfill Geosynthetics: Static and Dynamic*”, Ph. D. Thesis, Rensselaer Polytechnic Institute, Troy, NY, 1996.

"*Engineering Applications to Common Utility Systems*", M.S. Thesis, Illinois Institute of Technology, Chicago, 1991.

"*Common Utility Placement Systems (CUPS)*", Geotechnical Engineering Series, IIT-CE 91-02, Illinois Institute of Technology, Chicago, 1991, (with S. K. Saxena).

Exhibit D

RESUME - Muriel S. Robinette, P.G.

Senior Consultant

Education

MS, 1980, Engineering (Groundwater), Washington State University

BA, 1974, Geology, University of New Hampshire

Ph.D. Studies, 1982, Mining Engineering, University of Idaho

Registrations

Professional Geologist – 2002, New Hampshire, #00219

Professional Geologist – 1990, Maine, #GE258

Professional Geologist – 2018, New York,#00-1060-1

Areas of Specialization

- Hydrogeology
- Cost Allocation
- Brownfields' Redevelopment
- Forensic Field Studies
- Fate and Transport of Contaminants
- CERCLA Sites
- Remediation

Work History

Senior Consultant, CALEX Environmental, LLC, 2020 – present.

Senior Consultant, GZA GeoEnvironmental, Inc., 2017-2020

Senior Principal, Terracon Consultants, Inc., 2013-2017

Founder and President, New England EnviroStrategies Inc., 2007-2013

Sr. Vice President, Haley & Aldrich, Inc., 1996 – 2007

Vice President and Branch Manager, GEI Consultants, Inc., 1986 – 1996

Head, Hydrogeological Investigation Unit, Water Supply & Pollution Control Commission, 1983-1986

Instructor Hydrogeology and Assistant Prof. Geol. Engineering, U. of Idaho, 1978 – 1982

Summary of Experience

Ms. Robinette serves as a senior environmental hydrogeologist for Calex's Colebrook, New Hampshire office. She is responsible for technical strategy development and management of complex hazardous waste permitting, remediation and redevelopment projects. Ms. Robinette has extensive experience in designing and implementing forensic field studies for evaluation of contaminant impacts to environmental media in support of source determination and fate and transport of contaminants. She has served as consultant to many PRP groups addressing CERCLA sites, internal allocation, and as a testifying expert for numerous cases involving contaminant source determination, cost allocation and site remediation. She has led stakeholder negotiations regarding permitting strategies for site redevelopment and obtained federal funding for Brownfields' assessments and remediation.

Example Project Expérience – Landfill/NPL Sites

Senior Project Manager, Cost Allocation, Parker Landfill NPL Site, Vermont. Technical evaluation of waste stream contributions to landfill and determination of cost drivers to remedy. Assisted PRP Group with cost allocation negotiations and developed quantitative model for allocation computations.

Testifying Expert, Laurel Park and Beacon Heights NPL Landfills, Naugatuck and Beacon Falls, Connecticut. Developed cost allocation model which fairly accounts for more than 100 waste streams which were cost drivers to the CERCLA remedy components, including toxicity, mobility, and persistence characteristics. Expert opinions and models prepared with more than 6 weeks of expert testimony in fact finding case for Special Master.

Senior Project Manager, Bennington Landfill NPL Site, Bennington, Vermont. Technically evaluated PRP waste stream contributions to landfill and determined cost drivers to remedy. Performed focused feasibility evaluation of leachate treatment for PCBs and disposal options, and gas treatment and O&M costs for remedial action. Managed Natural Resource Damages negotiation, SOW development and oversaw successful implementation of wetlands mitigation measures.

Testifying Expert, Forensic Evaluations and Cost Allocation, Centredale Manor NPL Site, Rhode Island. Evaluation, historical topographic development and 3D visualization modeling completed to present a comprehensive conceptual site model for this (2,3,7,8-TCDD) driven site that encompasses acres of upland source area including landfilled wastes and drums, ponds and flood plains.

Project Director, Independent Quality Assurance Oversight of Remedial Action, Old Springfield Landfill NPL Site, Vermont. IQA Team overseeing the Remedial Action contractor on behalf of PRPs. Construction season was 18 months divided into two operable units comprised of the following components: waste area preloading, capping and closure; seep control through French drain construction using biopolymer wall technology; and leachate collection, pretreatment and discharge to POTW.

Testifying Expert, Auburn Road NPL Landfill – Londonderry, New Hampshire Expert opinion and deposition was provided regarding closure, regulatory and remediation requirements for CERCLA listed landfills during the mid 1980's.

Exhibit D

Muriel S. Robinette, P.G.

Senior Consultant

Allocation Expert - Combe Fill South NPL site – New Jersey Provided expert allocation support for municipal defendants in cost recovery case regarding contribution of contamination from MSW to site remediation costs at this co-disposal landfill.

Officer in Charge, **ACBM Solid Waste LF Closure, Nashua, New Hampshire.** Investigation and regulatory negotiations regarding closure of historical fill containing ACBMs for confidential utility.

Officer in Charge, CV Landfill, East Montpelier – Vermont Scope included negotiations, permitting, design and construction of remedial action to address slope failure, gas and leachate migration for closed 15-acre MSW landfill.

Proposed MSW Investigation – Barre, Vermont Officer-in-charge on investigation of proposed 25-acre MSW site.

Project Director - Landfill Investigations – Vermont, High Priority Landfills

Project Director for simultaneous design and implementation of hydrogeological studies at 14 landfills in Vermont. Study elements included file reviews, aerial photo interpretation, geological mapping, geophysical surveys, monitoring well installations and hydraulic testing, hydrogeological identification of contaminated pathways, limits of refuse determinations, and recommendations for closure/expansion.

Officer in Charge, Manchester MSW Landfill – Manchester, New Hampshire

Multiyear hydrogeologic investigation to develop closure alternatives for 50-acre MSW landfill. GMZ permit developed with monitoring plan to address leachate issues. Oversight of construction, gas harvesting, and long term O&M ongoing.

Senior Project Manager, Dover Landfill NPL Site – Dover, New Hampshire Performed geotechnical evaluation and costing of design closure requirements of 55-acre landfill for confidential industrial client. Successfully challenged groundwater HRS scoring with site data to reduce the remedial requirements to MNA of the landfill/leachate

Testifying Expert, Bennington Landfill – Bennington, New Hampshire Technical testimony was provided to a state appeals board and arbitrator to determine damages from the encroachment, land-taking and closure of town landfill on abutter’s property. Testimony was provided about local geology, landfill closure steps, permitting, groundwater impacts and commercial value of sand and gravel deposits used in closure design and construction.

Project Manager, Coakley Landfill NPL Site – Hampton, New Hampshire Performed design and implementation of a hydrogeological study of contamination of the fractured bedrock aquifer. Geophysical reconnaissance techniques were used to locate bedrock wells including gravity, magnetic, EM and seismic refraction. Installation of additional wells confirmed migration pathways and served as basis for remedial action decisions and targeted multilevel monitoring program.

Onondaga Lake and Salina LF NPL Sites, Onondaga, NY Provided a technical evaluation, scope and cost projections for sediment remediation at this NPL site, in addition to Salina LF and Lower Lay Creek sites. Mediation and Testimony provided (in bankruptcy court) on behalf of General Motors in conjunction with CERCLA cost allocation for these NPL sites.

Technical Expert, Confidential Minnesota Landfills Technical expert in evaluating environmental harm, waste in information and remedial costs associated with remediation of two co-mingled landfills in Minnesota in cost recovery case on behalf of selected PRPs.

Officer in Charge, F. O'Connor NPL Site, Maine. RI/FS and bench and pilot testing of exsitu stabilization of PCB contaminated soil. VLF EM surveys designed and implemented for siting fractured bedrock monitoring wells for recovery of free product PCB oils.

Testifying Expert, DNAPL Contamination due to Fire Response, PAK 2000 site, Melvin Village, New Hampshire.

Officer-in-Charge, Missouri Electric Works NPL Site, Cape Girardeau, Missouri. Innovative technology (ISTD) pilot demonstration at a PCB-contaminated site for a utility PRP consortium. Responsible for work plans, regulatory interactions, field health and safety, QA/QC and expanding the Insitu Thermal Desorption (ISTD) TSCA permit.

Chlorinated Solvents in Fractured Bedrock Technical Impracticability, Union Chemical NPL Site – So. Hope, Maine

Project manager for settling PRPs in performing long term quarterly monitoring and gaging program for surface and groundwater quality at this thermal desorption NPL site. Developed Technical Impracticability report regarding offsite remedy expansion into fractured bedrock contaminated with solvents.

Exhibit E

Case History of an Exhumed Landfill Double Liner System

George R. Koerner, Ph.D., P.E.[1];
and Robert M. Koerner, Ph.D., P.E., NAE, D.GE, Dist.M.ASCE[2]

[1]Geosynthetic Institute, 475 Kedron Ave., Folsom, PA 19033-1208. E-mail: gsigeokoerner@gmail.com
[2]Geosynthetic Institute, 475 Kedron Ave., Folsom, PA 19033-1208. E-mail: rmk27@drexel.edu

ABSTRACT

The opportunity of exhuming and evaluating various components of a double lined landfill system after 23 years of service is presented herein. The primary geomembrane (textured, 1.5 mm thick, HDPE) was evaluated and all eleven test properties were very close to the original properties and within current specification values. This was likewise the case for both extrusion and hot wedge seams. The geonet leak detection layer (4.4 mm thick, biplanar, HDPE) was in its original condition since no evidence of leachate was indicated. That said, the plastic cable ties holding the geonet sheets together were all broken in a brittle manner. The compacted clay liner beneath the secondary geomembrane was observed to have numerous long vertical cracks up to 15 mm wide throughout its thickness. The intact sections between the longer vertical cracks were striated with smaller cracks in all directions. While the clay's moisture content was 12%, the moisture content was likely higher during placement and subsequent shrinkage is the probable cause of the cracking.

REGULATORY BACKGROUND

In 1982, the U.S. Environmental Protection Agency promulgated its regulations on hazardous waste landfills designated as Subtitle "C" to the Resource Conservation and Recovery Act (RCRA). In 1985, the EPA set its minimum technology guidance for liner systems beneath the hazardous waste mass which must consist of the following items (top to bottom):

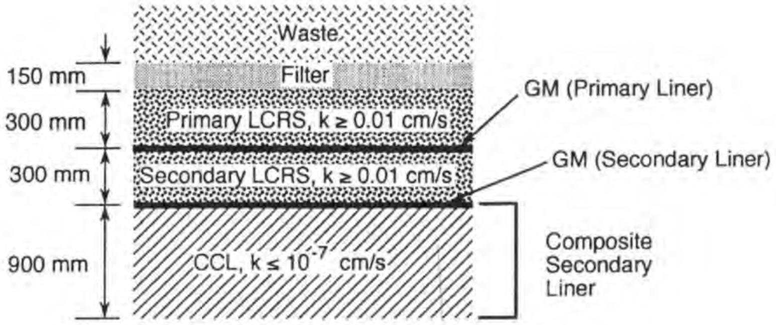
- Waste
- Filter
- Leachate collection and removal system (primary LCRS)
- Upper (or primary) geomembrane (GM)
- Leak detection system (secondary LCRS)
- Lower (or secondary) geomembrane (GM) in direct contact with 900 mm of compacted clay (i.e., compacted clay liner, or CCL), i.e., a two-component composite liner

Some ten years later, the EPA regulations were promulgated for municipal solid waste liner systems (RCRA Subtitle "D"), which consisted of only a leachate collection and removal system and a single composite liner with a geomembrane over 600 mm of compacted clay. The two liner systems are shown in Figure 1.

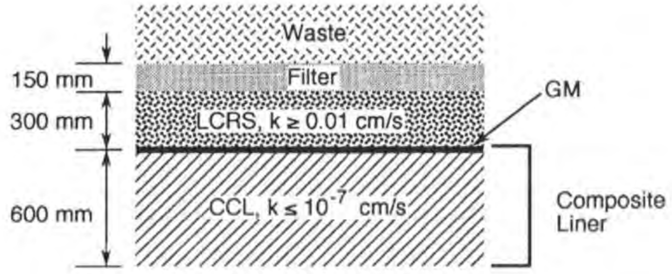
While minimum technology guidance for municipal solid waste landfills via the federal Subtitle D regulations calls for a single composite liner beneath the waste, many states have chosen to use double liners with an intermediate leak detection network of sand, geonet, or geocomposite. In this regard, these states go beyond minimum technology guidelines. The following twenty states are in this group: AR, CT, DE, FL, KY, LA, ME, MA, MI, MN, NH, NJ, NY, OR, PA, RI, TN, VT, VA, and WV. There are, however, large variations in the type of primary liner, secondary liner, and leak detection material (see Koerner and Koerner (2007) for

Exhibit E

details in this regard). The case history reported in this paper is within this category of using a double liner system with a geonet leak detection capability for a municipal solid waste landfill.



(a) Hazardous waste landfill (Subtitle C)



(b) Municipal solid waste landfill (Subtitle D)

Notes:
LCRS = Leachate Collection and Removal System
CCL = Compacted Clay Liner
GM = Geomembrane
k = Hydraulic Conductivity

Figure 1. Minimum liner system requirements (a) beneath hazardous waste landfills; and (b) beneath nonhazardous municipal solid-waste landfills.

CASE HISTORY OVERVIEW

As with most incrementally expanding landfills filled with waste over a long time period, the entire site is subdivided into discrete sections called "cells", which are separated by small soil berms. These berms are typically 2 to 3 m in height. Each cell is sequentially lined, tested, and filled with solid waste in a progressive manner. Once a cell is filled, or nearly filled, with waste, the construction of the adjacent cell is required. As such, it is necessary to uncover the edges of the liner system of the existing cell on the horizontal top of the separating berm. Here existing-to-new liner components are connected to one another from the lowest layer to the uppermost. The case history presented in this paper has such a liner system. It was constructed in 1993 and exhumed for the continuation cell in 2016, hence the existing liner components have had about 23-years of service. A cross section of the old and new cell's liner system are shown in Figure 2a and b respectively. Figure 3 is a mosaic of photographs taken at the time of the exhuming of the existing liner components along the top of the separation berm.

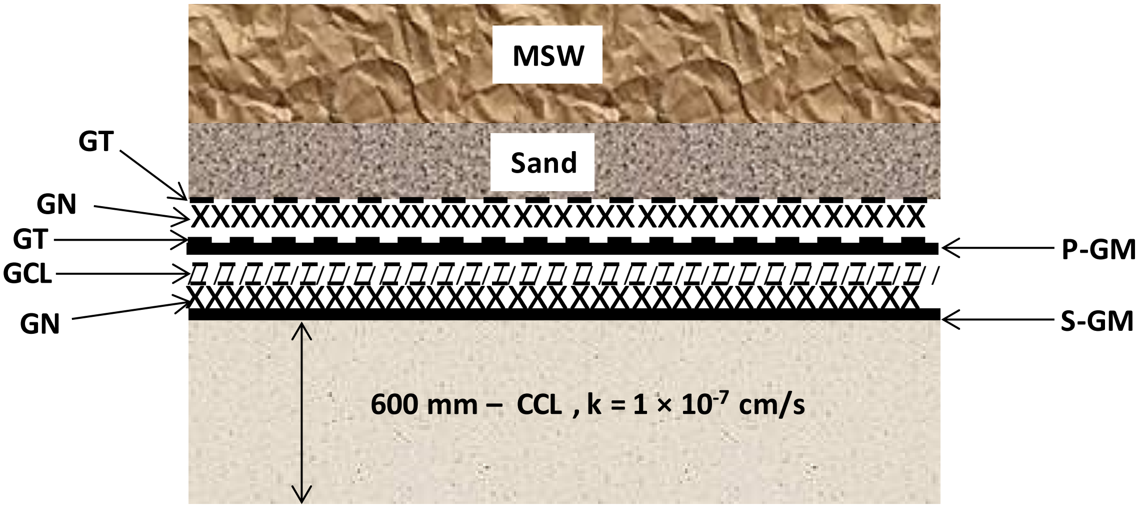


Figure 2a. Cross section of the old 1993 double lined MSW landfill system.

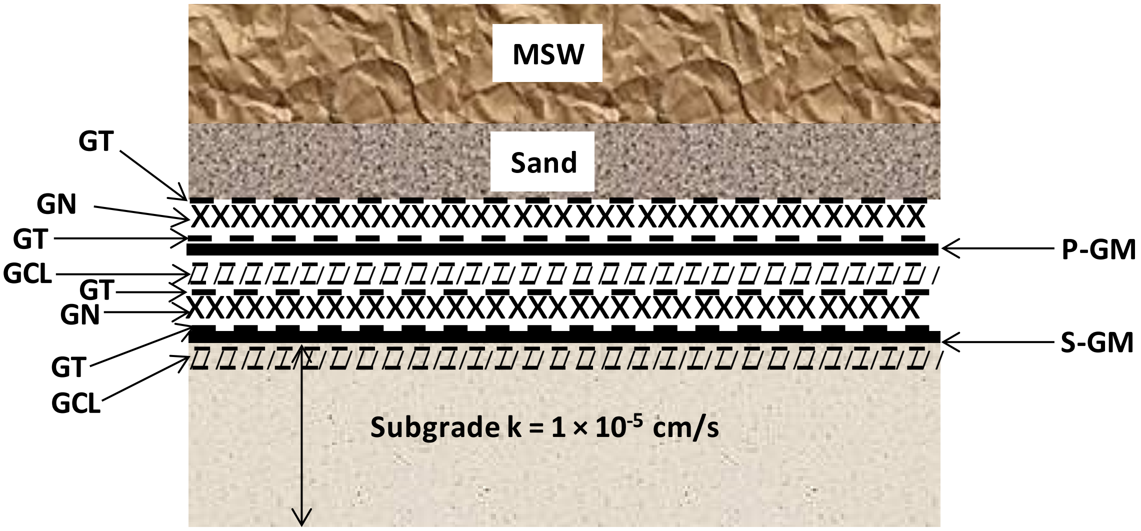


Figure 2b. Cross section of the new 2016 double lined MSW landfill system.

DETAILS OF FINDINGS

After 23-years of service life, the focus was on three specific components; primary geomembrane and its seams, the secondary leachate collect ion (leak detection) geonet and the compacted clay liner; recall Figure 2. These three are described and evaluated accordingly.

Primary Geomembrane: The geomembrane (only the primary was evaluated) was a 1.5 mm thick double sided textured high density polyethylene made to conform to the project specification. Both extrusion fillet seams and dual track hot wedge seams were available for evaluation. The sheet and both seam types were sampled and brought to the laboratory for testing and comparison to the original properties and to the current GRI-GM13 and GRI-GM19a specification properties (see Figure 4 for the relevant photographs and Tables 1 and 2 for the resulting test values). It should be clearly stated that samples were obtained near the bottom of the sump, in the leachate splash zone (labeled as wet-dry) and at the crest of the berm. The last location is assumed to be always dry. These three locations are envisioned to bracket the conditions that the liner experienced.

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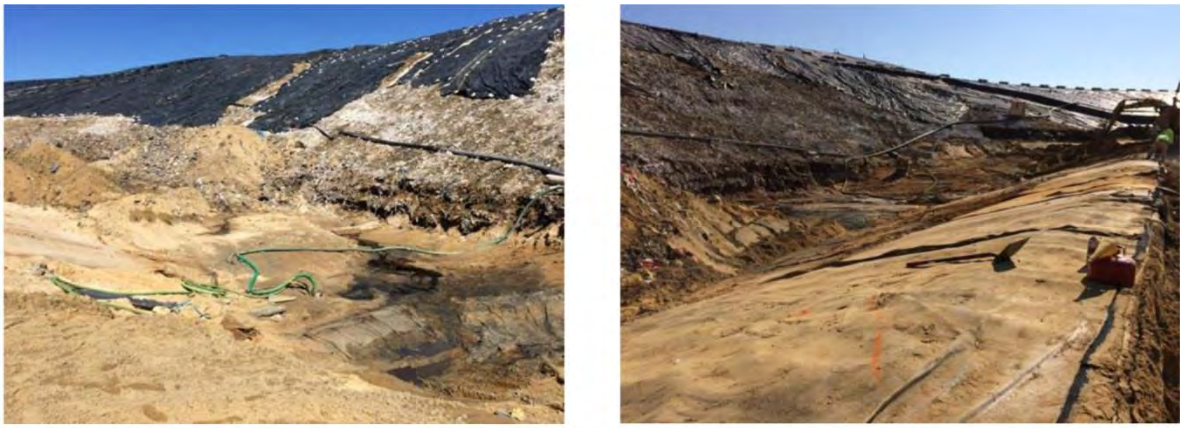

(a) Existing landfill at its full height

(b) Excavated separation berm where tie-in to new cell is required

(c) Bulldozer cutting into separation berm for compacted clay component extension

(d) Various existing layers prepared for new cell geosynthetic tie-ins

Figure 3. Site photographs of liner system materials where connections are to be made from existing-to-new landfill cell components.

The comparison of the aged geomembrane sheet test values to original values and to the current specification values indicate:

- original and aged thicknesses are similar and both are above the specification value,
- density of the aged material is the same as the original value and above the specification value,
- original and aged tensile properties (yield and break stress, and yield and break elongation) are similar to original values and above specification values,
- original and aged tear resistances are similar and above the specification value,
- original and aged puncture resistances are similar and above the specification value,
- stress crack resistance is at, or above, original values and higher than the specification value,
- original and aged carbon black contents are similar and meet the specification range of values,
- original and aged carbon black dispersion categories are similar and meet the

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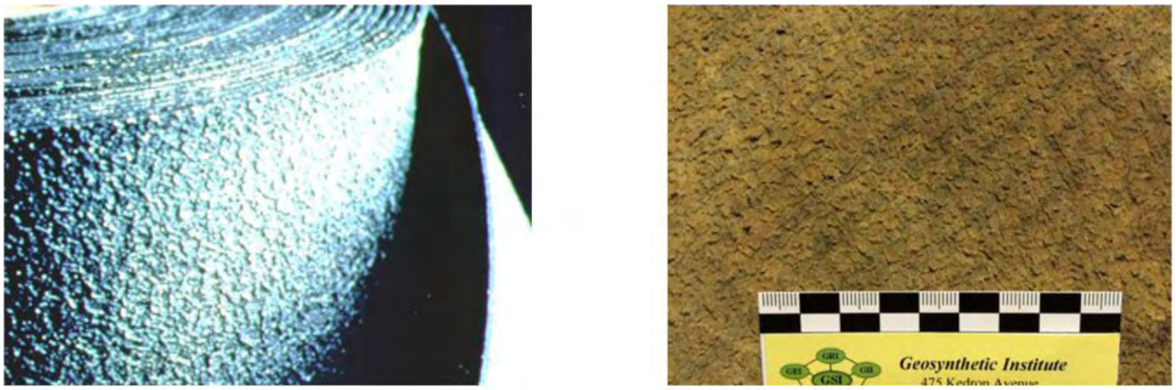
specification value, and
- oxidative induction times have remained constant over time.



(a) Roll of new textured geomembrane (b) 23-Year old site geomembrane

(c) Sampling of field geomembrane (d) Sampling of extrusion geomembrane seam

Figure 4. Photographs of field exhuming of primary geomembrane and seam.

Of all of the property values, very little has changed after the 23-year exposure period time and to the particular environment. It should be noted that until OIT values decrease and are eventually depleted, no changes are anticipated in the mechanical test properties of tensile, tear, or puncture values (Hsuan and Koerner 1998).

Regarding both the fillet extrusion seams and hot wedge, both shear and peel strengths pass the current GRI-GM19a seam specification. Also, seam elongation and type of break are acceptable. No information was available as to original required values. All seams were in excellent shape after the 23 years of service.

Geonet Leak Detection Layer: The leak detection layer was as specified, a 4.4 mm thick, biplanar, high density polyethylene, geonet placed directly between primary and secondary geomembranes with no associated geotextiles. Note that the design for the new cell called for geotextiles to be thermally bonded to both sides of the geonets, i.e., thereby becoming geocomposites, recall Figure 2. When exposed, as seen in Figure 5, the geonet ribs and apertures

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were completely clean. No leachate had ever passed within the adjacent set of ribs. This was as expected since the sampling area was on the top horizontal surface of the soil berm separating the existing-to-new cells. What was completely surprising was that every plastic cable tie holding the adjacent geonet sheet ends together was broken.

Table 1. Test Results for Field Exhumed Textured HDPE Sheet in Comparison to Original Values and Current GRI-GM13 Specification

Property	ASTM Test Method	Units	GM13 Values	Original Values	Sample 1 Primary Sump	Sample 2 Primary Wet-Dry	Sample 3 Primary Crest
Core Thickness	D5994	mm	1.35	1.59	1.57	1.59	1.58
Asperity Height	D7466	mm	0.4	0.6	0.71	0.70	0.73
Density	D792	g/cc	0.940	0.946	0.947	0.946	0.947
Tensile Properties	Type IV						
• yield stress	D6693	kN/m	29	40	33	29	30
• break stress	D6693	kN/m	26	28	30	32	33
• yield elongation	D6693	%	12	15	15	16	15
• break elongation	D6693	%	100	127	147	162	153
Tear Resistance	D1004	N	187	231	237	240	248
Puncture Resistance	D4833	N	481	641	586	665	591
Stress Crack Resistance	D5397 (App.)	hr.	200	>300	339	426	411
CB Content	D1603	%	2.0-3.0	2.3	2.2	2.4	2.3
CB Black Dispersion	D5596	Cat.	1 or 2	1	1	1	1
Oxidative Time OIT by STD DSC	D3895	min.	100	104	157	118	166

This prompted a new study on cable tie testing and resulting tensile strengths (see Koerner and Koerner 2018). Tension tests were conducted on ties, their heads and in complete loops. The latter appears to be the preferred configuration since all components interact in a field simulated manner. A test standard is in draft form for testing geonet cable ties. Additional tests were conducted on overlapping samples of biplanar geonet attached with a looped plastic cable tie and tested in wide width tension. Details are given in Table 3 and Figure 6. It is believed that the nylon tie used in 1993 did not age well. Currently we are recommending polyethylene ties with an improved service life.

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Table 2. Test Results for Field Exhumed HDPE Field Seams per ASTM D6392 in Comparison to Current GM19a Specification Values

Property	GRI-GM19a Values	Extrusion	Hot Wedge
Shear strength (kN/m)	44	50	49
Shear elongation (%)	50	>50	>50
Locus of Break	FTB	FTB (SE1)	FTB (SE1)
Peel strength (kN/m)	33	39	40
Peel separation (%)	25 (max.)	0	0
Locus of break	FTB	FTB (SE1)	FTB (SE1)

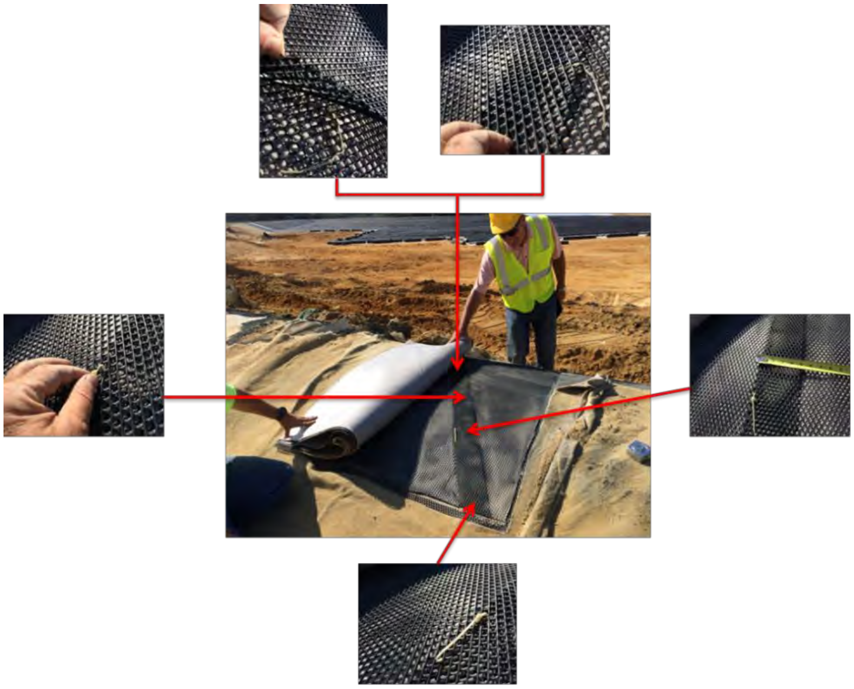

Figure 5. Sampling of geonet leak detection material showing broken plastic cable ties.

Table 3. Details of Plastic Cable Tied Geonet Test Specimens

Operational Details	Node or Rib Connections
Gage Length	100 mm
Strain Rate	50 mm/min
Specimen Size	Two 100 × 125 mm rectangular specimens, 100 mm overlap, connected with cable tie at center of specimens
Grip Face Details	Serrated facings of 100 × 25 mm size

Based upon the test results, it is suggested that several items should be followed insofar as geonet installation is concerned;

- polyethylene, not nylon, ties should be used in such applications,
- plastic cable ties should be looped around several adjacent ribs,

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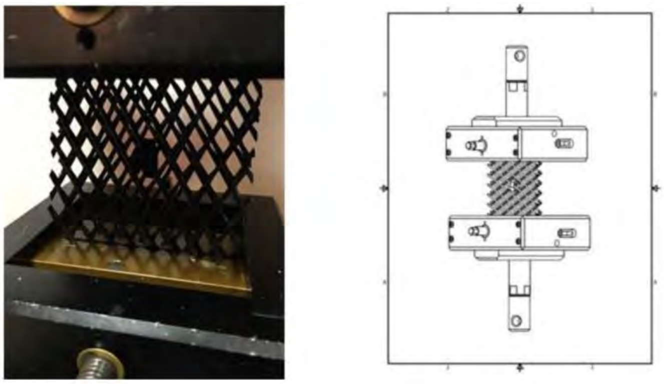
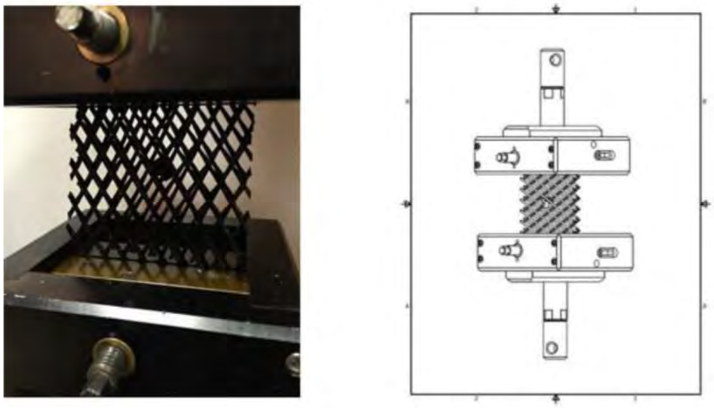
- the tie connection (called the "panduit") should be oriented so as to result in the minimum protrusion above the rib surfaces particularly when placed directly adjacent to geomembranes,
- the Panduit should not contain a metal keeper,
- tie spacings must follow the installation QA plan; they are usually closer attaching at the roll ends (≃ 150 mm) than when attaching the sides of the cores or longitudinal seams (≃ 1.5 m), and
- the individual strength required of the plastic cable ties depends on the site-specific stress imposed on the geonets and the site designer has discretion in this regard.



(a) Cable tie connecting geonet node



(b) Cable tie connecting geonet rib

Figure 6. Various tension tests of joined biplanar geonets.

Compacted Clay Liner: The compacted clay liner beneath the secondary geomembrane was observed in its full thickness (≃ 600 mm) cross section for the entire distance of the new cell tie-in which was approximately 75 m. The photographs of the field observations were alarming to say the least. See the photograph of Figure 7 to which we add some commentary. Vertical cracks up to 15 mm wide and extending 50 to 75% of the clay layer thickness were seen throughout the length of the tie-in. Even further, the intact clay between the large vertical cracks were striated with small cracks at various orientations throughout.

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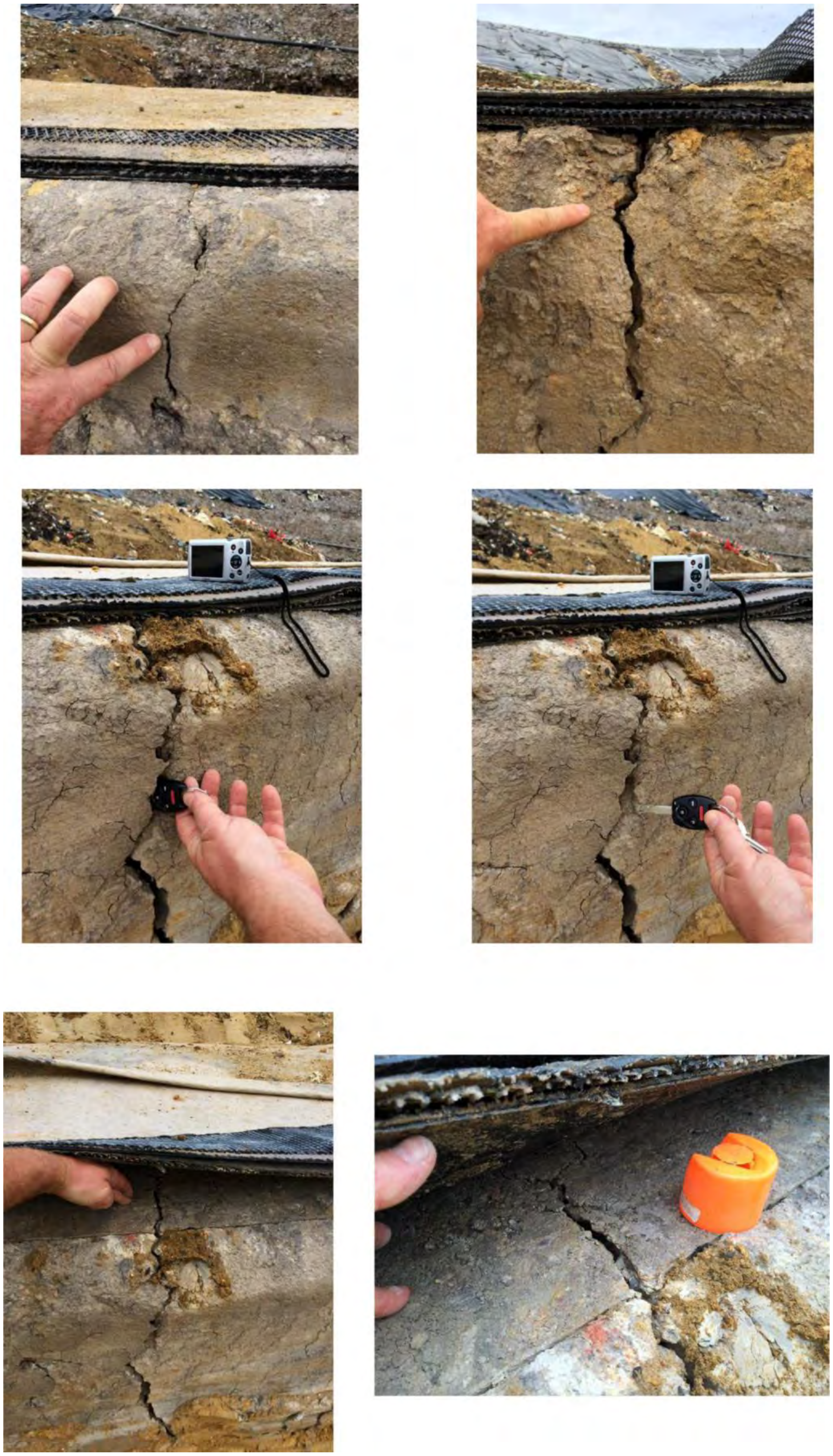

Figure 7. Condition of compacted clay liner (CCL) beneath secondary geomembrane after 23-years of service.

Laboratory testing of selected regions of the uncracked clay component resulted in the following:

- specific gravity = 2.5
- liquid limit = 56%
- plastic limit = 29%
- shrinkage limit = 12%
- dry unit weight = 18 kN/m^3
- hydraulic conductivity (of intact samples) = 8.3×10^{-8} cm/sec
- moisture content = 12%
- moisture content as placed = unknown

Please note that the hydraulic conductivity for the sections containing cracks was not determined. These sections were wetted and covered with a GCL to facilitate construction. No sampling or testing of the cracked CCL was undertaken.

SUMMARY

The opportunity of exhuming and testing various geosynthetic and clay components of a double-lined landfill liner system after 23-years of service is rare. This paper describes such an opportunity. The following conclusions are offered from observations and laboratory testing.

- The primary geomembrane showed no statistical meaningful signs of degradation or loss of properties from the original properties. Furthermore, all values were significantly higher than the prevailing current HDPE specification, GRI-GM13.
- Both extrusion fillet and hot wedge seam tests result in values meeting the current specification, GRI-GM19a.
- The biplanar geonet was observed to be in perfect condition based on visual observation although specific tests were not conducted.
- The plastic cable ties connecting ends and edges of the geonet, however, were all broken. This prompted a separate study for understanding the mechanisms of the bonds and development of a test method.
- The observed condition of the compacted clay liner was surprising and disturbing. It appears that the CCL desiccated over the alluvial silty sand subgrade. Major vertical cracks up to 15 mm wide and extending through most of the clay's thickness were observed. A smaller subset of randomly oriented cracks was also observed in regions between the major vertical cracks.

ACKNOWLEDGEMENTS

This research project was sponsored by members of the Geosynthetic Institute. As such, the authors sincerely appreciate the current (and past) members, affiliated members and associate members. The current list is available on the GSI website at <www.geosynthetic-institute.org> along with the current board of advisors and other contact information.

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ASTM D4833, "Standard test method for index puncture resistance of geomembranes,"

ASTM D5397, "Standard test method for evaluation of stress crack resistance of polyolefin geomembranes using notched constant tensile load test,"

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Data in brief 26 (2019) 104488

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Data in brief

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Data Article

Long-term groundwater protection efficiency of different types of sanitary landfills: Data description

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ABSTRACT

Data presented in this paper are related to the research article “Long-term risk assessments comparing environmental performance of different types of sanitary landfills” (Madon et al., 2019). Overall environmental risks were quantitatively assessed by calculating probabilities that an assumed aquifer lying directly below the landfill of a particular type will be polluted due to landfill-derived impacts as long as the pollution potential referring to each of the four types which were compared exists. A specific model was built for the purpose, described in the companion MethodX article (Madon et al., 2019). Uncertainty was taken in consideration by attributing input parameters required for modeling with probability distributions. When loosely defined groups of landfills are to be compared, which was the objective of the related research article, these distributions can be nothing but approximate and spread out, however, the values tend to cluster together around the averages which are characteristic for particular landfill types. Secondary data from scientific literature were mostly used to estimate probability density functions for the inputs, however, when referring to one of the four landfill types which were compared, primary data were used as well. The resultant outputs derived by running Monte Carlo simulations are given as time dependent variables. In this article, probability

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distributions for the outputs are graphically presented comparing environmental performance of different landfill types.

Specifications Table

Subject	Environmental science
Specific subject area	Waste disposal, Groundwater protection, Quantitative risk assessment, Comparative risk analysis
Type of data	Figures Tables
How data were acquired	Input data were acquired by - filtering and preprocessing secondary data obtained by means of scientific data mining (referring to 3 types of sanitary landfills) - performing long-term research and monitoring at a relatively small, full scale waste disposal and recycling site (referring to one sanitary landfill type) Output data were acquired by - simulation of input data using specific risk assessment model built within the @Risk software environment, product of Palisade Corporation
Data format	referring to the inputs to the model: - preprocessed secondary data - primary raw data referring to the outputs from the model: - simulated data derived from the input data mentioned above
Parameters for data collection	Secondary data were collected from the selected peer reviewed articles where reasonably well defined systems were studied, however, vaguly defined information derived from large number of sources was also taken into account when considering spread of possible values. Primary raw data were collected at the Ajdovščina waste disposal and recycling site performing environmental monitoring which lasted long enough for establishing long-term waste stabilization trends.
Description of data collection	When using @RISK software program, uncertain input variables are entered as probability distribution functions in cell formulas. Data used to construct these best-fit input probability curves were mainly collected from (1) specific peer reviewed studies where raw data derived from large number of landfills of a particular type have already been processed for different purposes and/or (2) from primary raw data. Output data were derived by performing Monte Carlo simulations utilizing above mentioned probability distributions for the inputs. Distribution of possible outcomes is obtained by letting a computer recalculate the worksheet repeatedly, each time using different randomly selected sets of values.
Data source location	for raw secondary data: - global sources (data related to 3 landfill types) for raw primary data: - Ajdovščina low-cost waste disposal and recycling site, Slovenia (data related to one landfill type) for processed input and output data: - KSD Ajdovščina, Slovenia
Data accessibility	With this article.
Related research article	Igor Madon, Darko DREV, Jakob LIKAR Long-term assessments comparing environmental performance of different types of sanitary landfills Waste Management https://doi.org/10.1016/j.wasman.2019.07.001

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Value of the Data

The acquired simulated data—

- can be valuable when uncertainty is appropriately acknowledged, but misleading when not
- could be of interest for local waste-management developers in low-income countries who want to upgrade their dumpsites
- can be helpful for hydrogeologists who perform long-term environmental risk assessments for already closed- or new landfill sites
- can provide landfill operators with new ideas before upgrading or closing their facilities
- can be used as thought-provoking material for landfill designers and regulators

1. Data

Compilation of all of the possible modeling outputs is presented in Table 1.

Resultant graphs for the outputs "$MLP_{starting}$", "MLP_{ending}", "$SLP_{starting}$", "SLP_{ending}", "$ILP_{starting}$" and "$CUMQRP_{max}$" are presented in Figs. 1–6. Each figure consists of 4 graphs supplied with explanation text in order the differences in environmental performance between particular landfill types (i.e., above-ground dumpsite, high-permeability landraise, modern dry-type landfill and modern wet-type landfill, respectively) can be more easily seen.

Comparative graphs for the output "QRP_t" are presented in Figs. 7–10 demonstrating "QRP" during the characteristic post-closure years (which includes particular post-closure years during which "QRP_{max}" is reached). Each figure refers to one of the four antagonistic types of landfills which were compared.

Sensitivity analises for parameters "QRP_{max}" and "$CUMQRP_{max}$" are provided as a supplementary material (Appendix-A).

2. Experimental design, materials, and methods

Waste disposal is one of those industries that generate data of considerable variety, veracity, and variability. These properties make secondary data analysis a big problem for the researchers in the field. Information describing hydrogeological configuration of landfill sites is usually missing or is deficient. Eventual leakages into the subsoil are usually undetected. It is therefore not surprising that no programs or code files for filtering and analyzing raw data from secondary sources exist that can be used to find reasonable correlations between environmental performances of landfills on one side and variables which contribute to these performances on the other side. This kind of approach is intrinsically unfit anyway, because too little post-closure time has expired so far in order to observe long-term groundwater protection effectiveness of most objects which can be hystorically described as modern landfills.

According to the model which was developed [1,2], there are just two decisive quantities which have to be known in order to perform long-term risk assessments from landfills: 1) primary leachate losses into the subsoil "Q_t" and 2) concentration of pollutants in primary leachate at the bottom of the landfill '"C_t". Both of these parameters generally change over time after landfill closure. They already represent quantities on the output side of the model. Important point however is that these outputs can be obtained by simulation modeling utilizing rather small number of input variables which can be convincingly attributed with probability density functions processing already available data and information. Simulated data for parameters "Q_t" and "C_t" are needed to derive many other, more complex outputs, however, once the model is established, all of the outputs are acquired in a single simulation step. Flowchart demonstrating the applied concept is presented in the related MethodX article [2].

Probability distributions for the inputs can be directly fitted to already available raw data from secondary and/or primary sources when such data exist. However, this is usually not the case. All direct and indirect information which is available has to be used to construct an input model instead. The goal is to obtain an approximation that captures the key characteristics of the underlying input process. @Risk program software [3] includes vast assortiment of probability functions which can be readily

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Table 1
Compilation of outputs obtained by simulation.

	Outputs	Units
C_t	Concentration of a specific pollutant within the leachate at the bottom of the landfill	Concentration (probability distribution of values for the selected post-closure year)
Q_t	Yearly leachate losses into the subsoil	Volume (probability distribution of values for the selected post-closure year)
QRP_t	Yearly release of a specific pollutant into the subsoil ("quantity of a reference pollutant")	Mass (probability distribution of values for the selected post-closure year)
QRP_{max}	Maximal quantity of a (reference) pollutant annually discharged into the aquifer (i.e., emissions during the post-closure year when the emitted quantity appears to be the largest: $QRP_t = QRP_{max}$)	Mass (probability distribution of values for the most polluting post-closure year)
$CUMQRP_{max}$	Quantity of reference pollutant cumulatively emitted into the subsoil considering overall life span until the landfill of a certain type exhibits pollution potential for causing moderate level of aquifer pollution.	Mass (probability distribution of values)
$MLP_{starting}$	Moderate level of aquifer contamination - commencement of the unfolding event	Required number of post-closure years for the "event" to happen (probability distribution of values)
MLP_{ending}	Moderate level of aquifer contamination - cessation of the unfolding event	Required number of post-closure years for the "event" to happen (probability distribution of values)
$SLP_{starting}$	Severe level of aquifer contamination - commencement of the unfolding event	Required number of post-closure years for the "event" to happen (probability distribution of values)
SLP_{ending}	Severe level of aquifer contamination - cessation of the unfolding event	Required number of post-closure years for the "event" to happen (probability distribution of values)
$ILP_{starting}$	Irreversible level of aquifer pollution - commencement of the event	Required number of post-closure years for the "event" to happen (probability distribution of values)
P_{MLP}	Probability for MLP to happen considering overall life span until the landfill of a certain type exhibits pollution potential for causing moderate level of aquifer pollution.	Probability (discrete value) $P_{MLP} = MLP_{starting\ max} = MLP_{ending\ max}$
P_{SLP}	Probability for SLP to happen considering overall life span until the landfill of a certain type exhibits pollution potential for causing severe level of aquifer pollution.	Probability (discrete value) $P_{SLP} = SLP_{starting\ max} = SLP_{ending\ max}$
P_{ILP}	Probability for ILP to happen considering overall life span until the landfill of a certain type exhibits pollution potential for causing "irreversible" level of aquifer pollution.	Probability (discrete value) $P_{ILP} = ILP_{starting\ max}$

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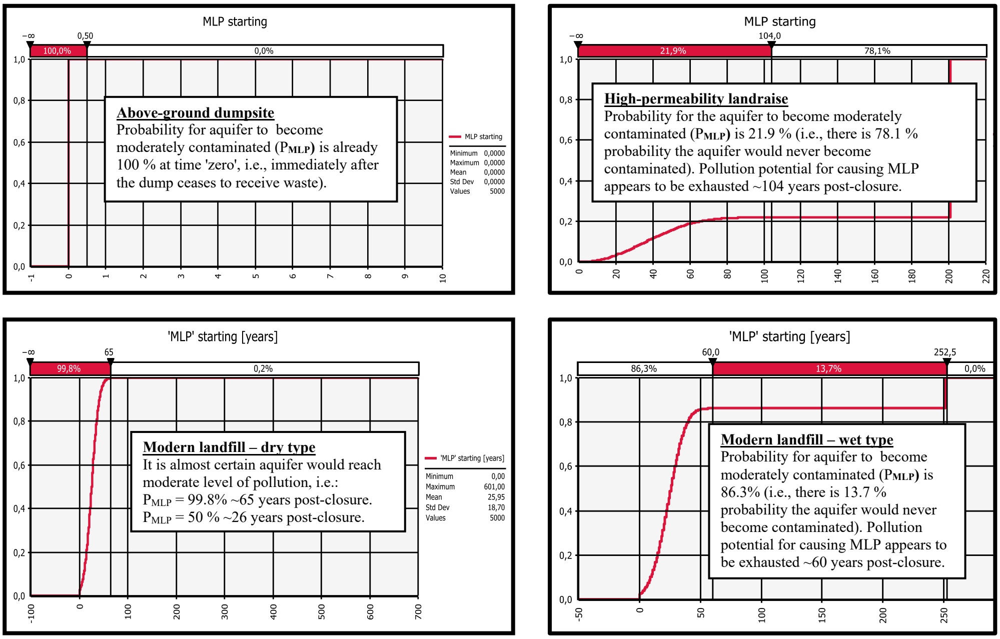

Above-ground dumpsite
Probability for aquifer to become moderately contaminated (P_{MLP}) is already 100 % at time 'zero', i.e., immediately after the dump ceases to receive waste).

High-permeability landraise
Probability for the aquifer to become moderately contaminated (P_{MLP}) is 21.9 % (i.e., there is 78.1 % probability the aquifer would never become contaminated). Pollution potential for causing MLP appears to be exhausted ~104 years post-closure.

Modern landfill – dry type
It is almost certain aquifer would reach moderate level of pollution, i.e.:
P_{MLP} = 99.8% ~65 years post-closure.
P_{MLP} = 50 % ~26 years post-closure.

Modern landfill – wet type
Probability for aquifer to become moderately contaminated (P_{MLP}) is 86.3% (i.e., there is 13.7 % probability the aquifer would never become contaminated). Pollution potential for causing MLP appears to be exhausted ~60 years post-closure.

Fig. 1. Derived comparative graphs for the output "moderate level of aquifer pollution – commencement of the unfolding event".

used to attribute input variables with estimated probability distributions. Several options for fitting distributions to raw data are available as well.

A common hydrogeological and hydrological setting was set up for modeling purposes in order to compare environmental performance of different landfill types. This was done in a way that the expected differences between the four antagonistic landfill types would show up as clearly as possible. The presumed common setting is described below:

- an aquifer exists immediately below the landfill subgrade, separated only by a thin vadose zone
- the local terrain is semipermeable (including the above mentioned vadose zone)
- the landfill is placed in a humid region.

Input variables needed for performing model simulations are compiled below:

- C_0 [mg/L]: initial concentration of the reference pollutant immediately after landfill closure
- $T_{0.5}$ [years]: half-life period characterizing reference pollutant concentration decline within the leachate at the bottom of the landfill
- $t_{failure}$ [years]: post-closure time which has to pass for composite liner system to fail
- q_0 [liters per hectare per day [lphd]]: initial specific leachate losses into the underground soon after the liner has failed
- T_2 [years]: time needed for leachate losses to double after the system fails
- q_{max} [lphd]: maximal possible leachate losses into the subsoil per unit area of landfill footprint
- k_{sat} [m/s]: hydraulic conductivity coefficient of a bottom clay liner
- d [m]: bottom clay liner (or natural clay stratum) thickness
- Q_{precip} [mm]: annual precipitation
- p_{undg} [%]: part of annual precipitation which is infiltrated into the landfill generating landfill leachate, but only that portion which percolates further down to the aquifer

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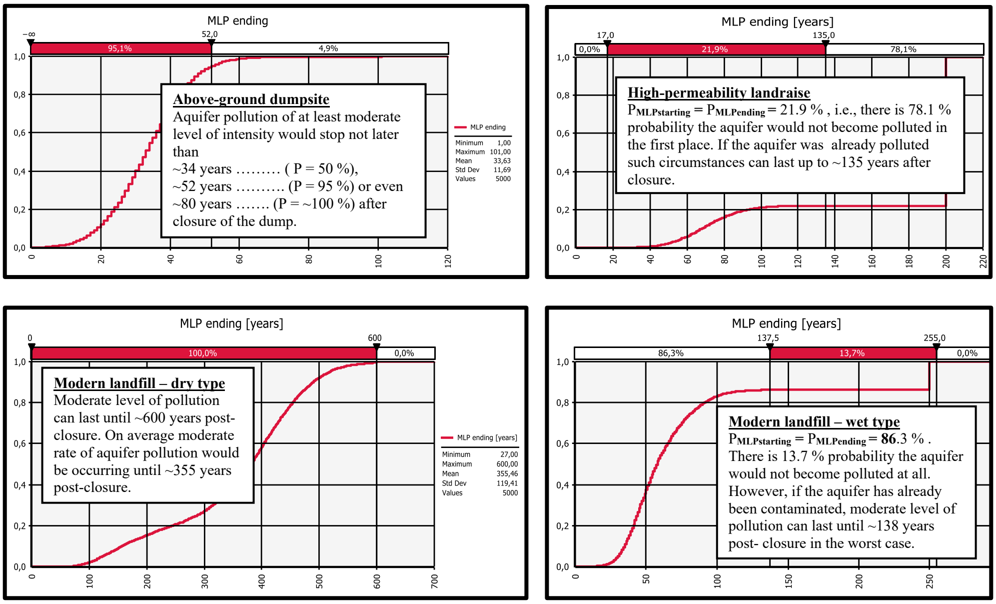


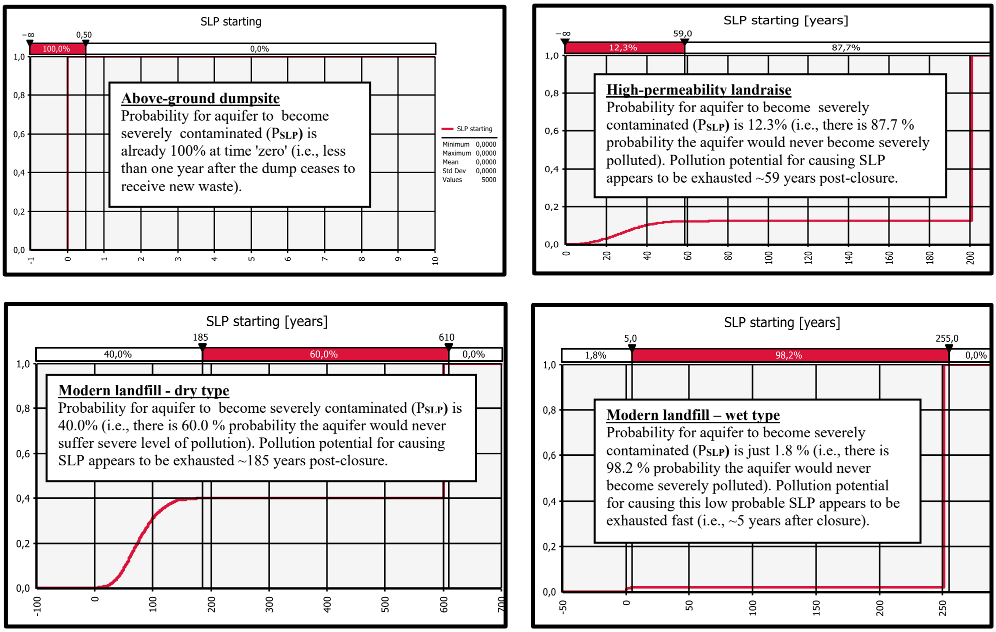
Above-ground dumpsite
Aquifer pollution of at least moderate level of intensity would stop not later than
~34 years ……… (P = 50 %),
~52 years ………. (P = 95 %) or even
~80 years ……. (P = ~100 %) after closure of the dump.

High-permeability landraise
$P_{MLPstarting} = P_{MLPending}$ = 21.9 % , i.e., there is 78.1 % probability the aquifer would not become polluted in the first place. If the aquifer was already polluted such circumstances can last up to ~135 years after closure.

Modern landfill – dry type
Moderate level of pollution can last until ~600 years post-closure. On average moderate rate of aquifer pollution would be occurring until ~355 years post-closure.

Modern landfill – wet type
$P_{MLPstarting} = P_{MLPending}$ = **86**.3 % .
There is 13.7 % probability the aquifer would not become polluted at all. However, if the aquifer has already been contaminated, moderate level of pollution can last until ~138 years post- closure in the worst case.

Fig. 2. Derived comparative graphs for the output "moderate level of aquifer pollution – cessation of the unfolding event".



Above-ground dumpsite
Probability for aquifer to become severely contaminated (P_{SLP}) is already 100% at time 'zero' (i.e., less than one year after the dump ceases to receive new waste).

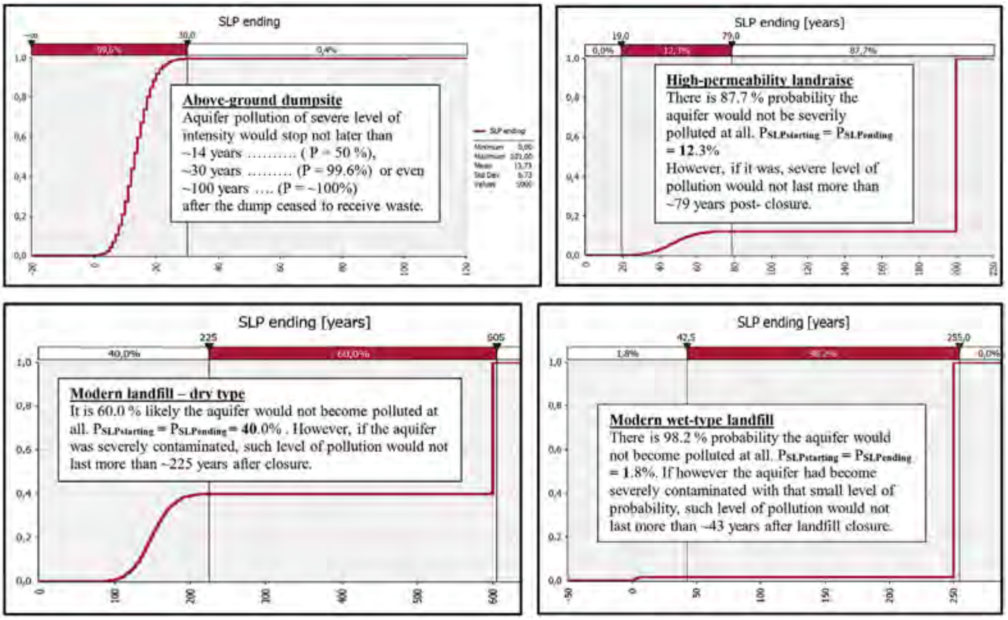
High-permeability landraise
Probability for aquifer to become severely contaminated (P_{SLP}) is 12.3% (i.e., there is 87.7 % probability the aquifer would never become severely polluted). Pollution potential for causing SLP appears to be exhausted ~59 years post-closure.

Modern landfill - dry type
Probability for aquifer to become severely contaminated (P_{SLP}) is 40.0% (i.e., there is 60.0 % probability the aquifer would never suffer severe level of pollution). Pollution potential for causing SLP appears to be exhausted ~185 years post-closure.

Modern landfill – wet type
Probability for aquifer to become severely contaminated (P_{SLP}) is just 1.8 % (i.e., there is 98.2 % probability the aquifer would never become severely polluted). Pollution potential for causing this low probable SLP appears to be exhausted fast (i.e., ~5 years after closure).

Fig. 3. Derived comparative graphs for the output "severe level of aquifer pollution – commencement of the unfolding event".

Exhibit E



Above-ground dumpsite
Aquifer pollution of severe level of intensity would stop not later than
~14 years ………. (P = 50 %),
~30 years ……… (P = 99.6%) or even
~100 years …. (P = ~100%)
after the dump ceased to receive waste.

High-permeability landraise
There is 87.7 % probability the aquifer would not be severily polluted at all. $P_{SLPstarting} = P_{SLPending}$ = **12**.3%
However, if it was, severe level of pollution would not last more than ~79 years post- closure.

Modern landfill – dry type
It is 60.0 % likely the aquifer would not become polluted at all. $P_{SLPstarting} = P_{SLPending}$ = **40**.0% . However, if the aquifer was severely contaminated, such level of pollution would not last more than ~225 years after closure.

Modern wet-type landfill
There is 98.2 % probability the aquifer would not become polluted at all. $P_{SLPstarting} = P_{SLPending}$ = **1**.8%. If however the aquifer had become severely contaminated with that small level of probability, such level of pollution would not last more than ~43 years after landfill closure.

Fig. 4. Derived comparative graphs for the output "severe level of aquifer pollution – cessation of the unfolding event".

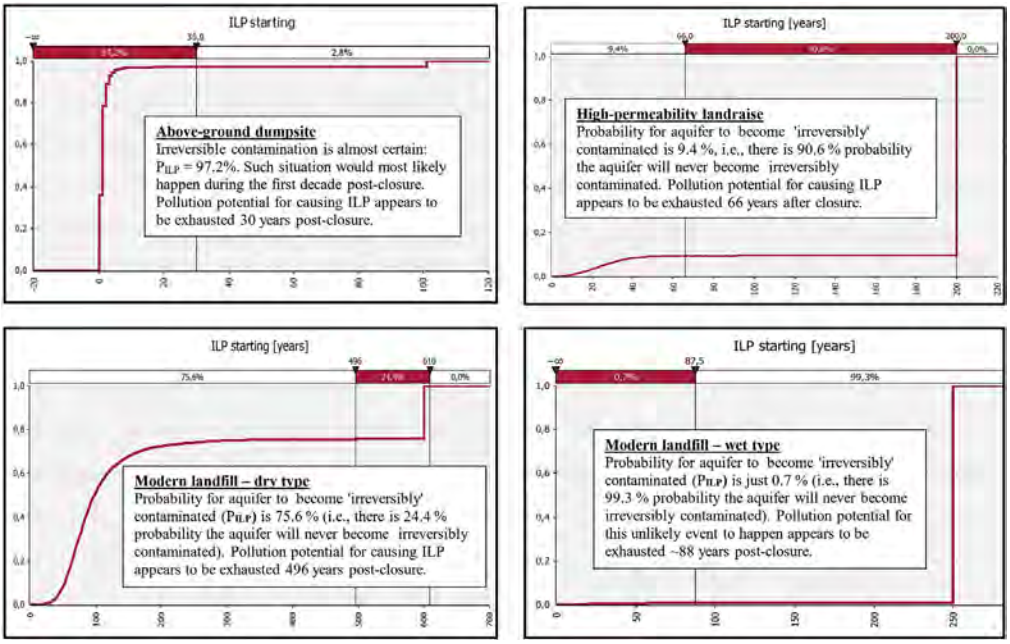
Only parameters required to calculate pollutant concentrations "C_t" (i.e.,"C_0" and "$T_{0.5}$") are invariably involved as modeling inputs for all landfill types. Other parameters, i.e. those which are required to calculate leakages "Q_t" appear to be rather specific for particular landfill types, i.e.:

- when referring to dry- and wet-type modern landfills, leachate losses into the subsoil are considered to be a stochastic phenomenon; "$t_{failure}$", "q_0","T_2" and "q_{max}" are the related variables needed for performing simulations of long-term leakages
- hydraulic system at the bottom of a high-permeability landraise (HPL) type of landfill is however deterministic; leakages are calculated using the Darcy law; nevertheless, the required inputs "k_{sat}" and "d" are considered to be variables not just due to uncertainties which exist when dealing with permeability measurements of small specimens in laboratory, etc., but to consider the expected diversity among the landfills of this type when comparing landfill types as groups
- "Q_{precip}" and "p_{undg}" are exclusively used to simulate annual leakages emanating from the uncontained landfills (dumpsites); leachate losses from contained landfills are only indirectly related to local hydrologic and hydrogeologic factors

Input variables were quantifyed as described below:

1. Probability density functions for parameters "K_{sat}" and "d" were selected according to the characteristics which define HPL as a landfill type.
2. Probability density functions for parameters "Q_{precip}" and "p_{undg}" were selected according to the characteristics of the presumed common hydrogeological and hydrological setting.
3. Probability distribution-estimations for the inputs "C_0" and "$T_{0.5}$" were mostly acquired by processing large amounts of secondary data which are only indirectly related to the parameters "C_0" and "$T_{0.5}$". When referring to HPL, raw primary data were used for the purpose instead. The main sources are presented below:
   - Laner [4] for modern landfills

Exhibit E



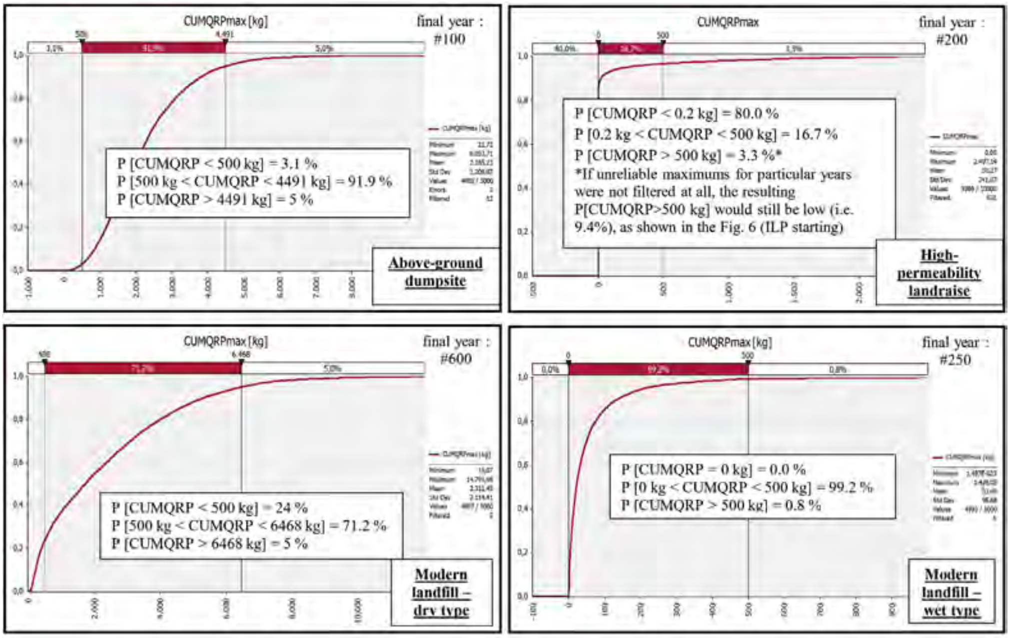
Above-ground dumpsite
Irreversible contamination is almost certain: P_{ILP} = 97.2%. Such situation would most likely happen during the first decade post-closure. Pollution potential for causing ILP appears to be exhausted 30 years post-closure.

High-permeability landraise
Probability for aquifer to become 'irreversibly' contaminated is 9.4 %, i.e., there is 90.6 % probability the aquifer will never become irreversibly contaminated. Pollution potential for causing ILP appears to be exhausted 66 years after closure.

Modern landfill – dry type
Probability for aquifer to become 'irreversibly' contaminated (P_{ILP}) is 75.6 % (i.e., there is 24.4 % probability the aquifer will never become irreversibly contaminated). Pollution potential for causing ILP appears to be exhausted 496 years post-closure.

Modern landfill – wet type
Probability for aquifer to become 'irreversibly' contaminated (P_{ILP}) is just 0.7 % (i.e., there is 99.3 % probability the aquifer will never become irreversibly contaminated). Pollution potential for this unlikely event to happen appears to be exhausted ~88 years post-closure.

Fig. 5. Derived comparative graphs for the output "irreversible level of aquifer pollution – commencement of the unfolding event".



P [CUMQRP < 500 kg] = 3.1 %
P [500 kg < CUMQRP < 4491 kg] = 91.9 %
P [CUMQRP > 4491 kg] = 5 %

Above-ground dumpsite

P [CUMQRP < 0.2 kg] = 80.0 %
P [0.2 kg < CUMQRP < 500 kg] = 16.7 %
P [CUMQRP > 500 kg] = 3.3 %*
*If unreliable maximums for particular years were not filtered at all, the resulting P[CUMQRP>500 kg] would still be low (i.e. 9.4%), as shown in the Fig. 6 (ILP starting)

High-permeability landraise

P [CUMQRP < 500 kg] = 24 %
P [500 kg < CUMQRP < 6468 kg] = 71.2 %
P [CUMQRP > 6468 kg] = 5 %

Modern landfill – dry type

P [CUMQRP = 0 kg] = 0.0 %
P [0 kg < CUMQRP < 500 kg] = 99.2 %
P [CUMQRP > 500 kg] = 0.8 %

Modern landfill – wet type

$CUMQRP_{max}$: Quantity of reference pollutant cumulatively discharged into the aquifer considering at least overall life span until the landfill of a particular type exhibits pollution potential for causing moderate level of aquifer pollution (i.e., probability distributions of CUMQRP acquired by performing simulations referring to final post-closure years are presented).

Fig. 6. Derived comparative graphs for the output "quantity of reference pollutant cumulatively discharged into the aquifer".

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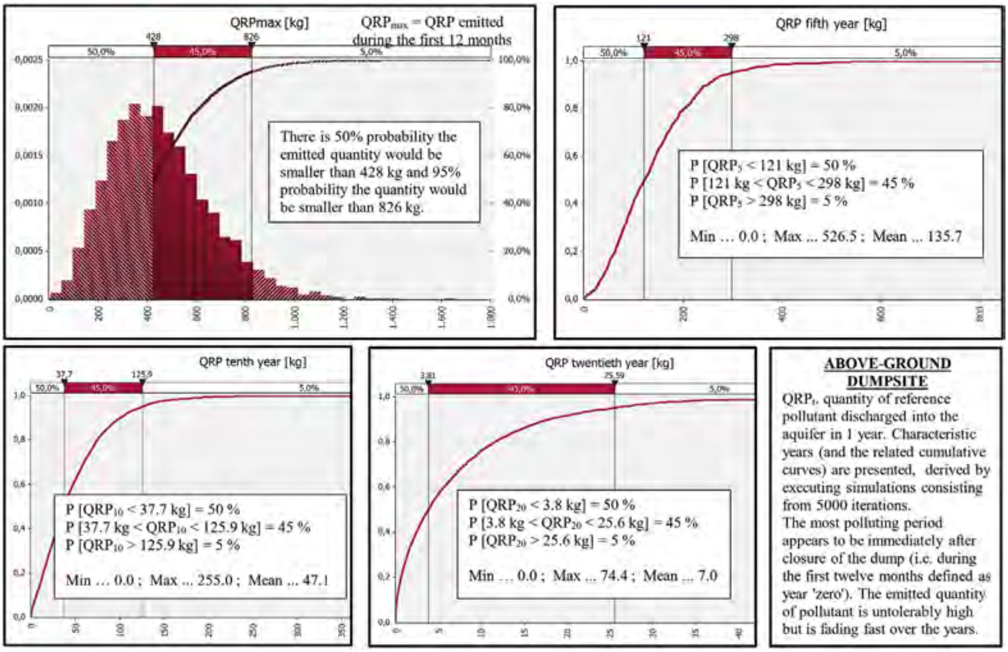

Fig. 7. Derived comparative graphs for the output "quantity of reference pollutant discharged into the aquifer" referring to above-ground dumpsites characteristic post-closure years.

- Kjeldsen and Christophersen [5] for dumpsites
- Madon [6] for high permeability landraises

Specific approaches and techniques were occassionally used to obtain the desired information, which would be otherwise unattainable.

4. Leakage rate from modern landfills is considered to be zero until the post-closure time when bottom liner system fails. Pivato [7] constructed failure probability curve based on groundwater monitoring data from 30 landfill sites in northern Italy. Distribution of "$t_{failure}$" values appeared to be approximately normal with average time approximately 25 years and standard deviation approximately 12.5 years. This density distribution was attributed to parameter "$t_{failure}$" to build an input model.
5. Typical leakage rates from modern landfills occuring immediately after the bottom liner fails appear to be very low. According to the measurements performed on double-lined landfills (Geoservices Inc., [8], EPA/600/R-02/099, [9], Moo-Young et al., [10]), frequencies of leakage-rates ranges appear to be distributed as follows (in liters per hectare per day)
   - 0 lphd (few cases)
   - 0–10 lphd (most of cases)
   - 10–100 lphd (a lot of cases)
   - 100–1000 lphd (few cases)
   - 1410 lphd (one case)

Measurement 1410 lphd most probably represents the case where clay liner functioned as a sole element of waste containment system, i.e., as if geomembrane has not existed due to some major failure. This value could be a good estimate for "q_{max}".

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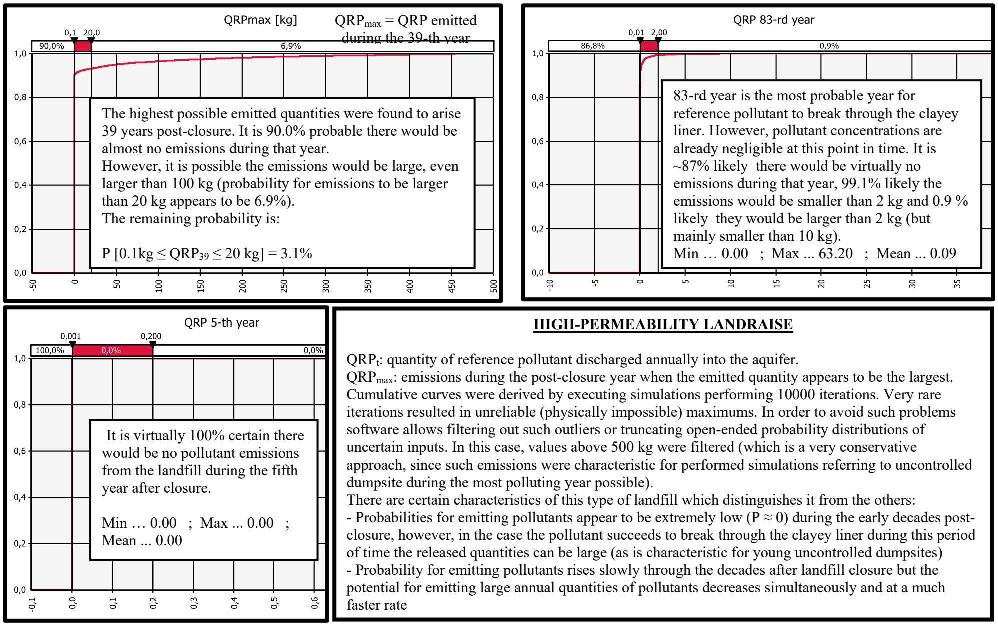


QRP_{max} = QRP emitted during the 39-th year

The highest possible emitted quantities were found to arise 39 years post-closure. It is 90.0% probable there would be almost no emissions during that year.
However, it is possible the emissions would be large, even larger than 100 kg (probability for emissions to be larger than 20 kg appears to be 6.9%).
The remaining probability is:

$P\ [0.1\text{kg} \le QRP_{39} \le 20\ \text{kg}] = 3.1\%$

83-rd year is the most probable year for reference pollutant to break through the clayey liner. However, pollutant concentrations are already negligible at this point in time. It is ~87% likely there would be virtually no emissions during that year, 99.1% likely the emissions would be smaller than 2 kg and 0.9 % likely they would be larger than 2 kg (but mainly smaller than 10 kg).
Min … 0.00 ; Max ... 63.20 ; Mean ... 0.09

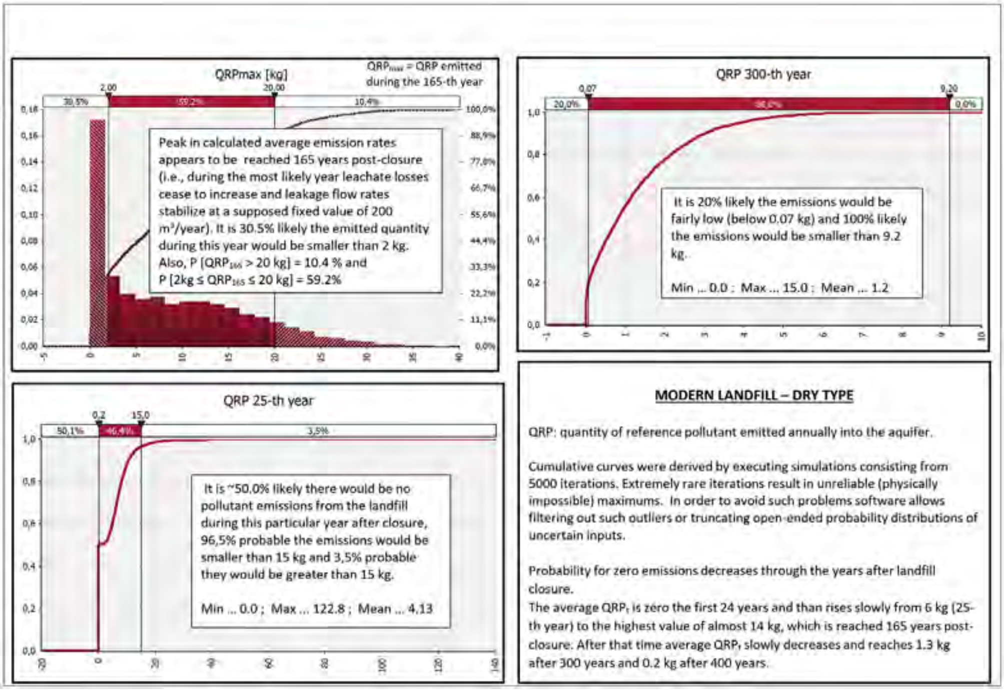
It is virtually 100% certain there would be no pollutant emissions from the landfill during the fifth year after closure.

Min … 0.00 ; Max ... 0.00 ; Mean ... 0.00

HIGH-PERMEABILITY LANDRAISE

QRP_t: quantity of reference pollutant discharged annually into the aquifer.
QRP_{max}: emissions during the post-closure year when the emitted quantity appears to be the largest.
Cumulative curves were derived by executing simulations performing 10000 iterations. Very rare iterations resulted in unreliable (physically impossible) maximums. In order to avoid such problems software allows filtering out such outliers or truncating open-ended probability distributions of uncertain inputs. In this case, values above 500 kg were filtered (which is a very conservative approach, since such emissions were characteristic for performed simulations referring to uncontrolled dumpsite during the most polluting year possible).
There are certain characteristics of this type of landfill which distinguishes it from the others:
- Probabilities for emitting pollutants appear to be extremely low (P ≈ 0) during the early decades post-closure, however, in the case the pollutant succeeds to break through the clayey liner during this period of time the released quantities can be large (as is characteristic for young uncontrolled dumpsites)
- Probability for emitting pollutants rises slowly through the decades after landfill closure but the potential for emitting large annual quantities of pollutants decreases simultaneously and at a much faster rate

Fig. 8. Derived graphs for the output "quantity of reference pollutant discharged into the aquifer" referring to high-permeability landraises characteristic post-closure years.



QRP_{max} = QRP emitted during the 165-th year

Peak in calculated average emission rates appears to be reached 165 years post-closure (i.e., during the most likely year leachate losses cease to increase and leakage flow rates stabilize at a supposed fixed value of 200 m^3/year). It is 30.5% likely the emitted quantity during this year would be smaller than 2 kg.
Also, $P\ [QRP_{165} > 20\ \text{kg}] = 10.4\ \%$ and
$P\ [2\text{kg} \le QRP_{165} \le 20\ \text{kg}] = 59.2\%$

It is 20% likely the emissions would be fairly low (below 0.07 kg) and 100% likely the emissions would be smaller than 9.2 kg.

Min ... 0.0 ; Max ... 15.0 ; Mean ... 1.2

It is ~50.0% likely there would be no pollutant emissions from the landfill during this particular year after closure, 96,5% probable the emissions would be smaller than 15 kg and 3,5% probable they would be greater than 15 kg.

Min ... 0.0 ; Max ... 122.8 ; Mean ... 4,13

MODERN LANDFILL – DRY TYPE

QRP: quantity of reference pollutant emitted annually into the aquifer.

Cumulative curves were derived by executing simulations consisting from 5000 iterations. Extremely rare iterations result in unreliable (physically impossible) maximums. In order to avoid such problems software allows filtering out such outliers or truncating open-ended probability distributions of uncertain inputs.

Probability for zero emissions decreases through the years after landfill closure.
The average QRP_t is zero the first 24 years and than rises slowly from 6 kg (25-th year) to the highest value of almost 14 kg, which is reached 165 years post-closure. After that time average QRP_t slowly decreases and reaches 1.3 kg after 300 years and 0.2 kg after 400 years.

Fig. 9. Derived graphs for the output "quantity of reference pollutant discharged into the aquifer" referring to modern landfills of dry type characteristic post-closure years.

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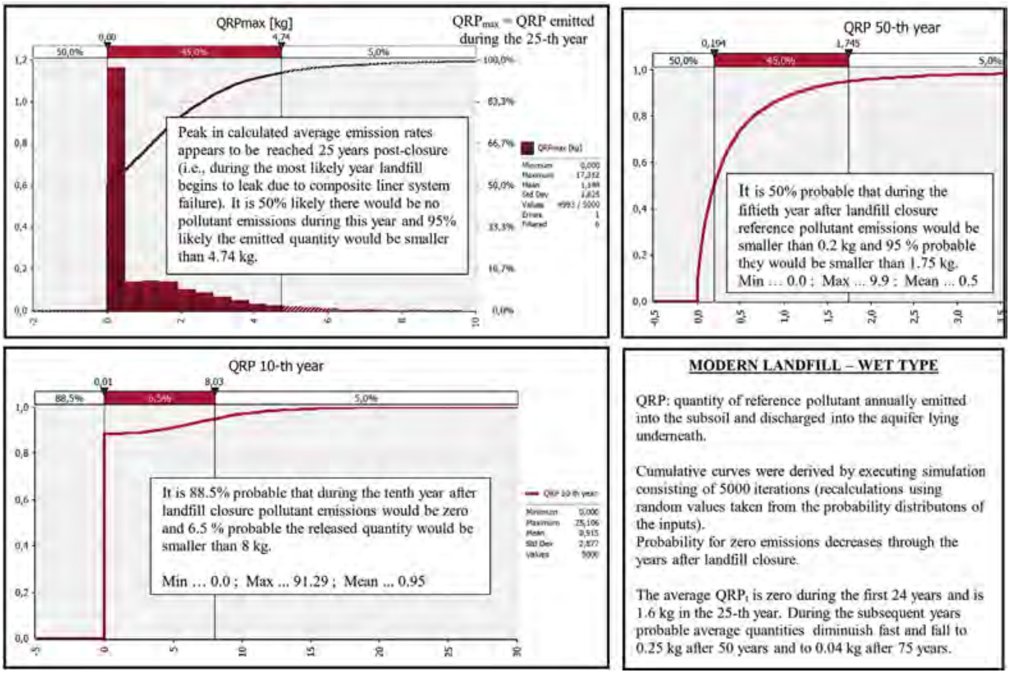

Peak in calculated average emission rates appears to be reached 25 years post-closure (i.e., during the most likely year landfill begins to leak due to composite liner system failure). It is 50% likely there would be no pollutant emissions during this year and 95% likely the emitted quantity would be smaller than 4.74 kg.

It is 50% probable that during the fiftieth year after landfill closure reference pollutant emissions would be smaller than 0.2 kg and 95 % probable they would be smaller than 1.75 kg.
Min ... 0.0 ; Max ... 9.9 ; Mean ... 0.5

It is 88.5% probable that during the tenth year after landfill closure pollutant emissions would be zero and 6.5 % probable the released quantity would be smaller than 8 kg.

Min ... 0.0 ; Max ... 91.29 ; Mean ... 0.95

MODERN LANDFILL – WET TYPE

QRP: quantity of reference pollutant annually emitted into the subsoil and discharged into the aquifer lying underneath.

Cumulative curves were derived by executing simulation consisting of 5000 iterations (recalculations using random values taken from the probability distributons of the inputs).
Probability for zero emissions decreases through the years after landfill closure.

The average QRP$_t$ is zero during the first 24 years and is 1.6 kg in the 25-th year. During the subsequent years probable average quantities diminish fast and fall to 0.25 kg after 50 years and to 0.04 kg after 75 years.

Fig. 10. Derived graphs for the output "quantity of reference pollutant discharged into the aquifer" referring to modern landfills of wet type characteristic post-closure years.

Generally, buried HDPE geomembranes have an estimated service life that is measured in terms of hundreds of years. The three stages of degradation and approximate associated durations for each as obtained from the laboratory testing program described in the report [9], are: (i) antioxidant depletion (≈200 years), (ii) induction (≈20 years), and (iii) half-life (50% degradation) of an engineering property (≈750 years). Therefore, with ageing, geomembranes deteriorate by definition and eventual leakages on average slowly increase.

The inputs were attributed with values as described below:

- Initial leakages "q_0" were chosen to fall mainly within the 0–10 lphd range (mean value = 4.4 lphd, st.dev. = 1.4 lphd)
- Leakage rates were considered to increase slowly through the decades (average doubling time "T_2" was set to be 30 years and st. deviation also 30 years)
- Maximal leakage "q_{max}" could have also been attributed with a probability distribution function in order to include highest possible leakage rates which were already measured (such as those higher than 1000 lphd), however, a discrete cut-off value of 110 lphd was used instead in order to be somewhat complaisant to conventional dry-type landfills comparing them to others when running simulations

Simulated data referring to average leachate flow rates into the subsoil during the characteristic post-closure years comparing performances of different landfill types are shown in Table 2. Simultaneously occuring values for reference-pollutant- concentrations in primary leachate are presented, too.

The applied methodology, including the approaches used to derive probability distribution estimates for input variables is more thoroughly described in the companion MethodX article [2].

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Table 2
Leachate fugitive flow rates into the subsoil and simultaneously occuring ref. pollutant average concentrations within the primary leachate (average values derived from simulations).

Post-closure year	Mean values for Q_t and C_t variables	Above-ground dumpsite	High-permeability landfill (HPL)	Modern dry-type landfill	Modern wet-type landfill
10th	Q_t [lphd]	1233	426	0	0
	[mm/year]	45	15.6	0	0
	C_t [mg/L]	20	(62)	1009	446
50th	Q_t [lphd]	1233	426	7.8	15.6
	[mm/year]	45	15.6	0.3	0.6
	C_t [mg/L]	<1	(<1)	505	8
100th	Q_t [lphd]	1233	426	24.6	49.2
	[mm/year]	45	15.6	0.9	1.8
	C_t [mg/L]	<1	<1	221	<1
200th	Q_t [lphd]	1233	426	109.6 (max value)	219.2 (max value)
	[mm/year]	45	15.6	4 (max value)	8 (max value)
	C_t [mg/L]	<1	<1	38	<1

Note that -
1.) flow through the clayey liner underneath the HPL's does not result into emissions until the pollutants penetrate the liner and break through on its bottom side (until this happens, reference pollutant concentration values within the leachate at the bottom of the landfill are shown in parentheses).
2.) upperbound (max) leachate rates of flow into the subsoil are reached 165 years after closure on average for modern landfills according to simulation results.
3.) water losses from the landfill into the subsoil "Q_t" are expressed in liters per ha per day as well as in units commonly used to describe amount of precipitation (mm per year).
4.) leakage rates from above-ground dumpsites situated in humid climates are generally high (however, pollutant concentrations within the primary leachate are generally low and decline rapidly after landfill closure).
5.) leakage rates from modern landfills are generally very low or even non-existent (but pollutant concentrations within the primary leachate are generally high and decline very slowly in the case of dry-type landfills).

Conflict of interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.dib.2019.104488.

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Exhibit E

Article:

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THE ROLE OF NATURAL CLAYS IN THE SUSTAINABILITY OF LANDFILL LINERS

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ABSTRACT

Engineered synthetic liners on their own cannot protect the environment and human health against landfill leachate pollution. Despite their initial impermeability, they are susceptible to failure during and after installation and have no attenuation properties. Conversely, natural clay liners can attenuate leachate pollutants by sorption, redox transformations, biodegradation, precipitation, and filtration, decreasing the pollutant flux. Depending on the clay, significant differences exist in their shrinkage potential, sorption capacity, erosion resistance and permeability to fluids, which affects the suitability and performance of the potential clay liner. Here, the physico-chemical, mineralogical and geotechnical characteristics of four natural clayey substrata were compared to discuss their feasibility as landfill liners. To study their chemical compatibility with leachate and rainwater, hydraulic conductivities were measured every ≈2 days spread over 7 weeks of centrifugation at 25 gravities. At field-scale, this is equivalent to every 3.4 yrs spread over 80 yrs. All the clayey substrata had favourable properties for the attenuation of leachate pollutants, although different management options should be applied for each one. London Clay (smectite-rich) is the best material based on the sorption capacity, hydraulic conductivity and low erodibility, but has the greatest susceptibility to excessive shrinkage and alterable clay minerals that partially collapse to illitic structures. Oxford Clay (illite rich) is the best material for buffering acid leachates and supporting degradation of organic compounds. The Coal Measures Clays (kaoline-rich) have the lowest sorption capacity, but also the lowest plasticity and have the most resistant clay minerals to alteration by leachate exposure.

1. INTRODUCTION

Leachates produced in municipal landfills constitute a health and environmental problem due to the different pollutants they content. For this reason, liners are required to minimise offsite migration of leachate. Two types of liners are currently used in modern landfills: synthetic liners, typically made of HDPE, and natural liners, typically made of compacted clay (Adar and Bilgili, 2015; Wei et al., 2018). Synthetic liners offer long-term impermeability to leachate but imply a high technology input and can be affected by slope stability, interface shear strength (Kavazanjian et al., 2006) and physico-chemical, thermal and mechanical problems (Kong et al., 2017), which may result in failure within 10 yrs of service (Rowe and Sangam, 2002; Rowe et al., 2003). Compacted clay liners are puncture-resistant and have advantageous reactive properties, but can be unstable in contact with leachate and susceptible to cracking under repeated wetting and drying cycles (Louati et al., 2018; Yesiller et al., 2000).

Because containment liners eventually fail independently of their low permeability properties, landfills are potential “ticking time bombs” that store and isolate waste until the confined pollutants are accidentally released to the environment in leachate. However, the intrinsic reactive properties of clays means they can biogeochemically interact with pollutants in leachates to decrease their availability and potential hazards over time. This reactivity (or attenuation) is enhanced if rainwater is allowed to enter the waste because then waste degradation is boosted, which accelerates its stabilization (Allen, 2001). The attenuation capacity of natural liners results in shorter periods of (1) potential release of pollutants and (2) aftercare monitoring, with subsequently lower landfill cost and less risk of environmental contamination. However, most attention has traditionally

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focused on the impermeability properties of liners as a performance characteristic. Here we focus on both impermeability and attenuation capacities, without relying solely on the impermeability (or containment) role, as a basis to improve liner design and performance. This dual capability can in principle be included in the engineering design of compacted clay liners to manage both organic and inorganic pollutants in leachate (Thornton et al., 1993; 1997).

The attenuation capacity, low cost and ease of implementation of compacted clay liners makes them more attractive than synthetic geomembranes on their own in landfill liner systems. This is particularly important in low-income countries where >90% of waste is openly dumped (Kaza et al., 2018), and in removing organic pollutants (Beaven et al., 2009). However, clays are very diverse in their physico-chemical properties and the suitability of the clayey substratum as a potential liner must be properly evaluated (Widomski et al., 2018). This task is complex and, in order to avoid any adverse effects, must consider the factors and the interactions between them, which affect leachate-liner system. There are many factors involved, such as liner mineralogy, shrink/swell potential, sorption capacity, dispersive/erosion behaviour and fluid permeability. If the clay plasticity is too high, construction of the liner becomes more difficult and the swelling/shrinking/cracking potential more significant as a failure mechanism.

In this study, the feasibility of four natural clayey substrata as landfill liners was evaluated. Their physico-chemical, mineralogical and geotechnical characteristics were studied and the results were discussed in terms of strengths and weaknesses as candidate materials for landfill liners. Finally, the potential for attenuation of pollutants in leachate by each material was evaluated for sustainable landfill applications. The aim was to characterise the relevant properties of the different clays in order to identify those which are geotechnical stable and effective in pollutant attenuation for liner design. This is essential to prevent pollution of the environment and protect human health from leachate spreading over groundwater aquifers or adjacent rivers and lands.

2. MATERIALS AND METHODS

2.1 Materials

Four clayey substrata from the United Kingdom were studied: London Clay (LC), Oxford Clay (OC), and shallow and deep Coal Measures Clays (SCMC and DCMC) (Table 1). The LC originated from shale, greensand, chalk, and lateritic soils during a sea level rise over the Northern Sea Basin. It is a silty to very silty clay, slightly calcareous with disseminated pyrite. The OC, collected from the Peterborough Member, contained many visible fossils (vertebrate and invertebrate), particularly bivalves (Meleagrinella). In contrast to the two previous clays, the Coal Measures Clays originated in a fluvio-deltaic environment and also have a relatively high proportion of iron sulphides (pyrite, marcasite) and gypsum, the latter following pyrite weathering. These Coal Measures Clays consist of interbedded clay, shales, silt and sand, interstratified with coal.

Approximately 100, 73, 25 and 20 kg of respectively LC, OC, SCMC and DCMC were recovered in-situ between June and July 2018. The pore water and cation exchange complex compositions were analysed in several subsamples before oven drying. The exchangeable cations were analysed in air-dried and powder samples (prepared with agate mortar and pestle) after applying 3 cycles of 10 sec of ultrasonification to a suspension of 0.15 mg clay in 50 mL deionized water. The elemental composition and mineralogy were determined after oven drying and grinding to a fine powder. For geotechnical tests the conglomerates were oven dried to remove residual moisture and the dry lumps broken up until a particle size <0.2 cm was achieved. For this, a rammer and several perforated screen trays fitted in a CONTROLS sieve shaker (Model 15 d040/a1) were used and the clays first reduced into approximately 2 cm aggregate lumps. Next, the <0.2 cm particles were recovered separately and the 0.2-2 cm lumps put into a bench soil grinder (Humboldt Co) and broken up to achieve <0.2 cm size. All results are expressed as a function of dry mass.

2.2 Analyses

The concentrations of nitrogen, carbon, hydrogen and sulphur were analysed in duplicate samples ground to ≤0.1 cm (0.005 g) using a Thermo Scientific FLASH 2000 Elemental Analyzer (CHNS). The remaining elements except oxygen and the halogens were analysed using a Spectro-Ciros-Vision radial ICP-OES instrument after acid digestion of 0.031 and 0.094 g at 150°C. For this, 12 mL of aqua regia was applied for 30 min followed by two 1 mL volumes of HF for 10 min, and the resulting solution was eluted up to 50 mL with 1 mass % HNO_3. The mineralogy was determined by X-ray diffraction (XRD) using a Ni-filtered Cu Kα radiation (k = 0.15406 nm) in a Philips X'Pert diffractometer,

TABLE 1: Information about the natural clayey substrata samples.

	London Clay (LC)	**Oxford Clay from Peterborough Member (OC)**	**Shallow Coal Measures Clay (SCMC)**	**Deep Coal Measures Clay (DCMC)**
Location (UK)	North Essex	Northwest Buckinghamshire	West Yorkshire, collected close to the surface	West Yorkshire, collected at a greater depth
Age	Eocene: 47.8 - 56.0 Ma	At the end of the Middle Jurassic: 164-166 Ma	Upper Carboniferous: 310 Ma	Upper Carboniferous: 310 Ma
Origin	Deep marine sediments	Deep marine sediments	Fluvio-deltaic sediments	Fluvio-deltaic sediments
Colour / appearance	Uniform, firm, brown colour	Grey colour with carbonaceous shells and rootlets	Dark grey-dark brown colour	Two-coloured: orange-light brown and dark brown
Selected references	Fannin 2006; Kemp and Wagner, 2006	Fannin 2006; Hudson and Martill, 1994; Scotney et al., 2012	Freeman, 1964, McEvoy et al., 2016	Freeman, 1964, McEvoy et al., 2016

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operating at 40 kV and 40 mA, with a step size of 0.016 and a speed of 2 s/step. The samples were prepared by both sprayed random powder (after grinding down to 1-3 µm) and flat oriented slides (after obtaining the <2-µm fraction by dispersant and Stokes' law). Each oriented sample was prepared from a suspension of 0.1 g of the clay-fraction in 2 mL of a solution in three ways: (1) in water and air drying, (2) in water and 550°C drying for 2 h, and (3) in a glycerol solution and air drying (Moore and Reynolds, 1997). The software PDF-4+ 2019 (version 4.19.0.1) and the database v. 4.1903 were used for data interpretation. The content of organic matter, sulphides, hydroxyl groups and carbonates phases was determined by termogravimetrical analysis (TGA). Replicates between 0.015-0.030 g were heated from 30 to 995°C at a rate of 20°C/min with a TGA 4000 Perkin Elmer under two atmospheres: N_2 and O_2 gas (20 mL/min). The results were interpreted in combination with the CHNS, ICP-OES and XRD results. The external specific surface area was measured in 0.2-0.5 g of degassed material (60°C) by the Brunauer-Emmett-Teller (BET) method of nitrogen gas sorption at 77 K in both a Micromeritics Tristar II 3020 and Beckman Coulter SA-3100. The material was prepared from 1 g of original sample gently ground to <400 µm (at least 10 cycles) and discarding the fraction below 64 µm (Bertier et al., 2016). The particle size distribution as volume percent was determined by the Malvern Mastersizer 3000® (double) Laser Diffraction (software version 3.62) assuming the refractive index and density of silica SIO_2 (respectively 1.457 and 2.65 g/cm^3). Samples were dispersed in distilled water by stirring at 2500 rpm and ultrasonic treatment. Measurements of 10 min duration were repeated in the same sample until the results were constant and an average taken.

The pore water chemistry was obtained by mixing 20 mL of deionized water to 10 g of wet clay at room temperature. Sample pH was measured with a pH glass electrode in the water:clay mixture after settling for 24 h and shaking prior to the analysis. The solution was then centrifuged and filtered (0.45 µm) to measure the electrical conductivity with a 0.4-cm sensor, and the soluble elements. The soluble anions and cations were analysed by ion chromatography (Dionex ICS-3000), the alkalinity by titration with H_2SO_4 (HACH digital titrator) and the carbon soluble species using a TOC-V-CSH analyser (Shimadzu ASI-V). The cations in the exchange complex were determined as the difference between the cations extracted with a 1.26 M $SrCl_2$ solution (80 mL) minus the soluble fraction extracted with water (80 mL) after shaking with 5 g of clay for 10 minutes (Edmeades and Clinton, 1981). Due to the high ionic strength of the $SrCl_2$ solutions, sodium, potassium, calcium and magnesium in these extracts were analysed by atomic absorption spectroscopy, AAS (HITACHI Polarized Zeeman Z2300), whereas ammonium was analysed by atomic emission spectroscopy. $LaCl_3$ was added at 20% to standards and samples for the AAS analyses of calcium and magnesium. The cation-exchange capacity (CEC) was determined by copper complex with Cu-triethylenetetramine at pH 7-8, with a photometer at a wavelength for maximum extension of 579 nm (Holden et al., 2012; Stanjek and Künkel, 2016).

To study the consistency and engineering behaviour of the materials, the clay samples were hydrated with different amounts of water for 24 hours in sealed plastic bags prior to index property tests (Head, 2006). The consistency was studied in the <425-µm fraction (250 g) by the determination of two specific water (or moisture) contents: the liquid limit, LL (water content that separates the plastic and liquid states) and the plastic limit, PL (water content that separates the semi-solid and plastic states). The change of clay consistency from plastic to liquid state was determined by the free-falling cone test at a penetration of 2 cm into the wet sample, with duplicates differing ≤0.05 cm (BS 1377:2:4.3, 1990). The change of clay consistency from semi-solid to plastic state was determined by manual rolling wet samples (20 g) until threads of 0.3-cm diameter begin to crumble, with four replicates differing ≤2% moisture content of their PL (BS 1377:2:5.3, 1990 and ASTM D 4318, 2015). To know the range of water content in which the clayey material has a plastic consistency, the plasticity index (PI) was calculated as the difference between the LL and the PL (Head, 2006). All actual moisture contents were determined on a mass % dry basis (Equation 1) after oven drying 5-10 g of material (105°C, 48 h) with duplicates that differ ≤0.5%.

$$\mathrm{MC}(\%) = \frac{m_0 - m_d}{m_d} \times 100 = \frac{m_{0,c} - m_{d,c}}{m_{d,c} - m_c} \times 100 \qquad (1)$$

where MC is the moisture content dry basis (%), m_0 is the mass of wet sample before moisture removal (g), m_d is the mass of sample after drying (g), $m_{0,c}$ is the mass of wet sample plus container before moisture removal (g), $m_{d,c}$ is the mass of sample plus container after drying (g) and m_c is the mass of the container (g).

The optimal condition of the clays at which the susceptibility to settlement is reduced was studied by applying the same compactive effort in different hydrated samples (240-540 mL water in 1600-1800 g clays). The compaction was placed into a mould of 5.25 cm radius by 11.55 cm height, in three equal layers subjected to 27 blows each one, by a 2.5 kg rammer of 2.5-cm radius that dropped from a height of 30 cm (BS 1377:4:3.3, 1990). The optimum moisture content (OMC) was selected on the basis of the maximum dry (bulk) density (MDD) after the compaction. To calculate the particle density of the solids, the specific gravity (G_s) was obtained by triplicate tests at 20°C, in desiccated materials of <0.2 cm size (50 g) using air-dried pycnometers of 50 mL (BS 1377:2:8.3, 1990 but 20°C instead of 25°C). The porosity (n) was calculated as a percentage following Equation 2 (Equation 3 for the optimal conditions). The slight difference between n and void ratio (e) is that the latter measures the void volume (the sum of V_{air} and V_w) in relation to the volume of the solid instead of the total volume. Thus, e (normally expressed as a ratio) can be >1, but n cannot be higher than 100%.

$$n(\%) = \frac{V_{air} + V_w}{V_T} \times 100 = \frac{V_T - V_s}{V_T} \times 100 \qquad (2)$$

$$n_{opt}(\%) = \frac{V_T - \frac{m_{d,OMC}}{G_s}}{V_T} \times 100 \qquad (3)$$

where V_{air} is the volume of the air (mL), V_w is the volume of the water (mL), V_T is the total volume (mould of 1000 mL),

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V_s is the volume of the solid particles (mL), $m_{d,OMC}$ is the dried mass of sample at the OMC (g) and Gs is the specific gravity (unitless).

Assuming that volumes of voids filled with air are constant ($\eta_{air,i}$), lines at different air void ($\eta_{air,1}$, $\eta_{air,2}$…) and saturation values can be drawn as a function of dry bulk density ($\gamma_{d,i}$) relative to the moisture content ratio (Equation 4). The difference between air void line (η_{air}) and saturation (s) is that the latter ratio measures the volume of water in relation to the void volume instead of the total volume. The zero-air void line ($\eta_{air} = 0$) corresponds to the maximum saturation ratio (s = 1).

$$\gamma_{d,i} = \frac{(1 - \eta_{air,i}) \cdot G_s \cdot \gamma_w}{1 + MCi \cdot G_s} \quad \text{being} \quad \eta_{air,i} = \frac{V_{air,i}}{V_T} \qquad (4)$$

where $\gamma_{d,i}$ and MC_i are the dry bulk densities (g/cm^3) and the moisture contents (ratio) corresponding to the air void constant i, $\eta_{air,i}$ is the line corresponding to an air void and saturation constant i related to the total volume (ratio), G_s is the specific gravity (unitless) and γ_w is the density of water (1 g/cm^3).

The specific value for the air void and saturation line after compaction at the optimal conditions ($\eta_{air,opt}$) was calculated with the $\gamma_{d,i}$ and MC_i equal to MDD and OMC (ratio), respectively (Equation 5).

$$\eta_{air\ opt}(\%) = \left(1 - \frac{MDD\ (1 + OMC \cdot G_s)}{G_s \cdot \gamma_w}\right) \times 100 \qquad (5)$$

The potential swell (S %) was determined based on its relationship with the Atterberg limits by the well-defined empirical Equation 6 (Seed et al., 1962):

$$\mathrm{S}(\%) = 216 \cdot 10^{-5} \cdot \mathrm{PI}^{2.44} \qquad (6)$$

where PI is the plasticity index (%).

The hydraulic conductivity or permeability coefficient (K) was measured in aluminium permeation cylinders by centrifuging at 25 gravities (Regadío et al., 2020). Model liners were compacted into of 5 cm radius by 10 cm height cylinders after being hydrated with tap water at the OMC. Leachate from a municipal solid waste landfill and rainwater were used as permeating fluids. Rainwater was normally used for permeating model liners previously permeated with landfill leachate. Eleven cylinders on average were assembled per centrifuge test, each one connected to an intake line. All intake lines came from a common tank that provided continuous permeation to all the cylinders by applying a pressure of 1.1 bar. The tests were conducted under a 50% CO_2/N_2 anaerobic gas (for leachate permeation) or under compressed air (for rainwater permeation). The fluid head in the tank that provided the permeating fluid was measured every ≈2 days during 2.5 weeks under leachate permeation, or 4.5 weeks under rainwater permeation. The K measured in the centrifugal permeability tests ("experimental model") had a 25-fold enhanced gravity. To calculate the corresponding real value in the field (K "prototype"), the scaling law (Ng, 2014) was applied in the falling head equation for less permeable soils (Head, 1994) adapted to this method (Equation 7):

$$K = \frac{K_{exp.m} \cdot n}{n^2} = \frac{\frac{a\,L}{A\,t}\ \ln\left(\frac{h_0}{h_1}\right)}{n} \text{, being } h_1 = \frac{h_0 - (h_0 - h_{1\#})}{\#} \qquad (7)$$

where $K_{exp.m}$ is the hydraulic conductivity in the experimental model (m/s), n is the enhanced gravity applied in the centrifugal experiment (25), a is the cross area of the tank (0.06158 m^2), L is the lengh of the liner specimen (0.10000 m), A is the cross area of the liner specimen (0.00785 m^2), t is the time period considered for the calculation (seconds), h is the head in the tank at the initial (if subscript 0) and final (if subscript 1#) points, # is the number of model liners connected to the tank.

3. RESULTS

3.1 Elemental composition and mineralogy

The four clayey substratum were mainly composed of silicium and aluminium, followed by iron, potassium, hydrogen and magnesium (Figure 1). This agreed with the expected high presence of clay minerals, potentially higher in Coal Measures Clays (see below). Silica, potassium, titanium, and especially magnesium were higher in the LC. The OC was notable for its high content in calcium, carbon, sulphur (g/kg) and strontium (mg/kg), with lower silica, iron and phosphorus content. The Coal Measures Clays were notable for their high concentration of aluminium, nitrogen and manganese, whereas the concentration of calcium, sodium, potassium, strontium and boron were the lowest within the four samples. In the case of SCMC, there was more carbon, nitrogen and sulphur than in DCMC. (Figure 1).

All samples contain smectite, illite, kaolinite and chlorite but in different proportions (Figure 2). Smectite was most important in LC, illite together with kaolinite in OC, and kaolinite (followed by illite) in the Coal Measures Clays. To a lesser extent, phlogopite mica was detected in LC, chlorite in both LC and OC, and interstratification (mixture of layers) of illite/smectite in OC and the two Coal Measures Clays.

Quartz and feldspars were the most important phases in all materials. These are accompanied by oxides except in the OC, which mainly contained calcium carbonate and iron sulphide (calcite and pyrite). Also relatively high levels of sulphides were found in SCMC, whereas, there were fluorides and oxide-fluoride in DCMC (Figure 3). The mass loss through heating due to dehydroxylation (associated with the mass of clay minerals) was the highest in the Coal Measures Clays (5-9%), while the highest mass loss due to decomposition of organics, sulphides and carbonates phases corresponded to OC (2, 4 and 5% respectively). Particulate organic matter as an associated material in these clays was especially high in the OC. It varied from 1.1 to 3.5% in the OC, in contrast to LC, SCMC and DCMC, which gave steady values of 1.7, 1.5 and 1.8%, respectively. The variability in the particulate organic matter content in the OC was due to its presence in many diverse forms: disseminated organic matter, coarse lignite fragments and fossils. Similarly, the carbonate phases in the OC varied from 4.5 to 6% due to the spread of carbonaceous shells.

3.2 Pore water and mineral surface characteristics

The LC had the highest natural moisture content followed by the OC (39 and 25 ± 2%, respectively), whereas SCMC and DCMC had the lowest values (10 and 12 ± 1%, respectively). This indicates a decreased water absorption and porosity from LC > OC > Coal Measures Clays. The pore water composition of the clayey materials of the OC was

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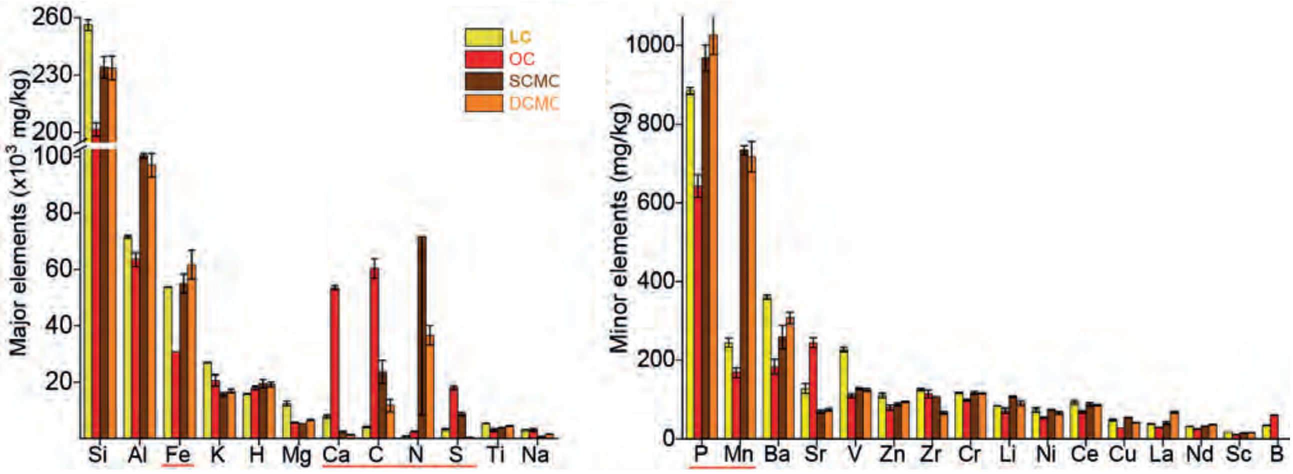

FIGURE 1: Elemental composition of London Clay (LC), Oxford Clay (OC), shallow Coal Measures Clay (SCMC) and deep Coal Measures Clay (DCMC).

the most basic due to the presence of calcium carbonate phases (pH 9.0) and the LC was close to neutral (pH 7.3). In contrast, the SCMC and DCMC were acidic (pH 3.8 and 5.4, respectively). Consistent with this, alkalinity was only present in the OC (10.3 mmol/kg as $CaCO_3$) and LC (1.7 mmol/kg as $CaCO_3$). The total dissolved ion content in terms of electrical conductivity in aqueous extracts (L/S 1:2.5) was between 1-3 mS/cm, except for DCMC (0.1 mS/cm) and for OC (5 mS/cm). The predominant soluble anion in all samples was sulphate (SO_4^{2-}), mainly balanced by calcium (Ca^{2+}) and sodium (Na^+) in both the LC and OC, by magnesium (Mg^{2+}) and Ca^{2+} in the SCMC and mostly Na^+ in the DCM. In all cases the concentration of potassium (K^+) was very low and ammonium (NH_4^+) was not detected. Only the OC had a significant content of soluble carbon in the pore water (10 mg/g).

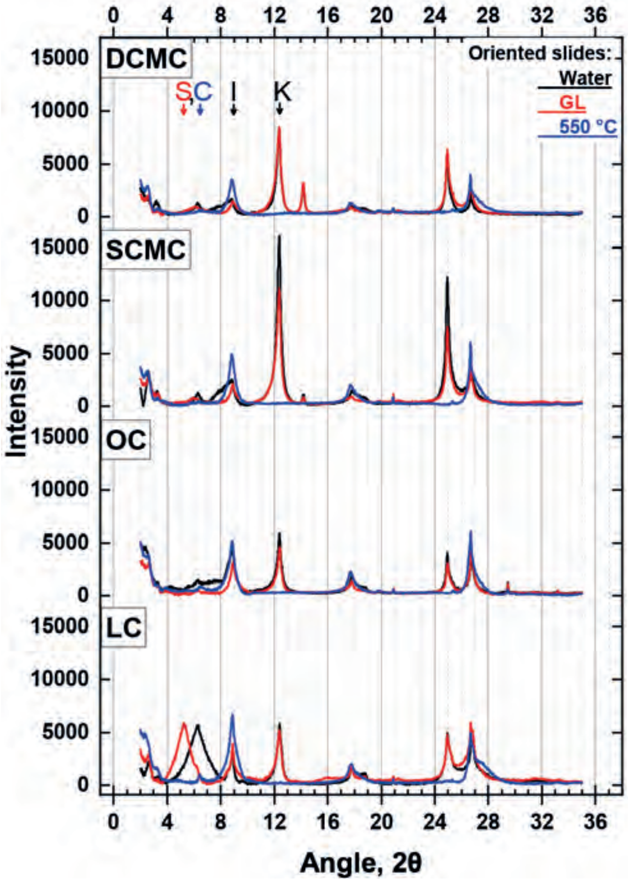

FIGURE 2: Sheet-silicate mineralogy of London Clay (LC), Oxford Clay (OC), shallow Coal Measures Clay (SCMC) and deep Coal Measures Clay (DCMC). Water: water and air drying preparation, GL: glycerol and air drying preparation, 550°C: water and 550°C drying preparation. S: smectite d001 reflection under GL preparation, C (chlorite) and I (illite) d001 reflections under all three preparations. K: kaolinite d001 reflection under water and GL preparations.

As expected the exchangeable cations on the negatively charged sites of the clays and particulate organic matter were similar to the most abundant in the pore water. The sum of exchangeable cations often exceeded the total charge of the clay (CEC), due to high concentrations of Ca^{2+} released by dissolution of carbonate minerals. Thus, the CEC was measured directly instead of estimating this from the sum of exchangeable cations, to avoid bias from Ca^{2+}. The CEC at pH 7-8 decreased in the order: LC (26 cmol+/kg) > OC (16 cmol+/kg) > Coal Measures Clays (13 cmol+/kg). The external specific surface area increased in the order: LC < OC < DCMC < SCMC (9.3 ± 0.3, 12.8 ± 3. 6, 31.0 ± 1.0, 53.7 ± 1.0 m^2/g, respectively). The highest values corresponded to the material with the highest amount of hydrous aluminium phyllosilicates minerals (Coal Measures Clays), followed by the material with the highest amount of particulate organic matter (OC). Nonetheless, the total surface area (external plus internal) of the LC may be one of the largest due to its higher content of expandable clay minerals (illite + smectite) than non-expandable ones (kaolinite + chlorite).

3.3 Consistency classification and properties

The moisture contents at PL and LL were determined to identify clays susceptible to dispersion and excessive shrinkage in the field (Table 2). These parameters can distinguish between silt- and clay- size, and organic or inor-

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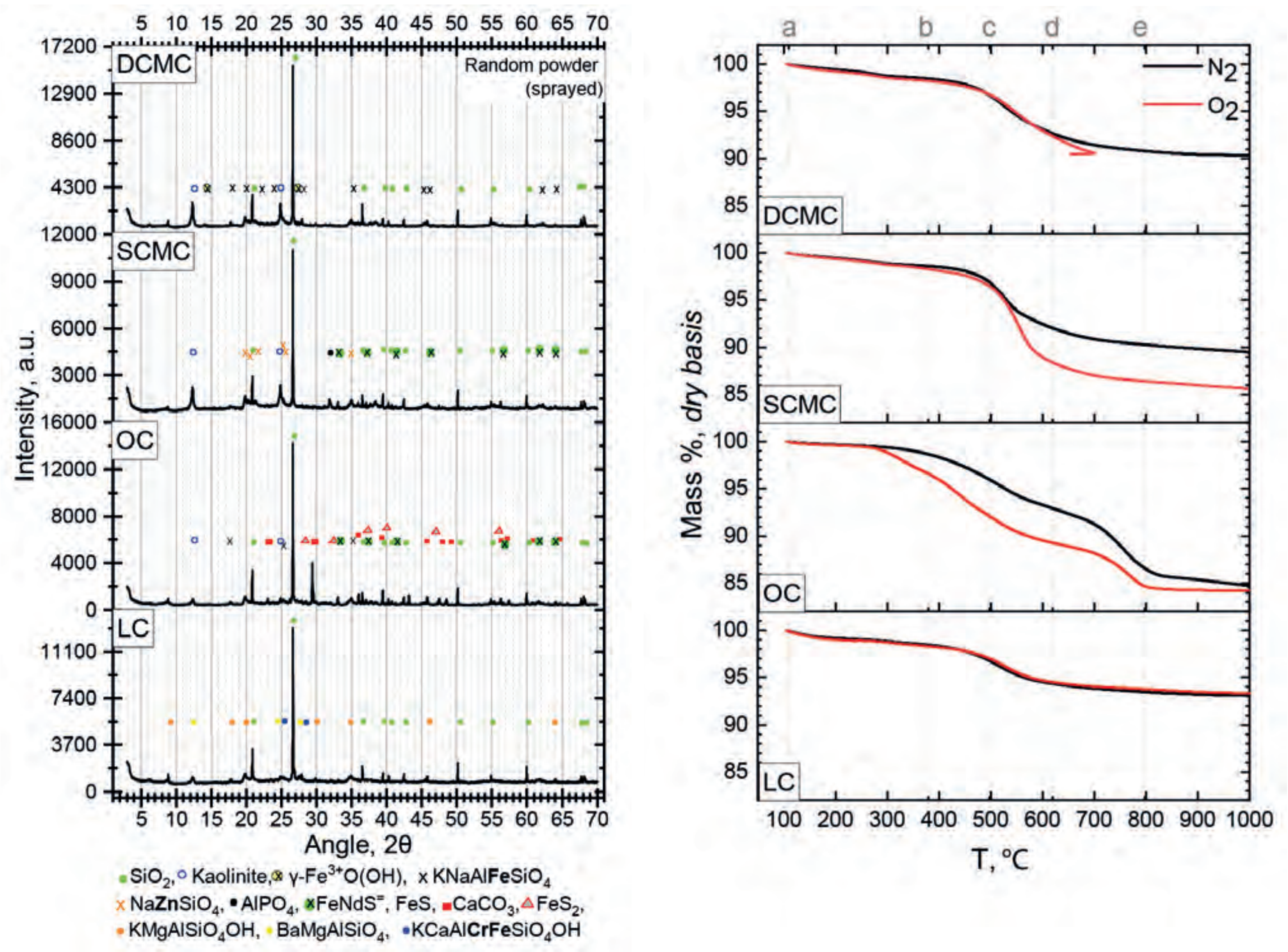

FIGURE 3: Left: Global mineralogy by sprayed random powder of London Clay (LC), Oxford Clay (OC), shallow Coal Measures Clay (SCMC) and deep Coal Measures Clay (DCMC). Right: TGA curves with mass relative to the mass after dehydration (removal of interlayer water): (a-b) mass loss mainly due to thermal decomposition of organic matter, (b-c) mass loss due to thermal decomposition of sulphides, (c-d) mass loss due to dehydroxylation, (d-e) mass loss due to thermal decomposition of carbonate and (e-end) materials vitrification and formation of new phases (recrystallization).

ganic character. All clays had a LL >20%, confirming that they were cohesive materials. The LL and PI varied in the order: LC > OC > Coal Measures Clays, consistent with the dominant sheet silicate in each material: smectite, illite/kaolinite and kaolinite, respectively. The LC and OC had high plasticity, high toughness and high to very high dry strength (Figure 4). The high plasticity of LC was notable for the broad range of water contents at which this clay had plastic consistency (from 28 to 79%, i.e., PI = 51%), twice that of the OC. This is due to the presence of smectite (expandable clay mineral) and the higher content of clay-size particles in the LC compared with the other clays with a higher silt content. Ninety vol% of the LC was composed of particles ≤52 µm, whereas 90 vol% of the DCMC, SCMC and OC were made up of particles ≤130 µm, ≤136 µm and ≤185 µm, respectively. The two Coal Measures Clays gave similar results: intermediate plasticity, medium toughness and high dry strength. The potential to swell decreased from LC >> OC > SCMC > DCMC (30.2, 5.3, 2.6, 2.4%), as expected from the mineralogy and PI results. All studied materials had no dispersive clay fines as these do not occur in clays from intermediate to high plasticity with smectite. On the contrary, dispersive clays typically appear in soils classified as clayey of low plasticity (CL), sometimes also in silty and/or sandy soils with low plasticity (ML, CL-ML) (Figure 4).

The "A-line" on the plasticity chart (Figure 4) denotes the empirical boundary between inorganic materials and clays (above line) and organic clays and clastic silts (below line). The OC fell on the dividing line between inorganic and organic categories, while Coal Measures Clays and the LC fell above the line in the inorganic region, being the DCMC close to the organic silts, and the LC the most inorganic clay.

3.4 Compaction and permeability behaviours

Clays are normally compacted for placing and constructing the clay liners because to increase the shear strength and bearing capacity, which limits future settlement. In addition, the void ratio and permeability is decreased, and variations in volume change are less pronounced. Consequently, clays are less susceptible to cracking that would offer preferential flow paths for leachate leakage and groundwater seepage. To optimise this, clays should be compacted close to the OMC, the quantity of water nec-

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TABLE 2: Moisture contents corresponding to the Atterberg consistency limits (<425-µm fraction).

	Linear regression		LL, %	PL, %		PI, %
	Slope	Intercept	Value (X when Y= 20)	Value	RSD, percent	Value
LC	0.552	-23.339	79	28	4.4	51
OC	1.136	-40.404	53	29	4.3	24
SCMC	1.758	-49.944	40	22	4.0	18
DCMC	1.368	-40.052	44	25	0.9	19

Linear regression: relationship of the cone penetration (Y-axis in mm, as a reverse measure of the shear strength) on the moisture content (X-axis in %), LL (or WL): liquid limit, PL (or WP): plastic limit, PI (or Pi): Plasticity index, RSD: relative standard deviation (the standard deviation divided by the average and multiplied by 100), LC: London Clay, OC: Oxford Clay, SCMC: shallow Coal Measures Clay, DCMC: deep Coal Measures Clay.

essary to achieve the maximum dry (bulk) density. Under the same compaction effort, the OMC followed the order LC > OC > Coal Measures Clays, while the maximum dry (bulk) densities followed the inverse sequence (Figure 5). The clay sequence for OMC agreed with those for air void lines and for porosity (both after compaction at the optimal conditions), and with the higher plasticity of LC, followed by OC, which could accommodate more water to achieve their maximum dry densities than the Coal Measures Clays. The particle density of the solids, in terms of specific gravity, followed the order LC > Coal Measures Clays > OC due to the higher particulate organic matter content of the last one (Figure 5). Both Coal Measures Clays had very similar consistency and engineering behaviour (Figure 4 and Figure 5).

The K for leachate and rainwater through the most plastic clays (LC and OC) amended with sandy materials was measured over time. In all three tests run with landfill leachate, K slightly increased from initial values of 0.1 and $0.3 \cdot 10^{-9}$ m/s to a maximum of 0.6 and $0.8 \cdot 10^{-9}$ m/s after an initial time equivalent to 8-15 yrs. Then, K decreased to comparable values at the start (Figure 6). Only on three separate occasions during leachate permeation through liners of 20% sand, K exceeded the maximum legal limit: in the beginning (between 0 and 3.1 yrs), in the middle (between 8.2 and 10 yrs) and towards the end (between 25.4-27.1 yrs). However, the average of K measurements taken in 9 different periods over a total modelled time equivalent to 32 yrs prototype of leachate through the liners of 20% sand was $0.8 \cdot 10^{-9}$ m/s (± $0.6 \cdot 10^{-9}$), and lower through the liners of 10% sand ($0.3 \cdot 10^{-9}$ m/s (± $0.2 \cdot 10^{-9}$)). When changing to rainwater though liners of ≈6% sand, there was also in the beginning a slight increase of K with time up to $0.5 \cdot 10^{-9}$ m/s, followed by a decrease with a stabilization around $0.2 \cdot 10^{-9}$ m/s (±$0.1 \cdot 10^{-9}$) from year 44 onwards (30 yrs of leachate permeation followed by 14 yrs of rainwater, Figure 6). The average of K for rainwater permeation taken over 16 periods of time within the total time modelled (53 yrs prototype) was $0.3 \cdot 10^{-9}$ m/s (±$0.1 \cdot 10^{-9}$) though the liners of ≈6% sand. The accumulated K calculated as a single measurement over the entire test time (≈19 days each test) was very close to the average K calculated with all intermediate measurements taken every ≈2.3 days over the 19-day tests (Table 3). This together with the small standard deviations of the K in liners with 10% or less sand, denotes that their K variation describe above was not very significant.

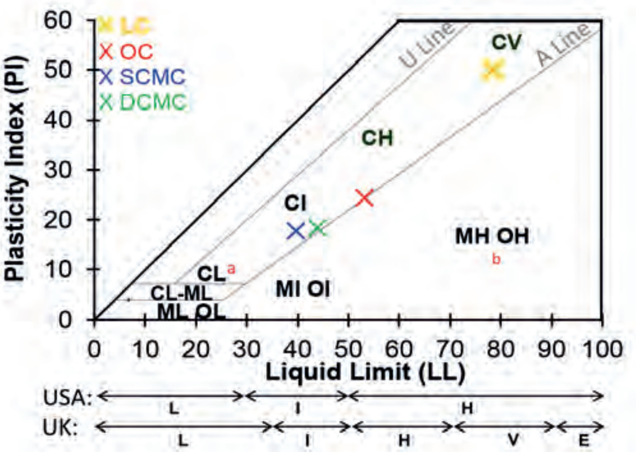

FIGURE 4: Plasticity chart for soil classification (<425-µm fraction) of London Clay (LC), Oxford Clay (OC), shallow Coal Measures Clay (SCMC) and deep Coal Measures Clay (DCMC). Divisions of plasticity in: L: low, I: intermediate, H: high, V: very high and E: extremely high, according to USA and UK. O: significant organic material; C: clayey; M: silty and/or sandy (Unified Soil Classification System, USCS). [a] dispersive clay fines, [b] non dispersive clay fines. U-line: upper reference bound of PI for natural soils defined by two equations: PI = 7 if LLs ≤16, and PI = 0.9 (LL- 8) if LLs >16. A-line: reference boundary of PI between the clay soils (above line, mostly inorganic) and the silt soils (below it) defined also by two equations: PI = 4 if LLs ≤25.5, and PI = 0.73 (LL- 20) if LLs >25.5 (Casagrande, 1947).

4. DISCUSSION

Based on the previous analysis, the feasibility of the four natural clayey substrata to attenuate landfill leachate is discussed below. Although its composition varies, landfill leachate always contains high concentrations of Na^+, K^+, bicarbonate and chloride, with significant NH_4^+ and organic compounds. The heavy metal content is generally relatively low, often of no major concern and limited to chromium, nickel and zinc (Aucott, 2006; Kjeldsen et al., 2002). As NH_4^+ and K^+ are major elements in landfill leachate and virtually absent in these Ca-clay mineral liners, both can be used as tracers in leachate migration studies. The differences between the clayey substrata on porosity, density, sorption, surface, plasticity, permeability are due to their origin, particle size and mineralogy (Table 1 and from Figure 1 to 3). The presence of carbonaceous material is characteristic of clays formed in alluvial or shallow waters, as is the case with Coal Measures Clays (Bain, 1971). Smectite is often found interstratified with illite and in mixtures with chlori-

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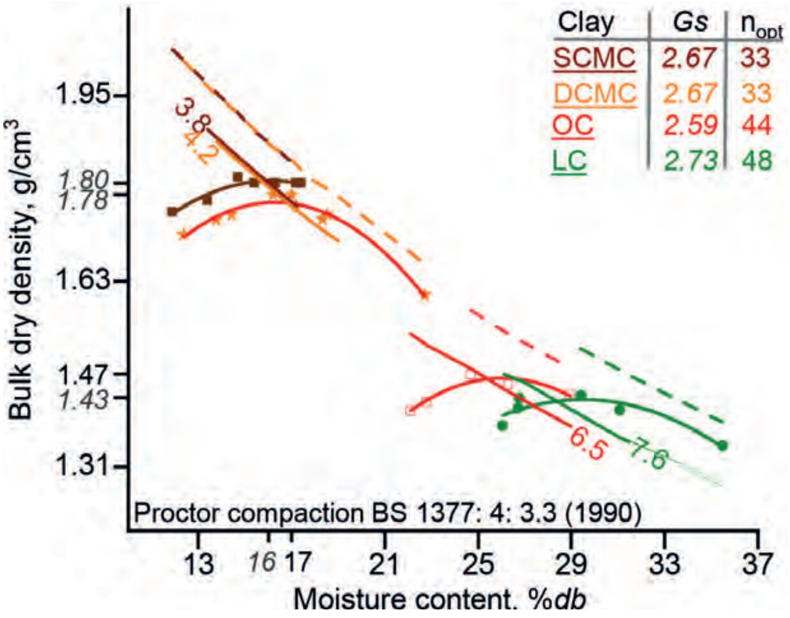

FIGURE 5: Air void lines (air vol% of the total volume) and compaction curves under Proctor BS 1377:4:3.3 (1990) to estimate the (optimum) moisture contents at which the dry bulk densities are maximum. Dashed straights: zero air line or full (water) saturation lines (s=1). Solid straights: air void lines at the optimum. n_{opt}: porosities at the optimum (air plus water vol% of the total volume). Gs: specific gravity (unitless). LC: London Clay, OC: Oxford Clay, SCMC: shallow Coal Measures Clay and DCMC: deep Coal Measures Clay.

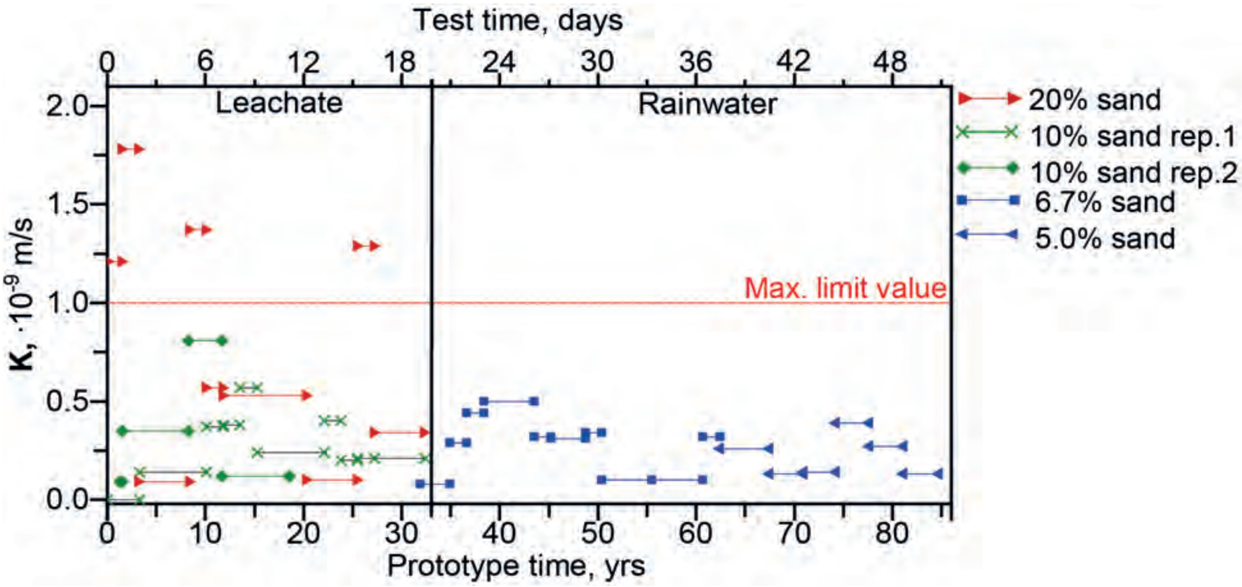

FIGURE 6: Hydraulic conductivities (K) of landfill leachate (from year 0 to 33) and rainwater (from year 33 to 82) through model liners (≈11) of averaged compositions made of clays and mixtures of clays with sandy non-cohesive materials. The mixtures were used to decrease the plasticity of London and Oxford clays and therefore its associated risk of shrinkage.

te and sometimes kaolinite in deep sea marine sediments, as for the LC and OC. A high silica-to-aluminium ratio is characteristic of clays with smectite minerals (Weaver and Pollard, 1973), agreeing with that the LC had the highest values of this ratio and of smectite.

4.1 Evaluation as attenuation liners

In addition to the low permeability that they provide, compacted clays can attenuate leachate pollutants by sorption, dilution, redox transformations, biodegradation, precipitation and filtration (Allen, 2001; Griffin et al., 1976; Thornton et al., 1993). Attenuation here refers to a reduction of the mass of pollutants by naturally-occurring processes (Regadío et al., 2015). These attenuation processes occur simultaneously and can affect more than one pollutant in leachate. By sorption, pollutants are attached to mineral phases or particulate organic matter by a physical or chemical process, which encompasses ion exchange, adsorption, absorption and chemisorption. By redox transformations, organic and metal compounds are converted

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TABLE 3: Hydraulic conductivities in m/s (K) as a single accumulated measurement within the entire test and as an average of the intermediate measurements taken every 2-3 days throughout the test.

Average liner composition	Permeating test time	Permeating fluid	One accumulated measurement	Average (± standard deviation) of intermediate measurements
Clays with 20% sand	From day 1 to 19	Landfill leachate	$0.45 \cdot 10^{-9}$	$0.81 \cdot 10^{-9}$ ($\pm 0.61 \cdot 10^{-9}$)
Clays with 10% sand (1)	From day 1 to 19	Landfill leachate	$0.21 \cdot 10^{-9}$	$0.25 \cdot 10^{-9}$ ($\pm 0.17 \cdot 10^{-9}$)
Clays with 10% sand (2)	From day 1 to 19	Landfill leachate	$0.29 \cdot 10^{-9}$	$0.27 \cdot 10^{-9}$ ($\pm 0.33 \cdot 10^{-9}$)
Clays with 6.7% sand	From day 19 to 36	Rainwater	$0.25 \cdot 10^{-9}$	$0.28 \cdot 10^{-9}$ ($\pm 0.14 \cdot 10^{-9}$)
Clays with 5.0% sand	From day 36 to 48	Rainwater	$0.22 \cdot 10^{-9}$	$0.22 \cdot 10^{-9}$ ($\pm 0.11 \cdot 10^{-9}$)

(1) and (2) are replicates.

into less toxic or immobile forms by electron transfer reactions. By biodegradation, organic pollutants are chemically decomposed by microorganisms. By precipitation, metallic pollutants become less bioavailable or mobile. By filtration, larger pollutants such as metal-organo complexes in the leachate remain physically trapped within the liner fabric.

The surface of soil particles is critical for the chemical reactions, sorption, colloid filtration, and transport of contaminants. All clayey materials and especially the OC contained particulate organic matter (Table 1, Figure 3 right, Figure 4) which has a large surface area and CEC. Particulate organic matter is important for the attenuation of contaminant molecules by sorbing them to its surface or fostering microbial communities that would breakdown the contaminants to less toxic or nontoxic compounds (see biodegradation below). The CEC in particulate organic matter and also in clay minerals is especially important for sorption. In this case cations in the pore water are sorbed by clays to neutralize their negative charge created by unbalanced substitutions of their structural cations. Sorbed native cations can be replaced by cationic pollutants in the leachate. Illites (present in the four clays here) have high affinity for selective sorption of NH_4^+ and K^+ due to their size compatibility with the interlayer (exchange) sites in this clay lattice (Griffin et al., 1976). Smectites (in the LC) also fix these cations but this destabilizes smectitic minerals, resulting in illitization, i.e., partial collapse of smectites with their subsequent conversion into illite. In the case of larger cations, organic cations or organometallic complexes in leachate, smectites sorbed these species preferentially relative to smaller, inorganic or uncomplexed metals (Koutsopoulou and Kornaros, 2010). This is because for the same valence these weakly hydrated cations are the easiest to sorb in the exchange sites than stronger hydrated small cations (Teppen and Miller, 2006), and only smectites have an exchanger interlayer space large enough to accommodate them. Smectite, along with vermiculite (interlayer Mg), has a high CEC, while illite has mid-range values and kaolinite very low values. Thus, the capacity to reduce the concentration of cationic pollutants in leachate by cation exchange reactions follows the order LC > OC > Coal Measures Clays. CEC generally increases with pH due to the development of greater negative charge (average pH in leachate is 7-8).

Anion sorption (bicarbonate, chloride, sulphate from leachate) is less efficient and very similar for the different clay minerals (kaolinite, smectite). It occurs at OH^- ions exposed on the mineral edges and is enhanced by positively charged iron-oxide colloids (present in LC and Coal Measures Clays) associated with clays (Raymahashay, 1987). Bicarbonate is the major inorganic anionic compound in leachate and largely determines the acid-base neutralisation potential of the system. This is good for Coal Measures Clays which have no pH buffering capacity to attenuate acidic episodes caused for example by oxidation of sulphides (pyrite) by infiltrating rainwater (Thornton et al., 2001). This oxygenated water can re-oxidized sulphide phases, resulting in the release of previously attenuated metals that precipitated earlier in such immobile phases (Regadío et al., 2013). Bicarbonates in the leachate itself would provide acid neutralization capacity to Coal Measure Clays which lack calcite. The acidity in Coal Measures Clays most likely arises from oxidation of pyrite in the upper, weathered zone, which produces a low pH, gypsum and amorphous iron oxides as by-products. Chloride is not significantly attenuated and mainly diffuses through the clay liner, together with Na^+ and the cations displaced from the exchange sites of clays (usually Ca^{2+} and Mg^{2+} substituted by NH_4^+, K^+) (Regadío et al., 2012; Zhan et al., 2014). These elements are diluted by the receiving groundwater and are generally not a problem due to its low toxicity even at relatively high concentrations. Sulphate in leachate is attenuated by anaerobic microbial reduction, a common redox process in landfills (Batchelder et al., 1998). All the studied clayey substrata contain redox-sensitive species, the most important being pyrite in the OC and SCMC, and iron oxides in the LC, SCMC and DCMC. As a result, these clays support the metals to precipitate as sulphides in the liner and the sulphate is in low concentration in leachate.

Biodegradation is also accompanied by changes in redox potential in the landfill, which results in transformation of organic and inorganic species by reactions under aerobic and a range of anaerobic conditions. Depending on the specific redox conditions in the landfill and liner (aerobic, nitrate-reducing, iron-reducing, sulphate-reducing, etc.), one or other organic compounds can be biodegraded (Bright et al., 2000). The concentration of the oxidising agents and their reduced species in the leachate indicates the redox conditions (Taylor and Allen, 2006). Differences in clay minerals have a minor effect on the biodegradation

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of organic pollutants than on the sorption of inorganic pollutants. This is because organic pollutants are attenuated mainly by anaerobic biodegradation (Thornton et al., 2000; Bright et al., 2000; Adar and Bilgili, 2015), rather than by sorption to clay minerals, in which case only smectite, chlorite and vermiculite would show significant organic sorption (Koutsopoulou and Kornaros, 2010). The decomposition of organic compounds down to water, methane and carbon dioxide, depends on the establishment of an appropriate microbial population. The native particulate organic matter of clay materials is essential to support in situ biological activity in liners, with the highest organic matter content found in the OC (followed by SCMC), sampled from a fossiliferous location (Martill et al., 1994). Anaerobic degradation in the liner is also sustained by the microbial inoculum in the leachate itself.

The attenuation of heavy metals in leachate is associated with particulate organic matter and mineral phases, including clay minerals in liners, and occurs by a combination of sorption, redox transformation and precipitation processes (Fannin, 2006). These processes are supported by specific mineral phases such as sulphate-bearing species (pyrite, gypsum), iron and manganese oxides and oxyhydroxides, and clays (mainly smectite and illite) (Fisher and Hudson, 1987). The studied materials all contain a high content of clay minerals which assists retention of heavy metals. The OC and SCMC contain pyrite, and the LC, SCMC and DCMC contain iron/metal oxides. The high native particulate organic matter content of the OC favours sorption of metals, whereas the dissolved organic compounds in leachate favour the formation of soluble metal-organo complexes. Despite the fact that metal-organo complexes are dissolved in leachate and therefore mobile, they can be attenuated by filtration due to their larger size (Christensen et al., 1996; Gregson et al., 2008). However, a proportion of metals complexed with dissolved organic matter or associated with colloids in leachate may not be attenuated (Thornton et al., 2001).

4.2 Evaluation as containment liners

None of the clays here were identified susceptible to dispersion in the field. Dispersive clays resemble normal clays but can be highly erosive and susceptible to severe damage or failure. Soils of high plasticity silt (MH in the USCS classification, Figure 4) and smetite-rich materials (LC) rarely contain dispersive clays. In the case of the LC, smectites are responsible for the adhesion forces between particles, which helps to prevent dispersion and thus soil erosion. The locations of the clays on or above the "A-line" on the plasticity chart (Figure 4), denotes a relatively low silt content so they are easy to compact well, resulting in low erodibility. The high OMCs of the OC and LC (25-29% with maximum dry bulk densities of 1.43-1.47 g/cm^3), indicate the abundance of clay-sized particles (heavy clays) as silt-rich soils have medium values and sandy materials have very low values. Coal Measures Clays had 16-17% of OMC with maximum dry bulk densities of 1.78-1.80 g/cm^3, being more characteristics of sandy-clay materials. In the case of shrinkage potential, only LC presented high risk because of the smectites. Concordantly, the LC was classified as high shrinkage (average shrink limits of 16.8±4.8%) compared to the OC as medium shrinkage (14.5 ±2.0%) in Hobbs et al. (2019). In addition, smectites can also sorb larger quantities of water that decrease the soil strength, causing destructive landslides and slope failure (Borchardt, 1977; Wagner, 2013; Yalcin, 2007). To ensure landfill liner stability, clays should have PIs of 15-30% (25% is good) and clays with PI >40% should not be used on their own.

The LC and OC are plastic clays and thus contain little sand and much clay, with a particular abundance of swelling minerals (illite and smectite). These are expandable sheet silicates with desirable properties such as erosion resistance, low permeability and excellent ability to attenuate pollutants, due to high surface area and CEC (e.g., the LC). Thus, they have been used globally to improve compacted soil liners (Ruiz et al., 2012) and to achieve permeabilities in geosynthetic clay liners in the low range of $0.10\cdot10^{-9}$-$0.01\cdot10^{-9}$ m/s (Egloffstein, 2001). A key limitation is that smectites are plastic minerals very sensitive to the cation occupying the hydrated interlayer, which results in a high potential for swelling or shrinkage in water or leachate, respectively. This property can induce instability and cracks in compacted clays and increase leakage through liners (Borchardt, 1977; Wagner, 2013; Yalcin, 2007). This risk can be reduced by compaction and by addition of sand (Tanit and Arrykul, 2005; Varghese and Anjana, 2015). No consensus exists though on whether applying a water content lower (Widomski et al., 2018) or higher (Benson et al., 1999) than the optimum, will limit the shrink potential and thus desiccation cracking, ensuring K values $\leq 1\cdot10^{-9}$ m/s. A further drawback of smectites is that their alteration to newly formed illite or even kaolinite results in much less chemo-mechanical stable materials than kaolinite-rich and illite-rich samples that are not originally derived from smectite (Zhao et al., 2007). This illitization at the expense of the smectite content can occur after ammonium and potassium sorption from the landfill leachate (Regadío et al., 2015), reducing the CEC of the clay by ≤10%.

The Coal Measures Clays were easily compacted until negligible air was present in their voids (4%), which is convenient to achieve a low permeability in the liner. The OC and LC can achieve the lowest K (Maritsa et al., 2016) due to their high plasticity, but also have a higher shrinkage risk, with consequent risk of increased K due to desiccation cracks. This is especially critical in the LC as its PI is >30%: the low K of compacted clay liners with such high plasticity could increase above the design specification after repeated cycles of shrinkage-by-drying and swelling-by-wetting, and never recover its initial value even after rewetting (Widomski et al., 2018). Conversely, low plasticity clays have a K that remains nearly constant and within the design specification, even after several drying/wetting cycles. Another advantage is that non-plastic clays exhibit predominant vertical instead of horizontal deformation, the latter being predominant in plastic clays. Vertical deformation presents a lower risk of desiccation cracking in a compacted clay liner. Thus, for the centrifuge permeability tests the sandy materials were added to both clays to decrease their plasticity (Mansouri et al., 2013; Tanit and Arrykul, 2005; Varghese and Anjana, 2015).

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Adding non-cohesive materials decreases the LL and swell index, but should be done with caution to avoid an excessive increase in K (Lee et al., 2005). The K varies depending on the solid properties (surface area, particle sizes, porosity, tortuosity…), and many factors such as:

- Lab or field measurements (Allen, 2000; Benson et al., 1999; Shackelford and Javed, 1991);
- Compaction (Herrmann et al., 2009);
- (liquid) saturation ratio (Benson et al., 1999; Widomski et al., 2018);
- Other minor construction variables (Benson et al., 1999);
- Permeating liquid (di Emidio et al., 2017; Francisca and Glatstein, 2010; Jo et al., 2001; Lee et al., 2005; Singh and Prasad, 2007; Stepniewski et al., 2011; Uma Shankar and Muthukumar, 2017);
- Methodology (Sandoval et al., 2017);
- Passing of time and wet-dry seasonal variations (di Emidio et al., 2017; Egloffstein, 2001; Mitchell and Jaber, 1990; Stepniewski et al., 2011; Widomski et al., 2016).

The low K measurements ($0.2\text{-}0.8 \cdot 10^{-9}$ m/s) showed that these clayey substrates are chemically compatible with landfill leachates and promising candidates for use in the design of landfill bottom liners to minimize leachate migration as dual impermeability-attenuation barriers. The K values in the clay liners with ≤10% sandy materials under long-term leachate and rainwater permeation were below the most common maximum regulatory criterion ($1 \cdot 10^{-9}$ m/s) over a time equivalent to 85 yrs. These experimental results are in line with the graphical and multivariate regression of Benson et al. (1994), which estimates K values of $<1 \cdot 10^{-9}$ m/s for materials with at least 20% LL, 7% PI, 30% fines and 15% clays. No significant differences were found between the K values measured between different periods of time. The little variation is most likely due to the not complete (but almost) saturation of the compacted liners at the beginning (Darcy, 1856). This results in measurements of unsaturated K whose values are typically lower than those of saturated K as the water would be strongly attracted by the tension of the dry soil. The possible loss of the hydraulic connection when the pore water at the bottom of the model liner is transferred to the collector during spinning would also promote unsaturated conditions with lower K. Additionally, there are other processes that can also be affecting K. The leachate, with a high concentration and valence of ions, would decrease the net particle charge (Chorom and Rengasamy, 1995) and thickness of the Diffuse Double Layer (di Emidio et al., 2017; Schmitz, 2006; Stepniewski et al., 2011) in an initial stage. The former is due to the decrease in the dispersion of clays and the latter is relevant for the high porosity of freshly compacted soils. For Ca-clay minerals like here, the maximum dispersion occurs at pH 6.5-7.7 (Chorom and Rengasamy, 1995), which is the pH for most leachates. As a result, the transport of charged species in clays with high plasticity is enhanced, resulting in an increase of K in the first years. This supports earlier observations of an increase of K with the leachate concentration (Mitchell and Soga, 2005). In a later stage the precipitation of mineral phases and the growth of microbial activity may contribute to pore clogging (Francisca and Glatstein, 2010; Stepniewski et al., 2011) and therefore the decrease of K after its maximum during the previous stage (Figure 6). Calcite is likely to precipitate within the liner due to the basic pH, the high leachate bicarbonate concentration and additional dissolved calcium released over time by cation exchange reactions with the liner (de Soto et al., 2012; Thornton et al., 2001).

5. CONCLUSIONS

The performance of four natural clayey substrata as potential landfill liners was assessed by measuring their physico-chemical properties and stability and alterability upon contact with leachate, followed by rainwater. The attenuation of pollutants in leachate depends on the pollutant species and liner mineralogy. Potassium, ammonium, (dissolved) organic compounds and heavy metals (chromium, nickel and zinc) are the most representative leachate pollutants, according to their concentration, toxicity or persistence. All studied clayey materials are useful for the attenuation of leachate pollutants in sustainable waste landfills. These pollutants are mainly attenuated in the clayey materials by anaerobic biodegradation and sorption mechanisms, especially cation exchange. Chloride and sodium in leachate and native cations released from exchange sites on the clay liner after sorption of pollutants can be diluted by groundwater. However, different management options should be applied depending on the clayey material. The LC is the best material based on the sorption capacity and erosion resistance. However, the LC has a large plasticity (high susceptibility to excessive shrinkage) and easily alterable smectite clay minerals that partially collapse to illitic structures. Illitization has less impact on the CEC of the liner than on its chemo-mechanical stability and could be countered by compacting and mixing LC with sands. The OC is also plastic but to a lesser extent, with an acceptable PI. This substratum has a significant sorption capacity and is the best material for buffering acid leachates (due to native calcite) and supporting biodegradation of organic compounds. On the negative side, Coal Measures Clays have the lowest sorption capacity and zero neutralization power. However, they have the lowest plasticity and the most resistant clay minerals (kaolinite accompanied by illite) to alteration by exposure to leachate. In addition, both Coal Measures Clays are easily compacted until negligible air voids, which favours the achievement of a low K. The SCMC contained sulphate-bearing species (resulting from oxidation of pyrite) that enhance the retention by precipitation of heavy metals through bacterial sulphate reduction in the liner. The DCMC had very low mineral phases or inorganic salts that are readily dissolved in water. This is advantageous as it results in less mobilization of leachable salts from the liner itself. The LC and Coal Measures Clays have associated iron/metal oxides and oxyhydroxides that can enhance anion exchange and the removal of metals by sorption. Redox-sensitive species such as pyrite (OC and SCMC) and iron oxides (LC and Coal Measures Clays) can

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enhance the removal of metals by bacterially-mediated redox transformation and precipitation processes. The presence of pyrite and iron oxides also determines to a large extent the acid-base neutralisation potential, together with native carbonates in OC and bicarbonates in the leachate. After permeation with landfill leachate and rainwater during several weeks (equivalent to years under field conditions), the model liners achieved long-term sustainable low K, that rarely surpassed the maximum value specified for liner design.

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Evaluation of an HDPE geomembrane after 14 years as a leachate lagoon liner

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Evaluation of an HDPE geomembrane after 14 years as a leachate lagoon liner

R. Kerry Rowe, Henri P. Sangam, and Craig B. Lake

Abstract: A geomembrane – compacted clay composite liner system used to contain municipal solid waste (MSW) landfill leachate for 14 years is evaluated. Field observations of the geomembrane revealed many defects, including holes, patches, and cracks. Physical, chemical, and mechanical tests conducted on samples collected from five different locations of the liner suggest that samples continuously exposed to sunlight and high temperatures experienced more degradation compared to samples that were covered by leachate or soil. Sorption and diffusion tests revealed that the permeation coefficients of volatile organic compounds were in the range of 4×10^{-12} to 6×10^{-11} m^2/s and that, with respect to these parameters, there was no significant difference between samples with different exposure levels. However, the permeation coefficients were between four and five times lower than values obtained for unaged HDPE geomembranes typical of present day production. Contaminant modelling of the entire lagoon liner suggests that the geomembrane liner most likely stopped being effective as a contaminant barrier to ionic species sometime between 0 and 4 years after the installation.

Key words: liquid containment, composite liner, diffusion, HDPE geomembrane, performance.

Résumé : On évalue un système de membrane étanche composite, comprenant une géomembrane et une couche d'argile compacte, utilisé pour confiner le lixiviat des enfouissements municipaux solides pour 14 ans. Des observations de la géomembrane sur le terrain ont révélé plusieurs défauts comprenant des trous, des piéces et des fissures. Des essais physiques, chimiques et mécaniques faits sur des échantillons prélevés de différentes positions sur la membrane suggèrent que les échantillons continuellement exposés aux rayons solaires et aux températures élevées ont subi plus de dégradations par rapport aux échantillons qui étaient couverts de lixiviat ou de sol. Des essais de sorption et de diffusion ont révélé que les coefficients de percolation des composés organiques volatiles étaient de l'ordre de 4×10^{-12} à 6×10^{-11} m^2/s et que, en ce qui concerne ces paramètres, il n'y avait pas de différence significative entre les échantillons ayant différents niveaux d'exposition. Cependant, les coefficients de percolation étaient entre 4 à 5 fois plus faibles que les valeurs obtenues pour les géomembranes HDPE non vieillies typiques de la fabrication actuelle. La modélisation du contaminant de l'entière membrane étanche du bassin suggère que la géomembrane a arrêté très probablement d'être efficace comme barrière de contaminant aux espèces ioniques quelque part entre 0 à 4 ans après l'installation.

Mots clés : confinement de liquide, membrane composite, diffusion, géomembrane HDPE, performance.

[Traduit par la Rédaction]

Introduction

The use of a geomembrane in conjunction with compacted clay has been widely accepted as a composite liner system for modern landfills and wastewater lagoons (Rowe 2001). The level of understanding associated with the design, selection of materials, construction quality control, and long-term protection of composite liners has improved considerably in recent years. The importance of some of these factors can best be illustrated with reference to case records. Because of the relatively short history of high-density polyethylene (HDPE) geomembrane usage in landfill applications, most of the reported case records are related to their use in liquid containment applications (Schmidt et al. 1984; Hsuan et al. 1991; Adams and Wagner 2000). Limited cases of HDPE geomembranes in landfill bottom liner applications found in the literature have been provided by Rollin et al. (1994) and Eith and Koerner (1997).

Issues regarding the hydraulic or diffusive performance of the geomembrane liner have not been directly addressed despite the fact that the primary function of a geomembrane is to act as a barrier against the migration of landfill leachate contaminants. Thus, the objective of this paper is to provide a case record based on the exhumation of a 14-year-old geomembrane from a leachate lagoon. Preliminary data for this particular case record was presented by Rowe et al. (1998). This investigation expands upon this preliminary in-

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formation and examines (*a*) the difference in geomembrane properties that can arise from different exposure conditions, and (*b*) the influence of such exposure on the effectiveness of the geomembrane as a barrier to contaminant migration.

The lagoon

The leachate lagoon discussed in this study began to collect leachate in 1982 and was subsequently decommissioned after 14 years of service. Decommissioning was required to relocate the lagoon as part of ongoing landfill expansion. The lagoon was at a location in Ontario, Canada where the average temperatures during the winter and the summer were 1 and 25°C, respectively, and the latitude and longitude were 43°06′00″N and 79°04′00″W, respectively. The lagoon had a storage capacity of approximately 2500 m^3 with side slopes of 3H:1V.. It had been used to store leachate generated from a nonhazardous industrial, municipal, and commercial landfill. The leachate contained typical inorganic constituents, including transition and heavy metals (see Table 1). Volatile organic compounds were infrequently observed during the monitoring program, probably because of the nature of the waste in the landfill and (or) their volatilization during lagoon aeration.

The lagoon liner system consisted of a smooth 1.5 mm thick HDPE geomembrane overlying an approximately 3 m thick compacted clay liner constructed from “silty clay” borrow material obtained from near the landfill site. There was no protection layer above the geomembrane, which was directly exposed to the leachate and, above the leachate level, to the sunlight and the atmosphere. The original physical, chemical, and mechanical properties of the geomembrane and installation, as well as construction information, were not available to the authors. The hydrogeological conditions existing beneath the lagoon and on the site have been described by Lake (2000).

Field observations of the geomembrane and compacted clay liner

Geomembrane liner

After the lagoon was taken out of service, it was drained to examine the surface of the geomembrane. A significant amount of liquid at the bottom of the lagoon was trapped between the geomembrane and the clay giving the appearance of a “waterbed”. An odorous black sludge was present at the bottom, especially near the influent pipe system. According to the landfill operators, the geomembrane component of the lagoon liner had a history of problems. During its lifespan, the lagoon had been drained several times to remove sludge and to patch geomembrane liner defects.

For investigation purposes, the exposed geomembrane liner was divided into five areas (north, east, south, and west side slopes and the bottom of the lagoon) with each of these five areas subdivided into 5 m × 5 m grid sections to map any features such as wrinkles, holes, cracks, and patches on the liner. Wrinkles were observed in the geomembrane at the top of the slopes of the lagoon, the diagonal intersection of side slopes, and at various locations on the bottom.

Detailed mapping of the liner revealed many defects (cracks, holes, and patches), as summarized in Table 2. Cracks observed on the slopes where the HDPE geomembrane liner was not covered by the leachate and hence was exposed to the sunlight and climate extremes were typically oriented down the slope and located near either seams or patches. Figure 1 shows a typical crack located near the edge of a seam. The cracks observed at this site were similar to the field observations reported by Peggs and Carlson (1989) and Hsuan (1999) who attributed the cracks to high thermal contraction stresses along the top of the slope adjacent to the trench where the geomembrane is completely restrained from contraction. Some of these cracks were up to 30 cm long suggesting a high susceptibility of the geomembrane to cracking and hence the geomembrane as being relatively brittle. As shown in Table 2, four (19%) of the reported cracks were on the east, two (10%) on the west, eight (38%) on the north, and seven (33%) were on the south slope. No existing cracks were visible on the bottom. Of the cracks observed, only one was located below the leachate level.

Table 1. Leachate characteristics from 1989 to 1995 (based on Gartner Lee Ltd., 1995).

Parameter	Mean concentration (mg/L)*
pH (–)	8.08
Conductivity (µs/cm)	15 200
Total dissolved solids (TDS)	11 300
Alkalinity	4 610
Hardness	1 040
Chemical oxygen demand (COD)	670
Biochemical oxygen demand (BOD)	200
Cl^-	630
SO_4^{2-}	3 110
Na^+	4 160
K^+	300
Mg^{2+}	150
NH_3-N	170
Al	140
Fe	1.3
Pb	3.3
Mn	0.025
Phenols	0.24

*Except as otherwise noted.

Most of the holes recorded were located on the slope portion above the leachate level (see Table 2). However, in contrast to the cracks, the majority of the holes were found on the east side where the service way was located. A total of 54 patches (i.e., repaired former holes or cracks) were also observed on the liner (see Table 2). As with the other defects already mentioned, most of the patches (31 of 54) were found at the upper part of the liner. A few patches were observed at the bottom of the liner.

In summary, a total of 82 cracks, holes, and patches having different forms, patterns, and sizes were observed in the geomembrane over an area of 1552 m^2. This yields an average of 528 defects per hectare over the 14-year period of operation. Of these, 70% (348 defects per hectare) were above the leachate level and 30% (180 defects per hectare) were below the leachate level. Many scratches were also observed

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Table 2. Distribution of defects (cracks, holes, and patches) on the geomembrane around the lagoon.

	Locations* (Area[†])						
	East ($293\ m^2$)	West ($289\ m^2$)	North ($289\ m^2$)	South ($291\ m^2$)	Bottom ($390\ m^2$)	Total ($1552\ m^2$)	Defects per hectare
Crack							
Slope above leachate level ($148\ m^2$)	4	1	8	7	—	20	1351[‡]
Slope below leachate level ($1014\ m^2$)	0	1	0	0	—	1	10
Bottom ($390\ m^2$)	—	—	—	—	0	0	0
Total cracks	4	2	8	7	0	21	
Cracks per hectare	136[§]	69	277	241	0		135
Hole							
Slope above leachate level ($148\ m^2$)	5	0	1	0	—	6	405
Slope below leachate level ($1014\ m^2$)	0	1	0	0	—	1	10
Bottom ($390\ m^2$)	—	—	—	—	0	0	0
Total holes	5	1	1	0	0	7	—
Holes per hectare	171	35	35	0	0	—	45
Patch							
Slope above leachate level ($148\ m^2$)	17	4	5	5	—	31	2095
Slope below leachate level ($1014\ m^2$)	5	4	5	3	—	17	168
Bottom ($390\ m^2$)	—	—	—	—	6	6	154
Total patches	22	8	10	8	6	54	—
Patches per hectare	751	277	346	275	154	—	348

*The “north” slope faces south etc.

[†] Geomembrane area.

[‡] Formula $\dfrac{\text{Total cracks (20)}}{\text{Slope above leachate level } (148\,\text{m}^2)}$.

[§] Formula $\dfrac{\text{Total cracks (4)}}{\text{Area East } (293\,\text{m}^2)}$.

on the geomembrane at the bottom of the lagoon and may be attributable to either construction or maintenance activities during the service period of the facility.

Even though the majority (93%) of unrepaired cracks and holes were above the leachate level, the remaining cracks and (or) holes (7%) in the geomembrane along the side slopes appear to have been sufficient to allow liquid to get between the geomembrane and the clay liner. There were no cracks or holes found in the geomembrane at the bottom of the lagoon at the time of decommissioning, although 6 of the 54 patches were on the bottom.

Compacted clay liner

After examining the geomembrane portion of the lagoon liner, portions of it were removed to expose the underlying clay liner. It was observed that significant portions of the clay liner were desiccated above the leachate level. This phenomenon has been observed by others (Corser et al. 1992; Basnett and Brungard 1992). Below the leachate level, the clay appeared saturated and was covered by a thin layer of black sludge (~25 mm).

Five locations on the bottom of the lagoon were chosen for continuous borehole sampling. The details can be found in Lake (2000). The properties of the sampled clay material are summarized in Table 3. The water contents measured from samples taken from borehole samples ranged from 38% at the top of the compacted clay liner to about 20–24% at a depth of about 0.8 m. These latter water contents agree with unpublished construction reports that indicate that the clay liner was compacted at 2–4% wet of optimum with water contents ranging from 15.5 to 23% and densities ranging between 1.562 and 1.747 Mg/m^3. The higher water contents obtained at the upper part of the clay liner may be attributed

Table 3. Properties of compacted clay.

Physical parameters	
Relative density	2.68
Sand	Trace
Silt	63%
Clay	37%
Liquid limit	41%
Plastic limit	23%
Plastic index	18%
Activity	0.2
Water content	20–38%
Hydraulic conductivity	2×10^{-10} m/s
Mineral Composition	
Quartz	36%
K-Feldspar	4%
Na-Feldspar	5%
Calcite	18%
Dolomite	4%
Illite	20%
Chlorite	10%
Vermiculite	3%
Chemical Properties (on <75 μm fraction)	
Total organic carbon (TOC)	0.2%
pH	8.1
Cation exchange capacity (CEC)	12.0 mequiv./100g

Exhibit E

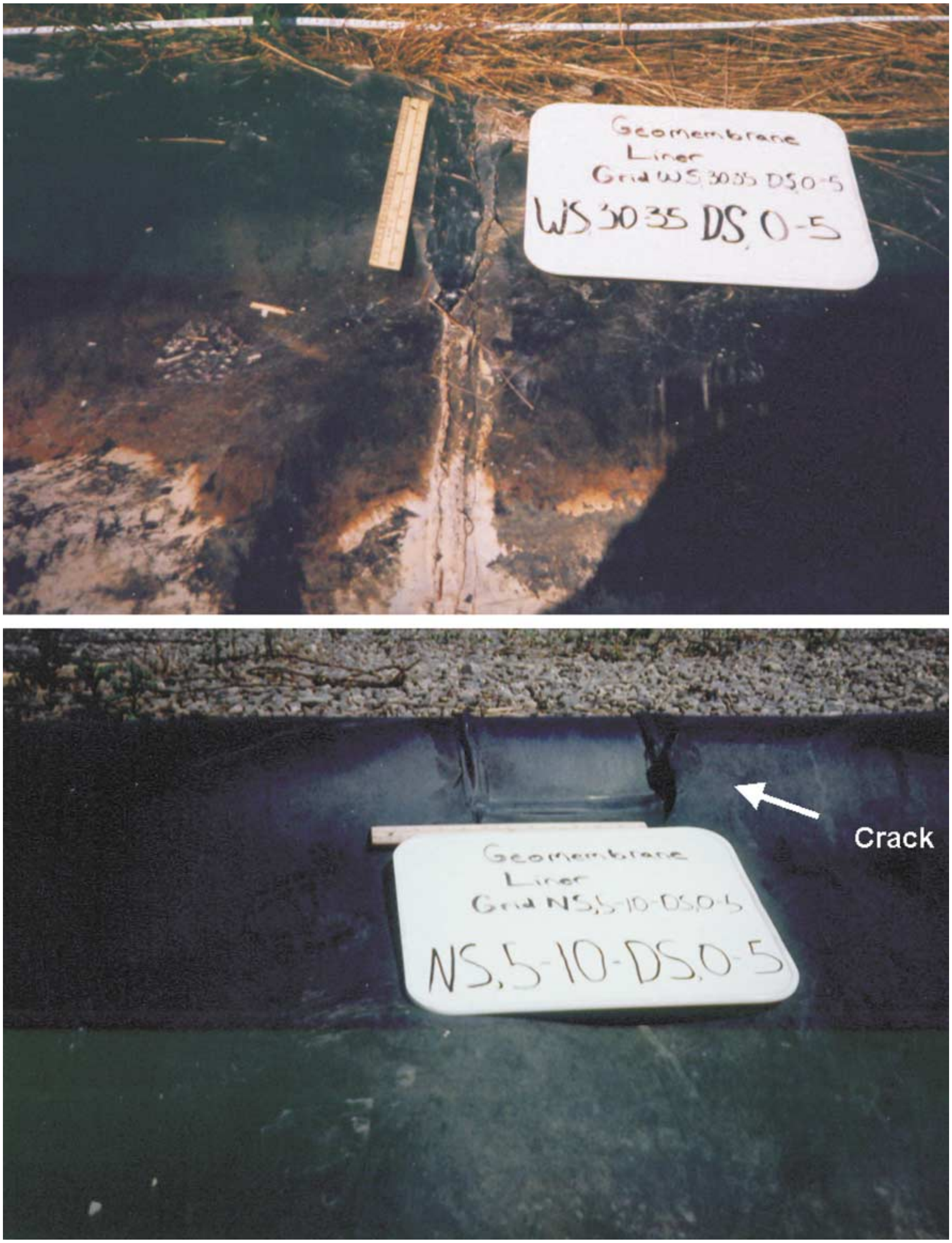

Fig. 1. Photograph of a typical crack located at the edge of a seam.

to the trapped water observed between the geomembrane and the compacted clay along with negligible effective stress at and near the clay surface that may have caused the clay to swell at the surface and hence increase the water content. This may also be partially due to the increase in void ratio from the biological activity that has taken place at and near the interface (in the form of the aforementioned black sludge) similar to the observations reported by Hrapovic (2001) for laboratory tests on clay plugs under negligible effective stresses.

Properties of the geomembrane after 14 years

Geomembrane samples were taken from the anchor trench (NSNL: no sunlight exposure, no leachate exposure), above

Exhibit E

the leachate levels in the lagoon (SNL: sunlight but no leachate exposure), at the leachate level interface (SLI: sunlight and leachate exposure), and below the leachate level (NSL: no sunlight but leachate exposure). Selected samples were also taken from the bottom of the lagoon (NSLB: no sunlight but leachate and significant sludge exposure). Figure 2 schematically shows the different locations from which the samples were collected.

ASTM methods

The following ASTM methods were used to evaluate the samples:

ASTM D 883	Standard definitions of terms relating to plastics, Vol. 08.01
ASTM D1004	Standard test method for initial tear resistance of plastic film and sheeting, Vol. 08.01
ASTM D1238	Flow rates of thermoplastics by extrusion plastometer, Vol. 08.01
ASTM D1603	Standard test method for carbon black in olefin plastics, Vol. 08.01
ASTM D3350	Standard specification for polyethylene plastics pipe and fittings materials, Vol. 08.02
ASTM D3895	Standard test method for oxidative-induction time of polyolefins by differential scanning calorimetry, Vol. 08.02
ASTM D4437	Standard practice for determining the integrity of field seams used in joining flexible polymeric sheet geomembranes, Vol. 04.09
ASTM D5397	Standard test method for evaluation of stress crack resistance of polyolefin geomembranes using notched constant tensile load test, Vol. 04.09
ASTM D5885	Standard test method for oxidative induction time of polyolefin geosynthetics by high-pressure differential scanning calorimetry, Vol. 04.09
ASTM D638–90	Standard test method for tensile properties of plastics, Vol. 08.01
ASTM D792	Standard test methods for density and specific gravity (relative density) of plastics by displacement, Vol. 08.01
ASTM E794	Standard test method for melting and crystallization temperatures by thermal analysis, Vol. 14.02

Geomembrane sheet samples

Oxidative induction time (OIT)

The first step of HDPE oxidative degradation is the consumption of the antioxidant used to hinder oxidation of the geomembrane. The amount of the antioxidant in the geomembrane is usually evaluated in terms of the oxidative induction time (OIT) using either the standard (Std) OIT test (ASTM D3895: 200°C, 35 kPa) or the high pressure (HP) OIT test (ASTM D5885: 150°C, 3500 kPa). A discussion of these two test methods has been presented by Hsuan and Koerner (1998).

The OIT values for modern HDPE geomembranes are typically in the range of 100 or more minutes. As shown in Table 4, average OIT (standard) values for all exposure conditions were very low implying that there were only small amounts of antioxidant in the geomembrane at the time of sampling. Of all the sampling locations, those denoted "SNL" were exposed to the greatest amounts of sunlight, the highest temperatures, and the most abundant amounts of oxygen. Thus these samples might be expected to have experienced the greatest photo-oxidation (UV) and thermo-oxidation (temperature), and indeed the average OIT of 1.8 min (based on 12 tests) was well below that of the other exposure conditions (see Table 4). The OIT of 1.8 min is close to the OIT value of 0.5 min measured by Hsuan and Koerner (1998) for an unstabilized (without any antioxidant) HDPE geomembrane, and the possibility that degradation might already have started in the exposed geomembrane cannot be excluded.

The OIT values were slightly higher (5–6 min) for samples below the leachate level (NSLS and NSLB) than for SNL samples, suggesting that more antioxidant remained in these samples. Factors that can affect antioxidant consumption include temperature and the availability of oxygen (Hsuan and Koerner 1998; Sangam 2001). The samples below the leachate level would experience the most consistent temperature and the lowest maximum temperature in the entire liner system. The leachate temperature would remain relatively constant throughout the year unlike the surface temperature, which would vary significantly. Secondly, oxygen would not be as abundant in the leachate as in the air even though the lagoon was aerated.

The SLI samples that had been subjected to intermittent sunlight and leachate exposure had an average OIT of 3 min, which was intermediate between the values obtained for full sun and full leachate exposure. A similar value was obtained for the anchor trench sample (NSNL) that was obtained from a shallow depth (approximately 0.75 m). At this depth, the temperature would reach 28°C during the summer and, as a consequence, the degradation would be expected to be faster than for samples covered by leachate.

Since the initial OIT of the original material at the time of installation was not available, it was rather difficult to infer the exact rate at which the antioxidant had been depleted. However, Adams and Wagner (2000) indicated that in the 1980s (i.e., the period when the geomembrane being discussed was manufactured and installed), the OIT of HDPE geomembranes was typically around 50 min (not the typical value of 100 min or more for modern geomembranes). Using that value as a basis and assuming that the depletion of antioxidants follows the first order decay kinetics as shown by Hsuan and Koerner (1995, 1998) and Sangam (2001), it can be estimated that the depletion of these specific antioxidants present in the geomembrane proceeded at approximately 0.24 year^{-1} for the exposed samples and at about 0.15 year^{-1} for samples covered by the leachate. The depletion rate for exposed samples compared very well with the rate of 0.28 year^{-1} based on data provided by Hsuan et al. (1991).

Density, carbon black content, and crystallinity

Since HDPE is a semicrystalline material, its density may be related to its degree of crystallinity. The density of five specimens cut from each sample was obtained according to ASTM D792, and the average values are presented in Ta-

Exhibit E

Fig. 2. Localization of geomembrane samples (not to scale).

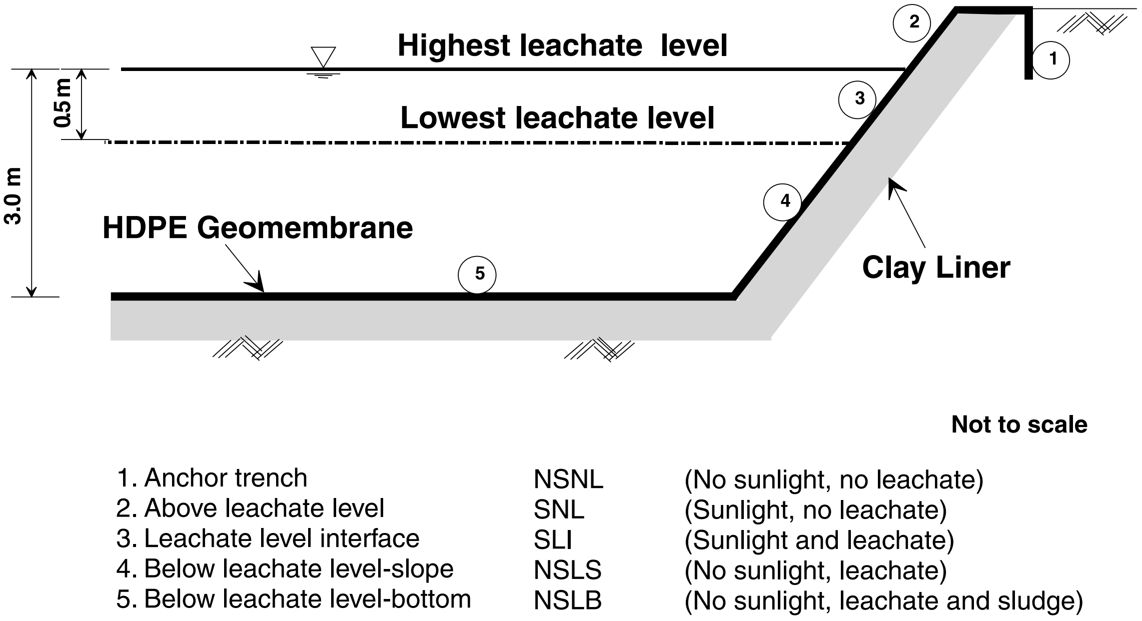

Table 4. Summary of the physical, chemical, and mechanical properties (modified from Rowe et al. 1998) of the samples according to various ASTM methods.

							D638				
							Tensile yield		Tensile break		
Sample	D3895 Sdt-OIT (min)	D1603 CBC (%)	D792 ρ_g (g/cm^3)	E794 χ (%)	D5397 SCR (h)	D1238 MFI (g/10 min)	T (kN/m)	ε (%)	T (kN/m)	ε (%)	D1004 ITR (N)
NSNL	3.5	2.58	0.965		3.5	0.36	37	11	33	646	283
SNL	1.8	2.64	0.967	67.5	2.6	0.50	37	11	25	379	274
SLI	3.3	2.67	0.967	—	—	—	37	10	26	479	284
NSLS	6.3	2.73	0.966	65.7	3.1	0.41	37	11	32	703	282
NSLB	5.0	2.20	0.965	65.5	3.0	0.31	39	10	27	456	292

Note: The results represent the average of replicate tests for the area considered. Sdt-OIT, standard oxidative induction time; CBC, carbon black content; ρ_g, density; χ, crystallinity; SCR, stress crack resistance; MFI, melt flow index; T, strength; ε, strain; ITR, initial tear resistance.

ble 4. The results are very similar for all locations and vary slightly between 0.965 and 0.967 g/cm^3.

The measured densities include a contribution due to the carbon black content (CBC), which can increase the overall density of the geomembrane by 0.0044 for each 1% of carbon added (ASTM D3350). Back-calculating to estimate the effect of CBC gave estimated resin densities of about 0.954–0.955 g/cm^3. These values were higher than those suggested as typical values for copolymer HDPE (0.941–0.950 g/cm^3) and suggest a high degree of crystallinity and hence a stiffer and more brittle geomembrane than modern copolymer HDPE geomembranes. Thus, it may be expected that the geomembrane will have higher tensile strength and lower strains at yield and break and will be more susceptible to stress cracking than modern HDPE geomembranes. This likely reflects the manufacturing practice of the time and may not be necessarily attributable to ageing.

The crystallinity, as evaluated according to ASTM E794 using a differential scanning calorimeter (DSC), ranged from 65 to 67% (see Table 4). These results are indicative of a very high degree of crystallinity and are consistent with the high densities measured. One of the expected consequences of high crystallinity would be an increased susceptibility of the geomembrane to stress cracking. If this is the case, then the SNL samples with the highest crystallinity would be expected to have the lowest stress cracking resistance.

Tensile and tear characteristics

The tensile properties, obtained according to ASTM D638–90 (Type IV) and summarized in Table 4, show no significant difference with sample location in either strength or strain values at yield. The yield strength (37–39 kN/m) was higher than for typical modern geomembranes (30 kN/m), while the strains at yield (10–11%) were lower than for typical modern geomembranes (15%), implying a stiffer material than would be expected for a modern material.

Both the strength and strain values at break were lower than those expected for new modern material. The highest values of 33 and 32 kN/m were obtained for the anchor

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trench samples (NSNL) and the samples from the slope that were exposed to leachate (NSLS), respectively. The lowest values of 25 and 26 kN/m were measured for samples exposed to sun (SNL) and samples from the leachate–sunlight interface (SLI), respectively. However, a surprising low value of about 27 kN/m was also obtained at the bottom (NSLB). It is hypothesized that this low value is due to the scratched nature of bottom samples, probably induced by the maintenance activities of the lagoon. These results are consistent with those reported by Rollin et al. (1994) who observed, for a 7-year-old HDPE, an increase of strength at yield and a decrease of both strength and strain at rupture. This behaviour of HDPE geomembranes suggests that the material has become brittle, and it would be consistent with ageing of the geomembrane.

The initial tear resistance (ITR) of a geomembrane (ASTM D1004) is defined as the load required to initiate tearing of the material. The values obtained for samples from different locations (see Table 4) suggest that the sun exposed (SNL) samples had the lowest ITR and those from the bottom of the lagoon had the highest. This contrasts with the low break strength measured for the sample collected from the bottom of the lagoon that had been scratched. This is attributed to the fact that in the ITR test, samples are notched and therefore are less influenced by surface defects.

Melt flow index

The molecular weight of the HDPE is related to the melt flow index (MFI) of the polymer with a low MFI corresponding to longer average polymer chains. The MFI values obtained (ASTM D1238) from different locations (Table 4) ranged between 0.31 and 0.50 g/10 min, with the lowest value corresponding to samples fully covered by leachate (NSLS and NSLB), whereas the exposed samples (SNL) had the highest value of 0.50 g/10 min. This, like other evidence discussed earlier, is consistent with the most exposed (SNL) samples having experienced the greatest degradation (giving rise to the smallest molecular chains) and those near the bottom of the lagoon the least degradation. The findings are in stark contrast to the observations made by Hsuan et al. (1991) for a 7-year-old HDPE geomembrane where the lowest MFI was measured for exposed samples.

Stress cracking resistance (SCR)

Stress cracking has been defined (ASTM D883) as an external or internal rupture in a plastic caused by a tensile stress less than its short-term mechanical strength. In the present investigation, the SCR was assessed by the single notched constant load test (SP-NCLT) following the procedure described in ASTM D5397. The notch was introduced from the exposed side of the geomembrane to minimize surface effects such as scratches or any surface degradation.

The SCR, reflected by the failure time given in Table 4, is remarkably low with all specimens failing within 4 h compared to the 200 h specified for a new modern HDPE geomembrane (Hsuan and Koerner 1997). Since the SCR data for the original geomembrane was not available, one cannot assess whether or not the low cracking resistance is due to ageing. Nevertheless, it is apparent that the exposed geomembrane had a lower failure time (i.e., more susceptible to stress cracking) than that of the covered samples. This is consistent with other properties measured (MFI, tensile and initial tear resistance) suggesting that the exposed samples have experienced more degradation than samples from other locations.

Seams

Shear and peel tests (ASTM D4437) were used to evaluate the quality and the integrity of the seams. In general, as quality control criteria, it is recommended that the ratio between the shear strength of the seam and the tensile strength of the sheet at yield be greater than 90%, while the peel strength should be greater than 75% of the sheet strength at yield. Also, the seam strain at break must not be less than that of the sheet (ratio greater than 100%). The results of the shear and peel tests performed on five test specimens cut from seam samples collected from four different locations (SNL, SLI, NSLS, and NSLB) are summarized in Table 5.

Except for the NSLB sample, the shear strength ratios are below today’s typical quality control criteria with values less than 70%. The peel test results presented showed very low seam-sheet strength ratios (<30%) compared to today’s typical quality control criterion of 75%, suggesting either very poor initial welding or a significant loss of peel strength during the 14 years of exposure.

Contaminant diffusion through the geomembrane

Materials and methods

Sorption and diffusion tests were conducted on samples from locations SNL, NSLS, and NSLB (see Fig. 2). The tests examined seven organic chemicals (Table 6) representative of chlorinated hydrocarbons (dichloromethane (DCM); 1,2-dichloroethane (1,2-DCA); and trichloroethylene (TCE)) and aromatic hydrocarbons (benzene, toluene, ethylbenzene, and xylenes (BTEX)).

The tests were performed at room temperature (22 ± 2°C) using mixed dilute aqueous solutions with the concentration of each contaminant at about 5 mg/L. Solution samples collected from the cells during the test were analyzed using a Varian gas chromatography – mass spectrometer (GC/MS) consisting of a Saturn 2000 MS and a 3800 GC equipped with a 8200 CX autosampler used in solid phase microextraction (SPME) and headspace modes. The contaminant concentrations were quantified based on calibration curves obtained through analysis of standards of known concentrations that were regularly prepared during the tests. Details regarding the test and the analytical procedure used are given in Sangam and Rowe (2001).

In the sorption tests, geomembrane samples were immersed in glass cells filled with a mixed dilute solution of contaminants. The change in contaminant concentration in the solution was monitored with time until equilibrium was reached, and then the partitioning coefficients (S_{gf}) were deduced as described by Sangam and Rowe (2001).

The diffusion tests were performed in double glass compartment cells consisting of a closed system with source and receptor reservoirs separated by the geomembrane sample under investigation as described by Rowe (1998) and Sangam and Rowe (2001). During the test, concentrations in both source (a mixed aqueous solution with each contami-

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Table 5. Shear and peel test results on seams collected from different locations (ASTM D4437).

		Yield				Break				
		Strength		Strain		Strength		Strain		
Test	Sample	*T* (kN/m)	% Sheet	ε (%)	% Sheet	*T* (kN/m)	% Sheet	ε (%)	% Sheet	Type of failure*
Shear	SNL	24	65	6	55	24	73	7	2.1	1a, 3b, 1c
	SLI	20	54	3	27	20	80	3	0.6	5b
	NSLS	25	66	4	36	25	96	5	0.7	1a, 4b
	NSLB	36	92	7	70	35	130	9	2	4b, 1d
	SNL					6	16	65	17	1a, 4b
Peel	SLI					5	14	10	2	1a, 4b
	NSLS					4	11	70	10	5b
	NSLB					10	20	178	39	1a, 3b, 1d

Note: Values are the average of 10 samples tested.

*The number denotes the number of failures and the letter denotes the type of failure where: a is a failure in adhesion; b is a break through the fillet; c is a break at the seam edge (bottom sheet); and d is a break in the bottom sheet.

Table 6. The properties (from Montgomery and Welkom 1990) of organic contaminants and the range of partitioning coefficients, S_{gf}, deduced from sorption tests.

Chemicals	Formula	Molar weight (g/mole)	Density (g/cm^3)	Molar volume* (cm^3)	Aqueous solubility† (mg/L)	Octanol–water (logK_{ow})	Dipole moment (Debye)	Partitioning coefficient S_{gf} (–)
Chlorinated hydrocarbons								
Dichloromethane	CH_2Cl_2	84.93	1.3266	64.02	20 000	1.25	1.60	3–5
1,2-Dichloroethane	$C_2H_4Cl_2$	98.96	1.2530	78.98	8 690	1.45	1.44	6–8
Trichloroethylene	C_2HCl_3	131.39	1.4642	89.74	1 100	2.53	0.77	53–56
Aromatic hydrocarbons								
Benzene	C_6H_6	78.11	0.8765	89.11	1 780	2.13	0.00	20–24
Toluene	C_7H_8	92.14	0.8669	106.28	515	2.79	0.30	57–69
Ethylbenzene	C_8H_{10}	106.17	0.8670	122.46	152	3.13	0.36	130–156
m-Xylene	C_8H_{10}	106.17	0.8642	122.85	162	3.20	0.30	190–216
o-Xylene	C_8H_{10}	106.17	0.8802	120.62	152	3.13	0.63	170–180
p-Xylene	C_8H_{10}	106.17	0.8669	122.47	156	3.18	0.00	190–216

*Calculated based on chemical density and molar weight.

†At 20°C.

nant listed in Table 6 at 5 mg/L) and receptor (initially deionized distillate water) reservoirs were monitored with time and the results were plotted as normalized concentrations (i.e., the concentration at a given time divided by the initial source concentration), as shown in Figs. 3 and 4.

The governing differential equation in these diffusion tests can be expressed as

$$[1] \qquad \frac{\partial c_g}{\partial t} = D_g \frac{\partial^2 c_g}{\partial z^2}$$

where D_g is the diffusion coefficient of the geomembrane [L^2T^{-1}], c_g is the concentration of diffusing substance in the geomembrane [ML^{-3}], and z is the direction of diffusion [L]. Since the concentrations (c_f) in the reservoir are monitored, then the flux, f [$ML^{-2}T^{-1}$], associated with the process can be written as (Rowe 1998; Sangam and Rowe 2001)

$$[2] \qquad f = -S_{gf} D_g \frac{dc_f}{dz} = -P_g \frac{dc_f}{dz}$$

where P_g [L^2T^{-1}], referred to as the permeation coefficient, is a contaminant mass transfer coefficient and S_{gf} [–] is the partitioning coefficient of the contaminant between the geomembrane and the adjacent fluid and is dependent upon the chemical–geomembrane system.

The tests were analyzed following the procedure described in detail by Rowe et al. (1995*a*) using the finite layer analysis program POLLUTE$^©$ v6.3.6 (Rowe et al. 1999) that specifically allows the modelling of the phase change and the boundary conditions in these tests.

Test results

Sorption test

Partitioning coefficients calculated based on the sorption tests are summarized in Table 6 (full test data is given by Sangam 2001). For the chlorinated aliphatic compounds examined, TCE has the highest value of S_{gf} (53–56), followed by DCA with a S_{gf} of 5–8. The lowest S_{gf} (3–5) was measured for DCM. For aromatic compounds, the calculated S_{gf} is the highest for *m*- and *p*-xylenes with values between 190

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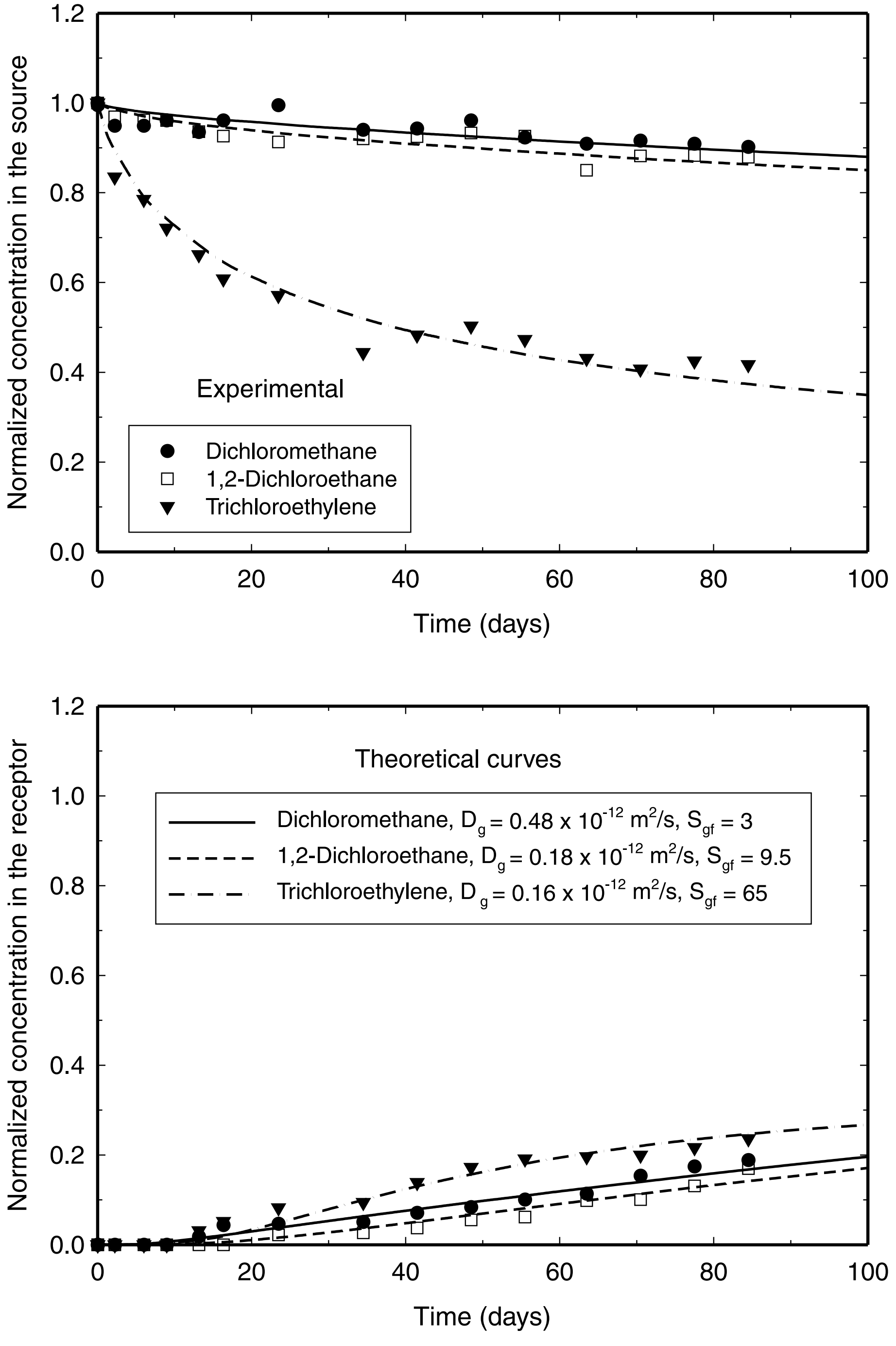
Fig. 3. Variation in the chlorinated hydrocarbons in the source and receptor during diffusion tests for sample SNL.



and 216, while benzene has the lowest S_{gf} at about 20–24. Although there was some (relatively small) variability in the results for a given compound, there was no significant or consistent difference among the results from the different sample locations. This may be attributed to the fact that the crystallinity of the samples was similar at the three locations (with the average ranging from 65.5 to 67.5%).

Diffusion test

Contaminant concentrations (measured in the source and the receptor over the 85 days of testing for the SNL sample) obtained for chlorinated hydrocarbons and aromatic hydrocarbons are shown in Figs. 3 and 4, respectively. In these plots, data points represent the average of triplicate values quantified with GC analyses. As previously discussed by Sangam and Rowe (2001), in this type of test the decrease in the source concentration is controlled by the partitioning parameter (S_{gf}) while the increase in the receptor concentration is dominated by the permeation coefficient (P_g). The diffusion curves were very similar for samples from all locations

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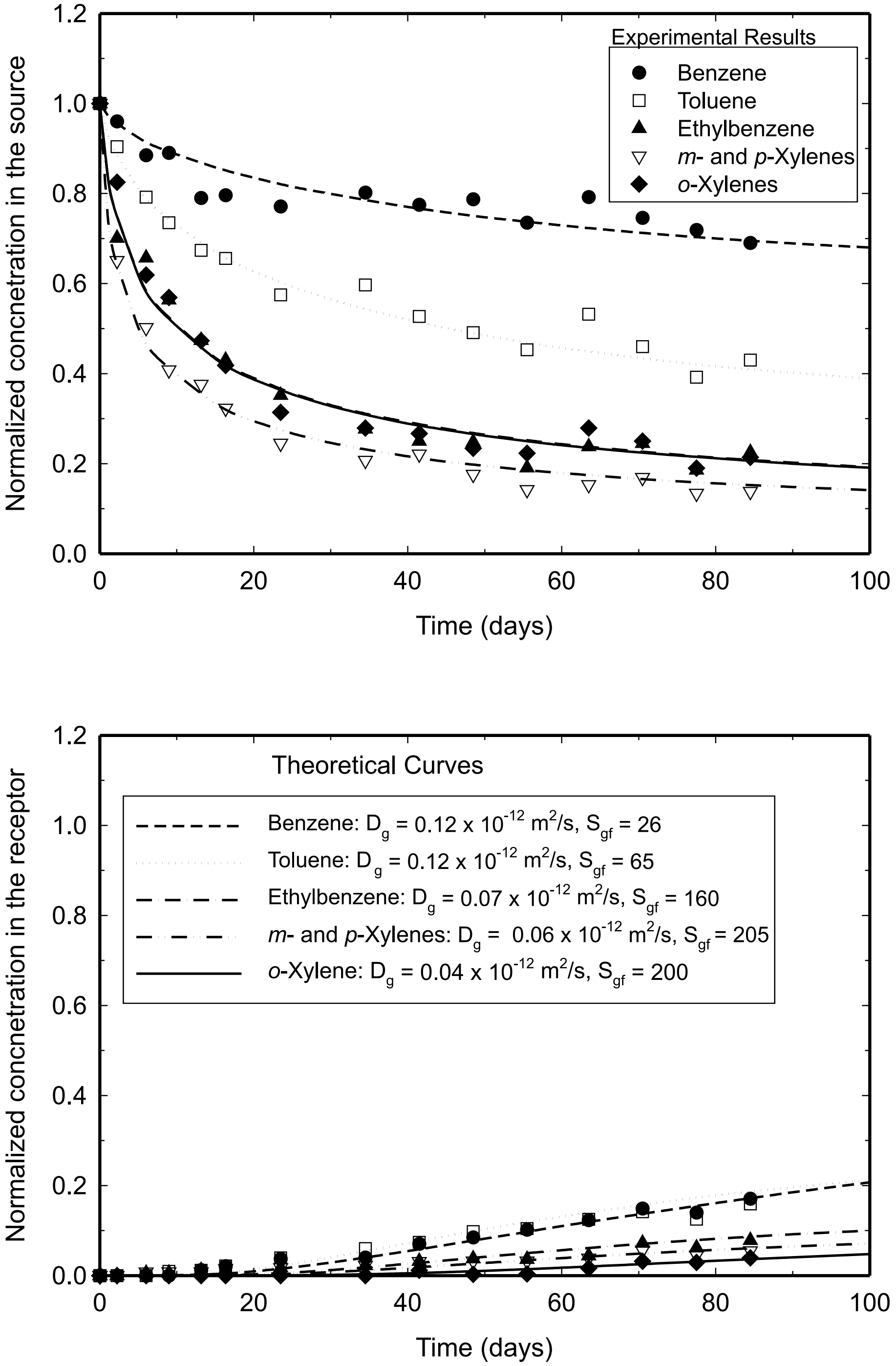
Fig. 4. Variation in the aromatic hydrocarbons in the source and receptor during diffusion tests for sample SNL.



(SNL, NSLS, and NSLB). Full data for all samples is provided by Sangam (2001).

Of the chlorinated compounds, the greatest (60%) decrease in the source solution concentration was for TCE (see Fig. 3), which dropped to 40% of the initial concentration after 85 days of testing. In contrast, the source concentrations of DCM and 1,2-DCA decreased by less than 10% over 85 days. In all cases, there was significant mass transfer to the receptor reservoir with the greatest increase being for TCE and the smallest for 1,2-DCA. The fact that the source concentration for 1,2-DCA decreased more than for DCM but the receptor increased less provides qualitative information about the sorption and diffusion coefficients, implying higher sorption and lower diffusion for 1,2-DCA than for DCM since there is greater uptake of 1,2-DCA by the geomembrane but less mass transfer through the geomembrane and into the receptor.

Figure 4 shows the variation in the concentration of aromatic hydrocarbons for the SNL sample during the diffusion test period. From the source data, it can be seen that after

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85 days of testing, the benzene concentration decreased by about 30% while that of toluene, *o*-xylene, and the *m*- and *p*-xylenes dropped by about 50, 80, and 85%, respectively. The increase in concentration in the receptor was greatest for benzene and toluene followed by ethylbenzene, the *m*- and *p*-xylenes, and *o*-xylene.

The theoretical curves generated for each of the compounds by solving the governing differential equation subject to the appropriate boundary conditions are also shown as lines in Figs. 3 and 4. By obtaining the best fit to the source and the receptor concentrations one can deduce the values of S_{gf} and D_g and hence calculated P_g as summarized in Table 7.

Discussion

The S_{gf} values (see Tables 6 and 7) generally increase with an increase in the *n*-octanol–water coefficient ($\log K_{ow}$) (which indicates the chemical hydrophobicity, and hence the ability of the chemical to partition with organic material). The partitioning coefficient varied somewhat from sample to sample in both the sorption (Table 6) and diffusion (Table 7) tests, however, the magnitude of the partitioning was very similar for both of the tests.

Comparing the diffusion test results obtained for samples from three different locations (see Table 7), it can be seen that while there is some small variability there is no consistent trend that could be attributed to location or to the small difference in crystallinity, and the range of values considered is more an indication of the variability that can be obtained among different samples of similar material in this type of test.

It is of some interest to compare the diffusion and sorption characteristics of the 14-year-old geomembrane (Table 7) with those obtained by Sangam and Rowe (2001) for an unaged modern HDPE geomembrane (see Table 8). The primary relevant difference between the two geomembranes is the crystallinity (65–68% and 47% for the old and new geomembranes, respectively). As is evident from Table 8, the permeation coefficient, P_g, is substantially higher for the new geomembrane than for the old one (by a factor of between 1.7 and 4.8). In fact, the difference in permeation coefficient between the two geomembranes is compound specific with the smallest difference being for DCM (which has the lowest molecular volume), and it generally increases with increasing molar volume. Benzene and TCE have a similar molar volume and a similar difference in permeation coefficients between old and new geomembranes. The greatest difference was for ethylbenzene and xylenes, which all have a similar molar volume (120.6–122.8 cm^3). This observed reduction in permeation coefficient may be attributed to the high crystallinity of the samples. As indicated by Naylor (1989) and Rogers (1985), the crystalline zones in semicrystalline polymers act as relatively impermeable barriers to the migrating molecules by (1) reducing the sorptive and diffusive regions, and (2) restraining the mobility of the polymer molecules required for the accomplishment of the diffusive jump. As a consequence, the segmental mobility of the chains required to achieve migration are restrained, and therefore the diffusion process becomes more dependent on the size and shape of the migrating molecule (Naylor 1989; Rogers 1985).

Effectiveness of the geomembrane liner

It is well recognized that an intact HDPE geomembrane is an excellent barrier to advective migration as well as an excellent diffusive barrier against inorganic and polar contaminants. Chloride is an inorganic ion that has a very low diffusion coefficient through HDPE geomembranes (Rowe et al. 1995*a*). Theoretically, if the HDPE geomembrane examined in this study stayed relatively intact for any length of time, very little break-through of chloride would be observed in the compacted clay liner. Conversely, if significant amounts of chloride (above background levels) were to be present in the compacted clay, this would suggest that the geomembrane had failed to perform its intended task.

Figure 5 shows the chloride concentration profile through the clay liner at the time of the investigation (i.e., after 14 years of service) measured from squeezed pore fluid obtained from five boreholes drilled into the clay liner. The profile shows an apparent back diffusion near the top, probably due to dilution of the leachate present in the bottom of the lagoon (rainwater that had accumulated during the one month period between decommissioning and the investigation). After 14 years of service, chloride had migrated approximately 1.7 m, which is consistent with expectations based on previous field cases in which the leachate was in direct contact with the clay liner (e.g., Rowe et al. 1995*b*). Although the clay liner appeared to have performed well (there was over 1.0 m of clay below the contaminated zone with no chloride) in protecting the environment during the service period, there are still questions about the effectiveness of this particular geomembrane liner in impeding the migration of chloride.

The effectiveness of the geomembrane with respect to contaminant migration was evaluated via contaminant transport modelling (using POLLUTE© v6.3.6, Rowe et al. 1999). Chloride leachate concentrations as shown in Fig. 6 were used to predict chloride pore-fluid concentrations throughout the compacted clay based on different assumptions regarding when the geomembrane failed. These profiles were then compared to chloride pore-fluid concentrations obtained from the field investigation.

For modelling purposes, the clay liner was subdivided into three layers (0–0.25, 0.25–0.50, and >0.50 m) with porosities of 0.48, 0.42, and 0.38, respectively, to account for the variation in water content with depth. The average value of the clay hydraulic conductivity (measured using flexible wall hydraulic conductivity tests with an effective stress ranging from 30 to 50 kPa and a gradient across the sample of 20) was about 2.2×10^{-10} m/s. The chloride diffusion coefficient for the clay measured in the laboratory was about 7×10^{-10} m^2/s.

Prediction of chloride pore-fluid profiles through the compacted clay requires consideration of the effectiveness of the geomembrane during the lifespan of the lagoon. If the geomembrane was intact (no defects), then chloride pore-fluid concentrations through the clay should be close to background levels because of the very low diffusion of chloride through geomembranes (Rowe 1998). For initial comparison purposes, it is interesting to examine the theoretical chloride contaminant profile through the clay for the unlikely scenario that the geomembrane was intact with only 2.5 holes

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Table 7. Inferred partitioning and diffusion coefficients based on diffusion tests with aqueous solutions.

	Sample SNL (χ = 67.5%)			Sample NSLS (χ = 65.7%)			Sample NSLB (χ = 65.5%)		
Chemicals	S_{gf} (–)	D_g (10^{-12} m^2/s)	P_g (10^{-12} m^2/s)	S_{gf} (–)	D_g (10^{-12} m^2/s)	P_g (10^{-12} m^2/s)	S_{gf} (–)	D_g (10^{-12} m^2/s)	P_g (10^{-12} m^2/s)
Chlorinated hydrocarbons									
Dichloromethane	3	0.48	1.4	3	0.5	1.5	5	0.45	2.3
1,2-Dichloroethane	10	0.18	1.8	10	0.16	1.6	10	0.16	1.6
Trichloroethylene	65	0.16	10.4	60	0.18	10.8	68	0.17	11.6
Aromatic hydrocarbons									
Benzene	26	0.12	3.1	32	0.12	3.8	32	0.13	4.2
Toluene	65	0.12	7.8	70	0.14	9.8	70	0.15	10.5
Ethylbenzene	160	0.07	11.2	160	0.08	14.4	150	0.08	12.0
m- and *p*-Xylenes	205	0.06	12.3	220	0.08	17.6	205	0.08	16.4
o-Xylene	200	0.04	8.0	190	0.06	11.4	180	0.06	13.3

Note: χ, crystallinity.

Table 8. Comparison of calculated permeation coefficients for the 14-year-old geomembrane (old GM) and the new modern geomembrane (new GM).

	New GM* (χ = 47%)			Old GM (χ = 65.5–67.5%)	
Chemicals	S_{gf}	D_g (10^{-12} m^2/s)	P_g (10^{-12} m^2/s)	P_g (10^{-12} m^2/s)	$\left[\frac{P_g\ (\text{new GM})}{P_g\ (\text{old GM})}\right]$ (–)
Chlorinated hydrocarbons					
Dichloromethane	6	0.65	3.9	1.4–2.3	1.7–2.8
1,2-Dichloroethane	12	0.40	4.8	1.6–1.8	2.7–3.0
Trichloroethylene	85	0.40	34.0	9.6–11.6	1.9–3.5
Aromatic hydrocarbons					
Benzene	30	0.35	10.5	3.1–4.2	2.5–3.4
Toluene	100	0.30	30.0	7.8–10.8	2.9–3.8
Ethylbenzene	285	0.18	51.3	9.8–12.0	3.6–4.6
m- and *p*-Xylene	347	0.17	59.0	12.3–17.6	3.4–4.8
o-Xylene	260	0.15	36.0	8.0–13.3	3.2–4.5

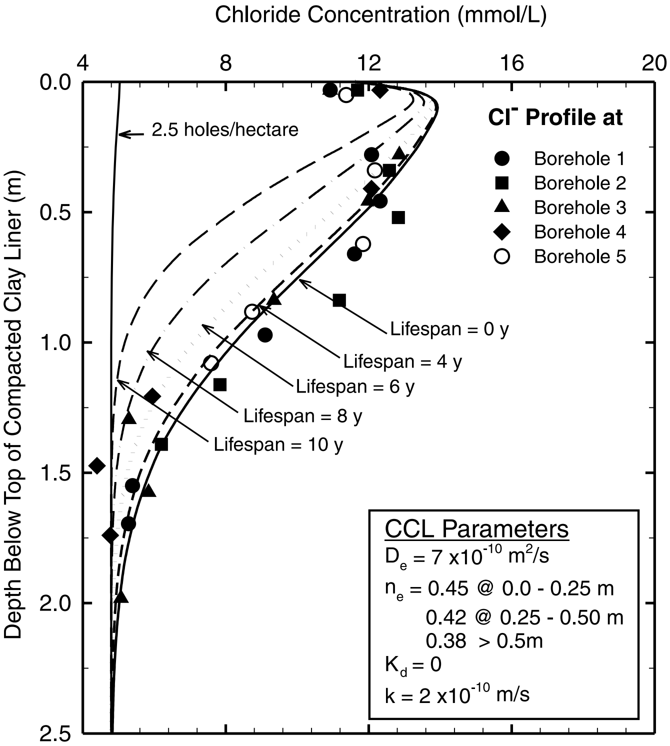
Note: χ, crystallinity.
*From Sangam and Rowe (2001).

(5 mm diameter) per hectare throughout the entire lifetime of the lagoon. It should be noted again that approximately 528 defects per hectare were actually found on the geomembrane at the time of the investigation. Based on the given leachate concentrations (Fig. 6) and a Darcy velocity (flux) of 3.5×10^{-4} m/a (1.1×10^{-11} m/s) through the geomembrane and clay, the resultant chloride profile through the clay is shown in Fig. 5. Leakage through the geomembrane was calculated with the LEAK program (Rowe and Lake 1997) using similar parameters to those summarized by Rowe (1998). As can be seen from Fig. 5, theoretical chloride concentrations are severely underpredicted through the compacted clay liner, and there is no match to the contaminant profiles obtained from the field investigation. This is because chloride leakage through a few small holes combined with a low chloride diffusion coefficient through the geomembrane gives rise to very little chloride flux through the geomembrane liner.

As a result of observations made during the field investigation, as well as discussions with maintenance staff, it is apparent that modelling of the composite liner by assuming leakage through only a few holes in the geomembrane is not very realistic. A significant amount of leachate was observed to be trapped under the geomembrane and was in direct contact with the compacted clay. It may be inferred that at some point during the lifetime of the lagoon, the geomembrane stopped functioning as an effective barrier and started to allow significant contact between the leachate and the compacted clay. Figure 5 shows contaminant profiles for chloride assuming the geomembrane was ineffective from the time of construction (lifespan equals 0 years) as well as various times after construction (4, 6, 8, and 10 years). In other words, after these time periods, modelling assumed that the leachate was in direct contact with the compacted clay and that the geomembrane had no influence on leachate contact with the clay. A comparison of the theoretical curves with the field data suggests that the geomembrane was effective for less than 8 years of the 14-year lifespan of the lagoon. Theoretical chloride pore-fluid profiles assuming geomembrane failure at 8 and 10 years provide a poor fit to

Exhibit E

Fig. 5. Chloride concentration profile through the compacted clay liner based on samples from five boreholes together with prediction of pore-fluid concentration for different assumed geomembrane service lives.



experimental chloride pore-fluid concentrations. However, assuming the geomembrane functioned effectively for elapsed times of 0, 4, and 6 years after construction provides a reasonable fit to the majority of the data.

Based on this chloride modelling, it is considered likely that the geomembrane ceased functioning effectively somewhere between 0 and 4 years after construction. However, there is some scatter in the field chloride pore-fluid concentrations that causes some uncertainty as to the actual time of failure of the geomembrane. It is also unlikely that the geomembrane failed at the same time for the entire lagoon, and hence the sequence by which the failure occurred would be expected to have some effect on the field profiles at different locations. Figure 5 contains data from five different locations and some scatter in field chloride concentration profiles is likely due to this effect. However, the general conclusion that the geomembrane failed to function effectively at some time 0–4 years after construction is consistent with discussions with the operators of the landfill, who indicated that frequent maintenance of the geomembrane was required almost from the time of installation.

Composite liner design implications

As previously mentioned, the level of understanding of using geomembranes with compacted clay for lagoons and landfills has improved considerably as results of case histories are published and discussed. The findings of this particular study reinforce existing design philosophies as well as the need for proper construction quality control and material selection. Below is a discussion of these items.

(1) The vintage of the geomembrane component of the lagoon liner discussed in this paper most likely did not fall within the time period where proper construction quality control was practiced for small lagoons such as this one. However, it is believed that observations of poor seam quality and geomembrane wrinkles were the result of construction practices. This reinforces the need for experienced installation personnel as well as qualified construction control – assurance procedures.

(2) The geomembrane material properties exhibited undesirable values with respect to OIT, CBC, crystallinity, and SCR. Because of a lack of knowledge of the original geomembrane properties, it is unknown whether this is the result of degradation or simply different geomembrane properties compared to similar products of that vintage. However, it does highlight the importance of proper geomembrane specifications (i.e., OIT, crystallinity, and SCR). Typical values for Std-OIT of 100 min, for CBC of 2–3%, for crystallinity of 45–50%, and for SCR of 200 h, as proposed by Hsuan and Koerner (1997) and Hsuan (2000), should be a minimum for lagoon liners such as this one.

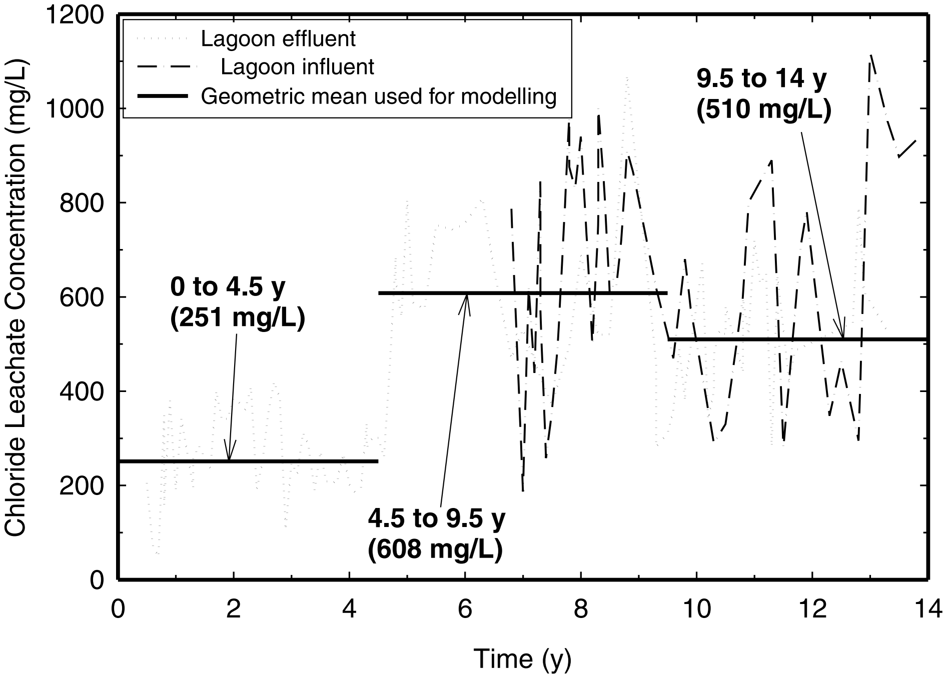
(3) It is believed that some of the defects observed in the liner were the result of maintenance activities. Material selection, such as a thicker geomembrane (e.g., 2.0 mm), may have helped with durability but may have made it more difficult to construct for the small geometry. Also, protection of the geomembrane with a thick geotextile and (or) sand layer would help during maintenance activities as well as providing protection from sunlight. Stability issues would have to be addressed as part of this process (Koerner 1999). Narejo et al. (1996), Koerner (1999), and Tognon et al. (2000) provide some insight regarding the design of protection layers. Maintenance of the lagoon should be part of the design and planning stage. Special care should be taken during sludge removal, and travel areas should be given additional protection for trucks and maintenance workers. Such care can help minimize maintenance-induced defects on the liner.

(4) Designing a lagoon for contaminant transport involves selection of the proper diffusion coefficient. The results obtained herein, along with those reported by Sangam (2001), suggest that volatile organic compound (VOC) diffusion coefficients will decrease with increasing crystallinity of the geomembrane. If the crystallinity does increase with geomembrane ageing as reported by several investigators (e.g., Sangam 2001), then it is conservative to use the diffusion coefficients of the unaged material. However, as shown in this paper, if diffusion coefficients decrease substantially with the increase of the crystalline zone in the geomembrane, other defects such as cracks, holes, and tears may result causing advective flow through these defects to control the overall contaminant transport through the geomembrane portion of the composite liner system.

(5) The importance of the compacted clay liner in minimizing advective and diffusive transport into the underlying groundwater system is emphasized from results presented herein. Without it, the lagoon would not have functioned properly.

Exhibit E

Fig. 6. Variation of chloride leachate concentration during the service of the lagoon.



Summary and conclusions

An evaluation of a 1.5 mm HDPE geomembrane used as a liner in a leachate lagoon for 14 years has been presented. The number of defects (holes, patches, and cracks) and wrinkles, the "waterbed" nature of the geomembrane at the time of decommissioning, and the chloride diffusion profile through the clay suggest that the geomembrane likely did not perform its design function for very long. The amount of antioxidant measured via the standard OIT indicated very short times, generally less than 7 min. The OIT also indicated that antioxidants were almost completely consumed for the exposed part of the geomembrane, with an OIT value of about 1 min. This suggests that some oxidation may have already occurred in this part of the geomembrane as confirmed by the low values measured for the tensile break properties and the stress cracking resistance. The relatively low permeation coefficients inferred for a high crystallinity geomembrane relative to that for a modern lower crystallinity geomembrane suggests that diffusion in an intact geomembrane may decrease with time if the degree of crystallinity increased with time. The results also suggest that the chloride measured in the compacted clay had migrated essentially through the different defects present in the geomembrane liner and that the geomembrane ceased to effectively perform its barrier function at a relatively short time after installation. However, because the compacted clay liner was 3 m thick and chloride had only diffused 1.7 m, failure of the geomembrane did not cause any adverse impact on the groundwater.

Acknowledgements

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Exhibit E

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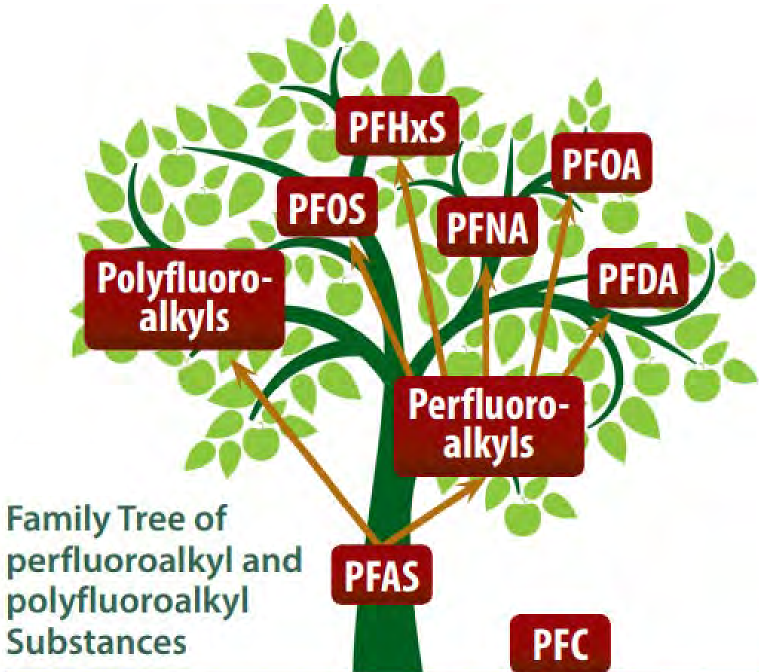
Per- and Polyfluoroalkyl Substances (PFAS) in Solid Waste



Credit: www.coastalreview.org

Bryan Staley, PhD, PE

President & CEO

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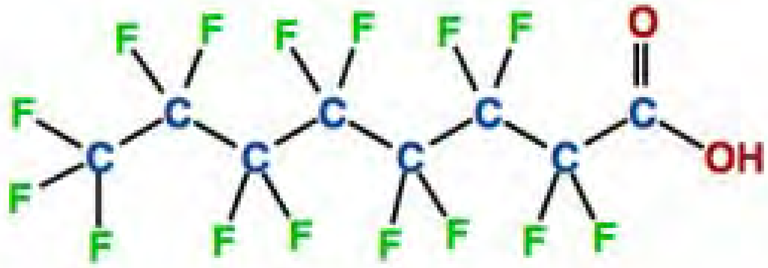
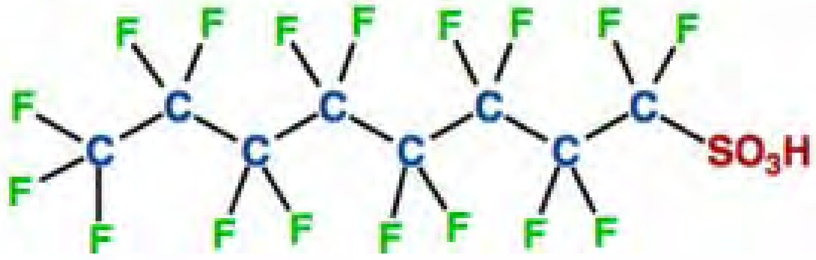
What are PFAS?

- Per- and polyfluoroalkyl substances (PFAS) are a group of man-made, highly fluorinated chemicals
- Varying length of carbon chain, from C4 – C16
  - C4 – C6 → typ. short chain
- Manufactured since the 1940's, but PFOA/PFOS voluntarily phased out in 2006 globally, but before this these were most common
- Manufacturers have developed new PFAS as others were phased out
- Currently many other PFAS compounds (possibly hundreds) are estimated to exist



PFOA - perfluorooctanoic acid



PFOS - perfluorooctanesulfonic acid

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PFAS Properties

- Have oil, stain and water repellant properties which makes them highly desirable for various products
- Flame retardance make them important for fire fighting
- Persistent and do not readily break down
  - Referred to as "forever chemicals"
  - Carbon-Fluorine bond is strong and stable
  - Some (fluorotelomer alcohols) degrade to more stable forms (PFCAs), making them more recalcitrant
- Highly mobile in the environment in both liquid and air
- Due to this, PFAS have been detected nearly everywhere on the globe, including the North Pole

Exhibit E

What Products Contain PFAS?

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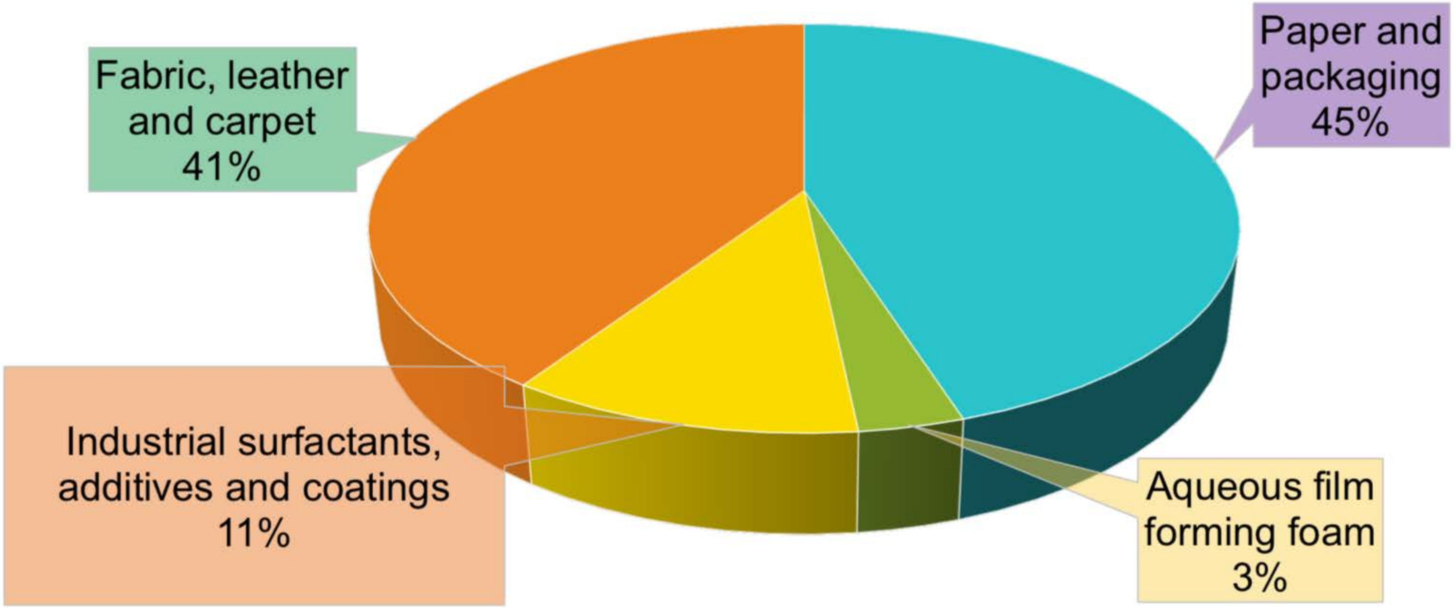
- PFAS are in hundreds of products we use frequently

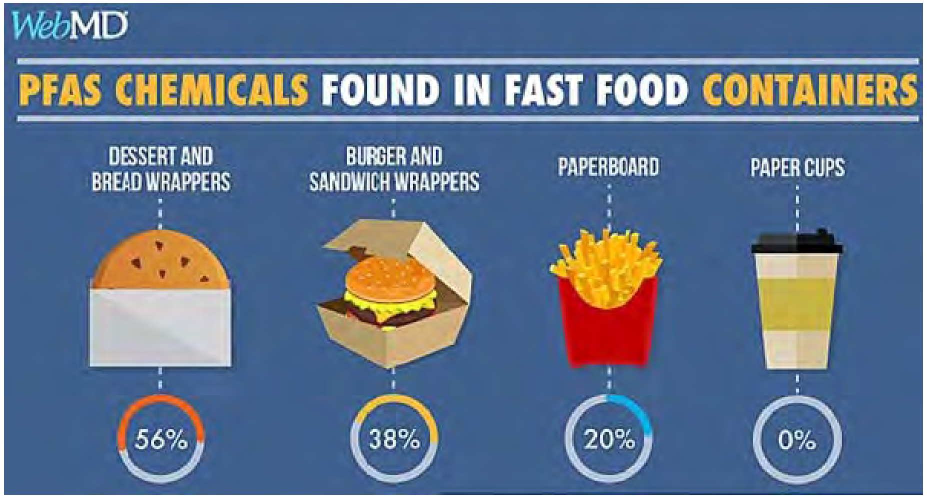
Credit: www.sixclasses.org

Exhibit E

PFAS Production



(Schultz, et al, 2003)



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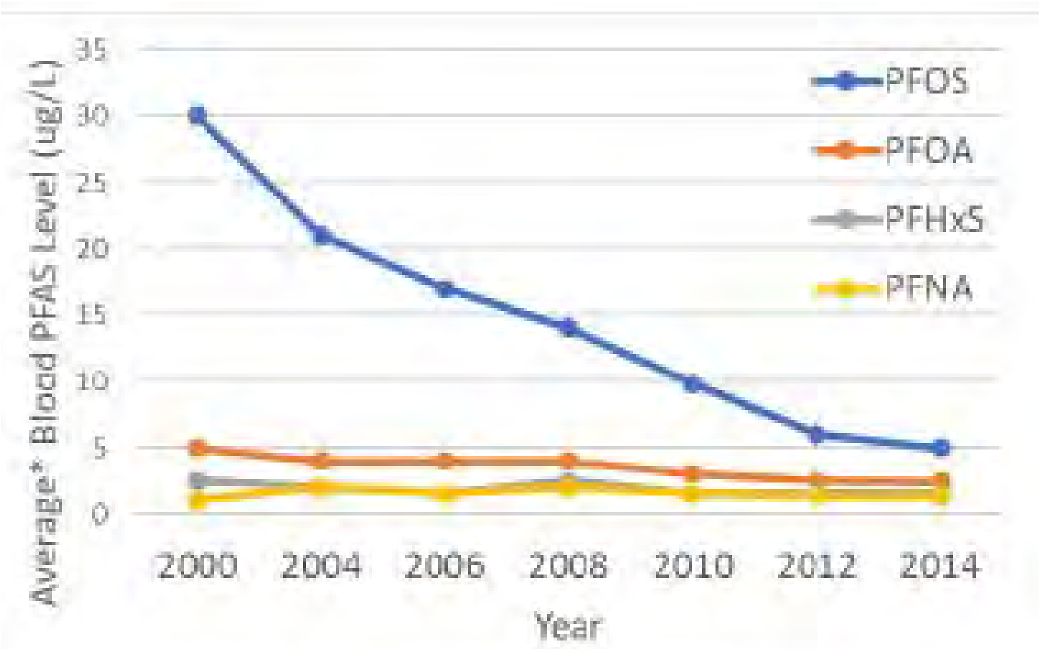
Health Implications

- Due to widespread use and exposure, PFAS are found in blood of > 99% of Americans
  - Long half-lives in human body (Kidneys: 3.8 yrs – PFOA; 5.4 yrs – PFOS)
- Levels of PFOS/PFOA in humans have been declining, but limited info is available for most other PFAS compounds
- Most research done on PFOA/PFOS at significant exposure levels (C8 Science Panel)
  - Cancer
  - Ulcerative colitis
  - Thyroid disease
  - Elevated cholesterol
  - Pre-natal impacts



Source: Center for Disease Control (CDC), 2017

Exhibit E

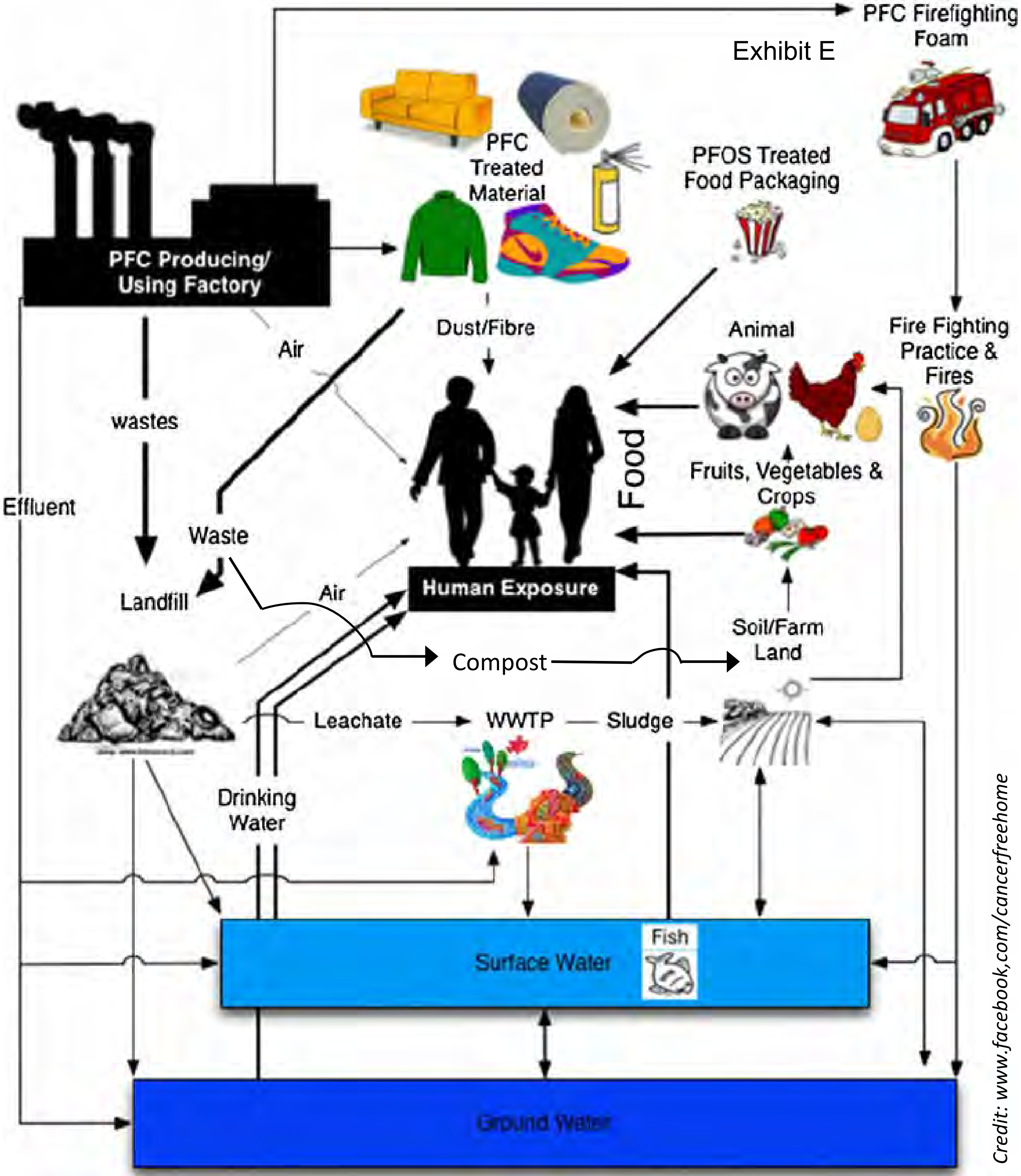
Health Implications *(cont.)*

- Much less research on short chain PFAS, which is being used more since phase-out of PFOS/PFOA
- Some research on other PFAS
    - 9 other PFAS tested show half-lives in humans ranging from 3 days to 15.3 years (Lau, 2015)
    - Confirmed/suggested toxic effects for 7 PFAS compounds beyond PFOA/PFOS (Ghisi et al., 2019)
- Research suggest behavior of PFAS can be VERY different depending on carbon length, functional group, etc.
    - Need to be cautious to extrapolate findings from PFOA/PFOS to all PFAS compounds

PFAS Exposure Pathways

- Bioaccumulates in food chain
- Inhalation
  - Indoor Dust
  - Airborne particulates
- Oral
  - Food
  - Drinking water
- Dermal *(suggested as unlikely) (MI PSAP, 2018)*

Exhibit E



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PFAS "Receiving Facilities"

PFAS are ubiquitous in engineered infrastructure

- Influent to publicly owned treatment works
    - Water Treatment
        - From surface water, runoff, air deposition(?)
        - From groundwater (typ. near 'hot spots')
    - Wastewater Treatment Plants (WWTPs)

- Solid Waste
    - Recycled materials
    - Compost
    - Discards to Landfill
        - Leachate
        - Landfill Gas

- As a sink for PFAS containing materials, WWTPs and landfills, in particular, may aggregate/collect PFAS
- Such facilities are also highly regulated, making it easy for agencies to control PFAS going to the environment

Exhibit E

PFAS in Recycled Materials

- Very little is known regarding whether or not PFAS persist in recycled materials
- Materials that are recycled may contain PFAS (e.g. food packaging)
- If they do, recycling could accumulate PFAS compounds in products that use recycled content
  - More research is needed to determine if this a significant issue
  - If reprocessed under higher temperatures, will this alter/destroy PFAS?

Exhibit E

PFAS in Compost

- Samples from 10 compost facilities in 5 states (WA, OR, CA, MA, NC) tested for 17 PFAS compounds (Choi et al., 2019)
- All had PFAS but significant differences between facilities that accepted food packaging
  - With food packaging = 28.7 – 75.9 µg PFAS/kg compost
  - Without food packaging = 2.4 – 7.6 µg PFAS/kg compost
  - > 68 % were short-chain PFAS
- Studies show PFAS accumulates in food crops and level of uptake directly correlates to levels in soil (Ghisi, 2019)

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PFAS in Leachate and Wastewater

- Most data is for PFOA and PFOS – limited data is available for other PFAS compounds more commonly in use today

Median PFOA/PFOS Concentrations (ng/L). Range is given in parentheses.

Type	PFOA	PFOS	PFOA + PFOS
Leachate[1]	712 *(30 - 5000)*	117 *(3 - 800)*	829
Wastewater Influent[2]	5.06 *(ND – 64.6)*	8.6 *(ND – 499.4)*	13.66

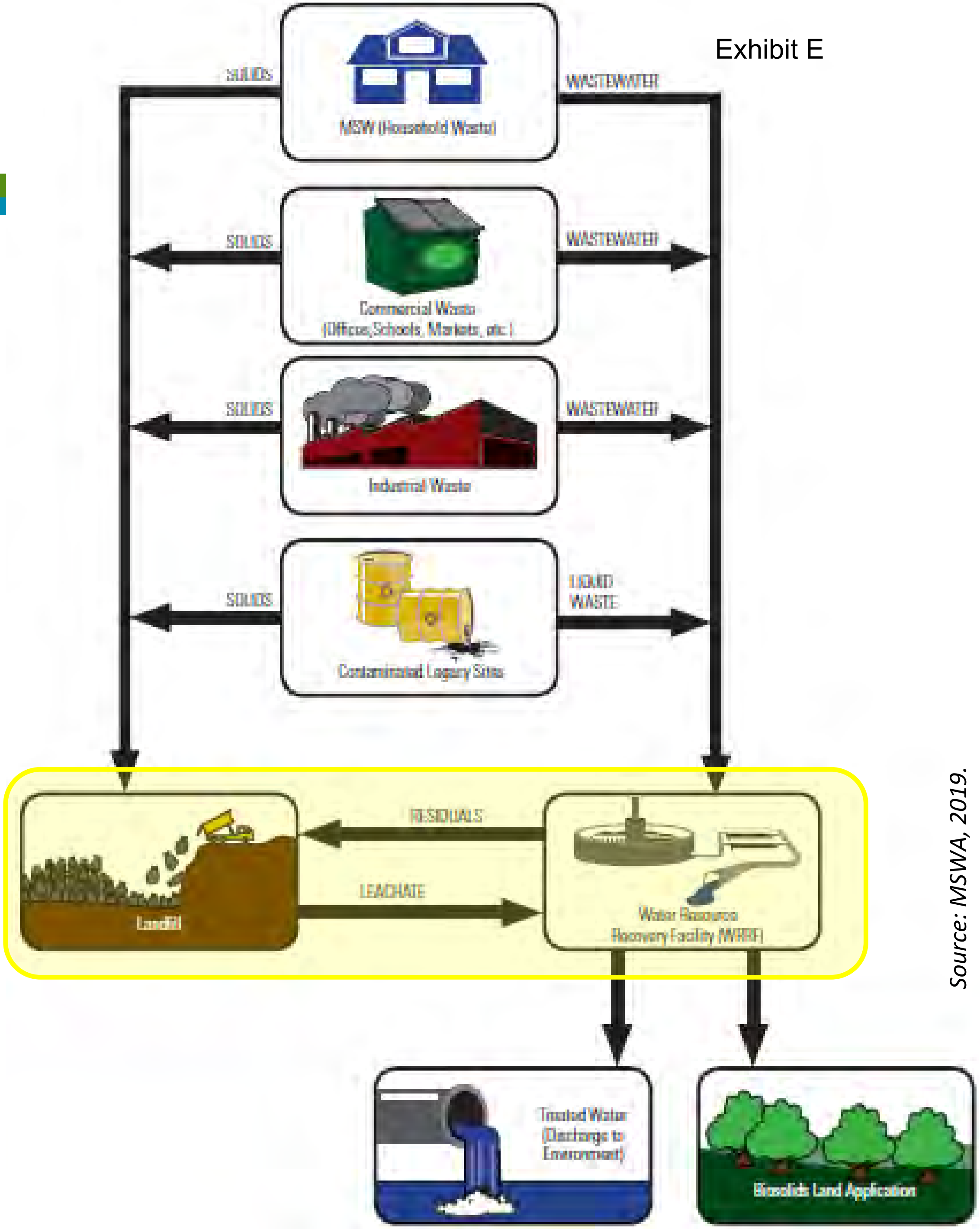
Source: MSWA, 2019. Notes: (1) Leachate is for the U.S. based on 3 studies and over 100 samples. (2) Wastewater values are from 39 Michigan WWTPs

- Leachate contribution to WWTP influent (mass loading)
  - PFOS: ~3.2% to WWTPs is from landfill leachate
  - PFOA: ~13.5% to WWTPs is from landfill leachate
- WWTP biosolids can contain significant PFAS concentrations
  - 0.7-241 ng/dry g PFOA; up to 110 ng/dry g PFOS (Arvaniti & Stasinakis, 2015)

Landfill/WWTP Interdependency

Exhibit E

- Landfills and WWTPs exchange materials
  - Biosolids to LFs
  - Leachate to WWTPs
- Generally there is no direct exposure to PFAS in leachate and wastewater as these are treated
- Treated liquids are released to bodies of water where further dilution occurs



Source: MSWA, 2019.

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Exposure Pathways to PFAS

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- Primary exposure to humans is from inhalation and orally (eating/drinking)

- Research is still evolving, but studies thus far suggest the following routine levels of exposure (per person)
  - Food consumption = 100 – 480 ng/day (Tittlemier, 2007)
  - Dust intake = 46 – 120 ng/day (Strynar & Lindstrom, 2008)
  - Total Dust & Food = 146 – 600 ng/day

- PFAS from diet dominated human intake when drinking water levels were < 40 ng/L (Vestergren & Cousins, 2009)

- Assuming PFAS concentrations in drinking water are equivalent to wastewater influent (13.66 ng/L)
  - a person would need to drink 10.7 to 44 L/day to same exposure as dust & food
  - represents 4.5% to 15.8% of total daily exposure

- Despite this perspective, relative assimilation in the body via these pathways is not well understood
  - it cannot be assumed that a minor exposure pathway is less significant

Exhibit E

What We Don't Know

- Health/toxicology/environmental
  - Health risks at lower doses and from other PFAS (aka. not PFOA or PFOS)
  - Which exposure pathways are most important
  - Very little work done to assess impacts to domestic animals, agricultural crops, wildlife
  - Minimal work done to assess impact to carbon cycle, climate change, soil, air water/oceans

- PFAS Pathways
  - Mass balance will help quantify risk and exposure
  - How much PFAS are in consumer products
  - How many products are sold annually that contain them
  - Which PFAS compounds are in each
  - Transport to receiving facilities (e.g. solid waste, wastewater, stormwater runoff, etc.)

Exhibit E

What We Don't Know - Related to Solid Waste

- How much PFAS are released from specific products
  - During use (human exposure, release to environment)
  - During waste management activities
    - Landfilling (during anaerobic decomposition)
    - Recycling processes/material reprocessing
    - Composting
    - Anaerobic Digestion

- PFAS measurement methods
  - Only accepted method is for drinking water; others are in development

- PFAS treatment/removal
  - Limited work has been done, mostly on reverse osmosis and activated carbon

- Influence on diversion policy
  - BPI, CMA, USCC are banning or recommending bans on PFAS to compost facilities
  - WWTP biosolids contain PFAS → could be banned from land application

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Key Takeaways

- PFAS is ubiquitous in our society and the environment
    - its presence in solid waste & leachate is not surprising
- We cannot assume research findings for PFOA/PFOS (most widely used prior to 2008) are applicable to other PFAS
- Primary human exposure appears to be from dust and food
- Leachate appears to represent a minor fraction of PFAS loading to WWTPs (the primary disposal method for leachate)
- There are many unknowns, more research is needed to quantify risks and management approaches

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Thank you!

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THE STRATIGRAPHY AND HYDRAULIC PROPERTIES OF TILLS IN SOUTHERN NEW ENGLAND

By Robert L. Melvin, Virginia de Lima, and Byron D. Stone

U.S. GEOLOGICAL SURVEY
Open-File Report 91-481

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WASTE MANAGEMENT DIVISION, REGION I

U. S. DEPARTMENT OF THE INTERIOR
March 3, 1849

Hartford, Connecticut
1992

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Exhibit E

CONTENTS

ILLUSTRATIONS

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ILLUSTRATIONS (Continued)

TABLES

CONVERSION FACTORS

Multiply	By	To obtain
	Length	
millimeter (mm)	0.0394	inch
centimeter (cm)	0.3937	inch
meter (m)	3.281	foot
kilometer (km)	0.6214	mile
	Flow	
centimeter per second (cm/s)	2,834	foot per day
	Mass	
kilogram (kg)	2.205	pound

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The Stratigraphy and Hydraulic Properties of Tills in Southern New England

By Robert L. Melvin, Virginia de Lima, and Byron D. Stone

ABSTRACT

The two widely recognized tills of southern New England were deposited during two late Pleistocene continental glaciations. The surface (upper) till consists of relatively sandy tills deposited during the late Wisconsin glaciation and includes compact subglacial lodgement and meltout units and a thin overlying supraglacial meltout (ablation) unit. The drumlin (lower) till is the locally preserved till deposited during the Illinoian glaciation and consists chiefly of a compact subglacial lodgement unit. These tills are highly variable in texture, composition, thickness, and structural features, reflecting the composition of the local bedrock and older surficial materials from which they were derived and the different modes of deposition.

The hydraulic properties of tills in this region are also variable because of the differences in texture, composition, and structural features that result from different provenance and genesis. Data on hydraulic properties at 92 sites were compiled from readily available sources. The horizontal hydraulic conductivities of tills derived from crystalline (metamorphic and igneous) rocks range from 1.4×10^{-6} *to* 2.3×10^{-2} *centimeters per second, whereas the vertical hydraulic conductivities of tills derived from these rock types range from* 4.7×10^{-6} *to* 3.4×10^{-2} *centimeters per second. The porosities and specific yields of 15 undisturbed till samples, also composed of crystalline-rock detritus, range from 22.1 to 40.6 percent and from 3.9 to 31.2, respectively.*

The horizontal hydraulic conductivities of tills derived from the Mesozoic (Triassic and Jurassic) sedimentary rocks of central Connecticut and west-central Massachusetts range from 2.8×10^{-7} *to* 1.2×10^{-3} *centimeters per second, whereas the vertical hydraulic conductivities range from* 1.8×10^{-7} *to* 1.2×10^{-3} *centimeters per second. The porosity of 58 samples of till derived from these sedimentary rocks ranges from 18 to 40.1 percent.*

INTRODUCTION

Till is the most extensive glacial sediment in southern New England. It mantles most of the uplands and also extends beneath stratified drift in valleys and lowlands. This ice-deposited sediment is highly variable in texture, composition, thickness, and structural features, and the variability is commonly reflected in hydraulic properties. Geologic studies over the last century have described the textural and structural features of tills and identified the genetic variants of till in most of the region. The establishment of stratigraphic relationships between tills of southern New England has been more difficult than in the midcontinent of North America where distinct lithostratigraphic units related to bedrock source and glacial ice lobes are recognized. Recently, work by Pessl and Schafer (1968), Stone (1974), Newton (1978), and Smith (1984), has led to development of a regional till stratigraphy, described in this report, that provides a framework for organizing and categorizing geotechnical data.

Till is not a major aquifer in southern New England, but nevertheless is an important geohydrologic unit because of its widespread occurrence and relation to bedrock and stratified-drift aquifers. Till generally extends from the land surface to the top of the underlying bedrock aquifers except in valleys underlain by stratified drift. In these valleys a thin (less than 3 m) layer of till commonly separates the stratified drift from the underlying bedrock. Over most of southern New England this geohydrologic unit, therefore, affects rates of recharge from precipitation and natural ground-water discharge from bedrock, as well as the subsurface transport of contaminants which may have been applied, spilled, or buried near the land surface. Till is also at most of the major sites of point-source contamination that are subject to investigation and remediation under Federal and State programs.

Knowledge of the hydraulic properties of till that control the movement of water and transport of contaminants in this region is sparse. A recent summary of regional hydrogeology (Randall and others, 1988) cited only three references containing limited data on the conductivity and storage properties of till. This type of information is useful to hydrologists and engineers investigating ground-water contamination and flow of ground water between hydrologic units or evaluating the suitability of potential disposal sites. In order to meet this need, the U.S. Geological Survey (USGS), in cooperation with the U.S. Environmental Protection Agency Region 1, Waste Management Division (USEPA), initiated a study of the hydraulic properties of tills in southern New England.

Purpose and Scope

The purpose of this report is to describe the stratigraphic framework for tills in southern New England and to summarize available information on their hydraulic properties. The stratigraphic framework consists of two tills, derived from two glaciations, that display textural and structural variability related to genesis and provenance. Hydraulic properties include reported values of hydraulic conductivity, porosity, and specific yield. The clay and silt content of the till matrix is also included in the reported data. These hydraulic properties, together with hydraulic gradient, are the principal controls on the rate and velocity of ground-water flow, whereas clay and silt content affects hydraulic conductivity and is an indicator of the type of till. Only existing data were compiled and no new data were collected for this study. The location of sites for which data were obtained are shown in figure 1.

Sources of Data and Methods

Data were compiled from published geologic, engineering, hydrologic, and soil science literature; consultants' reports on Superfund and Resource Conservation and Recovery Act (RCRA) sites prepared for the USEPA; unpublished theses and dissertations; and unpublished data from files of the USGS, U.S. Department of Agriculture Soil Conservation Service (SCS), and the Connecticut Department of Transportation (DOT). The hydraulic properties were determined by several laboratory and in-situ methods that have not been critically reviewed for this report with respect to accuracy of measurement, validity of analysis, or other possible sources of error. No attempt was made to calculate independently hydraulic conductivity from coefficients of consolidation determined by soil-mechanics laboratories. However, 56 values of porosity for Connecticut tills derived from Mesozoic sedimentary rocks, previously calculated from measurements of bulk and particle mass density by the USGS, are included in this compilation.

Acknowledgment

Mr. Rudy Chlanda of the SCS provided valuable assistance by reviewing, collating, and copying relevant SCS data for Massachusetts.

STRATIGRAPHY OF TILLS

Terminology

The tills of southern New England are correlated with two late Pleistocene continental glaciations of the region (Schafer and Hartshorn, 1965; Stone and Borns, 1986). Presently the tills of each glaciation are designated by informal stratigraphic names or by proposed formal names for local varieties of till (Stone and Borns, 1986). No regional study of lithologically distinct members of the surface (upper) till of late Wisconsinan age or the drumlin (lower) till of probable Illinoian age supports an inclusive formal nomenclature. In the field, physical criteria differ-

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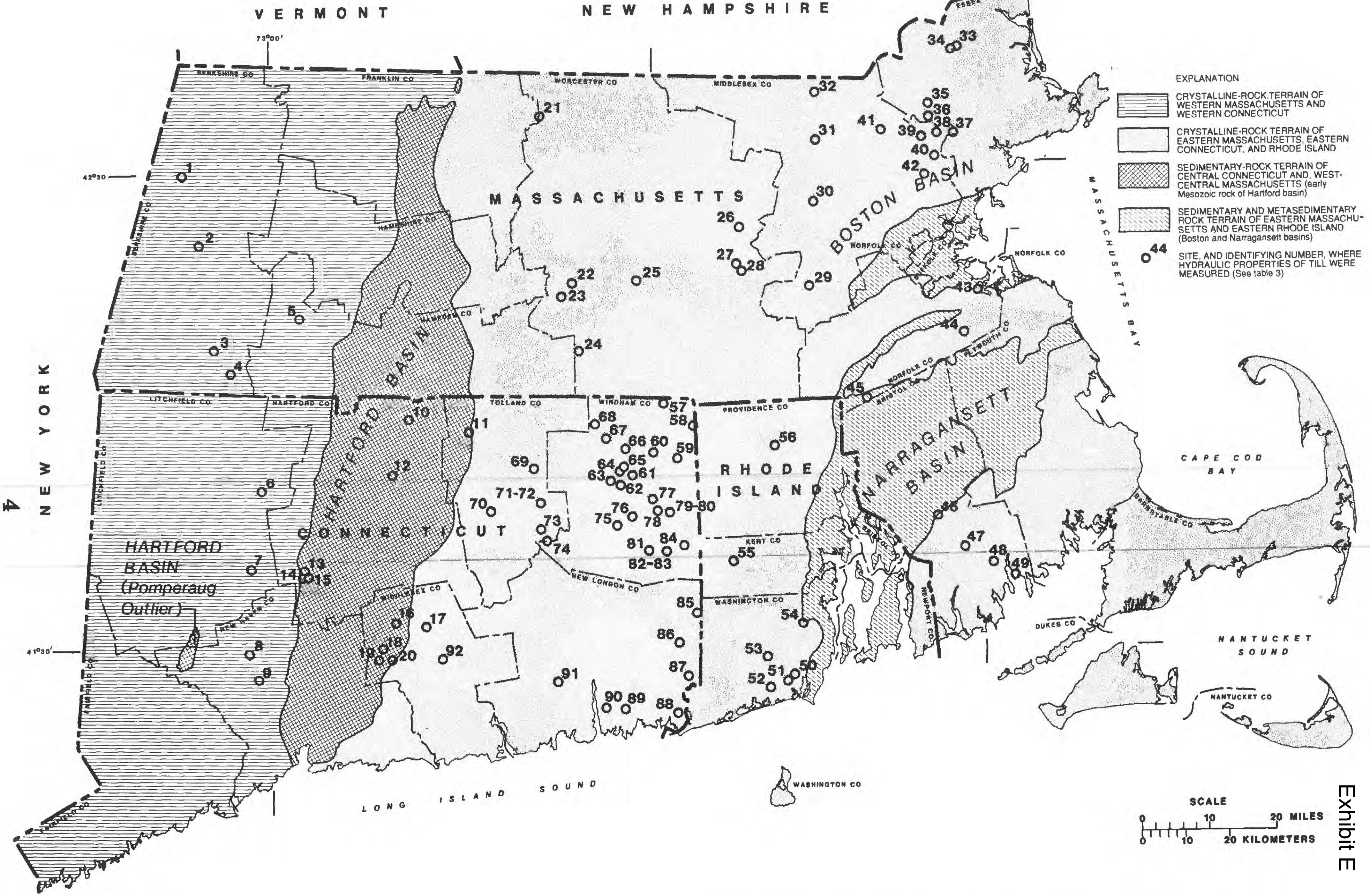


Base from U.S. Geological Survey.
Scale 1:500,000

Figure 1.--Sites where hydraulic properties of till were measured and approximate boundaries of differing provenance areas for the tills in southern New England.

Exhibit E

entiate local varieties of the tills, when comparisons are made of similar characteristics in areas of similar bedrock type. Bedrock control of till grain size, color, and composition is related to the very local distribution of bedrock units and physiography (Flint, 1930, 1961; Smith, 1984; Force and Stone, 1990). Because of the close relation of till composition and texture to local bedrock types, differences within one till unit may be greater in some areas than differences between varieties of both units.

The general terms "upper till" and "lower till" used by several recent investigators (Schafer and Hartshorn, 1965; Pessl and Schafer, 1968; Koteff and Pessl, 1985; Stone and Borns, 1986; discussion by Stone, in Weddle and others, 1989) refer to the chronostratigraphic relation between the two tills and, locally, to their stratigraphic position. The two-till stratigraphy evolved over more than a century of study of the glacial deposits of southern New England. Upham (1878) and Crosby (1891) ascribed all tills in the region to a single glaciation. Fuller (1906) first suggested that compact drumlin tills beneath the surface till are Illinoian in age. Judson (1949) proposed that the drumlin till in Boston was of early Wisconsinan age and this age assignment was retained in regional summaries (Muller, 1965; Schafer and Hartshorn, 1965; Stone and Borns, 1986). Further consideration of radiocarbon age constraints on the late Wisconsin glaciation (Stone and Borns, 1986), dated sediments of middle Wisconsinan and late "Eowisconsinan" ages on Long Island (Belknap, 1979, 1980; Sirkin, 1982), and weathering characteristics of the drumlin till (Stone, 1974; Newton, 1978; and Newman and others, 1990) has led to correlation of the drumlin till with the lower till at Sankaty Head on Nantucket Island, Massachusetts, which is of probable Illinoian age. The development and evolution of the two-till stratigraphy and related terminology is summarized in figure 2 and will aid in placing till discussed in earlier reports within the stratigraphic framework used in this report.

The upper till, referred to in this report as the surface till, comprises the relatively sandy surface tills that form the till sheet of the late Wisconsin glacial episode, which extended from about 24,000 BP (years before present) to deglaciation of the region about 14,000 BP. The till is dated by radiocarbon dating of preglacial subtill materials incorporated in the glacial sediments and of postglacial materials that overlie the sediments (Stone and Borns, 1986). The surface till is highly variable in composition, reflecting the composition of local bedrock and older surficial materials from which it is derived. The compact and weathered lower till, referred to in this report as the drumlin till, is the locally preserved till of the late Illinoian glaciation (Stone, *in* Weddle and others, 1989; Newman and others, 1990), which extended from about 180,000 BP to 150,000 BP (Richmond and Fullerton, 1986). Drumlin tills in drumlins throughout the region are correlated on the basis of the depth and degree of the weathering, and are further correlated with the Sankaty lower till which lies beneath dated marine beds of Sangamonian age on Nantucket Island, Massachusetts (Oldale and others, 1982). The weathering zone in the upper part of the drumlin till is the result of a relatively long or intense period of weathering that postdated drumlin formation.

The surface and drumlin tills are not laterally extensive, superposed, sheetlike bodies in the region. Throughout most of southern New England, only the sur-

Exhibit E

<table>
<tr><th colspan="2">SINGLE GLACIATION[1]
1880-1958
Southern New England New Hampshire and Long Island</th><th colspan="2">MULTIPLE GLACIATIONS[2]
1900-1949
Southern New England</th><th colspan="3">MULTIPLE WISCONSIN GLACIATIONS[3]
1949-1986
Southern New England and Long Island</th><th colspan="3">THIS REPORT WISCONSIN AND ILLINOIAN GLACIATIONS[4]
Southern New England and Long Island</th></tr>
<tr><td>WISCONSIN</td><td>Till,
Drumlin till</td><td rowspan="3">WISCONSIN</td><td rowspan="3">Thin till,
Surface till,
Upper till</td><td rowspan="3">WISCONSIN</td><td>Late</td><td>Upper till,
Surface till,
New till,
Proposed local formal units</td><td rowspan="3">WISCONSIN</td><td>Late</td><td>Surface till</td></tr>
<tr><td colspan="2" rowspan="3"></td><td>Middle</td><td></td><td>Middle</td><td></td></tr>
<tr><td>Early</td><td>Lower till,
Drumlin till,
Montauk Till,
Proposed local formal units</td><td>Early</td><td></td></tr>
<tr><td>ILLINOIAN</td><td>Drumlin till,
Lower till,
Montauk Till</td><td colspan="2">ILLINOIAN</td><td>Lower till at Sankaty Head</td><td colspan="2">ILLINOIAN</td><td>Drumlin till,
Montauk Till,
Lower till at Sankaty Head</td></tr>
</table>

References:

[1] Upham (1878, 1880, 1897)
Crosby (1891, 1908)
Alden (1924)
Flint (1930)
LaForge (1932)
Denny (1958)

[2] Woodworth (1901)
Fuller (1901, 1906, 1914)
Clapp (1908)
Woodworth and Wigglesworth (1934)

[3] Judson (1949)
Flint (1953)
Kaye (1961, 1982)
Muller (1965)
Schafer and Hartshorn (1965)
Newton (1978)
Sirkin (1982)
Oldale and others (1982)
Koteff and Pessl (1985)
Stone and Borns (1986)

[4] Stone, *in* Weddle and others (1989)

Figure 2.--Evolution of till stratigraphy in southern New England and Long Island. (Modified from Stone, *in* Weddle and others, 1989, fig. 2.)

face till is present. Thick, compact, gray surface till is present above oxidized and weathered drumlin till in relatively few exposures (Pessl and Schafer, 1968). More frequently, the superposed stratigraphy of the two tills consists of a sandy and stoney surface till less than 1 m thick overlying a mixed-till zone that contains discrete angular fragments of the drumlin till within a sandy matrix, which, in turn, overlies weathered and nonweathered drumlin till at depth.

Genetic Classification

Variants of tills of the region are also recognized within the framework of the genetic classification of tills (Till Work Group of the International Union for Quaternary Research Commission on Genesis and Lithology of Quaternary Deposits, in Dreimanis, 1989). As defined by the Commission, till is "sediment deposited by or from glacier ice without the intervention of running water" (Dreimanis, 1989, p. 35). In New England, areally extensive compact tills reported in mapping studies, hydrologic investigations, and topical research studies are subglacial (basal) lodgement till or subglacial meltout till of the genetic classification. The distinction of these compact tills is based on structural features and possibly grain-size distribution (Smith, 1984). Although the drumlin till consists entirely of a lodgement unit, studies of the surface till (Drake, 1971; Pessl and Schafer, 1968; Newton, 1978; Smith, 1984, 1988) have differentiated an upper, loose, sandy unit, containing boulders and cobbles and lenses of stratified sediments, from an underlying compact sandy unit. The loose, sandy unit is recognized genetically as a supraglacial meltout (ablation) till composed of debris of englacial or supraglacial origin. The compact varieties of surface tills are of subglacial lodgement or meltout origin, distinguished by clast fabrics and by minor differences in silt and clay content (Smith, 1984). A mixed-till zone, composed of eroded fragments of drumlin till in a sandy surface-till matrix, that overlies weathered drumlin till has been described throughout the region (Pessl and Schafer, 1968; Pease, 1970; Koteff and Stone, 1971; Stone, 1980; Mickelson and Newman, 1987; and Newman and others, 1987, 1990). Minor flowtill is found locally in stratified-drift deposits (Hartshorn, 1958; Smith, 1984); genetically, this is a supraglacial mass movement till.

Distribution and Thickness of Stratigraphic Units

The late Wisconsinan surface till forms an irregular blanket over bedrock uplands and beneath stratified-drift deposits. It is highly variable in composition and thickness because of differences in the composition and erodability of local bedrock and older surficial materials from which the till is derived. In areas of numerous or extensive bedrock outcrops, the topography of the till surface is controlled by bedrock-surface relief (fig. 3). Here the till is discontinuous, probably averaging less than 2 m thick, and contains numerous boulders. In other areas on north-facing lower valley slopes, the till forms smooth-to-bumpy patches of true ground mo-

Exhibit E

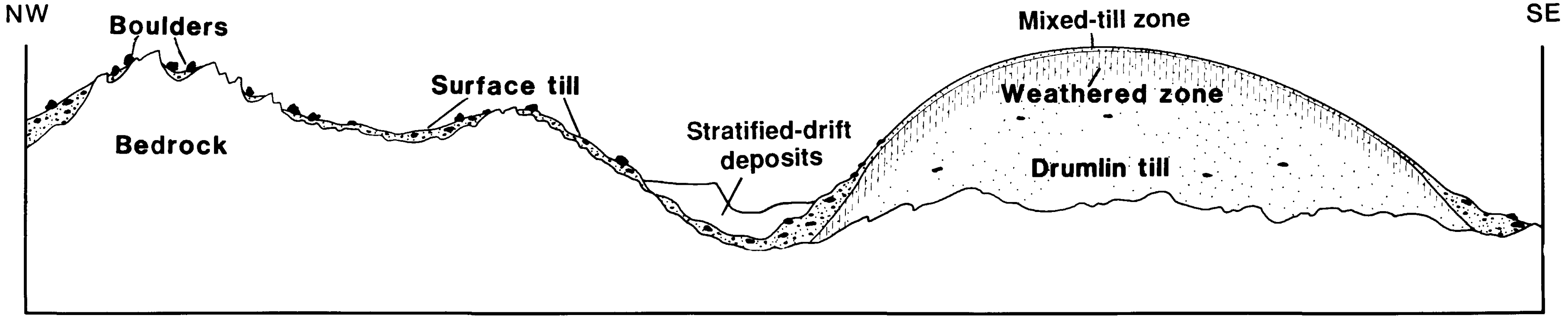
raine, ranging from 3 to 10 m thick. In these areas, the compact basal facies of lodgement and meltout origin form the bulk of the deposit. Loose, sandy, bouldery till of ablation origin forms a thin and discontinuous overlying unit in bedrock outcrop areas and areas of thicker till; locally, it is thick enough to form hummocky surface topography. In most drumlins in the region, the surface till consists of a thin mixed-till zone that overlies the weathered older till (as shown in fig. 3) but, in a few drumlins in the Cape Cod area, the surface till is apparently more than 15 m thick (Koteff, 1974). The late Wisconsinan surface till is the till unit mapped on State surficial geologic maps in the region and on numerous 7 1/2-minute-quadrangle geologic maps in southern New England.

The drumlin till is preserved almost exclusively in drumlins and related bodies of glacially smoothed and streamlined thick till which were resistant to subsequent late Wisconsin glacial erosion (fig. 3). The drumlin till is generally 10 to 30 m thick in these bodies and has a maximum reported thickness of 70 m. Exposures of weathered (oxidized) and some unweathered (nonoxidized) drumlin till are known widely across the region (Lougee, 1957; Castle, 1958; Flint, 1961; Kaye, 1961; Oldale, 1962; Pessl and Schafer, 1968; Stone, 1974; Thompson, 1975; Mulholland, 1976; Newton, 1978; Stone, 1980; Newman and others, 1990).

The distribution of the surface and drumlin tills with contrasting physical characteristics strongly reflects the local bedrock provenance. Four broad bedrock provenances are distinguished in this report (fig. 1): crystalline- (metamorphic and igneous) rock terrain of western Massachusetts and western Connecticut; sedimentary-rock terrain of the early Mesozoic Hartford basin in central Connecticut and west-central Massachusetts; crystalline-rock terrain of eastern Massachusetts, eastern Connecticut, and Rhode Island; and sedimentary- and metasedimentary-rock terrain of the Boston basin in eastern Massachusetts and the Narranganestt basin in southeastern Massachusetts and Rhode Island. This report does not treat the Narragansett and Boston basins as a separate till source area. Only one site (number 45) is in the Narragansett basin, and because it is at the northern boundary, the till may be derived from the crystalline rocks to the north. Till at three sites (numbers 43, 46, and 54), which are in the crystalline-rock terrain, are just south of the Boston or Narragansett basins and may be composed largely of sedimentary and low-grade metasedimentary rocks from these basins. However, because these four sites have not been field-checked by the authors and the origin of the till is not certain, none was categorized as being of sedimentary and metasedimentary rock provenance.

There are local variations in rock type within each provenance. For example, there is a marble belt within the crystalline-rock terrain of western Massachusetts and western Connecticut, and there are areas of schists and phyllites within the crystalline-rock terrains. These variations affect the physical characteristics, such as grain size, of the tills.

Exhibit E



Based on data from Jahns, 1953; Pessl and Schafer, 1968; Koteff and Stone, 1971; Newton, 1978; Stone, 1980; Weddle and others, 1989; Newman and others, 1990.

Figure 3.--Generalized geologic section showing distribution of surface and drumlin tills and weathered and mixed-till zones.

Exhibit E

Table 1.--*Selected characteristics of surface and drumlin tills that are derived from crystalline bedrock* (Modified from Stone, *in* Weddle and others, 1989, table 1)

[m, meter; mm, millimeter; %, percent; <, less than; >, greater than; USDA, SCS, U.S. Department of Agriculture, Soil Conservation Service]

CHARACTERISTIC	SURFACE TILL (late Wisconsinan)	DRUMLIN TILL (Illinoian)
Color (naturally moist material, Munsell color symbols)	Gray to light gray (2.5-5Y 6-7/1-2), to olive gray to light olive gray (5Y 4-6/2)	Olive to olive gray (5Y 4-5/2-3) to olive brown (2.5Y 4-5/3-5) in weathered zone, dark gray (5Y 3.5-5/1) in unweathered till
Texture of matrix (<2 mm range, fig. 4)	62-80% sand 20-38% silt and clay <1-7% clay	35-60% sand 40-65% silt and clay 11-38% clay
Stone content	10-54% >2 mm 5-30% >76 mm	19-42% >2 mm 1-11% >76 mm
Layering	Textural layering common, generally subhorizontal; consists of thin, lighter-colored sandy layers	Textural layering not common; thin, oxidized sand layers and vertical sand dikes locally with darker, silty layers; layering is laterally discontinuous
Jointing	None; subhorizontal parting is related to layering and fabric of till matrix	Well developed; closely-spaced subhorizontal joints and less numerous subvertical joints impart a blocky or thin platey structure to till
Distribution and thickness	Lies directly on bedrock; generally less than 3 m thick in areas of rock outcrop; commonly 3 to 6 m thick on lower valley slopes	Forms cores of drumlins and related bodies of thick till; generally >10 m thick, commonly 20 to 30 m thick; maximum reported thickness 70 m
Soils and weathering (representative USDA, SCS soil series)	Canton series, Charlton series (Typic Dystrochrepts)	Paxton series (Typic Dystrochrepts); soil developed in mixed-till zone that overlies weathered zone in drumlin till; weathered zone <9 m thick; zone is oxidized, leached in some areas, and contains altered clay minerals and iron-bearing minerals

Physical Characteristics Useful for Field Identification

Physical characteristics differentiate the two tills of southern New England (table 1). The color, texture, stone content, weathering and soil development, and geotechnical properties of the tills are related to source materials, glacial erosional and depositional processes, and weathering effects.

Color

The surface till in areas underlain by fresh, crystalline rocks consisting of granites, gneisses, schists, or quartzose metasedimentary rocks is generally gray below the present B horizon of the soil, reflecting composition of fresh, nonoxidized minerals. Local staining by iron minerals, probably limonite, may be controlled by water movement through materials of contrasting texture or around clasts. In the area of the Hartford basin of central Connecticut and west-central Massachusetts, the surface tills range from reddish brown to brownish red. In scattered areas of weathered-sulphitic schists, the tills are yellowish brown, and in other areas of weathered or stained rock, the tills are commonly pale brown.

The olive color of the weathered zone in the drumlin till is a pervasive oxidation stain that affects all parts of the silty till matrix. It commonly extends to depths of 5 to 9 m and through the zone of leached carbonate minerals in some exposures. The stain is darker around iron-bearing minerals. Dark iron-manganese staining is present on joint surfaces and around stones, but generally does not extend as deeply as the pervasive iron stain. In areas of crystalline-rock provenance the color of fresh, unweathered drumlin till commonly is dark gray, reported locally as blue gray. In the Hartford basin, the drumlin till is generally reddish brown to brownish red.

Texture and Stone Content

Particle-size analysis of the surface and drumlin tills (fig. 4) show that whole-till samples differ in stoniness, proportion of the dominant sand-sized particles, and silt and clay content. These analyses also show differences in grain-size characteristics within each of these tills that can be ascribed to differences in the lithology of the source rocks (fig. 4B). The volumetric content of stones larger than 5.1 cm in drumlin till is less than 10 percent and probably about 5 percent (Crosby, 1891; Pessl and Schafer, 1968; Fuller and Holtz, 1981). Boulders larger than 1 m are rare in large excavations of drumlin till. The stoniness, including large boulders, of the compact, surface till is 5 to 30 percent by weight. Boulders 1 to 2 m long are common in large excavations of compact surface till--these and smaller boulders are common in the ablation material at the surface of the late Wisconsinan till. The grain-size curves shown in figure 4A include these visual esti-

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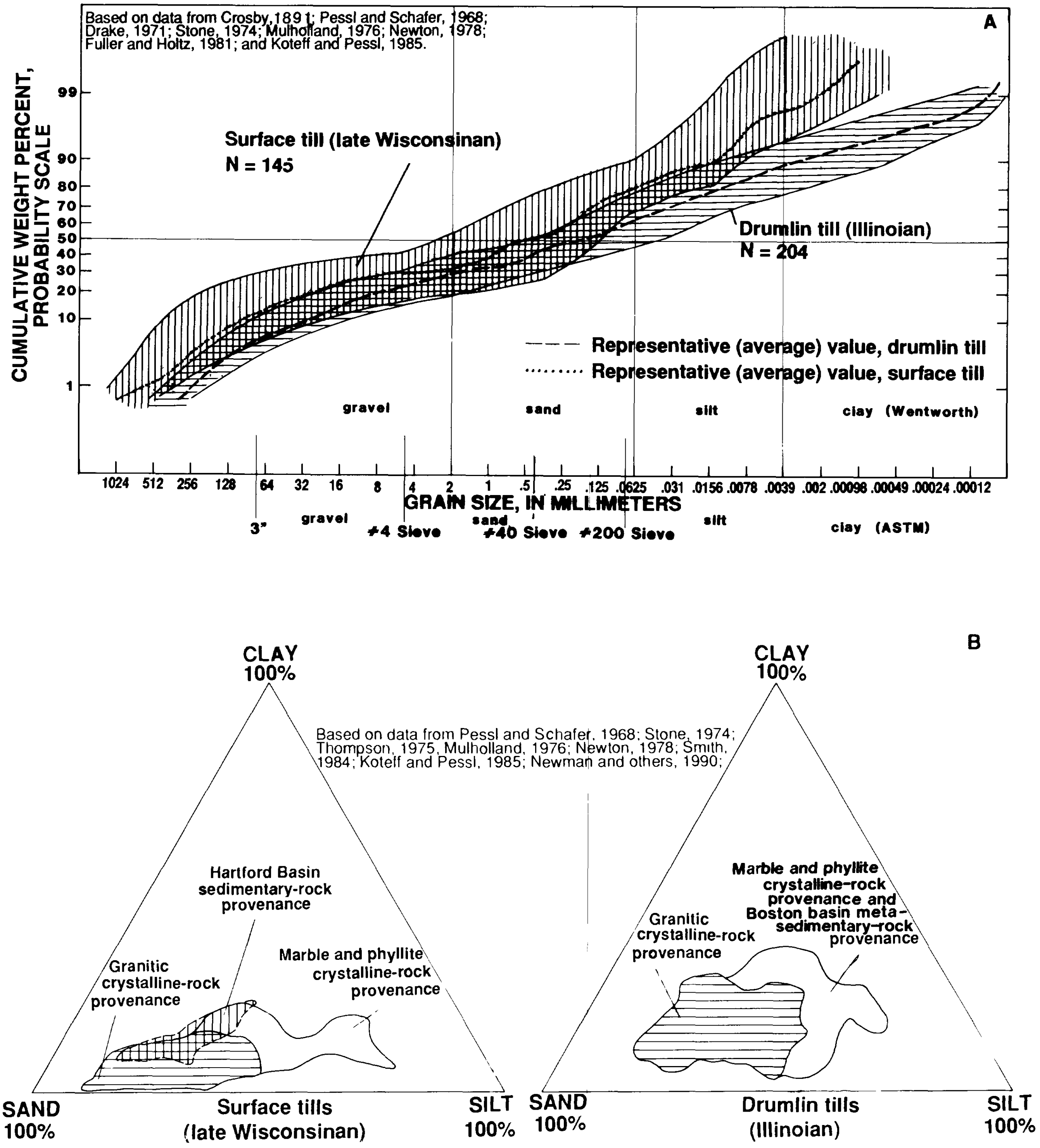

Figure 4.--Grain-size characteristics of the surface till and drumlin till: (A) ranges of cumulative-frequency curves of grain-size distributions of whole-till samples; and (B) ternary diagrams of sand-silt-clay percentages of the till matrix (particle sizes less than 2 millimeters).

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mates of stone content and sieved gravel data, adjusted for differences in densities of rock clasts and till matrix.

Fields of sand-size particles of the two till units overlap (fig. 4A). The proportion of sand differs greatly within each of the two till units, and locally more so than in samples between units. This variation in the relative amount of sand is related chiefly to the grain size and fabric of the local bedrock, and to the degree of comminution of the glacially eroded fresh rock fragments (Smith, 1984, 1988; Force and Stone, 1990).

The silt and clay contents of whole-till samples are distinguishing characteristics of the two tills. Although the ranges of the distributions overlap (fig. 4A), representative "average" values do not. Extreme values show that the surface till contains 9 to 31 percent silt and clay (69 to 91 cumulative weight percent, as shown in the figure), whereas the drumlin till contains 22 to 55 percent (45 to 78 cumulative weight percent). The proportion of clay likewise distinguishes the tills; surface till contains less than 1 percent to 6 percent clay, while drumlin till contains 6 to 24 percent clay. The drumlin till also contains a measurable amount of very fine clay (less than 0.2 microns in diameter) (Stone, 1974).

The silt and clay contents of the till matrix only (particles less than 2 mm in diameter) (fig. 4B) are different in samples of the till. The surface-till matrix contains 20 to 38 percent silt and clay, whereas the drumlin-till matrix contains 40 to 65 percent. The proportion of clay in the surface-till matrix is 1 to 7 percent, and in the drumlin-till matrix it is 11 to 38 percent.

Weathering and Soil Development

Soils developed in the upper 0.6 to 1.2 m of the surface till, mixed-till zone, and drumlin till (fig. 3) since late Wisconsinan deglaciation are inceptisols, characterized by B-horizons, which contain less than 20 percent more clay than overlying horizons, and weakly modified clay mineralogy. Typically Canton and Charlton soils series develop in the surface tills, and the Paxton soil develops in the mixed-till zone on drumlins (Fuller and Holtz, 1981 and Fuller and Francis, 1984).

The weathered zone in the upper part of nearly all drumlin-till exposures is 3 to 9 m thick. It is developed in the drumlin till, below the mixed till zone and the modern soil. The base of the weathered zone is subparallel to the surface of the landform, indicating soil genesis after glacial smoothing. Weathering effects are progressive upward through the zone; pH values decline (Stone, 1974), amount of leaching increases (Crosby and Ballard, 1894), color values of matrix stain increase (Crosby, 1891; Pessl and Schafer, 1968), degree and darkness of iron-manganese stain on joint faces increase, and blocky structure increases and is more densely developed (Pessl and Schafer, 1968). Laboratory data showing alteration of clay minerals and iron-bearing minerals further define the weathering gradient through the 3- to 9-m-thick zone. The weathering zone is the upper part of the C horizon of a probable well-developed soil (Stone, 1974; Newton, 1978; Newman and others,

Exhibit E

1990), the A and B horizons of which were removed by late Wisconsin glacial erosion.

Geotechnical Properties and Classification

Geotechnical properties of the surface and drumlin tills depend on the grain-size and plasticity-index (the water-content range of the material at which it is plastic) characteristics that are distinctly different in the two tills. The Unified Soils Classification System of soils for engineering purposes (American Society of Testing Materials, 1990) is commonly used to group soils on the basis of texture and plasticity-compressibility characteristics (table 2). In this classification system, the surface tills are either SM (silty sand with gravel with 3 to 17 percent cobbles and boulders by volume) or SP-SM (poorly graded sand with silt and with gravel and with 3 to 17 percent cobbles and boulders by volume). Reported variations in the textures of drumlin tills have led to their classification into four groups: SC (clayey sand with gravel, with 1 to 15 percent cobbles and boulders by volume); SM and SC-SM (silty sand with gravel, with 1 to 15 percent cobbles and

Table 2.--*Selected geotechnical properties of the surface and drumlin tills*

[S, sand; G, gravel; SP, poorly graded sand; SM, silty sand; SC, clayey sand; ML, sandy silt; <, less than; >, greater than]

	Unified Soil Classification System Group				
	SP-SM	SM	SC-SM	SC	ML
Relative fractions of sand and gravel	S>G	S>G	S>G	S>G	S>G
Percent fines	5-12	>12	>12	>12	>50
Percent (by volume) cobbles and boulders	3-17	3-17	1-15	1-15	1-15
Liquid limit (weight percent liquid content)	<10	>10		<30	<50
Plasticity index	low	low		10-30	low
Description	poorly graded sand with silt and gravel	silty sand with gravel		clayey sand with gravel	sandy silt with gravel

surface till

drumlin till

boulders by volume); and ML (sandy silt with gravel and with 1 to 15 percent cobbles and boulders by volume). Because clay content of surface tills is relatively low (fig. 4B), they are typically described as being nonplastic; whereas, the more clayey drumlin tills have plasticity indexes of 10 to 30 percent. In the field, naturally moist samples of the surface till exhibit low dry strength (a measure of "compaction" of fragments): fragments crumble or "pop" with some finger pressure. Drumlin till has medium dry strength; considerable finger pressure is required to pop fragments.

In most field and laboratory investigations of engineering properties, tills are described by criteria of the Unified Soil Classification System, without reference to stratigraphic units. In subsurface boring logs and in test-pit descriptions, tills are described as loose to loose and sandy, compact and sandy with boulders, or very compact and clayey. In the stratigraphic framework of the tills of southern New England, these materials are inferred to be surface till of supraglacial-meltout origin, surface till of subglacial lodgement or meltout origin or mixed-zone surface till, and drumlin till of subglacial-lodgement origin.

HYDRAULIC PROPERTIES OF TILLS

Hydraulic conductivity, porosity, and specific yield[1] are the hydraulic properties affecting the flow of ground water through till. The rate of flow depends on hydraulic conductivity if the flow is steady, and on both hydraulic conductivity and specific yield if flow is nonsteady. The average velocity of ground water is dependent on hydraulic conductivity, hydraulic gradient, and effective porosity (interconnected pore space) which, in the case of unconsolidated porous media, is considered identical to porosity (Todd, 1980, p. 27). Ground-water movement, including the governing equations, is described in detail in standard texts such as those by Bear (1972), Freeze and Cherry (1979), and Todd (1980).

This compilation is limited to data on hydraulic conductivity, porosity, and specific yield, although other till properties, such as dispersivity, can strongly affect transport of contaminants. Furthermore, if extensive secondary permeability and porosity has developed in tills through fracturing or other processes, the data on primary (matrix) hydraulic conductivity, porosity, and specific yield obtained from laboratory tests may not be representative of the "bulk" values required to analyze a flow problem. Secondary permeability and porosity are well developed in fractured till that underlies the Interior Plains Region of Canada. The hydraulic properties of the extensively fractured till that underlies this area and the effects of the secondary permeability on ground-water flow have been described by Grisak and others (1976) and Keller and others (1986, 1988).

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[1] Specific yield is considered equivalent to storage coefficient in the case of unconfined aquifers (Freeze and Cherry, 1979, p. 61).

The values for hydraulic properties of tills at 92 sites in southern New England are presented in table 3 (beginning on page 19). The data are organized into three broad groups that reflect geography and source area. The first group includes sites located in the western part of southern New England where the tills are derived from erosion of various types of crystalline rocks. The second group includes sites within or immediately adjacent to the Hartford basin where the distinctly red to brown tills consist mostly of material eroded from sedimentary rocks (largely sandstone and shale). The third group includes sites located in the eastern part of southern New England where tills also are derived from crystalline rocks. Parts of eastern Massachusetts and Rhode Island underlain by sedimentary and metasedimentary rocks of the Boston and Narragansett basins contain texturally distinct tills. Although none of the sites in table 3 have till which is known to be derived from rocks in these basins, they are shown as a separate till source area in figure 1.

Within each broad category, an attempt has been made to identify the stratigraphic unit (surface, surface-mixed zone, or drumlin till) and, in some cases, the general type of till (ablation, meltout, basal, and flow till). Criteria used to identify the stratigraphic unit and type of till include geomorphic and geologic setting of the sample sites as shown on detailed maps of surficial geology, depth of the sampled or tested interval, field descriptions of the till, and textural information (particularly the percents of silt and clay) contained in the source references. In most cases, the stratigraphic and genetic identifications given in table 3 are not certain because diagnostic features have not been adequately described in the references.

Values for hydraulic properties in table 3 were obtained from the referenced source material. The only changes are the conversions of all hydraulic-conductivity values to units of centimeters per second and depths to units of meters. All values are rounded to one decimal place.

Hydraulic Conductivity

Hydraulic conductivity values are organized into four categories in table 3. The first two are horizontal hydraulic conductivity (k_h) and vertical hydraulic conductivity (k_v). The third category (k_r) includes hydraulic-conductivity measurements made on repacked samples. Most of the repacked samples contain only till particles less than 0.42 mm (40 mesh) in diameter that have been compacted. The fourth category (k_u) includes hydraulic-conductivity measurements where the orientation and (or) degree of disturbance are unknown.

The type of test and method of analysis, if known, are given for the hydraulic-conductivity values in table 3 to assist the user of this report in judging their relevance to field problems. Stephenson and others (1988) have pointed out several factors that influence the hydraulic conductivity measurements of tills and their comparability, with consequent implications for field studies of flow and transport. Factors cited by Stephenson and others (1988) include (1) in-situ values of hydraulic conductivity determined in the field from aquifer tests and single-well water-level response tests (slug tests and constant-head tests) are commonly much greater than values determined in the laboratory for the same material; (2) laboratory-determined values can be representative of the till matrix but not of the bulk mass of the till; and (3) different laboratory methods can produce different values.

Comparisons of field- and laboratory-determined values of hydraulic conductivity have not been made using data in table 3. In fact, the suitability of the data for making such comparisons has not been evaluated. A number of features could increase hydraulic-conductivity values calculated from in-situ tests; these include fractures (both jointing and a subhorizontal fissility), widely observed and often well developed in drumlin till and locally (and less developed) in the compact basal facies of the surface till (Smith, 1984, p. 8 and table 1 of this report); macropores, such as root casts that are produced by soil-development processes in the zone 1 to 1.5 m below land surface; and small lenses or layers of stratified drift within the till. If secondary permeability and porosity are well developed locally in the tills of southern New England, the laboratory-determined values of till-matrix properties could differ considerably from the bulk values that control the rate and velocity of ground-water flow.

Weathered-till deposits are also recognized to have greater hydraulic conductivity than that of similar unweathered till (Stephenson and others, 1988, p. 309). Nearly all of the extensive drumlin-till exposures in southern New England contain a weathered zone at least 3 m thick. It has not been determined if this weathering has increased the hydraulic conductivity.

The laboratory-determined hydraulic conductivity of the till matrix has also been observed to have a strong relation to grain-size distribution (Stephenson and others, 1988, p. 306). The major effect of grain size appears to be related to the clay content; contents of 15 to 20 percent mark a threshold above which hydraulic conductivities are uniformly low. The clay content of the surface-till matrix in southern New England ranges from less than 1 percent to 7 percent, whereas the clay content of the drumlin-till matrix ranges from 11 to 38 percent (fig. 4). Data on the combined silt and clay content are available for most of the samples where hydraulic conductivity was estimated by laboratory analysis (table 3). The grain-size scales used by geologists, soil scientists, and engineers commonly differ and the boundary used to divide silt from sand size is, therefore, indicated in the table.

Porosity and Specific Yield

Porosity and specific-yield data are in two adjacent columns in table 3 to facilitate comparisons. The porosity values are all total porosities measured in or calculated for laboratory samples. The most extensive porosity data are the 58 values for tills derived from Mesozoic sedimentary rocks of the Hartford basin (sites 10-12, 16, and 18-20). Fifty-six of these values had been calculated by the USGS from the bulk mass density and particle mass density of the samples, using the formula given in Freeze and Cherry (1979, p. 337). Only 15 measurements of specific yield were found in the referenced sources. All these measurements were made on undisturbed samples of tills derived from crystalline bedrock that were collected and analyzed by the USGS.

The values in table 3 represent only the porosity and specific yield of the till matrix. If the till is fractured or contains other secondary openings, these matrix values from laboratory tests apply to till blocks between the secondary openings and not to the bulk mass of the till (Grisak and others, 1976, p. 311). In such cases, the storage (specific yield) and porosity characteristics imparted to the bulk of the till must also be determined if the ground-water-flow system and the directions, rates, and velocities of ground-water flow are to be understood.

Exhibit E

Table 3.--*Hydraulic conductivity, porosity, and specific yield values for till in southern New England*

Site number: A unique sequential number assigned to each locality where hydraulic conductivity has been determined. Site numbers are shown in figure 1.

Site name and location: Place name or facility name associated with the test site. Includes town and state, such as Durham-Middlefield Landfill, Durham, Conn.

Sample or well number: Number or alphanumeric characters used by the referenced sources to identify a till sample or well where a test was conducted to determine hydraulic conductivity.

Type of till: Estimated from physical descriptions, textural information, topographic setting, published geologic maps, and depth. Types include surface (undifferentiated), surface-ablation, surface-mixed, surface-basal, surface-morainal, drumlin, flowtill, unknown (estimate could not be made largely because of imprecise location).

Hydraulic conductivity:

k_h	measured in horizontal direction
k_v	measured in vertical direction
k_r	measured in repacked (disturbed) sample
k_u	measurement in sample where orientation and degree of disturbance (undisturbed to repacked) are not specified.

Type of test and analysis:

First code

P	permeameter
PT	aquifer test
PZ	piezometer
SI	slug injection
SW	slug withdrawal
O	other
U	unknown

Second code

BR	analysis by method described by Bouwer and Rice (1976) and Bouwer (1989)
H	analysis by method described by Hvorslev (1949 and 1951)
N	analysis by method described by Department of the Navy (1971, p. 7.4.8–7.4.9)
T	analysis by method described by Cooper and others (1967) and Papadopulos and others (1973) as modified by Torak (1979)
ch	constant head
fh	falling head

Percentage of silt and clay:

a	AASHO scale: silt and clay fraction less than 0.074mm (U.S. Standard Sieve number 200)
u	USDA scale: silt and clay fraction less than 0.05 mm
w	Wentworth scale: silt and clay fraction less than 0.0625 mm

References:

USDA, SCS	U.S. Department of Agriculture, Soil Conservation Service
USCOE	U.S. Army Corps of Engineers

Exhibit E

Table 3.--*Hydraulic conductivity, porosity, and specific yield*

[--, no data; <, less than; >, greater than; ≤, less than or equal to; mm, millimeters; cm, centimeter;

Site no.	Site name and location	Sample or well number	Depth below land surface (m)	Type of till	Hydraulic conductivity (cm/s)				Type of test and analysis
					k_h	k_v	k_r	k_u	
	Crystalline bedrock of western								
1	Rose Disposal Pit, Lanesboro, Mass.	5A-83	1.5-4.6	surface	3.2×10^{-5}				SW-BR
		5B-83	11.0-14.0	do.	2.4×10^{-5}				
		5C-83	27.7-30.8	do.	7.8×10^{-5}				
		8A-83	1.5-4.6	do.	1.2×10^{-3}				
		8B-83	9.8-12.8	do.	7.1×10^{-6}				
		8C-83	24.8-27.9	do.	4.7×10^{-4}				
		10A-83	1.5-4.6	do.	4.1×10^{-3}				
		10B-83	13.1-16.2	do.	9.5×10^{-6}				
		11A-83	1.2-4.3	do.	2.3×10^{-2}				
		11B-83	8.2-11.3	do.	1.2×10^{-5}				
		14A-83	1.5-4.6	do.	1.7×10^{-5}				
2	Washington Mountain Brook, site 3, Lee, Mass.	70W1292	0.9-3.7	surface?			1.4×10^{-5}		P-ch
		70W1290	0.9-3.7	do.			1.8×10^{-5}		
		70W1288	0.9-4.3	do.			1.4×10^{-5}		
		72W659	0.6-3.0	do.			1.4×10^{-6}		
		72W660	--	do.			7.1×10^{-6}		
3	Clam River watershed, Morley Brook site, Sandisfield, Mass.	DH No.8	4.6-4.9	surface?	4.7×10^{-3}				PT-ch
		do.	6.1-6.4	do.	9.9×10^{-4}				
4	Clam River watershed, Silver Brook site, Sandisfield, Mass.	DH-1	6.1-15.2	surface	1.2×10^{-4}				PT-ch
		65W210	--	do.			9.2×10^{-5}		P-fh?
		65W209	--	do.			8.8×10^{-6}		do.
		65W133	--	do.			2.2×10^{-5}		do.
		65W135	--	do.			1.8×10^{-6}		do.
		66W2568	--	do.			2.8×10^{-7}		do.
5	Bradley Brook watershed, Black Brook site, Russell, Mass.	70W1010	0.9-3.7	surface?			5.3×10^{-6}		P-ch
		70W1012	0.9-4.3	do.			1.4×10^{-6}		
6	Canton 1, stream cut at Bakersville Brook, New Hartford, Conn.	2C1 horizon	0.8-1.0	surface-ablation		7.5×10^{-3}			P
		2C3 horizon	1.5-1.7	do.		4.1×10^{-3}			
		2C5 horizon	2.1-2.3	do.		3.4×10^{-2}			
7	Thomaston Dam, Plymouth, Conn.	24	--	drumlin			9×10^{-6} to 8×10^{-8}		P
8	Laurel Park, Naugatuck, Conn.	TP3	0.9	surface				6.8×10^{-6}	P-fh
		TP4	0.9	surface-basal				5.3×10^{-6}	
		TP5	0.9	surface				1.5×10^{-5}	
9	Beacon Heights Landfill, Beacon Falls, Conn.	MW-14	2.4-3.9	surface	5.4×10^{-4}				SW-BR
		MW-15	2.4-3.9		1.5×10^{-4}				

Exhibit E

values for till in southern New England

m, meter; km, kilometer; cm/s, centimeter per second; lb/ft^2, pound per foot squared]

Porosity (percent)	Specific yield	Percent silt and clay	Remarks	References
Massachusetts and Connecticut				
				Geraghty and Miller, (1984, table 4)
			hydraulic conductivity determined on minus no. 4 fraction of samples under load of 2,000 lb/ft^2	unpublished data for the Washington Mountain Brook watershed, USDA, SCS
				SCS (1964a) and unpublished data for the Clam River watershed, USDA, SCS
		21 (u) 33 (u) 23 (u) 33 (u) 37 (u)	till thickness equal to or greater than 14.6 m	SCS (1966) and unpublished data for the Clam River watershed USDA, SCS
		31 (u) 42 (u)	sample may be schistose rock or mixed till; hydraulic conductivities measured on minus no. 4 fraction of samples under load of 2,000 lb/ft^2	SCS (1969) and unpublished data for the Bradley Brook watershed USDA, SCS
		11.1 (u) 15.5 (u) 16.8 (u)	one of six samples of Canton soils collected from C horizon at three localities; orientation of cores reportedly vertical (H.D. Luce, Univ. of Conn., oral commun., 1989)	Pelletier (1982)
		40 (a)	the hydraulic conductivities represent the range of values for several samples of till matrix (≤4.75 mm grain size) after standard compaction; tests conducted by New England Division, USCOE	Linell and Shea (1961)
		43.3 (a) 36.6 (a) 37.7 (a)	analysis performed on samples trimmed from block samples by method described by USCOE manual; data on plastic and liquid limits of samples also available.	Fred C. Hart, Assoc., Inc. (1983, unnumbered worksheet), USCOE (1970, appendix VII)
			slug test data available but not interpreted (Malcolm Pirnie, 1988, figs. 1 and 2)	
			till described as loose	NUS (1985b, chap. 4, p. 18)

Exhibit E

Table 3.--*Hydraulic conductivity, porosity, and specific yield*

Site no.	Site name and location	Sample or well number	Depth below land surface (m)	Type of till	Hydraulic conductivity (cm/s)				Type of test and analysis
					k_h	k_v	k_r	k_u	
	Sedimentary bedrock of central								
10	Suffield Meadows condominiums, between Rte. 159 and the Connecticut River, Suffield, Conn.	BB1-1	1	surface-mixed or drumlin	1.0×10^{-4}				P-ch
		BB1-2	2	drumlin	7.7×10^{-7}				
		BB1-3	1.8	do.	1.5×10^{-6}				
		BB1-4	2	do.		3.8×10^{-7}			
		BB1-5	3	do.	1.3×10^{-5}				
		BB1-6	3	do.		6.0×10^{-7}			
		BB1-7	2	do.	9.0×10^{-7}				
		BB1-9	3	do.	2.8×10^{-7}				
		BB1-10	4	do.	3.2×10^{-6}				
		BB1-11	2.5	do.	1.9×10^{-6}				
		BB1-12	2.6	do.		8.7×10^{-6}			
11	Parker Rd. east of Rte. 83, Somers, Conn.	E1-1	1	surface	8.9×10^{-4}				P-ch
		E1-2	2	do.	1.7×10^{-4}				
		E1-3	2	do.	1.4×10^{-4}				
		E1-4	3	do.	3.6×10^{-4}				
		E1-5	3	do.	3.8×10^{-4}				
		E1-7	2	do.		5.3×10^{-4}			
12	Day Hill, Windsor, Conn.	S48, C1 horiz	0.6	surface-mixed?				7.0×10^{-4}	P
		do.	0.6-0.7	do.				1.1×10^{-4}	
13	Superior Electric, Bristol, Conn.	MW7	2.7-4.3	surface	3.5×10^{-6}				SW-H
		MW8	3.0-4.6	do.	3.5×10^{-5}				
14	Cecos, Cross St., Bristol, Conn.	CR1	6.1-9.1	surface	3.7×10^{-4}				SW-H
		CR4	9.1-12.2	do.	1.2×10^{-3}				
15	Cecos, Broderick Rd., Bristol, Conn.	BR5	12.5-15.5	surface	1.2×10^{-3}				SW-H
16	Excavation for Farmers and Mechanics Bank, Main St., Middletown, Conn.	MT1-3	5	drumlin	1.0×10^{-4}				P-ch
		MT1-4	3	do.	6.0×10^{-7}				
		MT1-6	5	do.	1.3×10^{-6}				
		MT1-7	2	do.	6.6×10^{-6}				
		MT1-8	3	do.	7.5×10^{-6}				
		MT1-9	4	do.	1.6×10^{-6}				
		MT1-10	3	do.		2.5×10^{-6}			
17	Pratt and Whitney, Middletown, Conn.	MW1	23.5-25.0	surface	1.7×10^{-5}				SW-H
		MW1A	19.2-20.7	do.	8.5×10^{-5}				
		GZ5D	18.9	do.	2.8×10^{-4}				
18	Durham-Middlefield Landfill, Durham, Conn.	D1-1	--	drumlin		4.1×10^{-6}			P-ch
		D1-2	--	do.	9.5×10^{-6}				
		D1-3	--	do.		2.3×10^{-5}			
		D1-4	--	do.	3.8×10^{-6}				
		D1-5	--	do.	1.4×10^{-6}				
		D1-6	--	do.		4.8×10^{-6}			
		D1-9	--	do.	1.4×10^{-5}				
19	Town of Durham, open-space land at end of Dunn Hill Rd., Durham, Conn.	D13-1	1	surface?		1.2×10^{-3}			P-ch
		D13-2	1.3	surface-mixed?		2.1×10^{-5}			
		D13-3	4.5	drumlin		8.5×10^{-5}			
		D13-4	4.6	do.		5.4×10^{-4}			
		D13-5	4.8	do.		1.1×10^{-6}			
		D13-6	5.1	do.		4.4×10^{-6}			
		D13-7	5.3	do.		9.0×10^{-5}			
		D13-8	5.6	do.		1.0×10^{-6}			
		D13-9	10.5	do.		8.2×10^{-5}			
		D13-10	11.2	do.		8.2×10^{-7}			
		D13-11	11.3	do.		1.1×10^{-6}			

Exhibit E

values for till in southern New England--Continued

Porosity (percent)	Specific yield	Percent silt and clay	Remarks	References
Massachusetts and Connecticut				
29 21 28 21 27 23 25 20 27 25 26			part of a group of 58 till samples collected in the southern part of the Connecticut Valley Lowland by USGS; analysis by Univ. of Conn., Dept. of Civil Engineering; porosity calculated from bulk mass density and particle mass density ■ sample BB1-3 contained silt layer	unpublished file data USGS, Hartford, Conn.
32 32 32 32 32 --			do.	do.
40.1 31.0		71.6 (u) 71.6 (u)	core samples analyzed by the Connecticut Agricultural Experiment Station	Bourbeau and Swanson (1954)
			till is described as red at this site	Ground Water, Inc. (1987, p. 25)
		11 (a) 22, 6, and 28 (a)	screen of CR1 may be partly in sand; percent silt and clay in CR1 from 9.1-9.4 m; three sediment samples in CR4 taken from 9.1-9.7, 10.8-11.4 (described as containing only trace silt) and 12.3-12.8 m	Goldberg Zoino Assoc. (1990b, table 2)
		29 (a)		Goldberg Zoino Assoc. (1990a, table 2)
28 24 25 27 -- 23 24			part of a group of 58 till samples collected in the southern part of the Connecticut Valley Lowland by USGS; analysis by Univ. of Conn., Dept. of Civil Engineering; porosity calculated from bulk mass density and particle mass density ■ some silt laminae in samples MT1-3 and MT1-6	unpublished file data USGS, Hartford, Conn.
			underlying rock is crystalline, but till is largely derived from Mesozoic sedimentary rocks directly to the west; samples MW1A and GZ5D assumed to be in till; reference gave method as slug test; withdrawal is assumed	Charles T. Main (1990, chap. 3, table 8)
25 26 27 22 18 22 25			part of a group of 58 till samples collected in the southern part of the Connecticut Valley Lowland by USGS; analysis by Univ. of Conn., Dept. of Civil Engineering; porosity calculated from bulk mass density and particle mass density ■ sample D1-1 described as sandy and friable, others are compact	unpublished file data, USGS, Hartford, Conn.
28 27 29 25 27 21 22 25 25 20 21			do.	do.

Exhibit E

Table 3.--*Hydraulic conductivity, porosity, and specific yield*

Site no.	Site name and location	Sample or well number	Depth below land surface (m)	Type of till	Hydraulic conductivity (cm/s)				Type of test and analysis
					k_h	k_v	k_r	k_u	
20	West side of Cherry Lane near Durham Center, Durham, Conn.	D14-1	1.2	drumlin		1.6×10^{-5}			P-ch
		D14-2	6.3	do.		2.9×10^{-7}			
		D14-3	>6.3	do.		2.6×10^{-7}			
		D15-1	0.8	do.		1.6×10^{-5}			
		D15-2	1.1	do.		1.1×10^{-6}			
		D15-3	1.3	do.		2.4×10^{-6}			
		D15-4	1.4	do.		3.7×10^{-7}			
		D15-5	1.7	do.		5.2×10^{-7}			
		D15-6	4	do.		5.7×10^{-7}			
		D15-7	4.4	do.		3.8×10^{-7}			
		D15-8	4.6	do.		5.7×10^{-7}			
		D15-9	6.1	do.		6.3×10^{-7}			
		D15-10	6.7	do.		1.8×10^{-7}			
		D15-11	6.9	do.		4.2×10^{-7}			
		D15-12	7.1	do.		3.9×10^{-7}			
		D15-13	7.4	do.		2.1×10^{-7}			
					Crystalline bedrock of eastern Massachusetts,				
21	Athol Landfill, Athol, Mass.	MW2I	6.7-7.0	surface	1.2×10^{-4}				SW-H
		do.	7.9-8.2	do.	1.2×10^{-5}				
		do.	9.1-9.4	do.	1.2×10^{-4}				
		do.	10.4-10.7	do.	7.4×10^{-6}				
		do.	11.6-11.9	do.	1.4×10^{-6}				
		MW3I	6.7-7.0	do.	6.0×10^{-4}				
		do.	8.2-8.5	do.	3.3×10^{-6}				
		do.	9.1-9.4	do.	4.5×10^{-5}				
		do.	10.4-10.7	do.	1.2×10^{-5}				
		do.	11.6-11.9	do.	9.0×10^{-5}				
22	Upper Quaboag watershed Sucker Brook, West Brookfield, Mass.	DH6	6.7-7.2	surface-mixed?				1.1×10^{-4}	PT-ch
23	Upper Quaboag watershed Lamberton site, West Brookfield, Mass.	64W2909	0.3-1.2	surface-mixed?			5.3×10^{-6}		P
24	Galileo, Sturbridge, Mass.	MW8S	2.7-5.8	surface	2.4×10^{-3}				SW-BR
		MW11S	0.8-5.3	do.	4.7×10^{-3}				
25	Upper Quaboag watershed Shaw site, Spencer, Mass.	TH No.7	3.0-3.5	surface?				1.4×10^{-5}	U
		TH No.9	7.6-8.1	do.				4.2×10^{-3}	
		TH No.14	6.7-7.8	do.				1.4×10^{-5}	
26	SUASCO watershed North Brook (Ross) site, Berlin, Mass.	71W1078	--	surface			1.4×10^{-5}		P
		71W1074	--	do.			3.5×10^{-5}		
27	SUASCO watershed Assabet River, site A-4-C Northboro, Mass.	60W2069/ 219.1	0.5-0.8?	surface			7.1×10^{-5}		P

values for till in southern New England--Continued

Porosity (percent)	Specific yield	Percent silt and clay	Remarks	References
27 21 21 28 27 26 26 25 24 25 24 24 23 25 25 25			part of a group of 58 till samples collected in the southern part of the Connecticut Valley Lowland by USGS; analysis by Univ. of Conn., Dept. of Civil Engineering; porosity calculated from bulk mass density and particle mass density	unpublished file data USGS, Hartford, Conn.
Rhode Island, and eastern Connecticut				
			description of material is similar to that for a sample of till, although the material is not called till in the report	Tighe and Bond (1988, p. 17)
				SCS (1965b) and unpublished data for the Upper Quaboag River watershed, USDA, SCS
		38 (u)	sample may not be till; hydraulic conductivity determined on minus no. 4 fraction of sample compacted to 96 percent of maximum standard dry density	SCS (1964b) and unpublished data for the Upper Quaboag River watershed, USDA, SCS
			MW11S assumed to be in till	Applied Environmental Technologies Corp. (1989, p. E3-E4)
		30 (u)		SCS (1965a) and unpublished data for the Upper Quaboag River watershed, USDA, SCS
			hydraulic conductivities determined on minus no. 4 fraction of samples under load of 500 lb/ft^2	unpublished data on soil mechanics testing, USDA, SCS
			till above rock at emergency spillway; hydraulic conductivity determined on disturbed sample compacted to 95 percent of standard proctor density; both lab and field sample identification numbers given	SCS (1962) and unpublished data for SUASCO watershed, USDA, SCS

Exhibit E

Table 3.--*Hydraulic conductivity, porosity, and specific yield*

Site no.	Site name and location	Sample or well number	Depth below land surface (m)	Type of till	Hydraulic conductivity (cm/s)				Type of test and analysis
					k_h	k_v	k_r	k_u	
28	SUASCO watershed, Assabet River site A-3-C, Northboro, Mass.	62W814	1.2-1.7	surface			1.8×10^{-4}		P
29	Nyanza, Ashland, Mass.	MW10A	2.1-3.6	surface	2.1×10^{-4}				SW-N
30	Southeast side of Summer Hill, Maynard, Mass.	63MAS8	1.5-1.8	drumlin?			4.7×10^{-6}		P
31	Nashoba Brook Valley, Westford, Mass.	63MAS1	1.2-1.5	surface-flow till?			2.2×10^{-3}		P
32	Charles George, Tyngsborough, Mass.	MW8A JSU-1	1.8-3.4 1.7-3.2	surface do.	1.5×10^{-5} 5.1×10^{-5}				SW
		MW9A --	11.0-14.0 --	do. ?	1.9×10^{-6} 10^{-6}-10^{-4}				SW
33	Groveland Wells, Groveland, Mass.	ERT3 ERT12A	10.8-11.1 4.0	surface do.	1.0×10^{-3} 1.3×10^{-3}				SW
34	Haverhill Landfill, Haverhill, Mass.	MW6/S7	29.0-29.6	drumlin			3.0×10^{-5}		P
		MW1/S10	18.0-18.3	do.				2.0×10^{-8}	
35	West of Holt Hill, Andover, Mass.	3	1.8	surface	5.2×10^{-4}				P
36	Northwest corner of Reading Quad, Andover, Mass.	4	1.5	surface		9.4×10^{-5}			P
37	North side Rte. 62 near Middleton, North Reading, Mass.	6	1.1	surface?		4.7×10^{-6}			P
38	Wilmington-Reading area, Mass.	10	2.1	surface?	2.4×10^{-4}				P
39	West of confluence of Lubber Brook and Ipswich River, North Reading, Mass.	11	0.8	surface-flow till?		9.4×10^{-5}			P
40	East of North Main St. and north of Forest St., Reading, Mass.	7	2.1	drumlin?	1.0×10^{-2}				P
41	Iron Horse Park, Billerica, Mass.	OW-29	10.7-17.1	surface-basal	6.6×10^{-5}				O

Exhibit E

values for till in southern New England--Continued

Porosity (percent)	Specific yield	Percent silt and clay	Remarks	References
		22 (u)	hydraulic conductivity measured on minus no. 4 fraction of sample that had been compacted	SCS (1961) and unpublished data for SUASCO watershed, USDA, SCS
				NUS (1989, unnumbered worksheet)
40.4	9.7	50.9 (w)	one of two till samples collected and analyzed in the Assabet River basin by USGS	Pollock and Fleck (1964)
29.1	10.8	9.3 (w)	do. ■ this sample taken at an ice-contact stratified-drift exposure	do.
			MW8A described as in a silty drumlin deposit; JSU1 was in a sandy till	Ebasco (1988, p. F-1)
			described as silty till range given for sandy till at the site, not at a specific well	NUS (1986, chap. 5, p. 42)
			called ablation till in report; analysis by method described by U.S. Department of Interior (1978)	NUS (1985a, p. C-3)
		55 35	dense, silty till; MW6/S7 remolded, MW1/S10 undisturbed	Perkins Jordan (1981, p.3)
36.7	30.8	40.1 (w)	part of a group of six undisturbed till samples collected and analyzed by USGS	Baker and others (1964)
34.5	29.1	36.7 (w)	do.	do.
40.6	28.0	99.2 (w)	do.	do.
35.6	29.8	62.2 (w)	do. ■ location uncertain	do.
22.1	19.6	20 (w)	do. ■ sample appears to be taken from stratified-drift exposure near till contact	do.
33.7	31.2	23.8 (w)	do. ■ high hydraulic conductivity attributed to measurement parallel to parting planes of compact till	do.
			hydraulic conductivity determined from specific capacity using figure 3 on p. 12 of Walton (1962)	Camp, Dresser and McKee, Inc. (1987, chap. 5, table 4)

Exhibit E

Table 3.--*Hydraulic conductivity, porosity, and specific yield*

Site no.	Site name and location	Sample or well number	Depth below land surface (m)	Type of till	Hydraulic conductivity (cm/s)				Type of test and analysis
					k_h	k_v	k_r	k_u	
42	Wells G + H Woburn, Mass.	G1S	8.8-11.9	surface	1.8×10^{-3}				SW-N
		G2S	2.7-5.8	do.	1.4×10^{-4}				
		G2M	7.0-8.5	do.	3.5×10^{-5}				
		G3S	6.7-11.3	do.	3.5×10^{-5}				
		G4S	4.9-7.9	do.	3.5×10^{-5}				
		G5S	3.6-6.6	do.	8.1×10^{-4}				
		G7S	1.8-6.4	do.	2.1×10^{-4}				
		G8OW	10.4-13.4	do.	3.5×10^{-5}				
		G9S	3.7-5.2	do.	4.6×10^{-4}				
		G10S	1.5-4.5	do.	2.1×10^{-5}				
		G11S	4.9-7.9	do.	3.9×10^{-4}				
		G12S	4.6-7.6	do.	9.2×10^{-4}				
		G13S	5.3-8.3	do.	1.4×10^{-5}				
		G14S	3.7-6.7	do.	1.4×10^{-5}				
		G15S	4.4-7.4	do.	2.1×10^{-4}				
		G16S	6.7-9.7	do.	3.5×10^{-6}				
		G17S	12.0-15.0	do.	1.8×10^{-5}				
		G18S	7.2-10.2	do.	2.5×10^{-5}				
		G19S	3.4-6.4	do.	1.1×10^{-4}				
		G19M	12.8-15.8	do.	7.1×10^{-5}				
		G20S	7.9-10.9	do.	1.1×10^{-4}				
		G21S	5.9-8.9	do.	2.1×10^{-5}				
		G22S	5.2-9.8	do.	2.5×10^{-5}				
		G23S	4.3-7.3	do.	1.8×10^{-4}				
		G24S	5.2-8.2	do.	3.5×10^{-5}				
		G25S	6.4-9.4	do.	3.5×10^{-5}				
		G26S	3.8-6.8	do.	7.1×10^{-5}				
		G27S	3.7-6.7	do.	3.5×10^{-5}				
		G28S	4.8-7.8	do.	1.1×10^{-4}				
		G31S	5.5-8.5	do.	7.1×10^{-6}				
		G32S	4.9-7.9	do.	1.8×10^{-5}				
		GO-1S	2.4-5.4	do.	5.3×10^{-4}				
43	Clean Harbors of Braintree, Braintree, Mass.	CHI-5B	4.6-7.6	surface	6.3×10^{-4}				SW-BR
44	Baird & McGuire, Holbrook, Mass.	903A	16.8-18.3	surface	1.7×10^{-3}				SW-H
		904A	16.2-17.7	do.	4.9×10^{-3}				
		905A	15.7-17.2	do.	7.4×10^{-3}				
		906A	16.4-17.9	do.	1.8×10^{-3}				
		907A	17.9-19.4	do.	7.0×10^{-3}				
		910A	7.0-8.5	do.	5.6×10^{-3}				
		911A	10.7-12.2	do.	9.2×10^{-4}				
		913A	1.2-5.8	do.	3.1×10^{-4}				
		914A	13.4-14.9	do.	3.2×10^{-3}				
		915A	19.2-20.7	do.	2.8×10^{-3}				
		PW-5	12.2-15.2	do.	9.2×10^{-3}				PT
		PB-1	10.7-11.3	do.	--				
45	Engelhard, Plainville, Mass.	MW23A	1.2-2.0	surface	1.3×10^{-3}				SW-BR
		MW5	--	do.	3.6×10^{-5}				
		MW1	2.7-5.5	surface	3.8×10^{-4}				SW-H
		MW4	6.4-6.7	do.	3.5×10^{-4}				
		MW7	3.4-5.8	do.	4.8×10^{-4}				
		MW8	1.2-5.8	do.	3.3×10^{-4}				
46	Polaroid, Freetown, Mass.	GZ-5	1.4-4.4	surface	2.5×10^{-5}				SW-H
47	Re-Solve, Dartmouth, Mass.	D	5.3-8.3	surface	8.8×10^{-4}				SI

Exhibit E

values for till in southern New England--Continued.

Porosity (percent)	Specific yield	Percent silt and clay	Remarks	References
			all samples called lodgement till in report; value for percent silt and clay determined for well number G19M	Jonathan Bridge, GeoTrans, written commun., 1990
		41 (a)		
				Balsam Environmental Consultants, Inc. (1990, chap. 3, table 4)
			sandy, gravelly till with boulders; analysis by Hvorslev's method, as outlined in Lambe and Whitman (1969)	GHR (1985, chap. 3, table 1)
		11 (a)	aquifer test run in till layer, but results questionable because of recharge from overlying sand and gravel	Metcalf & Eddy (1989, p. 22-35)
		6(a)	MW5 is assumed to be in till	Environ Corp. (1990, p. F4)
			all samples assumed to be in till	Environ Corp. (1989, table 4)
			lodgement till, screen partly in sand and gravel	Goldberg Zoino Assoc. (1988, table 5)
			difficult to distinguish from outwash	Camp, Dresser, and McKee, Inc. (1983, chap. 2, p. 22)

Exhibit E

Table 3.--*Hydraulic conductivity, porosity, and specific yield*

Site no.	Site name and location	Sample or well number	Depth below land surface (m)	Type of till	Hydraulic conductivity (cm/s)				Type of test and analysis
					k_h	k_v	k_r	k_u	
48	Sullivan's Ledge, New Bedford, Mass.	---	---	surface	1.2×10^{-3}				PT and (or) SW
49	Atlas Tack Corp., Fairhaven, Mass.	MW5	1.5-3.0	surface	1.9×10^{-4}				SW-BR
		MW7	1.2-3.4	do.	1.6×10^{-4}				
		MW8	0.9-4.0	do.	1.1×10^{-3}				
50	Upper Pawcatuck River basin, east of Tuckertown, South Kingston, R. I.	Sok 894	19.2	surface-morainal?			2.4×10^{-5}		P
		do.	25.2	surface-basal			4.2×10^{-4}		
51	North shore Long Pond, South Kingston, R. I.	Sok 889	41.9	surface-morainal			4.7×10^{-4}		P
		do.	52.9	surface-basal			4.7×10^{-5}		
52	North shore Bull Head Pond, South Kingston, R. I.	Sok 891	17.4	surface-morainal			1.4×10^{-4}		P
		do.	25.3	do.			2.8×10^{-4}		
53	Upper Pawcatuck River basin, northwest corner Kingston Quad, Richmond, R. I.	Ric 322	34.0	surface-basal			4.7×10^{-5}		P
54	Upper Pawcatuck River basin, east edge Slocum Quad, North Kingston, R. I.	Nok 1231	30.2	flow till?			9.4×10^{-5}		P
		do.	48.9	surface-basal			3.3×10^{-5}		
55	Picillo Farm, Coventry, R. I.	MW5	5.5-8.5	surface	1.2×10^{-3}				SW-H
		MW39	9.1-14.9	do.	7.8×10^{-4}				
		MW28	3.0-3.5	do.	5.1×10^{-4}				SW-H
		MW28	6.1-6.6	do.	1.7×10^{-5}				
56	Davis Liquid, Smithfield, R. I.	OW74	2.1-5.2	surface	1.7×10^{-4}				SW-H
57	Canton 3, bank cut west side of Rte. 12, 1.13 km south of Conn.–Mass. border, Thompson, Conn.	C1horiz	0.5-0.8	surface-ablation		9.2×10^{-3}			P-fh
		2C2horiz	0.8-1.1	do.		2.6×10^{-3}			

Exhibit E

values for till in southern New England--Continued.

Porosity (percent)	Specific yield	Percent silt and clay	Remarks	References
			average of unknown number of samples with a range in conductivities of 1 x 10^{-3} to 1.7 x 10^{-3} cm/s; values were determined from either short-term pumping tests or slug tests	Ebasco Services, Inc. (1989, chap. 5, p. 37)
		14 (a)	both MW7 and MW8 include root zone; MW8 described as located in sandy till	Rizzo Assoc., Inc. (1989, unnumbered worksheet)
		28 (w) 6.9 (w)	group of till samples collected during drilling of wells in the Upper Pawcatuck River basin and subsequently analyzed by the USGS; till generally overlain by thick deposits of stratified drift ■ sample at 25.2 m at boundary between till and stratified drift on well log	Allen and others (1963)
		13.4 (w) 24.7 (w)	do. ■ surface morainal till in Charlestown moraine	do.
		15.9 (w) 8.6 (w)	do.	do.
		12 (w)	do.	do.
		22.4 (w) 20.4 (w)	do. ■ flowtill in "end moraine" a zone of collapsed stratified sediments and till	do.
				GCA (1985, chap. 8, p. 8)
				Mitre Corp. (1981, p. 38)
				Camp, Dresser and McKee, Inc. (1986, chap. 4, p. 19)
		61.5 (u) 27.6 (u)	one of six samples of Canton soils collected from C horizon at three localities; orientation of cores reportedly vertical (H.D. Luce, Univ. of Conn., oral commun., 1989)	Pelletier (1982)

Exhibit E

Table 3.--*Hydraulic conductivity, porosity, and specific yield*

Site no.	Site name and location	Sample or well number	Depth below land surface (m)	Type of till	Hydraulic conductivity (cm/s)				Type of test and analysis
					k_h	k_v	k_r	k_u	
58	Quaddick State Forest, Thompson, Conn.	Th57	5.2-6.6	surface-mixed and (or) drumlin	3.1×10^{-4}				SW-T
59	Southwest corner Thompson Quad, Putnam, Conn.	Pu34a	5.4-7.8	surface?	2.2×10^{-4}				SW-T
		Pu34b	1.3-2.1	surface	3.6×10^{-3}				
60	Excavation west of Quinebaug River, Putnam, Conn.	1-L	--	drumlin?	1.1×10^{-3}				P-fh
					1.5×10^{-3}				
61	Northwest corner Danielson Quad, Pomfret, Conn.	Po7	3.2-6.6	surface-mixed?	3.0×10^{-4}				SW-T
		Po10	1.9-3.7	do.	8.4×10^{-3}				
62	Northeast corner Hampton Quad, Pomfret, Conn.	Po57	3.6-4.8	surface	1.6×10^{-3}				SW-T
		Po58	5.4-6.3	drumlin?	2.5×10^{-3}				
		Po76	0.7-6.3	surface-mixed and (or) drumlin	1.4×10^{-3}				
63	Natchaug State Forest, Eastford, Conn.	3	1.8-3.7	surface-mixed?	8.2×10^{-5}				SI-T
		4	1.8-6.5	drumlin?	1.9×10^{-6}				
		6	1.1-2.5	surface-mixed?	1.0×10^{-4}				
		8	2.0-3.0	do.	1.1×10^{-4}				
		11	1.8-3.3	do.	1.1×10^{-4}				
		14	2.1-5.2	drumlin?	3.7×10^{-4}				
		15	1.4-3.6	surface-mixed?	5.5×10^{-5}				
		17	2.4-3.3	do.	4.2×10^{-5}				
		23	2.0-3.2	do.	1.6×10^{-4}				
64	Northeast corner Hampton Quad and southeast corner Eastford Quad, Pomfret, Conn.	Po63	3.3-4.3	surface-mixed and (or) drumlin	6.3×10^{-3}				SW-T
		Po69	4.2-5.5	do.	2.1×10^{-4}				
		Sirrine	3.7-5.5	drumlin?	3.5×10^{-4}				
		Po60	4.6-5.2	do.	3.8×10^{-4}				
		Po62	2.2-3.9	surface-mixed?	6.2×10^{-3}				
		Po64	3.1-3.7	do.	1.0×10^{-2}				
65	Mashmoquet Brook, Pomfret, Conn.	4-U	1.5	surface	7.8×10^{-4}				P-fh
66	West margin Putnam Quad and east margin Eastford Quad, Woodstock, Conn.	Wk19	3.2-4.4	surface	3.4×10^{-3}				SW-T
		do.	3.3-4.4	do.	3.2×10^{-3}				
		Wk21	3.8-4.7	do.	1.6×10^{-3}				
67	Eastford Quad, West Woodstock, Woodstock, Conn.	Wk200	2.3-3.7	surface-mixed?	6.6×10^{-4}				SW-T
		Wk200a	3.0-5.0	do.	1.4×10^{-4}				
		Wk202	2.4-4.6	surface-mixed or drumlin	2.4×10^{-3}				
		Wk203	1.8-5.6	surface-mixed and (or) drumlin	8.0×10^{-5}				
		Wk204	2.0-7.4	do.	5.7×10^{-5}				

Exhibit E

values for till in southern New England--Continued.

Porosity (percent)	Specific yield	Percent silt and clay	Remarks	References
			part of a group of eight dug wells originally tested by USGS (Thomas and others (1966); Randall and others (1966); data reanalyzed by Torak (1979))	Torak (1979)
			part of a group of 19 dug wells tested in eastern Connecticut	do.
		44 (w)	undisturbed sample from pit exposure	do.
			part of a group of 19 dug wells tested in eastern Connecticut	do.
			do.	do.
			group of nine small-diameter (5 cm) wells installed in Natchaug State Forest	do.
			part of a group of 19 dug wells tested in eastern Connecticut	do.
			part of a group of eight dug wells originally tested by USGS (Thomas and others (1966); Randall and others (1966); data reanalyzed by Torak (1979))	
		31 (w)	undisturbed sample collected from two-till locality described by Pessl (1966); adjacent sand lens had $k_h = 3.7 \times 10^{-3}$ cm/s	do.
			part of a group of 19 dug wells tested in eastern Conn. ■ Wk19 also tested by USGS (Thomas and others (1966); this value is from data reanalysis by Torak (1979))	do.
			do. ■ Wk200a is 53 m from Wk200	do.

Exhibit E

Table 3.--*Hydraulic conductivity, porosity, and specific yield*

Site no.	Site name and location	Sample or well number	Depth below land surface (m)	Type of till	Hydraulic conductivity (cm/s)				Type of test and analysis
					k_h	k_v	k_r	k_u	
68	Paxton 2, borrow pit west side Old Turnpike Rd., Woodstock, Conn.	2Cr1horiz	0.6-0.9	drumlin		4.2×10^{-4}			P-fh
		2Cr2horiz	0.9-1.3	do.		1.9×10^{-5}			
69	Willington, Conn.	--	--	unknown				1.5×10^{-3}	U
70	Near headwaters of Olsons Brook, Coventry, Conn.	basal till	--	drumlin	2.2×10^{-5}				PZ
71	Paxton 1, test pit 1.21 km south of intersection of Conn., Rtes. 275 and 195, Mansfield, Conn.	2Cr1horiz	0.8-1.0	drumlin		9.4×10^{-5}			P-fh
		2Cr2horiz	1.2-1.5	do.		2.5×10^{-4}			
		2Cr3horiz	2.1-2.4	do.		6.9×10^{-5}			
		2Cr4horiz	2.4-2.6	do.		7.5×10^{-4}			
		do.	2.6-2.8	do.		2.2×10^{-4}			
72	Paxton 3, test pit 0.5 km north-northeast of intersection Horsebarn Hill Rd. and Rte. 195, Mansfield, Conn.	2Crhoriz	0.7-.9	surface-mixed?		8.6×10^{-4}			P-fh
		do.	0.9-1.1	do.		1.0×10^{-3}			
73	Chestnut Hill, southwest corner of Spring Hill Quad, Mansfield, Conn.	Paxton11 Cxhoriz	0.2-0.3	drumlin?		8.3×10^{-6}			P
						7.8×10^{-5}			
		Woodbridge 11Cxhoriz	0.3-0.4	?		8.3×10^{-6}			
						1.4×10^{-5}			
		Ridgebury11 Cxhoriz	0.3	drumlin?		5.6×10^{-4}			
						1.4×10^{-4}			
		Whitman11 Cxhoriz	0.3-0.4	surface?		1.1×10^{-4}			
						1.3×10^{-3}			
		Well 1	--	drumlin	8.3×10^{-5}				PZ
		Well 2	--	do.	3.6×10^{-5}				
		Well 3	--	do.	3.6×10^{-5}				
		Well 4	--	do.	1.4×10^{-5}				
		Well 5	--	do.	8.3×10^{-5}				
		Well 6	--	do.	4.2×10^{-5}				
		Well 7	--	do.	4.2×10^{-5}				
		Well 9	--	do.	3.6×10^{-5}				
		Well 11	--	do.	8.3×10^{-5}				
74	Northwest ninth of Willimantic Quad, Windham, Conn.	64CON3	1.5?	surface	5.7×10^{-3}				P
75	Northeast side of drumlin located south of Rte. 6 and west of Brooklyn town line, Hampton, Conn.	Paxton11 Cx1horiz	0.7-0.8	drumlin?	4.3×10^{-3}	1.6×10^{-4}			P
						1.7×10^{-3}			
						1.7×10^{-3}			
		Canton11 C21horiz	0.8-0.9	surface	4.1×10^{-3}	1.2×10^{-3}			
						1.4×10^{-3}			
						4.0×10^{-3}			
		Ridgebury11 Cxhoriz	0.6-0.9	drumlin?	1.4×10^{-5}	6.9×10^{-5}			
						4.4×10^{-4}			

Exhibit E

values for till in southern New England--Continued

Porosity (percent)	Specific yield	Percent silt and clay	Remarks	References
		42.8 (u) 41.5 (u)	one of nine samples of Paxton soils collected from C horizon at three localities; orientation of cores reportedly vertical (H.D. Luce, Univ. of Conn., oral commun., 1989)	Pelletier (1982)
			exact location is not known; one of six samples identified as till on graph titled "Summary of permeability tests as of 8-6-42" compiled by Conn. Dept. of Transportation	unpublished file data, Conn. Dept. of Transportation, Rocky Hill, Conn.
			tested by piezometer method (Kirkham (1945))	Welling (1983)
		34.2 (u) 29 (u) 26.7 (u) 36.6 (u) 41.6 (u)	one of nine samples of Paxton soils collected from C horizon at three localities; orientation of cores reportedly vertical (H.D. Luce, Univ. of Conn., oral commun., 1989)	Pelletier (1982)
		34.8 (u) 35 (u)	do.	do.
			group of core samples collected from C horizons of soils developed on till	Pietras (1981)
			group of nine wells at same site tested by piezometer method; wells 1-3 and 5 are open to Paxton substratum, wells 6-9 and 4 are open to Woodbridge substratum and well 11 is open to Ridgebury substratum	do.
31.6	27.9	18.5 (w)	undisturbed sample collected and analyzed by USGS; field notes indicate minor disturbance	Thomas and others (1967) and file data from USGS, Hartford, Conn.
			group of core samples collected from C horizons of soils developed on till	Pietras (1981)

Exhibit E

Table 3.--*Hydraulic conductivity, porosity, and specific yield*

Site no.	Site name and location	Sample or well number	Depth below land surface (m)	Type of till	Hydraulic conductivity (cm/s)				Type of test and analysis
					k_h	k_v	k_r	k_u	
76	Brooklyn, Conn.	Bk20 Bk32	2.9-4.2 1.0-2.7	surface do.	2.1×10^{-3} 1.7×10^{-2}				SW-T
77	Central part of the Danielson Quad, Brooklyn, Conn.	Bk54	3.1-4.3	surface	7.4×10^{-3}				SW-T
78	Pit, 152 m north of Ennis Rd-Allen Hill Rd. intersection, Brooklyn, Conn.	E3/63CON4	1.5?	drumlin?		3.3×10^{-5}			P
79	Pit, west of Green Hollow Rd, 152 m south of Fall Brook, Killingly, Conn.	H6/63CON5	--	surface-mixed?		2.8×10^{-5}			P
80	East of new Rte. 12 expressway, north of Killingly Drive, Killingly, Conn.	K5/63CON6	1.8	surface?		1.9×10^{-5}			P
81	Black Hill Rd, 366 m east of Exley Rd., Plainfield, Conn.	T3/63CON1	5.2	drumlin		9.4×10^{-6}			P
82	Pit, 213 m east of Conn. Turnpike, south of Moosup River, Plainfield, Conn.	L1/63CON2	2.7	surface		8.0×10^{-4}			P
83	Road cut north of Evergreen St., east of Evergreen Cemetery, Plainfield, Conn.	K4/63CON3	0.9	surface-ablation?		1.4×10^{-3}			P
84	Revere Textiles, Sterling, Conn.	MW3	14.4-17.4	surface	9.4×10^{-4}				SW-H?
85	Central part of Voluntown Quad, Voluntown, Conn.	Vo88	1.4-3.4	surface?	2.8×10^{-3}				SW-T
86	Southwest part of the Voluntown Quad, North Stonington, Conn.	NSn25	6.6-8.4	drumlin?	8.0×10^{-5}				SW-T
87	Canton 2, test pit east side of Boombridge Rd., North Stonington, Conn.	2C1horiz 3C4horiz	0.8-1.0 1.4-1.6	surface-ablation do.		8.0×10^{-3} 3.6×10^{-3}			P-fh

Exhibit E

values for till in southern New England--Continued

Porosity (percent)	Specific yield	Percent silt and clay	Remarks	References
			part of a group of 19 dug wells tested in eastern Connecticut	Torak (1979)
			part of a group of eight dug wells originally tested by USGS (Thomas and others (1966); Randall and others (1966); data reanalyzed by Torak (1979))	do.
38	4.1	48.8 (w)	part of a group of six undisturbed till samples from the Quinebaug River basin analyzed by USGS (Randall and others (1966, p. 56)); both field and lab sample identification numbers given	Randall and others (1966)
28.6	3.9	44.8 (w)	do.	do.
29.9	12.2	39.5 (w)	do.	do.
27.6	4.6	39.4 (w)	do.	do.
35	20.3	32.9 (w)	do.	do.
36.1	20.9	30.8 (w)	do.	do.
			test described as "pumpout and recovery"	Camp, Dresser and McKee, Inc. (1989, chap. 9, p. 6)
			part of a group of eight dug wells originally tested by USGS (Thomas and others (1966); Randall and others (1966); data reanalyzed by Torak (1979)) ■ sand lens reportedly present in till (Thomas and others (1966, p. 41))	Torak (1979)
			do.	do.
		19.4 (u) 26 (u)	one of six samples of Canton soils collected from C horizon at three localities; orientation of cores reportedly vertical (H.D. Luce, Univ. of Conn., oral commun., 1989)	Pelletier (1982)

Exhibit E

Table 3.--*Hydraulic conductivity, porosity, and specific yield*

Site no.	Site name and location	Sample or well number	Depth below land surface (m)	Type of till	Hydraulic conductivity (cm/s)				Type of test and analysis
					k_h	k_v	k_r	k_u	
88	Montauk 2, bank cut 0.3 km southeast on Greenhaven Rd., from intersection with RR tracks, Stonington, Conn.	2Cr1horiz	0.9-1.4	surface-basal?		3.0×10^{-3}			P-fh
		do.	1.4-1.6	do.		3.8×10^{-3}			
		do.	1.6-1.8	do.		3.4×10^{-3}			
89	Montauk 1, test pit 0.2 km west-northwest of intersection of Noank-Ledyard Rd., and Interstate 95, Groton, Conn.	2Cr1horiz	0.6-0.9	surface-basal?		3.7×10^{-3}			P-fh
		2Cr2horiz	0.9-1.1	do.		3.3×10^{-3}			
90	New London Bypass, Groton, Conn. (?)	--	--	unknown				1.7×10^{-6}	U
91	Route 85, Waterford, Conn.	--	--	unknown				5.4×10^{-5}	U
92	Haddam, Conn.	--	--	unknown				3.8×10^{-4}	U

values for till in southern New England--Continued

Porosity (percent)	Specific yield	Percent silt and clay	Remarks	References
		21.1 (u) 20.4 (u) 17 (u)	one of five core samples of Montauk soils collected from C horizon at two localities; orientation of cores reportedly vertical (H.D. Luce, Univ. of Conn., oral commun., 1989)	Pelletier (1982)
		24.4 (u) 27.3 (u)	do.	do.
			exact location is not known; one of six samples identified as till on graph titled "Summary of permeability tests as of 8-6-42" compiled by Conn. Dept. of Transportation	unpublished file data, Conn. Dept. of Transportation, Rocky Hill, Conn.
			do.	do.
			do.	do.

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Quality of Water in the Fractured-Bedrock Aquifer of New Hampshire

By Richard Bridge Moore

In cooperation with the New Hampshire Department of Environmental Services

Scientific Investigations Report 2004-5093

U.S. Department of the Interior
U.S. Geological Survey

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Gale A. Norton, Secretary

U.S. Geological Survey
Charles G. Groat, Director

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Contents

Figures

1-10 Maps showing

Conversion Factor

Multiply	By	To obtain
	Volume	
milligram per liter (mg/L)	1,000	microgram per liter (µg/L)

Water-Quality Constituents and Acronyms

Concentrations of chemical constituents in water are given either in milligrams per liter (mg/L), micrograms per liter (µg/L)., or picoCurie per liter (pCi/L). Arsenic concentrations in rock are measured in milligrams per kilogram (mg/kg).

Acronyms Used in This Report

MCL	Maximum Contaminant Level
NHGS	New Hampshire Geological Survey
SMCL	Secondary Maximum Contaminant Level
USEPA	U.S. Environmental Protection Agency
USGS	U.S. Geological Survey

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ACKNOWLEDGMENTS

Special thanks are extended to the New Hampshire Department of Environmental Services (NHDES) for providing much of the water-quality and well-construction data used in this report. The project would not be possible without the wealth of well data recorded by the well drillers and reported to the New Hampshire Water Well Board. These data were compiled and computerized and the geographic coordinates of the well locations determined by NHDES. The author thanks Frederick Chormann, of the New Hampshire Geological Survey (NHGS), NHDES, for providing cross-referencing between the well and water-quality databases; Eugene Boudette, former New Hampshire State Geologist, and Stewart Clark, Jr., U.S. Geological Survey (USGS), for providing preliminary bedrock groupings for radon potential; David Chase, New Hampshire Department of Health and Human Services, Radon Program, for providing radon-in-air data relative to these groupings; Joseph Ayotte, USGS, for providing the water-quality data for public-supply wells; and to John Peper, USGS, for extending his categorization of lithochemical groups for the Connecticut River Basin to cover all of New Hampshire for this study.

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Quality of Water in the Fractured-Bedrock Aquifer of New Hampshire

By Richard Bridge Moore

Abstract

Over the past few decades, New Hampshire has experienced considerable population growth, which is forcing some communities to look for alternative public and private water supplies in the bedrock aquifer. Because the quality of water from the aquifer can vary, the U.S. Geological Survey statistically analyzed well data from 1,353 domestic and 360 public-supply bedrock wells to characterize the ground water. The domestic-well data were from homeowner-collected samples analyzed by the New Hampshire Department of Environmental Services (NHDES) Environmental Laboratory from 1984 to 1994. Bedrock water in New Hampshire often contains high concentrations of iron, manganese, arsenic, and radon gas. Water samples from 21 percent of the domestic bedrock wells contained arsenic above the U.S. Environmental Protection Agency (USEPA) 10 micrograms per liter (µg/L) drinking-water standard for public-water supplies, and 96 percent had radon concentrations greater than the USEPA-proposed 300 picocurie per liter (pCi/L) standard for public-water supplies. Some elevated fluoride concentrations (2 percent of samples) were above the 4 milligrams per liter (mg/L) USEPA drinking-water standard for public-water supplies. Water from the bedrock aquifer also typically is soft to moderately hard, and has a pH greater than 7.0.

Variations in bedrock water quality were discernable when the data were compared to lithochemical groupings of the bedrock, indicating that the type of bedrock has an effect on the quality of water in the bedrock aquifer of New Hampshire. Ground-water samples from the metasedimentary lithochemical group have greater concentrations of total iron and total manganese than do the felsic and mafic igneous lithochemical groups. Ground-water samples from the felsic igneous group have higher concentrations of total fluoride than do those from the other lithochemical groups. For arsenic, the calcareous metasedimentary group was identified, using the public-supply database, as having higher concentrations, on average, than the other lithochemical groups. The use of a radon-gas-potential classification of bedrock in the State indicated where high radon concentrations in the air and in water from private and public-supply wells were more likely to occur.

In general, samples from the bedrock aquifer tend to have higher pH (are less acidic), greater hardness, much higher concentrations of iron, similar concentrations of manganese, and higher concentrations of fluoride and arsenic than do samples from stratified-drift aquifers in New Hampshire. An understanding of the water-quality conditions of water in bedrock aquifers is important from a public-health perspective because an increasing number of domestic bedrock wells are being drilled and relied upon as a source of drinking water in the State.

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Introduction

New Hampshire has experienced considerable population growth over the past few decades (New Hampshire State Data Center, 2001), which has led many communities to search for new drinking-water supplies. Many of these communities experiencing population growth have limited stratified-drift (sand and gravel) aquifers that historically have been the most favorable aquifers for constructing municipal wells. As a result, communities are increasingly looking to the fractured crystalline bedrock aquifer for additional water supplies. Also, much of this new population, and accompanying development, is relying on the use of domestic wells that are drilled into the crystalline bedrock aquifer. Understanding the variability of water quality within the fractured crystalline bedrock aquifer (termed the bedrock aquifer throughout this report) may be an important consideration when evaluating this resource as a future drinking-water supply.

Ground-water chemistry in the fractured-bedrock aquifer is dependent on various hydrogeologic factors such as mineral composition, physical contact, residence time, and oxidation-reduction conditions; all factors that affect the solubility of bedrock minerals. Increased residence time and physical contact between the bedrock and the ground water increases the potential for the water to react with the rock, typically resulting in more dissolution of minerals. Fractures increase surface area, which in turn provides for a greater potential for the water to react with the bedrock. Residence time and oxidation-reduction conditions, which control mineral solubility, are affected by the amount of water moving through the ground-water system, and by recharge, discharge, and flow rates. Certain minerals dissolve much more readily if the oxygen has been depleted along the ground-water-flow path.

The quality of ground water from stratified-drift and bedrock aquifers in New Hampshire has been studied by numerous previous investigations. These studies include Morrissey and Regan (1988), Rogers (1989), Medalie and Moore (1995), and Ayotte and others (1999). Morrissey and Regan (1988) provide a generalized description of water quality in the bedrock and stratified-drift aquifers, and discussed the effects of land use on ground-water quality. Rogers (1989) provided a geochemical comparison of ground water in bedrock and stratified-drift aquifers in areas in New England, New York, and Pennsylvania. Medalie and Moore (1995) summarize water-quality data and conditions of stratified-drift aquifers throughout New Hampshire.

A number of recent studies have focused on the occurrence of arsenic and other metals in bedrock water for parts of New Hampshire. Ayotte and others (1999) used available data from a selected set of public-supply wells drilled in bedrock to determine the relation of arsenic, iron, and manganese in ground water to aquifer type, bedrock lithogeochemistry, and land use in parts of Eastern New England, including eastern New Hampshire. Ayotte and others (2003) described arsenic concentrations in ground water and factors that may be controlling arsenic in Eastern New England based on newly collected water-quality data from a variety of wells. Montgomery and others (2003) present the results of a study of arsenic in water samples from domestic bedrock wells in Stratford, Rockingham, and Hillsborough Counties of southeastern New Hampshire.

The New Hampshire Department of Environmental Services (NHDES) Environmental Laboratory (Laboratory) has been analyzing water samples from private domestic and public-water supply wells throughout the State when requested by the well owner. These analyses may be helpful for describing ground-water quality; however, there were no comprehensive assessments of the water-quality data from the Laboratory available before this study. The U.S. Geological Survey (USGS), in cooperation with the NHDES, assessed the variability of a number of water-quality measurements and constituents in domestic and public bedrock wells throughout the State using the well data from the NHDES Laboratory and other available data sets. This assessment is part of the New Hampshire Bedrock Aquifer Assessment Project, which is intended to provide information that can be used by communities, industry, professional consultants, and other interests to evaluate the potential for ground-water development of the bedrock aquifer. This report on the water quality of the bedrock aquifer is one of three companion reports that present the results of the USGS New Hampshire Bedrock Aquifer Assessment Project. The other two reports cover the topics of well yields, evaluated at a statewide and regional scale (Moore and others, 2002), and geophysical investigations at well fields (Degnan and others, 2001). These two reports were designed to identify relations that have the potential to increase the probability of successfully locating high-yield water supplies in the bedrock aquifer underlying New Hampshire.

Purpose and Scope

This report describes and summarizes bedrock ground-water-quality data that were available from the NHDES Environmental Laboratory from 1984 to 1994. Water-quality measurements and constituent data that were evaluated include pH, hardness, iron, manganese, fluoride, arsenic, and radon. These measurements and constituents are those most routinely analyzed by the Laboratory. Statistical analyses are used to quantify data variability, and to identify differences between groupings of mapped bedrock units. Comparisons are made to primary and secondary Federal and State drinking-water standards and to the water-quality conditions of the stratified-drift aquifers above the bedrock in some locations.

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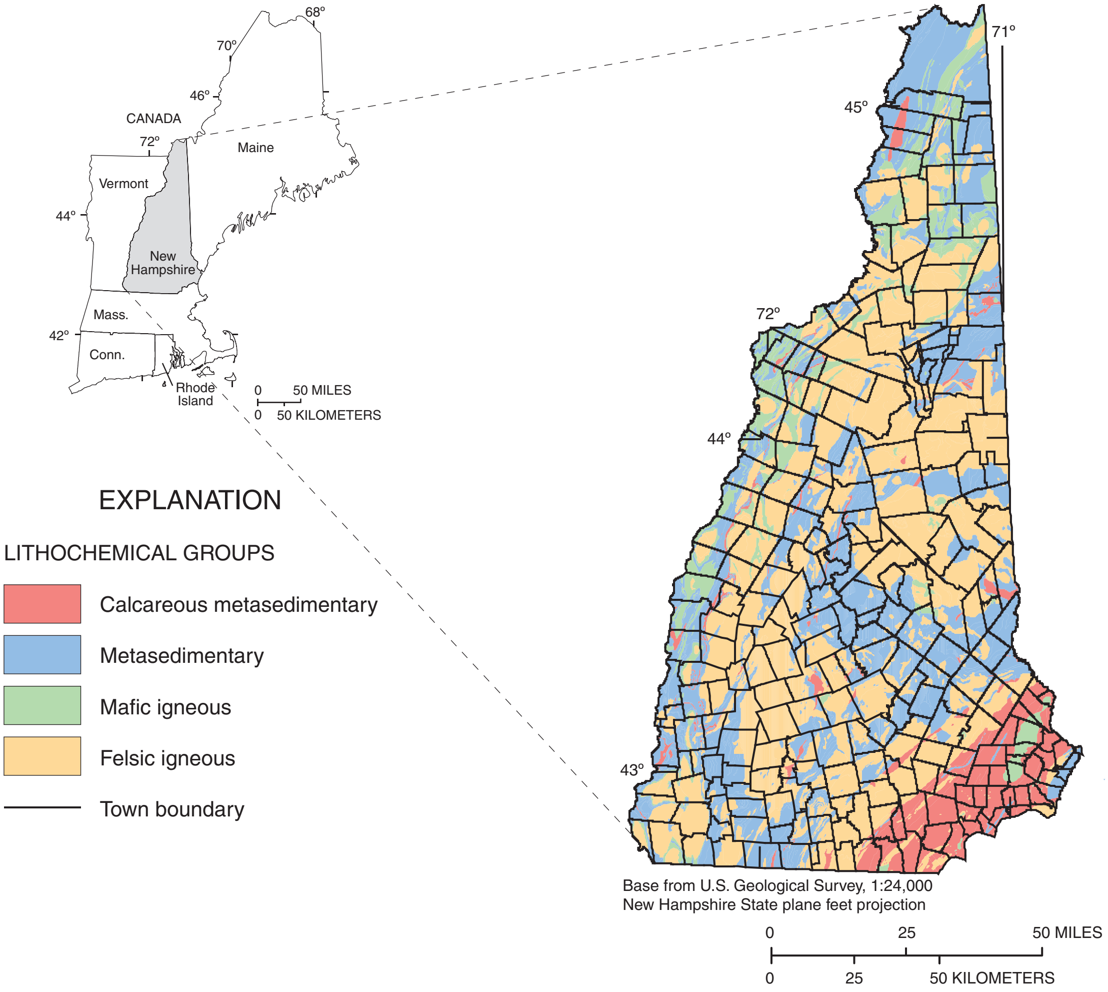
Characterization of New Hampshire Bedrock for Water-Quality Assessment

Bedrock units in New Hampshire have been characterized as to their potential effect on the chemical composition of ground water (Robinson, 1997, Montgomery and others, 2002) and classified into lithochemical groups. These characterizations are based on mineralogical and chemical characteristics relevant to water quality, which include the reactivity of constituent minerals to dissolution and the presence of carbonate or sulfide minerals (John D. Peper, U.S. Geological Survey, written commun., 1994 and 1996; Robinson and others, 2002; Montgomery and others, 2002). Carbonate and sulfide minerals are important to water quality because these are highly reactive minerals in solution. All 174 mapped bedrock units on the Bedrock Geologic Map of New Hampshire (Lyons and others, 1997) have been assigned to 4 major lithochemical groups. Major groups found in New Hampshire (fig. 1) are: (1) calcareous metasedimentary rocks; (2) primarily noncalcareous, clastic metasedimentary rocks at or above biotite-grade of regional metamorphism; (3) mafic igneous rocks and their metamorphic equivalents; and (4) felsic igneous rocks and their metamorphic equivalents. Nine percent of the State is underlain by calcareous metasedimentary rocks, 34 percent



Base from U.S. Geological Survey, 1:24,000
New Hampshire State plane feet projection

Figure 1. Areal distribution of major lithochemical groups in New Hampshire used for statistical analyses. Mapped bedrock units (Lyons and others, 1997) were grouped into lithologic categories on the basis of mineralogical and chemical characteristics relevant to water quality.

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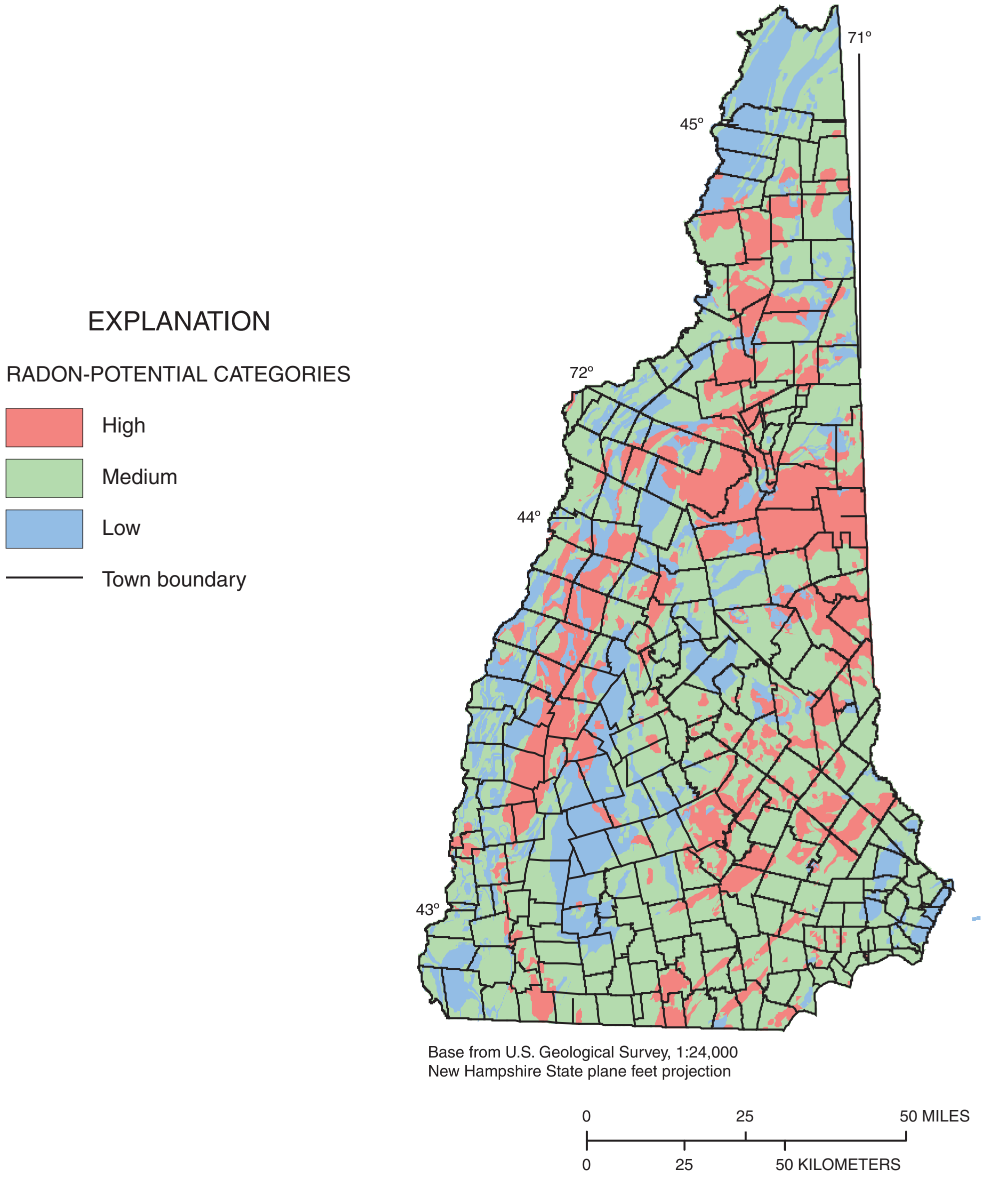
by noncalcareous metasedimentary rocks, 9 percent by mafic igneous rocks, and 48 percent by felsic igneous rocks.

Mapped bedrock units of New Hampshire have also been grouped for relative potential of producing radon gas (Eugene Boudette, New Hampshire State Geologist, written commun., to David Chase, New Hampshire Department of Health and Human Services, Radon Program, 1999; Stewart F. Clark, Jr., U.S. Geological Survey, written commun., 2000). Three broad categories of radon potential—high, medium, and low—were defined on the basis of lithology and mineralogy (fig. 2). New Hampshire is underlain mainly by granitic and metamorphic rocks, many of which have a high potential for containing uranium and its daughter products including radon (Boudette, 1994). Two-mica granites and associated pegmatites are identified especially with high levels (greater than 4,000 pCi) of radon (Boudette, 1977). Twenty-two percent of the State is underlain by the rocks in the high radon-potential category, 58 percent in the medium radon-potential category, and 20 percent in the low radon-potential category.



Base from U.S. Geological Survey, 1:24,000
New Hampshire State plane feet projection

Figure 2. Areal distribution of radon-potential categories in New Hampshire used for statistical analyses. Mapped bedrock units (Lyons and others, 1997) were grouped for relative potential of producing radon gas.

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Data Sources and Methods of Analysis

Water-quality data maintained by the NHDES Laboratory served as the primary source of data used in the analysis. This database consisted of 1,818 sample analyses from 1,353 domestic wells collected during 1984–94 throughout New Hampshire. Samples were collected and submitted to the NHDES Laboratory by homeowners or residents. Water-quality measurements and constituents provided in the database included pH, hardness, iron, manganese, fluoride, radon, and arsenic. In addition to water-quality data, radon air-concentration data were obtained from the New Hampshire Department of Health and Human Services, Radon Program, (David Chase, written commun., 1999) to assist in the characterization of radon variability in bedrock aquifers.

The water-quality data maintained by the NHDES Laboratory did not contain information on the location of the well. To identify a well's location, data describing the owner and address in the water-quality database were matched with similar data in a well-construction database maintained by the NHGS. This well-construction database contains information on the depth of the well, construction characteristics, geologic material encountered during drilling, and the geographic coordinates for over 21,000 bedrock wells in New Hampshire.

Most (68 percent) of the water-quality samples analyzed by the Laboratory were obtained within 2 years of well construction on the basis of a comparison of dates in the two databases. Therefore, the evaluation of a new water source appears to be the primary reason for the homeowners sampling their well water.

Analyses of arsenic and radon in water of public-supply bedrock wells were used in addition to the arsenic and radon data in the Laboratory database. The data for public-water supplies are the result of public-water-supply monitoring to determine compliance with Federal Safe Drinking Water Act requirements and are the same data used by Ayotte and others (1999). These data represent water suppliers that (a) had one supply source (a single well), and (b) were not required to do any treatment (Ayotte and others, 1999).

Applying these water-quality data to characterizations of the bedrock aquifer statewide required a number of assumptions. First, it was assumed that differences in laboratory analytical techniques produced results that were, for each constituent, directly comparable; thus, allowing the aggregation of the data into a single database. All analyses were done by a single U.S. Environmental Protection Agency (USEPA) certified laboratory that follows standard analytical procedures. To account for changing detection levels, all less-than values were set to the highest less-than value for each specific constituent. Second, it is assumed that sample-collection procedures by the homeowner or water supplier had no or minimal affect on sample results. Third, if a well had multiple values for the same measurement type or constituent analyzed, only the highest value was kept in the database. This highest value was assumed to be the best indicator of untreated well water; thus minimizing the incorporation of treated water samples. Treated water may not be reflective of the quality of water as it leaves the ground.

A number of statewide analyses were performed with the water-quality data. To allow for comparisons of water-quality conditions among the four major lithochemical groups, all bedrock wells with water-quality data other than radon concentrations were assigned to one of the four major lithochemical groups. This relation was accomplished with a geographic information system using the location of the well. Likewise, wells with radon data were assigned to one of the three radon-potential categories. The water-quality data, by measurement/constituent, were summarized statistically for each lithochemical group and radon-potential category and graphically displayed with cumulative-frequency distribution plots to display differences in the data sets. The cumulative-frequency distribution plots display the data ranked from lowest to highest. Measurements or concentrations of constituents are plotted on the x-axis and the cumulative frequency on the y-axis. Concentrations below the detection limit are assigned the same low rank and are not plotted individually. The cumulative frequency is essentially the inverse of the probability. For example, concentrations with a cumulative frequency of 0.1 are equaled or exceeded in 90 percent of the sample population and concentrations or values with a cumulative frequency of 0.5 are the median value.

After the analyses described above were completed, nonparametric tests then were used to define significant statistical differences between data associated with the lithochemical groups and radon-potential categories. A Kruskal-Wallis test (Helsel and Hirsch, 1992; SAS Institute, Inc., 1999) was used to test the null hypothesis that the water-quality data falling in the four major lithochemical groups (or three estimated radon-potential categories) are from the same population. The null hypothesis indicates that there is no significant difference among the means of the ranks of the concentrations of a chemical constituent between the groups. To detect specific significant differences between populations in pairs of lithochemical groups, a subsequent multiple-stage Kruskal-Wallis test was used. This multiple-stage test is valid only if the null hypothesis was rejected in the initial Kruskal-Wallis test (Helsel and Hirsch, 1992, SAS Institute, Inc., 1999). For all possible pair-wise comparisons (comparing two groups, one to another), a within-group variance is used in the multiple-stage test to calculate the minimum difference in mean rank that is necessary to consider groups significantly different (SAS Institute, Inc., 1999). For all statistical tests described in this report, rejection of the null hypothesis required that the attained significance level (p) be less than 0.05.

Statewide and lithochemical-group and radon-potential-category summary statistics were compared to appropriate USEPA drinking-water standards that apply to public-water supplies (U.S. Environmental Protection Agency, 2002a and b). Water-quality data from each measurement type or constituent were compared to the Maximum Contaminant Levels (MCL), which are enforceable USEPA primary drinking-water

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standards, or to Secondary Maximum Contaminant Levels (SMCL), which are USEPA-recommended health advisory levels for certain contaminants in public-water supplies (U.S. Environmental Protection Agency, 2002a and b). There are no enforceable statewide drinking-water standards for water from private domestic wells. Lastly, statewide median values for the bedrock aquifer were compared to the statewide median value of water from stratified-drift aquifers throughout New Hampshire as reported by Medalie and Moore (1995).

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Water Quality of the Bedrock Aquifer

Water-quality samples from a total of 1,713 wells from throughout New Hampshire were used to characterize water from the bedrock aquifer in the State. Although most wells are for private domestic use, 357 public-supply bedrock wells had arsenic data and 310 public-supply bedrock wells had radon data (Joseph Ayotte, U.S. Geological Survey, written commun., 1999). The total domestic-well database includes 1,078 wells with pH data, 1,076 wells with hardness, 1,078 with total iron, 1,076 with total manganese, 1,138 with total fluoride, 191 with total arsenic, and 221 wells with radon concentrations.

Most ground water from bedrock wells in New Hampshire is suitable for drinking. However, arsenic and radon concentrations frequently are greater than MCLs in some areas of the State, whereas fluoride concentrations occasionally exceed the MCL. Iron and manganese also are common nuisance contaminants but these do not pose a threat to human health. The following sections contain a description and statistical analysis on the occurrence of pH, hardness, iron, manganese, fluoride, arsenic, and radon in bedrock ground water.

Two potential biases, spatial and self-selection biases, may be present in the data analyzed in this report. The first potential spatial bias may result because of a greater frequency of sample collection in central New Hampshire than other parts of the State because people who live in this area are near the NHDES Laboratory (see figs. 3–9). As a result, the data used in these analyses could underrepresent wells that are remote from the NHDES Laboratory. For this reason, well-location plots are provided with a discussion for each chemical constituent to show where the samples were collected.

The second potential bias is that of sample self selection. Well owners may submit samples because they are experiencing a water-quality problem or suspect that they may have a problem. This particular situation is true of the arsenic and radon analyses, and to a lesser extent iron and manganese (Frederick Chormann, New Hampshire Department of Environmental Services, written commun., 2003). Peters and others (1999) evaluated this bias for an arsenic data set from New Hampshire and found that this bias is likely to increase the median value of arsenic, but it did not affect which areas or bedrock types had the highest concentrations. Self-selection bias is, therefore, unlikely to affect the comparisons presented in this report between samples from different lithochemical groups. Furthermore, it is possible that the self-selection bias is minimized in the data described in this report because the evaluation of a new water source appears to be the prime motivation for sampling the wells in the database.

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pH

The pH of water is a measure of the hydrogen-ion activity. The pH scale ranges from 0 to 14 where each unit increase in the scale represents a tenfold decrease in hydrogen-ion activity. Water with a pH of 7.0 is neutral, less than 7.0 is acidic, and greater than 7.0 is alkaline. A recommended SMCL range of pH for public-water supplies is 6.5 to 8.5 (U.S. Environmental Protection Agency, 2002b). At low pH, below 6.5, metal pipes can corrode introducing metallic contaminants and a bitter metallic taste to the water. At high pH, greater than 8.5, the water is apt to be hard imparting a slippery feel and soda taste, and create mineral deposits (U.S. Environmental Protection Agency, 2002b).

The bedrock aquifer of New Hampshire is typically alkaline, having a median pH of 7.7. Twenty-one percent of the pH data were less than 7.0 indicating slightly acidic conditions for water from these wells. Ten percent of the water samples had a pH less than 6.5, and 2 percent had a pH greater than 8.5 meaning that water from about 12 percent of the bedrock wells in the State may require treatment to adjust pH.

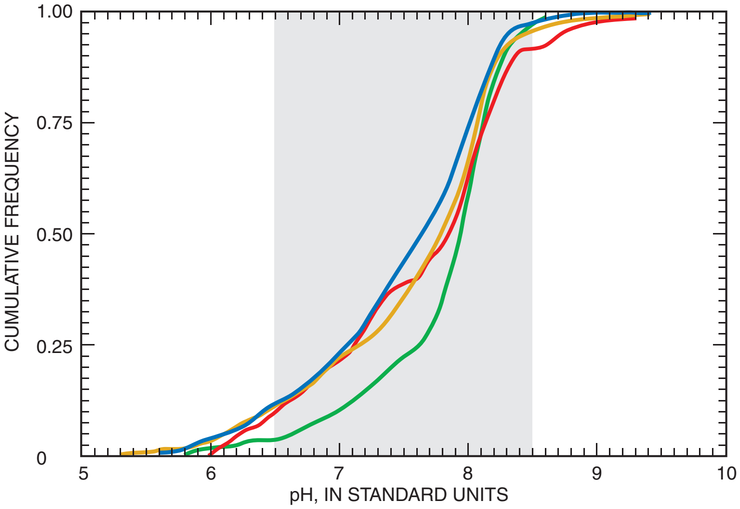
Statistically significant differences in pH values among lithochemical groups are evident (fig. 3). Ground-water samples from the mafic igneous group have higher pH values than do those either from the felsic igneous group or the metasedimentary group, whereas the pH for samples from calcareous metasedimentary do not differ significantly from any of the other groups (fig. 3).

The mafic igneous group had the lowest percentage of ground-water samples outside the range of the USEPA SMCL drinking-water standard for pH (6.5 to 8.5). Only 4 percent of the water samples from the mafic igneous group had pH below 6.5; compared to 10 to 12 percent of the water samples from the other lithochemical groups. The mafic igneous group also had the lowest percentage (1 percent) of pH values above 8.5; 2 and 3 percent of the samples from the metasedimentary and felsic igneous groups, respectively; and 7 percent from the calcareous metasedimentary were above 8.5.

Water from the bedrock aquifer typically has higher pH (is less acidic, more basic) than does water from stratified-drift aquifers locally above the bedrock. The median pH of water from stratified-drift aquifers in New Hampshire is 6.3 (Medalie and Moore, 1995) as compared to a median pH of 7.7 for water from the bedrock aquifer. Water in the stratified-drift aquifer is usually more reflective of water newly introduced to the ground-water system and, therefore, often is similar in quality to rainwater and is less chemically evolved than bedrock water.

Exhibit E

Cumulative frequency plot of pH by lithochemical group. Gray area is U.S. Environmental Protection Agency recommended range of pH (6.5 to 8.5).



Distribution of pH data by lithochemical group

Quantile, in percent	Calcareous metasedimentary [1]ab	Metasedimentary b	Mafic igneous a	Felsic igneous b
90	8.3	8.2	8.3	8.2
50 (median)	7.8	7.6	7.9	7.8
10	6.5	6.4	7.0	6.4

[1] Lithochemical populations with the same letter designation do not differ significantly at the 95-percent confidence level. Significance level attained for the multiple-comparison test is 0.0004.

EXPLANATION

LITHOCHEMICAL GROUPS

🟥	Calcareous metasedimentary [68]
🟦	Metasedimentary [417]
🟩	Mafic igneous [95]
🟧	Felsic igneous [498]
[68]	Number of samples
●	Domestic well sampled for pH

pH

(Domestic wells)

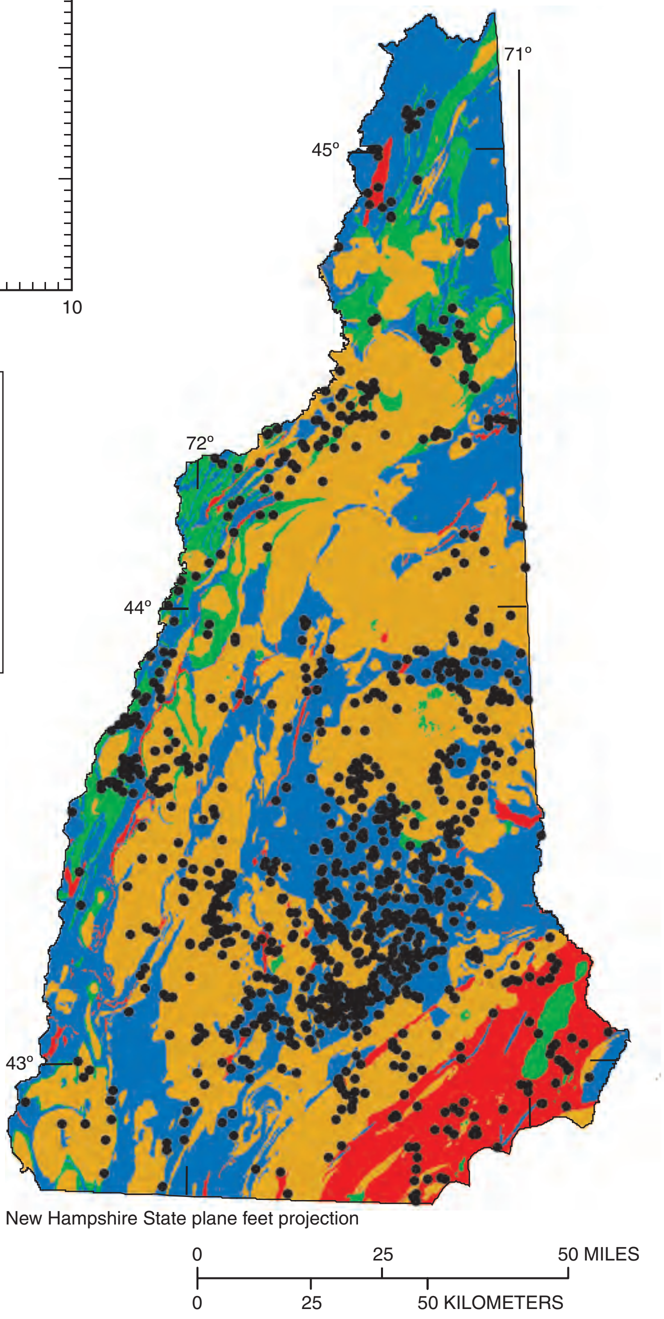


Figure 3. Location of domestic-bedrock-well sample sites in New Hampshire and statistical distribution of water-quality data in relation to lithochemical groups for pH.

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Hardness

Hardness of water is a property or characteristic not attributable to a single constituent or mineral and usually is expressed in terms of an equivalent concentration of calcium carbonate ($CaCO_3$. Hardness typically is calculated from calcium and magnesium concentrations) (Hem, 1985). Although a variety of categorization schemes are used in the water industry. Durfor and Becker (1964) define 60 mg/L $CaCO_3$ or less as soft; 61 to 120 mg/L $CaCO_3$ as moderately hard; 121 to 180 mg/L as hard, and greater than 180 mg/L $CaCO_3$ as very hard (fig. 4). Hardness in drinking water is not known to pose a health risk. Rather, hard water creates other problems such as soap scum (most noticeable on tubs and showers), white mineral deposits on dishes and plumbing fixtures, and reduced efficiency of water heaters. USEPA has not established a MCL or a SMCL for hardness.

Ground water from the bedrock aquifer in New Hampshire typically is soft to moderately hard (fig. 4), having a median hardness value of 65 mg/L. Of the 1,076 samples analyzed for hardness, 45 percent of the water is soft, 44 percent is moderately hard, 7 percent is hard and 4 percent is very hard.

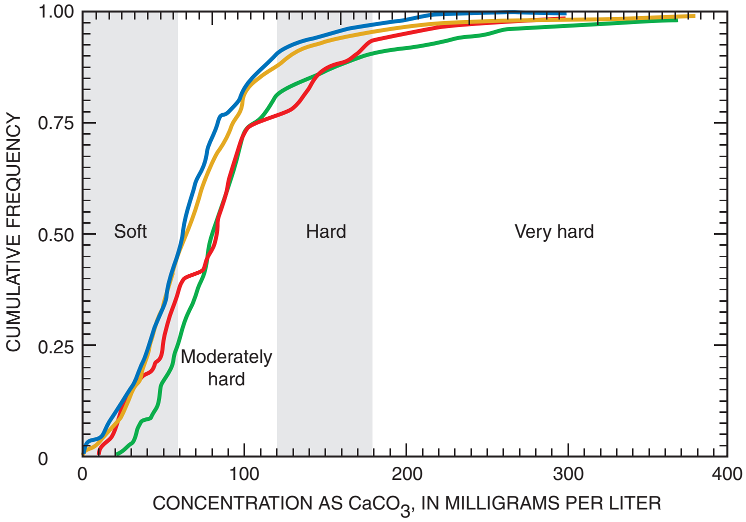
Hardness values are significantly different among lithochemical groups. Samples from the mafic igneous group indicate harder water than the metasedimentary and felsic igneous groups (fig. 4). Samples from the calcareous metasedimentary group were harder than samples from the metasedimentary group.

Water in the calcareous metasedimentary and mafic igneous groups were classified as hard or very hard water for 22 and 16 percent of the samples, respectively; this result compares to less than 12 percent of the water samples from the other two lithochemical groups. Conversely, 47 and 48 percent of the samples from the felsic igneous and metasedimentary groups, respectively, are considered soft. Only 25 percent of the samples from the mafic group are soft (fig. 4).

Water from the bedrock aquifer typically has greater hardness than does water from stratified-drift aquifers. The median hardness of water from stratified-drift aquifers in New Hampshire is 22 mg/L $CaCO_3$ (Medalie and Moore, 1995). This value compares to a median hardness of 65 mg/L $CaCO_3$ for water from the bedrock aquifer.

Exhibit E

Cumulative frequency plot of hardness concentrations by lithochemical group.



Distribution of hardness concentrations by lithochemical group

Quantile, in percent	Calcareous metasedimentary [1]ab	Metased-imentary c	Mafic igneous a	Felsic igneous bc
90	170	120	170	130
50 (median)	82	62	81	65
10	23	21	43	25

[1] Lithochemical populations with the same letter designation do not differ significantly at the 95-percent confidence level. Significance level attained for the multiple-comparison test is 0.0001.

EXPLANATION

LITHOCHEMICAL GROUPS

🟥 Calcareous metasedimentary [68]

🟦 Metasedimentary [415]

🟩 Mafic igneous [95]

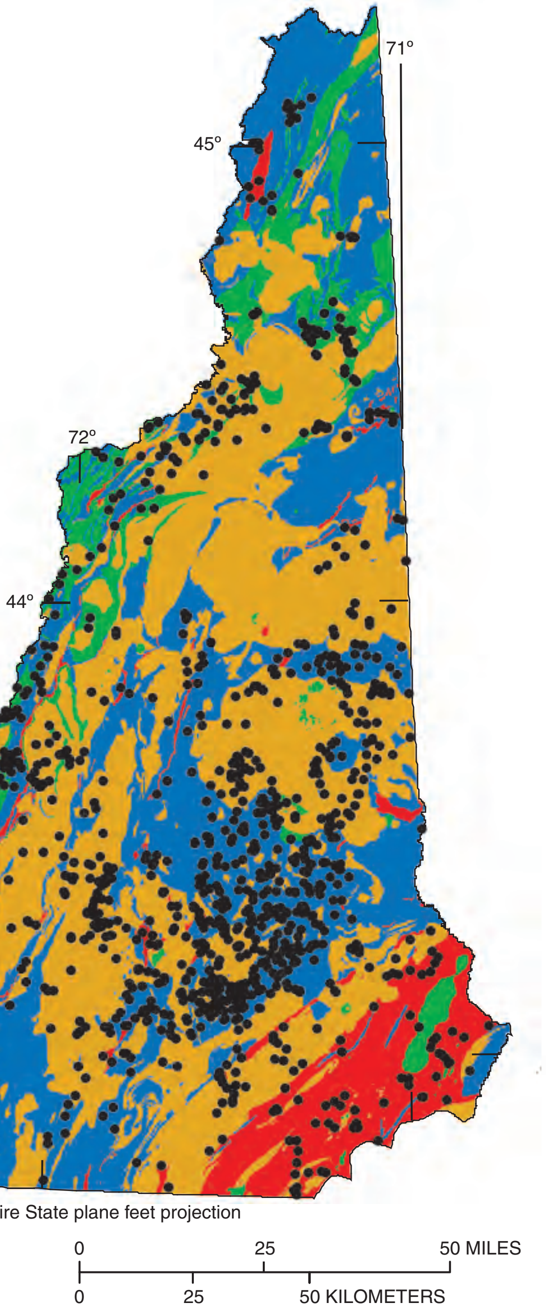
🟧 Felsic igneous [498]

[68] Number of samples

● Domestic well sampled for hardness

Hardness

(Domestic wells)



New Hampshire State plane feet projection

Figure 4. Location of domestic-bedrock-well sample sites in New Hampshire for total hardness concentration and statistical distribution of concentrations in relation to lithochemical groups.

Exhibit E

Iron

Iron is a naturally occurring element in New Hampshire's ground water. Igneous rock minerals with high iron content in the State include pyroxenes, amphiboles, biotite, magnetite, and olivine. Iron in these minerals is in the ferrous (Fe^{2+}) oxidation state, but ferric (Fe^{3+}) also may be present, such as in magnetite, ($Fe3O_4$) (Hem, 1985). According to Hem (1985), iron dissolves as acidic rain water percolates through soil and rock. The iron that is released in this process can remain dissolved in the ground water or be precipitated. The chemical behavior of iron and its solubility in water depend strongly on the oxidation and pH conditions in which it occurs. Iron is not known to have effects on human health even if present in water in excessive amounts; however, it can form red precipitates that stain laundry and plumbing fixtures. A recommended SMCL for iron in public-water supplies to prevent staining is 300 µg/L (U.S. Environmental Protection Agency, 2002b).

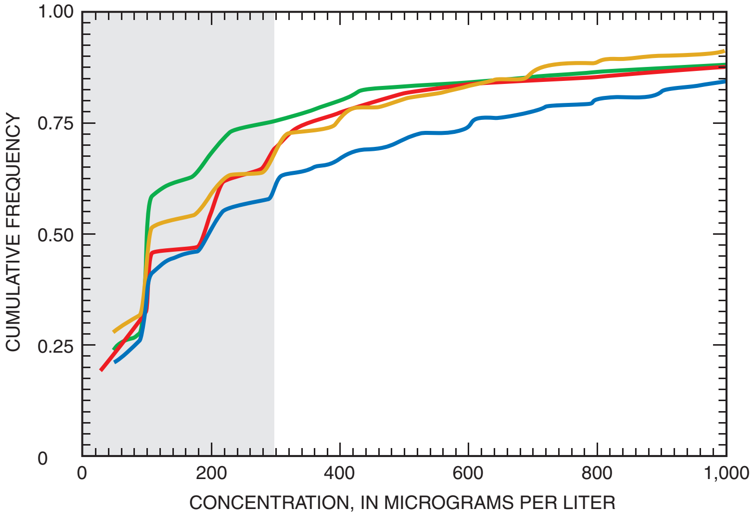
The median of 1,078 iron samples from throughout the State is 135 µg/L (0.135 mg/L). Thirty-one percent of these samples exceeded the SCML of 300 µg/L indicating that elevated iron concentrations in bedrock water is common.

Ground-water samples from the metasedimentary group have significantly greater concentrations of iron than do the felsic and mafic igneous groups (fig. 5). Ground-water samples with intermediate concentrations of iron in water from the calcareous metasedimentary group were not significantly different than concentrations in water from the other three lithochemical groups. Samples from wells in the metasedimentary group also had the highest percentage (37 percent) of ground-water samples exceeding 300 µg/L. This percentage compares to 22 percent for the mafic igneous group, 26 percent for the calcareous metasediments, and 28 percent for the felsic igneous group.

In New Hampshire, water from the bedrock aquifer has greater concentrations of iron than does water from stratified-drift aquifers. The median concentration of iron in water from bedrock wells is an order of magnitude greater (135 µg/L) than the reported median (10 µg/L) in stratified-drift aquifers (Medalie and Moore, 1995).

Exhibit E

Cumulative frequency plot of iron concentrations by lithochemical group. Gray area is less than the Secondary Maximum Contaminant Level of 300 micrograms per liter recommended by U.S. Environmental Protection Agency.



Distribution of iron concentrations by lithochemical group
[<, less than]

Quantile, in percent	Calcareous metasedimentary [1]ab	Metased-imentary a	Mafic igneous b	Felsic igneous b
90	1,400	1,700	1,300	900
50 (median)	200	200	100	100
10	<100	<100	<100	<100

[1] Lithochemical populations with the same letter designation do not differ significantly at the 95-percent confidence level. Significance level attained for the multiple-comparison test is 0.0011.

EXPLANATION

LITHOCHEMICAL GROUPS

🟥	Calcareous metasedimentary [68]
🟦	Metasedimentary [416]
🟩	Mafic igneous [95]
🟧	Felsic igneous [499]
[68]	Number of samples
●	Domestic well sampled for iron

Iron

(Domestic wells)

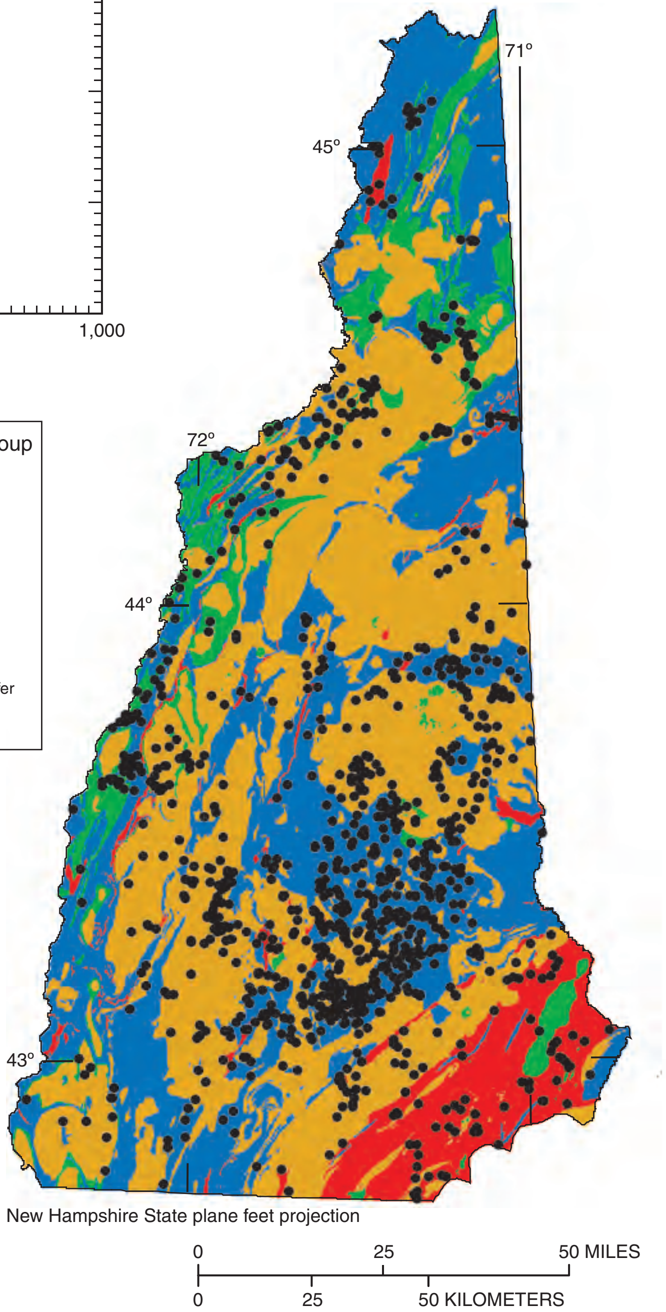


Figure 5. Location of domestic-bedrock-well sample sites in New Hampshire for total iron concentration and statistical distribution of concentrations in relation to lithochemical groups.

Exhibit E

Manganese

Manganese occurs naturally in New Hampshire's ground water and varies in concentration with the rock matrix through which the water flows. Manganese, like iron, is one of the most common elements in rocks and soils. Many igneous and metamorphic minerals contain manganese as a minor constituent (Hem, 1985). In New Hampshire, manganese is a major constituent of basalt and is found in pyroxene and amphibole minerals. According to Hem (1985), the chemistry of manganese is similar to iron in that both metals participate in reduction-oxidation processes in weathering environments. The most common forms of manganese in rocks and soils are oxides and hydroxides, which tend to strongly adsorb other metallic cations. Manganese is considered undesirable in water supplies because of the potential to deposit black oxide stains, clog fixtures, and cause a metallic taste. The recommended SMCL upper limit for manganese in public-water supplies in the United States is 50 µg/L (U.S. Environmental Protection Agency, 2002b).

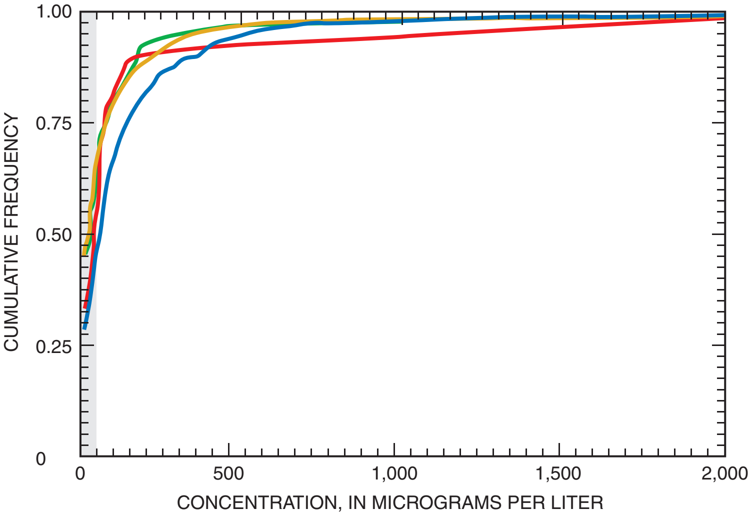
The median of 1,076 manganese samples from throughout the State is 40 µg/L (0.04 mg/L) with 40 percent of these samples exceeding the 50 µg/L SCML. Manganese concentrations are statistically different among the lithochemical groups (fig. 6). Ground-water samples from the metasedimentary group have higher manganese concentrations than do those either from the felsic or mafic igneous groups; samples from wells in calcareous metasedimentary rocks have water that statistically is not dissimilar to water from the other three lithochemical groups.

Water from the metasedimentary group also had the highest percentage (52 percent) of samples exceeding the SMCL of 50 µg/L. Forty percent of the calcareous metasedimentary group exceeded the SMCL. This result compares to exceedences of 32 and 34 percent for the felsic and mafic igneous groups, respectively (fig. 6).

Water from the bedrock aquifer has concentrations of manganese that are similar to, or slightly less than, water from stratified-drift aquifers. The median value of manganese concentrations in water from stratified-drift aquifers in New Hampshire is 63 µg/L (Medalie and Moore, 1995). This result compares to a median manganese concentration of 40 µg/L in water from the bedrock aquifer.

Exhibit E

Cumulative frequency plot of manganese concentrations by lithochemical group. Gray area is less than the Secondary Maximum Contamnant Level of 50 micrograms per liter recommended by U.S. Environmental Protection Agency.



Distribution of manganese concentrations by lithochemical group
[<, less than]

Quantile, in percent	Calcareous metasedimentary [1]ab	Metased-imentary a	Mafic igneous b	Felsic igneous b
90	170	330	180	220
50 (median)	40	60	30	26
10	<30	<30	<30	<30

[1] Lithochemical populations with the same letter designation do not differ significantly at the 95-percent confidence level. Significance level attained for the multiple-comparison test is 0.0001.

EXPLANATION

LITHOCHEMICAL GROUPS

🟥	Calcareous metasedimentary [68]
🟦	Metasedimentary [415]
🟩	Mafic igneous [95]
🟧	Felsic igneous [498]
[68]	Number of samples
●	Domestic well sampled for manganese

Manganese (Domestic wells)

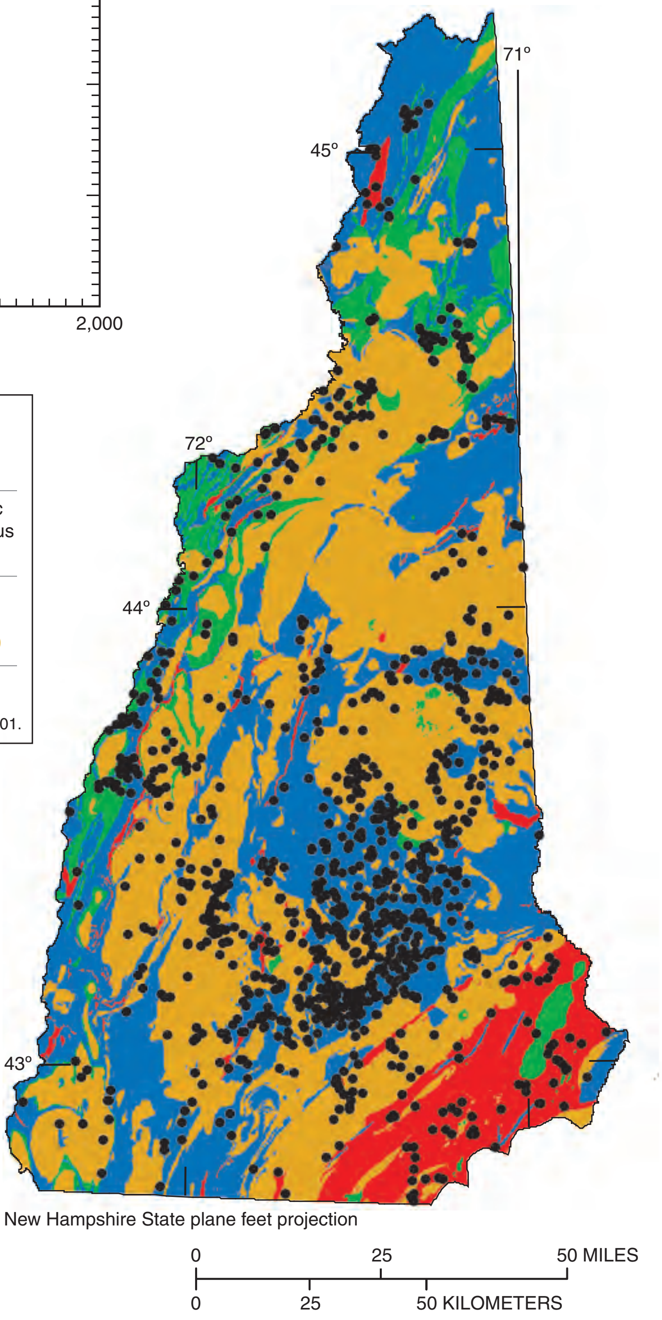


Figure 6. Location of domestic-bedrock-well sample sites in New Hampshire for total manganese concentration and statistical distribution of manganese concentrations in relation to lithochemical groups.

Exhibit E

Fluoride

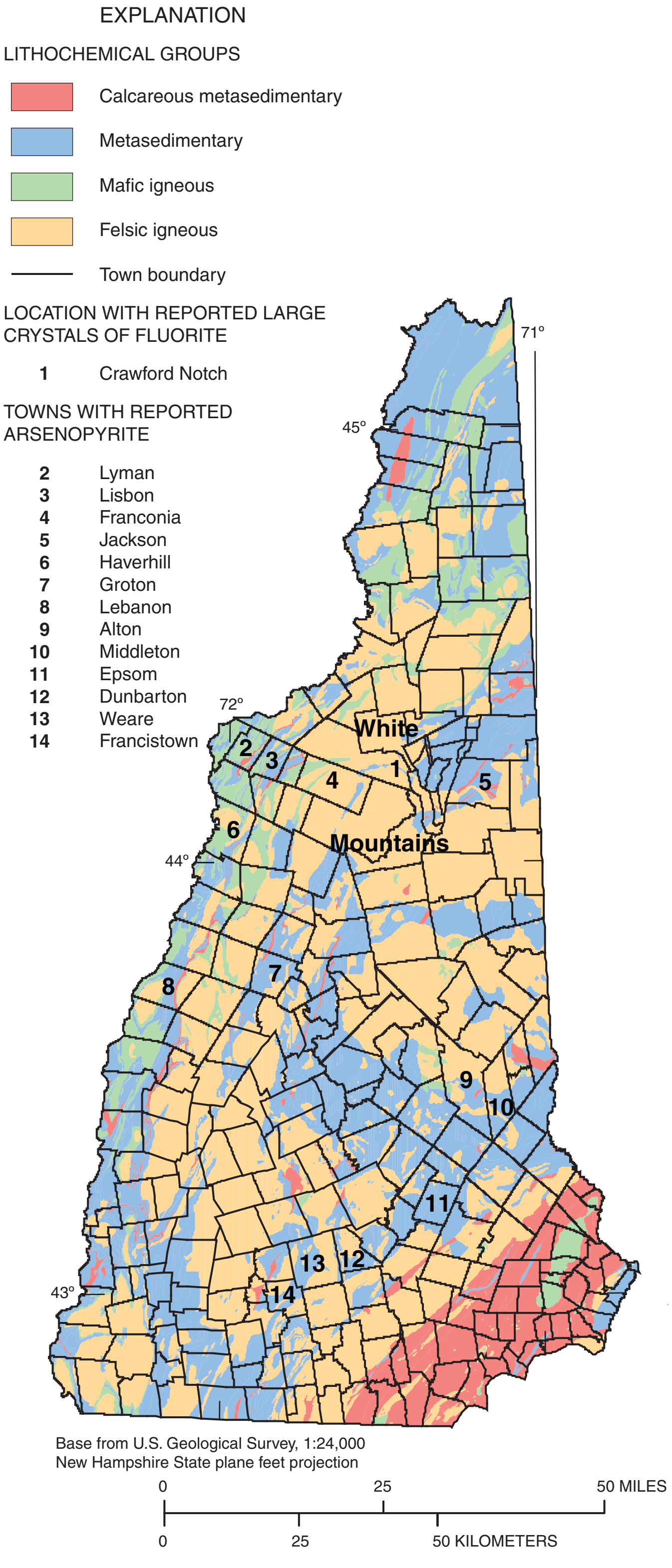
Fluoride is the negative ion of fluorine, an element that occurs commonly and naturally in rock minerals. Fluoride concentrations present in most natural waters generally are less than 1.0 mg/L because fluorine is relatively insoluble (Hem, 1985). Hem (1985) also reports that fluoride ions form strong complexes with many cations. In New Hampshire, various fluoride-containing minerals, such as fluorite (CaF^2), commonly are found. Large crystals of fluorite are found in Crawford Notch in the White Mountains (Hitchcock, 1878, part IV, p. 35) (fig. 7). Fluorite has a low solubility and occurs in igneous, metamorphic, and sedimentary rock. Other fluoride-containing minerals, commonly found in New Hampshire, include apatite, amphiboles (such as hornblende), and some micas.

Fluoride in drinking water is beneficial at concentrations less than 1.2 mg/L for dental protection. The Federal Centers for Disease Control have recommended 1.0 to 1.2 mg/L as the optimum beneficial concentration of fluoride in drinking water for dental protection (New Hampshire Department of Environmental Services, 2001). Drinking water with fluoride concentrations greater than 2.0 mg/L can cause staining of tooth enamel; at concentrations greater than 4.0 mg/L, fluoride may cause bone disease (skeletal fluorosis) (New Hampshire Department of Environmental Services, 2001; U.S. Environmental Protection Agency, 2002a). As a result, the USEPA has established a MCL of 4.0 mg/L for fluoride and a SMCL of 2.0 mg/L.

The median of 1,138 fluoride samples from throughout the State is 0.40 mg/L with 2 percent of these samples exceeding the 4.0 mg/L MCL and 9 percent exceeding the 2.0 mg/L SCML. Ground-water samples from the felsic igneous group have significantly greater concentrations of fluoride than do those from the other groups (fig. 8). Fluoride in ground-water samples from the mafic igneous and metasedimentary groups were similar to one another, and ground-water samples from the calcareous metasedimentary group had significantly lower concentrations of fluoride than the other groups.

Wells in the felsic igneous lithochemical group also had the highest percentage of ground-water samples exceeding USEPA drinking-water standards; 13 percent were greater than the SMCL of 2 mg/L and 3 percent were greater than the MCL of 4 mg/L. Wells in the calcareous metasedimentary group had the fewest number of samples exceeding the standards with just 1 percent exceeding the SMCL and none exceeding the MCL.

Water from the bedrock aquifer in New Hampshire typically has higher concentrations of fluoride than does water from stratified-drift aquifers. The median concentration of fluoride in water from the bedrock aquifer is 0.4 mg/L as compared to a median concentration of 0.1 mg/L for water from stratified-drift aquifers (Medalie and Moore, 1995).

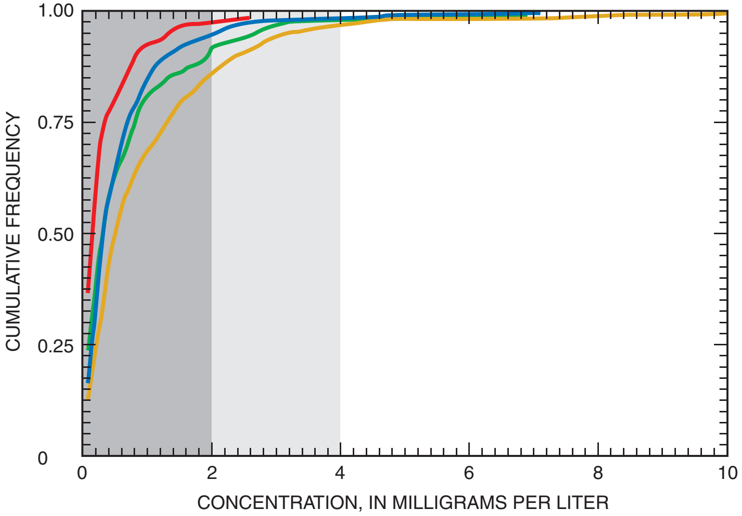


Base from U.S. Geological Survey, 1:24,000
New Hampshire State plane feet projection

Figure 7. Location of Crawford Notch with reported large crystals of fluorite, and towns in New Hampshire with reported noteworthy locations with arsenopyrite, shown in relation to lithochemical groups.

Exhibit E

Cumulative frequency plot of fluoride concentrations by lithochemical group. Darker gray area is less than the Secondary Maximum Contaminant Level of 2 milligrams per liter recommended by U.S. Environmental Protection Agency. Lighter gray area is less than the Maximum Contaminant Level of 4 milligrams per liter required by U.S. Environmental Protection Agency for public-water supplies.



Distribution of fluoride concentrations by lithochemical group
[<, less than]

Quantile, in percent	Calcareous metasedimentary [1]c	Metased-imentary b	Mafic igneous b	Felsic igneous a
90	0.8	1.3	1.9	2.4
50 (median)	.2	.3	.3	.5
10	<.1	<.3	<.1	<.1

[1] Lithochemical populations with the same letter designation do not differ significantly at the 95-percent confidence level. Significance level attained for the multiple-comparison test is 0.0001.

EXPLANATION

LITHOCHEMICAL GROUPS

🟥	Calcareous metasedimentary [71] (lowest)
🟦	Metasedimentary [439]
🟩	Mafic igneous [101]
🟨	Felsic igneous [527]
[71]	Number of samples
●	Domestic well sampled for fluoride

Fluoride (Domestic wells)

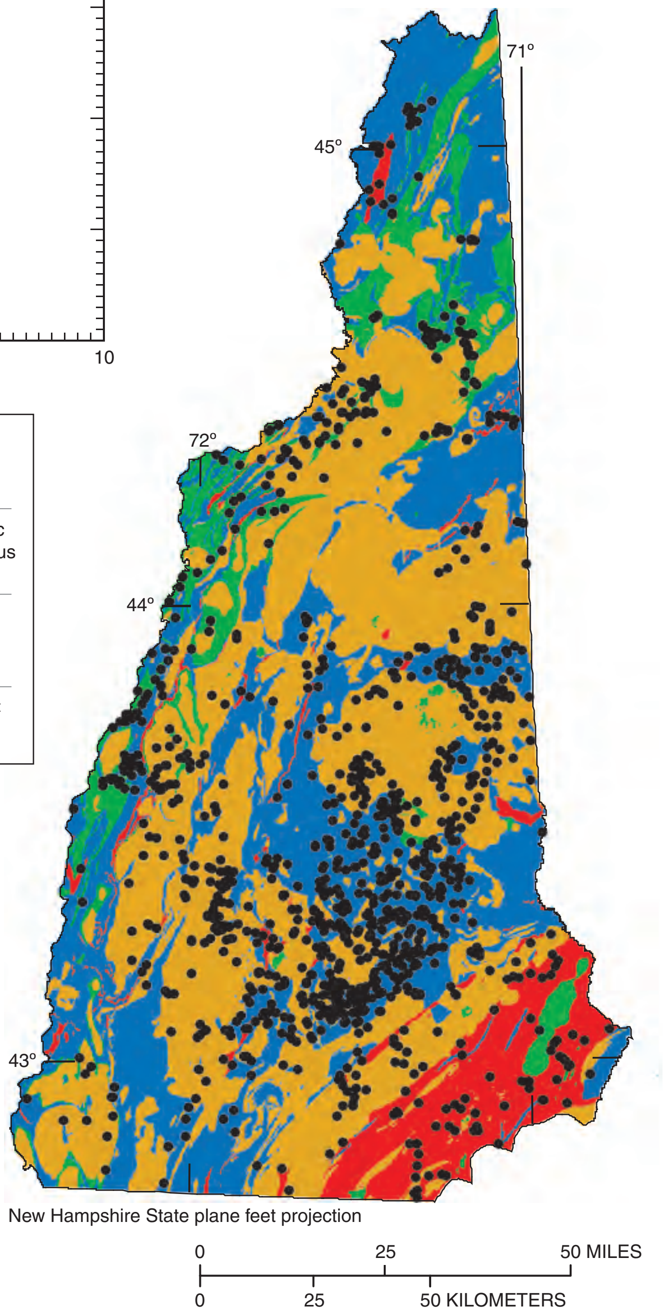


Figure 8. Location of domestic-bedrock-well sample sites in New Hampshire for total fluoride concentration and statistical distribution of concentrations in relation to lithochemical groups.

Exhibit E

Arsenic

Arsenic, a highly undesirable impurity in water supplies because of its potentially adverse effect on human health, occurs naturally in New Hampshire. Arsenic may be found in metal arsenide and sulfide minerals, and it can be present as native arsenic as an accessory element in sulfide ore deposits (Hem, 1985). Arsenic, in the form of arsenopyrite or other arsenic-rich pyrites, is sufficiently plentiful in New Hampshire to have justified small-scale mining in the past. Localities of note where arsenic minerals have been found are in "Jackson, Francistown, Haverhill, Lebanon, Weare, Groton, Lisbon, Lyman, Middleton, Dunbarton, Epsom, and Alton" (Hitchcock, 1878, part V, p. 68) and Franconia, N.H. (Hurlbut, 1971, p. 267) (fig. 9). New Hampshire also has some of the few localities in the United States (in Haverhill and Jackson) where native arsenic has been found "in thin layers in a dark blue mica schist, associated with iron and arsenical pyrites" (G.W. Hawes, in Hitchcock, 1878, part IV, p. 25). Widespread high arsenic concentrations in ground water are most commonly caused by release from phyllosilicate, iron oxide, and sulfide minerals (Welch and Ayotte, 2002).

Various geochemical processes regulate arsenic concentrations found in ground water. Adsorption of arsenic by hydrous iron oxide, or in combination with sulfide in reduced bottom mud, are processes that can maintain concentrations of arsenic at low levels in water (Hem, 1985). Aerobic geochemical conditions, in particular, appear to inhibit the solubility of arsenic in ground water. On the basis of the analyses of water samples from more than 100 domestic bedrock wells in Eastern New England, Ayotte and others (2003) found that dissolved arsenic concentrations were greatest in waters with high pH and low dissolved-oxygen concentrations. Few samples with dissolved-oxygen concentrations greater than 1 mg/L had arsenic concentrations greater than 1 µg/L. Conversely, anaerobic conditions, which can be associated with landfill leachates, tend to increase the solubility and mobility of arsenic in ground water (Colman and others, 2002; Wilkin and others, 2002).

Since 1999, a number of previous studies assessed the presence of arsenic in ground waters of New England and, collectively, these studies indicate that ground water in parts of New Hampshire are susceptible to elevated concentrations (above 10 µg/L) of arsenic (Ayotte and others, 2003; Ayotte and others, 2002; Montgomery and others, 2003; and Peters and others, 2002). These studies were stimulated by the known occurrence of elevated concentrations of arsenic in ground water from parts of New England and the change of the arsenic MCL from 50 µg/L to 10 µg/L (New Hampshire Department of Environmental Services, 2002; U.S. Environmental Protection Agency, 2002a). Ayotte and others (2003) reported that nearly 30 percent of domestic wells sampled in calcareous metasedimentary bedrock in eastern New England—including parts of New Hampshire—contained water with arsenic concentrations greater than 10 µg/L; this percentage compares to 7 percent of the sampled wells in other types of bedrock and 3 percent of wells in stratified-drift aquifers. Ayotte and others estimated that about 103,000 people in Eastern New England with domestic wells could have water with arsenic above 10 µg/L. Ayotte and others (1999) noted similar relations between arsenic concentrations in the water from public-supply wells in Eastern New England.

Montgomery and others (2003) sampled 353 randomly selected private bedrock wells for arsenic in 3 southeastern counties of New Hampshire (Hillsboro, Rockingham, and Strafford Counties) to better define the presence of arsenic in ground water from bedrock. Major findings from this study are (1) 19 percent of wells tested in the three counties had concentrations of arsenic that exceed the 10 µg/L MCL for public-water supplies, (2) the spatial distribution of arsenic concentrations that exceed 10 µg/L relates to geology, and (3) less than 14 percent of the wells had been previously tested for arsenic.

The distribution of bedrock types throughout much of New England closely matches, at a gross scale, the areas of elevated arsenic in ground water (Robinson and Ayotte, 2002). In central New Hampshire, the geographic distribution of elevated arsenic concentrations in the bedrock aquifer correlates with the presence of pegmatites that border the Concord Granite and which intrude metasedimentary rocks (Peters and others, 2002). Arsenic concentrations of the rock matrix in the pegmatites average 9.6 mg/kg, which is much higher than concentrations in the rock matrix of associated granites (0.24 mg/kg) and metasedimentary rocks (0.8 mg/kg). Peters and others (2002) proposed that pegmatites have the highest arsenic concentrations because the pegmatites are the last to crystallize during formation.

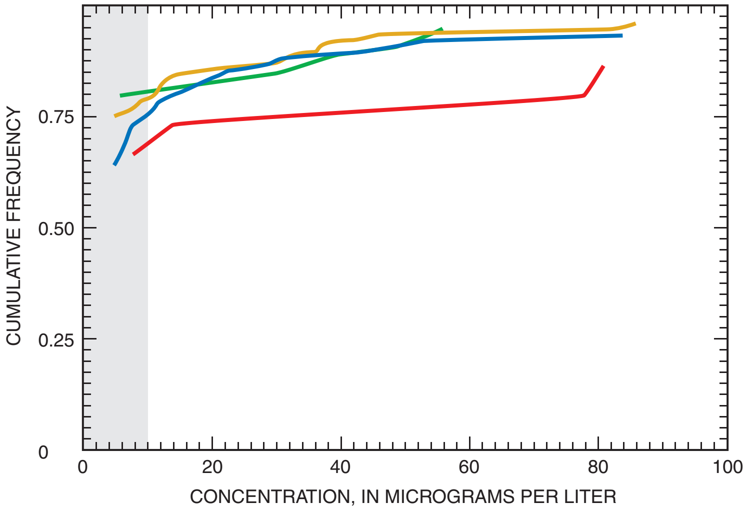
The source of the arsenic in ground water of New England is thought to be predominantly natural, originating from minerals within the rocks of the region (Robinson and Ayotte, 2002; Ayotte and others, 2003). Former pesticide use, treated lumber, and manufacturing also are sources of arsenic that may contribute to ground-water contamination (Ayotte and others, 2002; Robinson and Ayotte, 2002). In Maine, Loiselle and others (2002) concluded that the arsenic concentration of ground water is most likely the result of both natural processes and human activities.

Using well data from the NHDES Laboratory, the median of 191 arsenic samples from domestic wells throughout the State is less than 5.0 µg/L, with 21 percent of these samples exceeding the 10 µg/L MCL. These samples do not show statistically significant differences in arsenic concentrations among lithochemical units (fig. 8); this may be because of the limited number of samples in each lithochemical unit—just 15 samples from calcareous metasedimentary group, for example. Graphically, however, the calcareous metasedimentary group appears to have arsenic concentrations greater than the other groups.

Arsenic data from the 357 public-supply bedrock well samples have a median concentration of less than 5 µg/L with 12 percent exceeding the MCL of 10 µg/L. These data indicate

Exhibit E

Cumulative frequency plot of arsenic concentrations by lithochemical group for domestic bedrock wells. Gray area is less than the Maximum Contaminant Level of 10 micrograms per liter required by U.S. Environmental Protection Agency for public-water supplies.



Distribution of arsenic concentrations by lithochemical group[1]
[<, less than]

Quantile, in percent	Calcareous metasedimentary	Metasedimentary	Mafic igneous	Felsic igneous
90	81	42	39.5	36
50 (median)	5	<5	<5	<5
10	<5	<5	<5	<5

[1] Lithochemical populations do not differ significantly at the 95-percent confidence level. Significance level attained for the multiple-comparison test is 0.4310.

EXPLANATION

LITHOCHEMICAL GROUPS

🟥 Calcareous metasedimentary [15]

🟦 Metasedimentary [77]

🟩 Mafic igneous [20]

🟧 Felsic igneous [79]

[15] Number of samples

● Domestic well sampled for arsenic

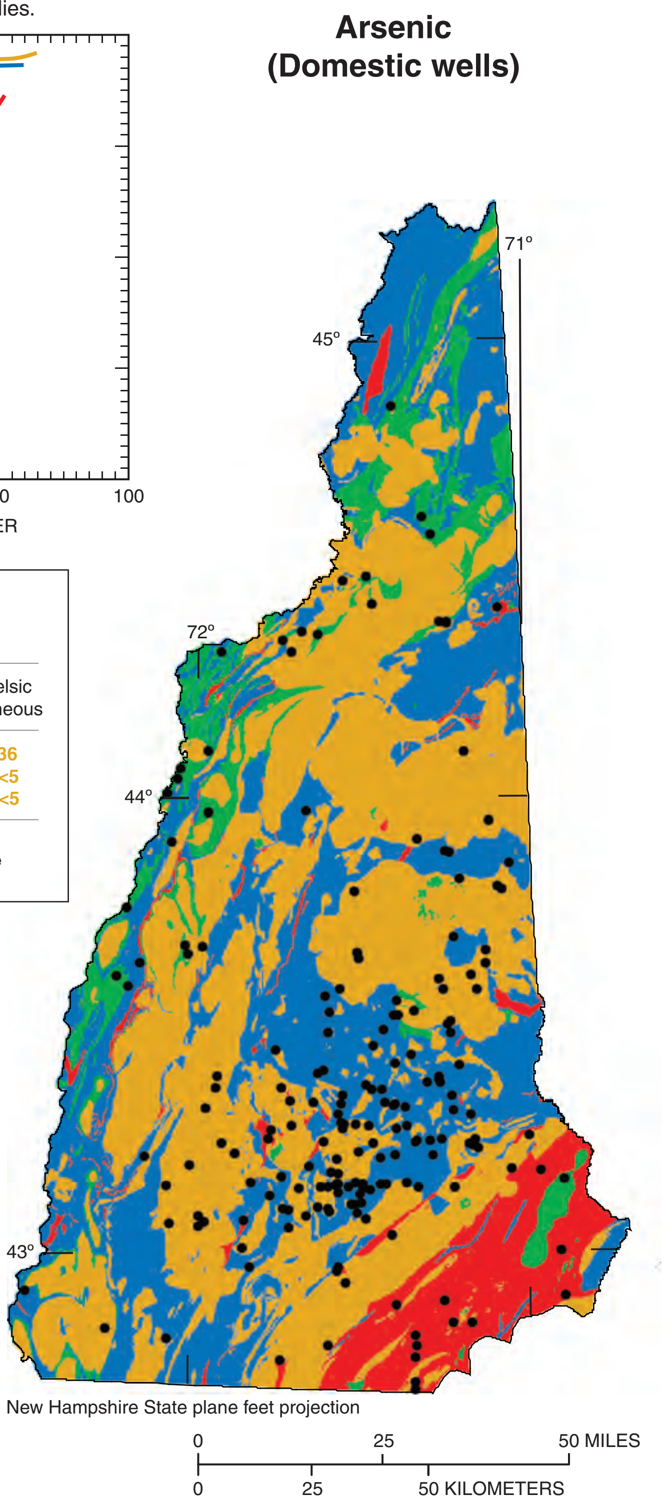


Figure 9. Location of domestic-bedrock-well sample sites in New Hampshire for total arsenic concentration and statistical distribution of concentrations in relation to lithochemical groups.

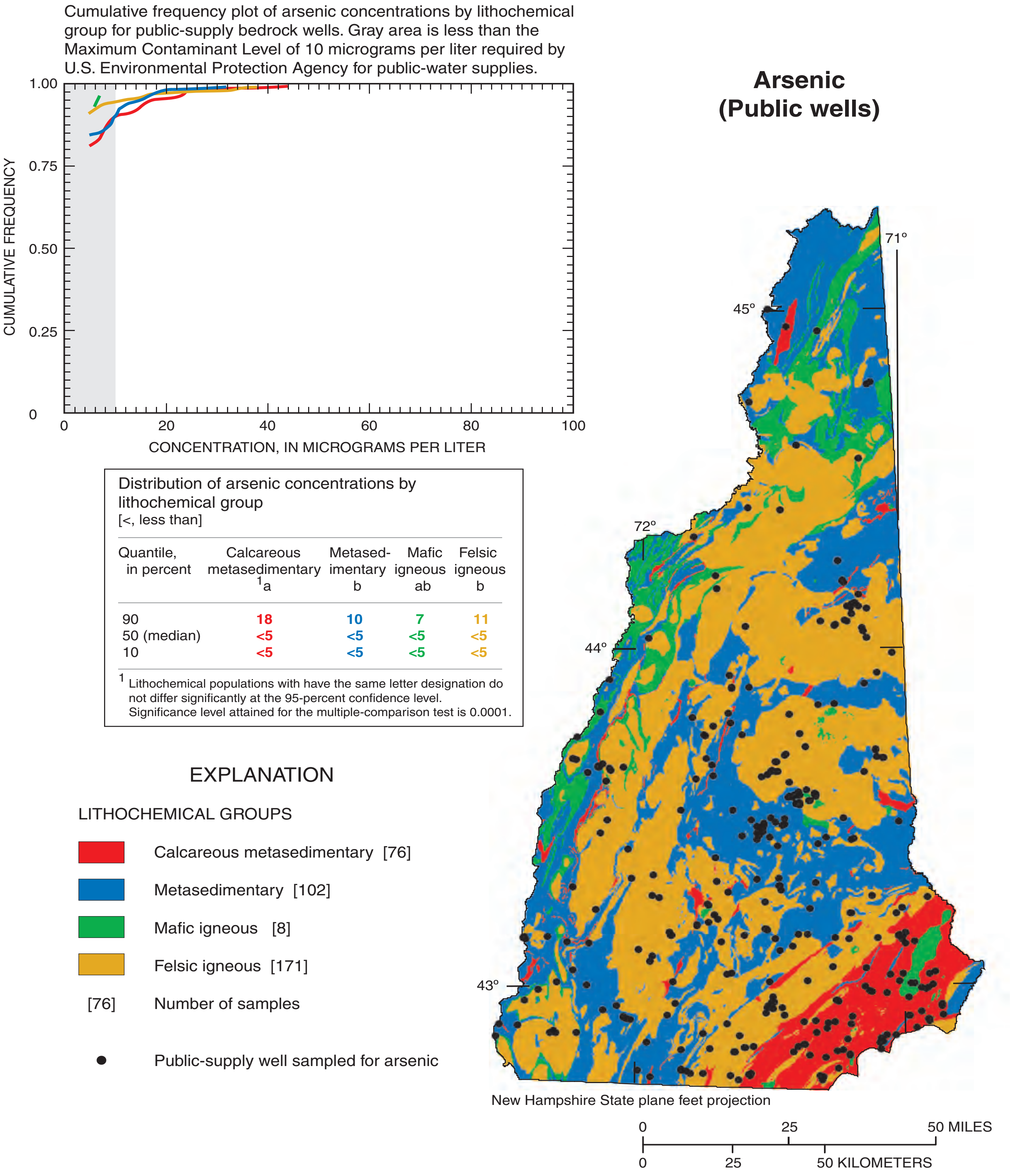
Exhibit E

statistically significant differences in arsenic concentrations among lithochemical units. Ground-water samples from the calcareous metasedimentary group have significantly greater concentrations of arsenic than samples from the other groups with the exception of the mafic igneous group. This result may be because of the lack of data with only eight public-supply bedrock wells in the mafic igneous group (fig. 10). The occurrence of high arsenic concentrations in public-supply wells in the calcareous metasedimentary bedrock of New Hampshire is similar to results reported by Ayotte and others (1999), and is expected because some of the arsenic data are used in both studies.

The calcareous metasedimentary group, for domestic and public-supply wells, had the highest percentage (27 and 21 percent, respectively) of ground-water samples exceeding the USEPA drinking-water MCL of 10 µg/L arsenic. These percentages compare to 23 and 9 percent for the domestic and the public-supply-well samples, respectively, from the metasedimentary group; 20 and 10 percent, respectively, for samples from the felsic igneous group, and 15 and 0 percent, respectively, for samples from the mafic igneous group.

Arsenic data for samples from wells in stratified-drift aquifers are not available from Medalie and Moore (1995); however, Ayotte and others (1999) report that the occurrence of arsenic concentrations of 5 µg/L or greater in public-water-supply bedrock wells was significantly greater than the occurrence in stratified-drift aquifer wells.

Exhibit E



Distribution of arsenic concentrations by lithochemical group
[<, less than]

Quantile, in percent	Calcareous metasedimentary [1]a	Metased-imentary b	Mafic igneous ab	Felsic igneous b
90	18	10	7	11
50 (median)	<5	<5	<5	<5
10	<5	<5	<5	<5

[1] Lithochemical populations with have the same letter designation do not differ significantly at the 95-percent confidence level. Significance level attained for the multiple-comparison test is 0.0001.

EXPLANATION

LITHOCHEMICAL GROUPS

🟥	Calcareous metasedimentary [76]
🟦	Metasedimentary [102]
🟩	Mafic igneous [8]
🟧	Felsic igneous [171]
[76]	Number of samples
●	Public-supply well sampled for arsenic

Figure 10. Location of public-supply bedrock-well sample sites in New Hampshire for total arsenic concentration and statistical distribution of concentrations in relation to lithochemical groups.

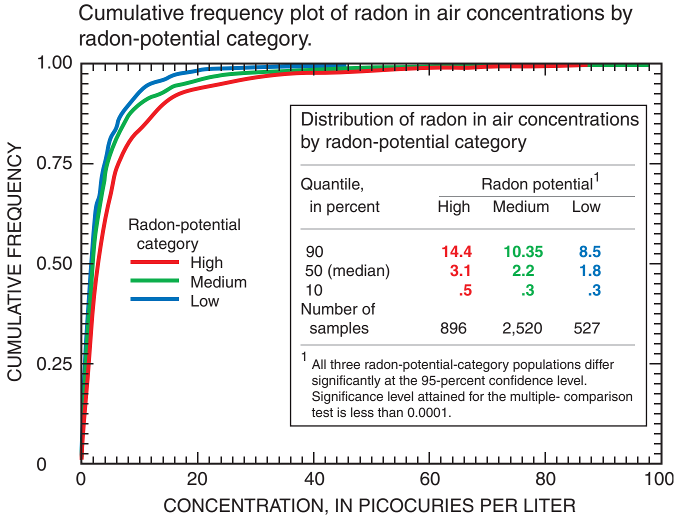
Exhibit E

Radon

Radon is a naturally occurring radioactive gas that is part of the uranium decay chain. Isotopes of radon are produced from the decay of radium isotopes 223, 224, and 226. Radon-222 produced in the decay of radium-226 has a half-life of 3.8 days and is the only radon isotope of importance in the environment because the other radon isotopes have half-lives of less than a minute (Hem, 1985). Radon, in addition to being transported in the gas phase, is soluble in water. According to Hem (1985), small amounts are present in the atmosphere; however, large amounts (when compared to the atmosphere) are present in gases below the land surface. As a result, radon can enter buildings and homes through foundations and well-water systems. Radon-222 decays through a series of short-lived daughter products to lead-210, which has a half-life of 21.8 years.

Two standards presently (2004) are being proposed by USEPA for radon in public-supply waters (U.S. Environmental Protection Agency, 1999). A standard of 4,000 pCi/L is proposed under the "multimedia mitigation" program (U.S. Environmental Protection Agency, 1999), which takes into consideration air and water sources of radon. Under this program, if the contribution in air is low, or treated to be low, higher concentrations in water are applied than otherwise would be allowed. When multimedia mitigation is not applied, the proposed USEPA MCL is 300 pCi/L for water. The State of New Hampshire recommends that homeowners take steps to lower indoor radon-air concentrations when these concentrations equal or exceed 4 pCi/L in the lowest part of the home (New Hampshire Department of Health and Human Services, 2004).

The median air-radon concentration, on the basis of data from 3,943 single family homes with bedrock wells, was 2.2 pCi/L. Air-radon concentrations are statistically different when grouped by the radon-potential categories (high, medium, and low) (fig. 11) with the highest concentrations associated with the high radon-potential category. These results indicate that the grouping of bedrock into radon-potential categories can be useful for determining where high air-radon concentrations are likely to be present.


Cumulative frequency plot of radon in air concentrations by radon-potential category.

Distribution of radon in air concentrations by radon-potential category

Quantile, in percent	Radon potential[1] High	Medium	Low
90	14.4	10.35	8.5
50 (median)	3.1	2.2	1.8
10	.5	.3	.3
Number of samples	896	2,520	527

[1] All three radon-potential-category populations differ significantly at the 95-percent confidence level. Significance level attained for the multiple- comparison test is less than 0.0001.

Figure 11. Statistical distribution of radon in air concentrations from single family homes with drilled wells in New Hampshire in relation to radon-potential categories.

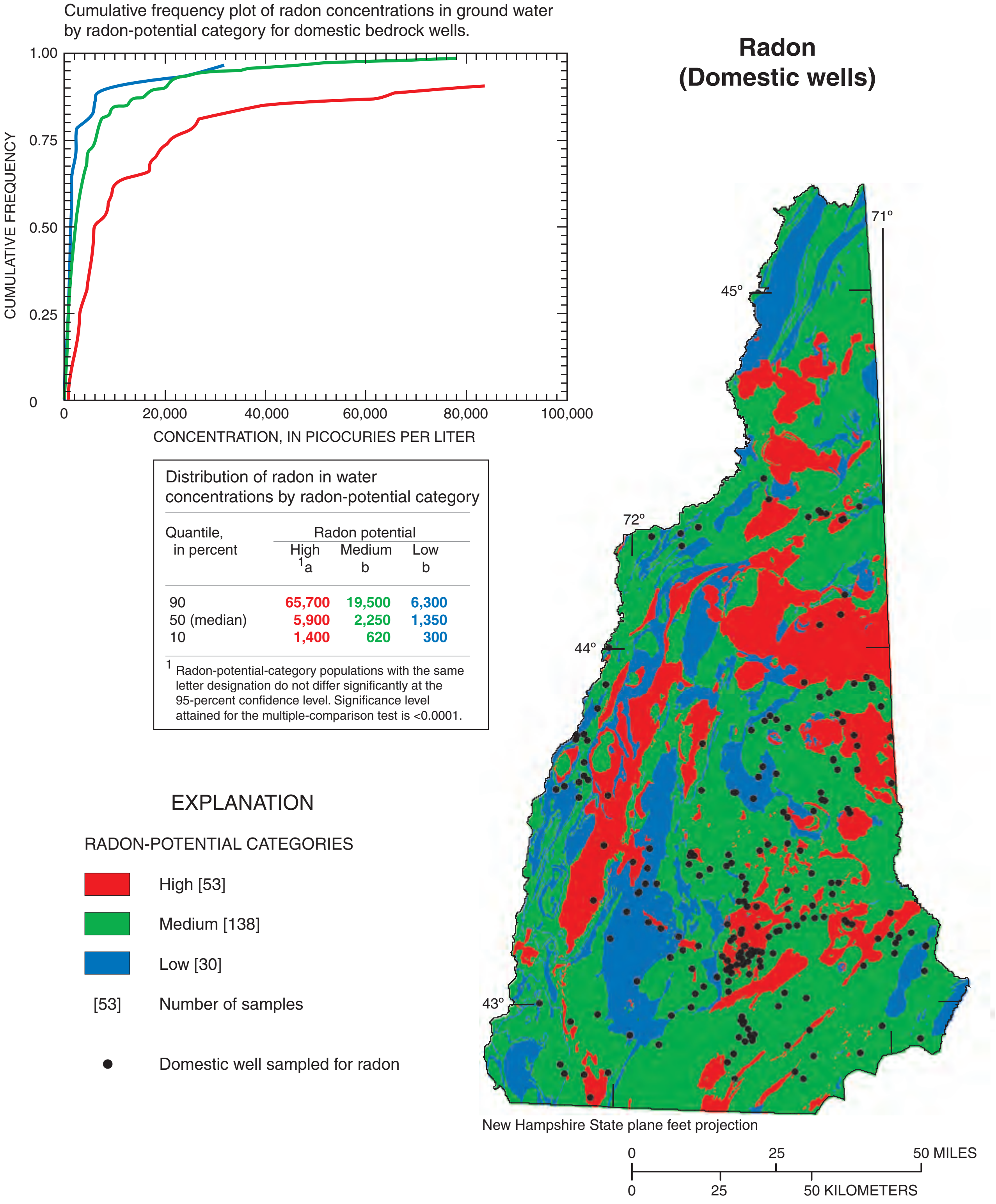
The median radon concentrations in ground-water samples from 221 domestic bedrock wells is 2,600 pCi/L, this compares to a median concentration of 2,000 pCi/L from 310 public-water-supply well samples. For the domestic and public-water-supply wells, radon concentrations were higher in bedrock grouped in the high radon-potential category than in the bedrock grouped as medium or low radon-potential categories (figs. 12 and 13). However, statistical differences in the domestic and public-supply-well data are not identified between the medium and low radon-potential categories. The lack of statistical difference may be because of the small number of samples in the low radon-potential categories for domestic and public-supply wells (30 and 45, respectively). By use of the generalized categories of radon potential, distinct differences in radon concentrations are identified from all three databases—air, domestic ground water, and public-supply ground water (Moore and others, 2000).

Nearly all of the ground-water samples from the bedrock aquifer in New Hampshire fail to meet the proposed USEPA standard of 300 pCi/L when multimedia mitigation is not implemented. All of the water samples from the domestic and public-supply bedrock wells in the high-radon potential exceeded 300 pCi/L; 97 and 98 percent of the water samples from the domestic and public-supply bedrock wells, respectively, in the medium radon-potential category exceeded 300 pCi/L, and 90 and 89 percent of the water samples, from domestic and public-supply bedrock wells, respectively, in the low radon-potential category exceeded 300 pCi/L.

Many (40 and 30 percent) of the ground-water samples from the bedrock aquifer from domestic and public-supply bedrock wells, respectively, also fail to meet the proposed standard of 4,000 pCi/L (when multimedia mitigation is implemented). In the high radon-potential category, 70 and 50 percent of the water samples from the domestic and public-supply bedrock wells, respectively, exceeded 4,000 pCi/L; in the medium radon-potential category, 34 and 27 percent from the domestic and public-supply bedrock wells exceeded 4,000 pCi/L, respectively; and in the low radon-potential category, 17 and 16 percent from the domestic and public-supply bedrock wells exceeded 4,000 pCi/L, respectively.

Radon concentrations in the water of bedrock aquifers typically are greater than the concentrations in stratified-drift aquifers (Hall and others, 1985, and Boudette, 1994). Hall and others (1985) reported that general ranges of radon in glacial deposits (including stratified drift) are less than 1,000 pCi/L. Data on radon concentrations in water from stratified-drift aquifers (Medalie and Moore, 1995) were not available for comparison to the bedrock radon data presented in this report.

Exhibit E



Cumulative frequency plot of radon concentrations in ground water by radon-potential category for domestic bedrock wells.

Distribution of radon in water concentrations by radon-potential category

Quantile, in percent	Radon potential High [1]a	Radon potential Medium b	Radon potential Low b
90	65,700	19,500	6,300
50 (median)	5,900	2,250	1,350
10	1,400	620	300

[1] Radon-potential-category populations with the same letter designation do not differ significantly at the 95-percent confidence level. Significance level attained for the multiple-comparison test is <0.0001.

EXPLANATION

RADON-POTENTIAL CATEGORIES

🟥	High [53]
🟩	Medium [138]
🟦	Low [30]
[53]	Number of samples
●	Domestic well sampled for radon

Figure 12. Location of domestic-bedrock-well sample sites in New Hampshire for radon concentration in ground water and statistical distribution of concentrations in relation to radon-potential categories.

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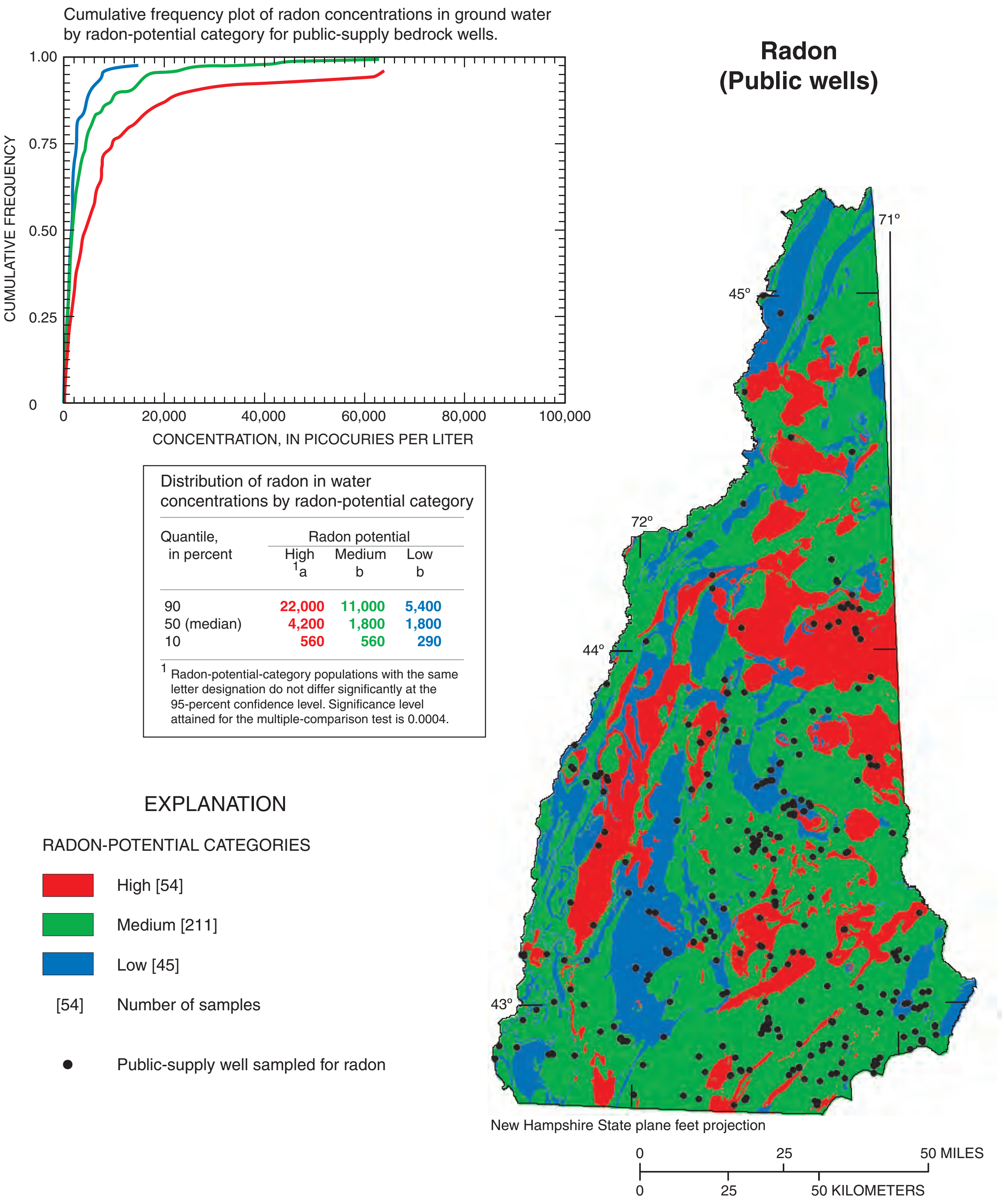

Distribution of radon in water concentrations by radon-potential category

Quantile, in percent	Radon potential High [1]a	Radon potential Medium b	Radon potential Low b
90	22,000	11,000	5,400
50 (median)	4,200	1,800	1,800
10	560	560	290

[1] Radon-potential-category populations with the same letter designation do not differ significantly at the 95-percent confidence level. Significance level attained for the multiple-comparison test is 0.0004.

EXPLANATION

RADON-POTENTIAL CATEGORIES

🟥 High [54]

🟩 Medium [211]

🟦 Low [45]

[54] Number of samples

● Public-supply well sampled for radon

Figure 13. Location of public-supply bedrock-well sample sites in New Hampshire for radon concentration in ground water and statistical distribution of concentrations in relation to radon-potential categories.

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Summary and Conclusions

Many New Hampshire communities are looking to the fractured crystalline bedrock aquifer for additional water supplies. Understanding the variability of water quality within the bedrock aquifer may be an important consideration when evaluating this resource as a future drinking-water supply. Bedrock-well data from throughout New Hampshire were used to characterize the water quality of the bedrock aquifer. This study was part of the New Hampshire Bedrock Aquifer Assessment by the U.S. Geological Survey, in cooperation with the New Hampshire Department of Environmental Services (NHDES).

Ambient water quality of ground water in the bedrock aquifer throughout New Hampshire varies by lithochemical groups and radon-potential categories. Information on the occurrence of pH, hardness, iron, manganese, fluoride, arsenic, and radon in bedrock ground water were compiled and statistically compared to the lithochemical and radon-potential groups from which the samples originated. A water-quality database for domestic bedrock wells was created by determining geographic coordinates for bedrock wells where water-quality samples had been collected. The database includes analyses for 1,078 wells with pH, 1,076 wells with hardness, 1,078 with total iron, 1,076 with total manganese, 1,138 with total fluoride, 191 with total arsenic, and 221 wells with radon. For arsenic and radon, a second database of public-supply wells was examined. Constituents available for analysis were limited to those routinely collected by the NHDES Environmental Laboratory.

Nonparametric statistical analyses were used to quantify relations between concentrations of the various chemical constituents in ground-water samples and the lithochemical groups, or radon-potential categories that characterize the bedrock aquifer at the sample locations. Bedrock wells with water-quality analyses of pH and total hardness, iron, manganese, fluoride, and arsenic concentrations were assigned to one of the four major lithochemical groups based on the location of the well. Likewise, bedrock wells with radon data were assigned to one of the three radon-potential categories. Statistical differences among the lithochemical groups (calcareous metasedimentary, metasedimentary, mafic igneous, felsic igneous) or the radon-potential categories (high, medium, and low) were identified for all seven water-quality constituents examined. These relations were used to identify areas with relative differences in water quality as a function of the general chemical and mineralogical characteristics of the bedrock.

Most ground water from bedrock wells in New Hampshire is suitable for drinking. However, a large percentage of the water samples (21 percent from the domestic well data set and 12 percent from the public-supply well data set) fail to meet the U.S. Environmental Protection Agency MCL drinking-water standard of 10 µg/L for arsenic. Similarly, radon is a common contaminant for which a large number of samples fail to reach proposed drinking-water standards, and for fluoride, 2 percent of the water samples from the domestic well data set fail to meet the fluoride MCL drinking-water standard of 4 mg/L. Iron and manganese also are common nuisance contaminants but these do not pose a threat to human health. For pH, hardness, iron, manganese, and fluoride domestic bedrock-well samples, differences among the lithochemical groups are as follows:

1. Ground-water samples from the mafic igneous group have higher pH values and greater hardness than do those from either the felsic igneous group or the metasedimentary group. The mafic igneous group also had the lowest percentage of ground-water samples outside the range of USEPA SMCL drinking-water standards (from 6.5 to 8.5 pH). Only 4 percent of the water samples from the mafic igneous group had pH below 6.5, which can cause metal pipes to corrode.
2. Ground water from the bedrock aquifer in New Hampshire is typically soft to moderately hard. The percentage of the water samples with hard or very hard water is 22 percent for the calcareous metasedimentary group and 16 percent for the mafic igneous group. This result compares to less than 12 percent of the water samples from the other lithochemical groups that are hard or very hard.
3. Ground-water samples from the metasedimentary group have greater concentrations of total iron than do the felsic and mafic igneous groups. The metasedimentary group also had the highest percentage (37 percent) of ground-water samples exceeding USEPA SMCL drinking-water standard of 300 µg/L iron. For the other lithochemical groups, samples exceeded the standard by 22–28 percent.
4. Ground-water samples from the metasedimentary group also have greater concentrations of total manganese than do the felsic and mafic igneous groups. The metasedimentary group had the highest percentage (52 percent) of ground-water samples exceeding USEPA manganese SMCL drinking-water standard of 50 µg/L. The calcareous metasedimentary group had the second highest percentage (40 percent) exceeding the USEPA SMCL drinking-water standard. This result compares to 32 and 34 percent for the felsic and mafic igneous groups, respectively.
5. Ground-water samples from the felsic igneous group have significantly greater concentrations of total fluoride than do those from the other groups. The felsic igneous group also had the highest percentage of ground-water samples exceeding USEPA drinking-water standards for fluoride, with 13 percent above the SMCL of 2 mg/L and 3 percent above the MCL of 4 mg/L.

The calcareous metasedimentary group was identified, utilizing the public-supply database, as having significantly higher concentrations of arsenic than the other groups. The calcareous metasedimentary group, for the domestic and the public-supply wells, had the highest percentage of ground-water samples exceeding the USEPA drinking-water MCL arsenic standard, with 27 and 21 percent, respectively, exceeding 10 µg/L.

Radon concentrations in the air and in water from private and public-supply wells are higher at sites underlain by high

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radon-potential category rocks compared to sites underlain by rocks in the medium and low categories. Likewise, the medium radon-potential category is higher for air samples and appears to be higher for water samples than do those samples from the low category. For water samples, this difference was not identified as statistically significant, possibly because of small sample sizes in the low potential category. USEPA standards are not presently (2004) finalized for radon.

In general, samples from the bedrock aquifer tend to have higher pH (are less acidic), greater hardness, much higher concentrations of iron, similar concentrations of manganese, and higher concentrations of fluoride, arsenic, and radon than stratified-drift aquifers. Further investigation is needed to develop less biased water-quality databases and to develop hydrochemical analyses of the complex interrelations between water quality and the lithochemistry and ground-water-flow systems in the bedrock aquifer.

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Migration behavior of landfill leachate contaminants through alternative composite liners

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Abstract

Four identical pilot-scale landfill reactors with different alternative composite liners were simultaneously operated for a period of about 540 days to investigate and to simulate the migration behaviors of phenolic compounds (phenol, 2-CP, 2-MP, 3-MP, 4-MP, 2-NP, 4-NP, 2,4-DNP, 2,4-DCP, 2,6-DCP, 2,4,5-TCP, 2,4,6-TCP, 2,3,4,6-TeCP, PCP) and heavy metals (Pb, Cu, Zn, Cr, Cd, Ni) from landfill leachate to the groundwater. Alternative landfill liners of four reactors consist of R1: Compacted clay liner (10 cm + 10 cm, $k=10^{-8}$ m/sn), R2: Geomembrane (2 mm HDPE) + compacted clay liner (10 cm + 10 cm, $k=10^{-8}$ m/sn), R3: Geomembrane (2 mm HDPE) + compacted clay liner (10 cm, $k=10^{-8}$ m/sn) + bentonite liner (2 cm) + compacted clay liner (10 cm, $k=10^{-8}$ m/sn), and R4: Geomembrane (2 mm HDPE) + compacted clay liner (10 cm, $k=10^{-8}$ m/sn) + zeolite liner (2 cm) + compacted clay liner (10 cm, $k=10^{-8}$ m/sn). Wastes representing Istanbul municipal solid wastes were disposed in the reactors. To represent bioreactor landfills, reactors were operated by leachate recirculation. To monitor and control anaerobic degradation in the reactors, variations of conventional parameters (pH, alkalinity,

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chloride, conductivity, COD, TOC, TKN, ammonia and alcaly metals) were also investigated in landfill leachate samples. The results of this study showed that about 35–50% of migration of organic contaminants (phenolic compounds) and 55–100% of migration of inorganic contaminants (heavy metals) to the model groundwater could be effectively reduced with the use of bentonite and zeolite materials in landfill liner systems. Although leachate contaminants can reach to the groundwater in trace concentrations, findings of this study concluded that the release of these compounds from landfill leachate to the groundwater may potentially be of an important environmental concern based on the experimental findings.

Research highlights

► Migration of phenolic compounds to the groundwater could be reduced by 35–50%. ► Migration of heavy metals to the groundwater could be reduced by 55–100%. ► The release of these compounds may potentially be of an important environmental concern.

Introduction

Landfill leachate contain a large number of hazardous compounds, including aromatics, halogenated compounds, phenols, pesticides, heavy metals, and ammonium, which can be assumed to be hazardous even in small amounts and their detrimental effects are often caused by multiple and synergistic effects (Christensen et al., 2001, Oman and Rosqvist, 1999). Particularly, phenolic compounds released into the environment are of high concern because of their potential toxicity. These compounds found in the leachate include phenol, cresols and substituted and chlorinated phenols. Phenol, cresols, short-chain phenols previously reported in leachates of municipal and industrial landfills (Benfenati et al., 1999) may originate from different types of wastes. Phenol and substituted phenols are common transformation products of several pesticides. Many substituted phenols, including chlorophenols, nitrophenols, and cresols, have been designated as priority toxic pollutants by the U.S. Environmental Protection Agency (Boopathy, 1997).

Contaminant transport through composite landfill liners can be considered in two problems: (1) advective and dispersive transport of inorganic and organic contaminants through defects in the geomembrane seams connecting geomembranes and through clay liner underlying the geomembrane, and (2) diffusive transport of organic contaminants through non-defective composite liners (Foose et al., 2002, Katsumi et al., 2001). Diffusive transport of organic contaminants through composite liners may be considered in two basic steps: (1) transport through the geomembrane, and (2) transport through the clay liner.

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Sakti, 1993, Park and Nibras, 1993 demonstrated that organic contaminants could diffuse through geomembranes at appreciable rates.

Contamination of groundwater by landfill leachate represents the major environmental concern associated with the landfilling of waste (El-Fadel et al., 1997). The impact of landfill leachate on the surface and groundwater has given rise to a number of studies in recent years (Abu-Rukah and Al-Kofahi, 2001, Saarela, 2003). Although numerous studies in literature (Foose et al., 2002, Kalbe et al., 2002, Baun et al., 2003, Edil, 2003 Lo et al., 2004, Haijian et al., 2009, Chalermtanant et al., 2009, Lu et al., 2011) have been conducted to investigate the migration of pollutants through landfill liners, however, relatively few of them include the interaction between biodegradation of contaminants in leachate during landfilling and migration of organic and inorganic contaminants through composite liners. A simulation investigation that couples the biodegradation processes to the transport processes, under realistic landfill conditions, can be considered as a key step to gain an understanding of chemical transport and behavior of pollutants (particularly phenolic compounds and heavy metals) in a specific landfill leachate-model groundwater system. Since the transport mechanisms of landfill leachate through liners are controlled by several complex interactions between various physical, chemical and biological processes, some simplifications may be needed for the preliminary estimation of the potential environmental risks and development of strategies for groundwater protection against contamination by landfill leachate, as well as for the understanding of chemical transport and behavior of pollutants in a specific landfill system.

Considering the above-mentioned facts, the specific objectives of this study were to evaluate the effectiveness of several landfill liner designs with regard to phenolic compounds transport through alternative landfill liners to model groundwater and to investigate the migration of contaminants through landfill liners including the interaction between biodegradation of contaminants in leachate during the landfilling operation.

Section snippets

Exhibit E

Reactor setup, operation and liner materials

Four identical pilot-scale landfill reactors (R1, R2, R3 and R4) were simultaneously run for a period of about 540 days to investigate the nature of diffusive transport of the selected organic and advective transport of inorganic contaminants. All parts of the reactors were made of HDPE pressurized pipes with a wall thickness of 5 mm. The diameter (D_R), height (H_R), effective volume (V_E) and total volume (V_T) of the reactors were 40 cm, 250 cm, 0.201 m^3 and 0.251 m^3, respectively. The reactors were…

pH and alkalinity

The pH values were in the range of 5.5–6.5 in the first 100 days of degradation in all reactors. With the leachate recirculation (after day 100), pH values reached almost neutral conditions after day 200 in all reactors. Thereafter, no considerable change was observed in pH of leachate from anaerobic landfill reactors (after day 200). These results are in accordance with the data stated by others (Bilgili et al., 2007, Cossu et al., 2003). The results indicated that the initial pH of leachate…

Conclusions

This study describes the performance of four alternative liner systems in migration of various organic and inorganic contaminants released from landfill leachate to the model groundwater. This study demonstrated that about 35–50% of transport of these contaminants to the model groundwater can be effectively reduced with the use of bentonite and zeolite materials in landfill liner systems. Although leachate contaminants can reach to the groundwater in trace concentrations, potential risks of…

Acknowledgements

This research has been supported by The Scientific and Technological Research Council of Turkey (TUBITAK—CAYDAG) (Project Number: 105Y334) Ankara-Turkey.…

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Exhibit E

Spatial and Temporal Migration of a Landfill Leachate Plume in Alluvium

Jason R. Masoner · Isabelle M. Cozzarelli

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Abstract Leachate from unlined or leaky landfills can create groundwater contaminant plumes that last decades to centuries. Understanding the dynamics of leachate movement in space and time is essential for monitoring, planning and management, and assessment of risk to groundwater and surface-water resources. Over a 23.4-year period (1986–2010), the spatial extent of the Norman Landfill leachate plume increased at a rate of 7800 m^2/year and expanded by 878 %, from an area of 20,800 m^2 in 1986 to 203,400 m^2 in 2010. A linear plume velocity of 40.2 m/year was calculated that compared favorably to a groundwater-seepage velocity of 55.2 m/year. Plume-scale hydraulic conductivity values representative of actual hydrogeological conditions in the alluvium ranged from 7.0×10^{-5} to 7.5×10^{-4} m/s, with a median of 2.0×10^{-4} m/s. Analyses of field-measured and calculated plume-scale hydraulic conductivity distributions indicate that the upper percentiles of field-measured values should be considered to assess rates of plume-scale migration, spreading, and biodegradation. A pattern of increasing Cl^- concentrations during dry periods and decreasing Cl^- concentrations during wet periods was observed in groundwater beneath the landfill. The opposite occurred in groundwater downgradient from the landfill; that is, Cl^- concentrations in groundwater downgradient from the landfill decreased during dry periods and increased during wet periods. This pattern of changing Cl^- concentrations in response to wet and dry periods indicates that the landfill retains or absorbs leachate during dry periods and produces lower concentrated leachate downgradient. During wet periods, the landfill receives more recharge which dilutes leachate in the landfill but increases leachate migration from the landfill and produces a more concentrated contaminant plume. This approach of quantifying plume expansion, migration, and concentration during variable hydrologic conditions provides increased understanding of plume behavior and migration potential and may be applied at less monitored landfill sites to evaluate potential risks of contamination to downgradient receptors.

Keywords Landfills · Plumes · Contaminant transport · Temporal · Migration · Groundwater contamination

1 Introduction

Migration of contaminants from closed or abandoned unlined landfills is a threat to groundwater and surface-water resources worldwide. Determining the risks posed by unlined or leaking landfills requires understanding of the dynamics of leachate movement in both space and time. Groundwater quality near closed unlined landfills can be affected for decades or centuries after cessation of a landfill operation (Cozzarelli et al. 2011; Bjerg et al.

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2011, and Bjerg et al. 2014). Landfill leachate typically contains high concentrations of ammonium, dissolved organic carbon (DOC), salts, trace metals, and organic contaminants of emerging concern (Christensen et al. 1994; Barnes et al. 2004; Van Breukelen and Griffioen. 2004; Buszka et al. 2009; Andrews et al. 2012; Masoner et al. 2014). Closed unlined landfills adjacent to surface-water bodies can discharge leachate into surrounding sediments and waterways, resulting in contamination of aquatic ecosystems (Báez-Cazull et al. 2007; Lorah et al. 2009).

Modern landfills in the United States are designed with liners and leachate-collection systems to prevent leachate from migrating into groundwater. Although the number of active landfills in the United States has decreased from about 7900 in 1988 to 1900 in 2009 (USEPA 2010), older closed landfills in the United States remain of greater concern; their numbers were estimated at more than 90,000 two decades ago (Suflita et al. 1992). These closed landfills are typically unlined and do not use leachate-collection systems. Exposure of buried waste to precipitation and subsequent groundwater seepage create leachate plumes containing complex mixtures of organic and inorganic contaminants (Bjerg et al. 2014). Prior to passage of Subtitle D of the Resource Conservation and Recovery Act in 1976, landfills commonly were located near rivers on active floodplains where erosion, inundation, active-channel migration, and climatic changes could have unpredictable effects on plume concentration and migration (Curtis and Whitney 2003).

Hydrologic conditions and geologic features exert substantial control on the composition and migration of leachate away from a landfill. Water-table mounds in a landfill cell can increase lateral spreading and downward seepage of leachate, and limited vertical mixing of leachate plumes in groundwater can result in relatively steep vertical concentration gradients of leachate constituents (Bjerg et al. 2011). Spatial heterogeneity in contaminant concentrations, up to 1000 fold, has been documented in groundwater affected by landfill leachate (e.g., Kjeldsen et al. 1998), underscoring the importance of installing extensive monitoring well networks to delineate leachate pathways and chemical gradients. At the Norman Landfill, near Norman, Oklahoma, previous studies have documented the presence of many organic compounds including detergents, pharmaceuticals, insect repellents, pesticides, plasticizers, fire retardants, hydrocarbons, and fecal indicators in groundwater downgradient from the landfill (Eganhouse et al. 2001; Cozzarelli et al. 2011; Andrews et al. 2012). Evaluating potential water-quality risks from these and other contaminants requires an understanding of how a plume expands, migrates, and changes chemically due to changing hydrologic conditions. Cozzarelli et al. (2011) identified specific conductance, chloride, tritium, and the isotopic composition of water as useful tracers of the leachate plume at the Norman Landfill. Other investigators have demonstrated the value of using non-reactive tracers such as chloride to study variability in plume movement on a time scale of several years (Freyberg 1986); geophysical approaches such as electrical resistivity tomography (Singha and Gorelick 2005) have been used to track contaminant plumes.

In this paper, we use horizontal patterns of chloride concentration, specific conductance measurements, and historical aerial photos and maps to quantify plume extent over time in order to meet our objective of understanding the dynamics of spatial and temporal migration of the leachate plume at the Norman Landfill at the time scale of years to decades. Previously, Arora et al. (2013) used wavelet analyses to study the connection between solutes in the plume and hydrologic variables such as water table elevation and precipitation on the time scale of months to years. In addition, we evaluate the effect of changing annual precipitation patterns on plume concentration using monitoring wells screened in the landfill and monitoring wells in the downgradient plume. The approach to quantifying spatial and temporal migration of the landfill leachate plume and the analysis of chemical variability related to changing precipitation amounts during wet and dry periods may be transferrable to tens of thousands of closed or abandoned landfills throughout the U.S. and worldwide.

1.1 Site Description and Hydrogeologic Characteristics

The Norman landfill is a closed municipal solid-waste landfill south of the city of Norman built on alluvial deposits of the Canadian River in central Oklahoma, USA (Fig. 1). The landfill does not have a liner or leachate-collection system and leachate seeps into groundwater in the underlying alluvial aquifer, forming a leachate plume. The U.S. Geological Survey (USGS) began a multi-disciplinary investigation of this landfill in 1994, as part of the Toxic Substances Hydrology Program (http://toxics.usgs.gov/). Scientists from the

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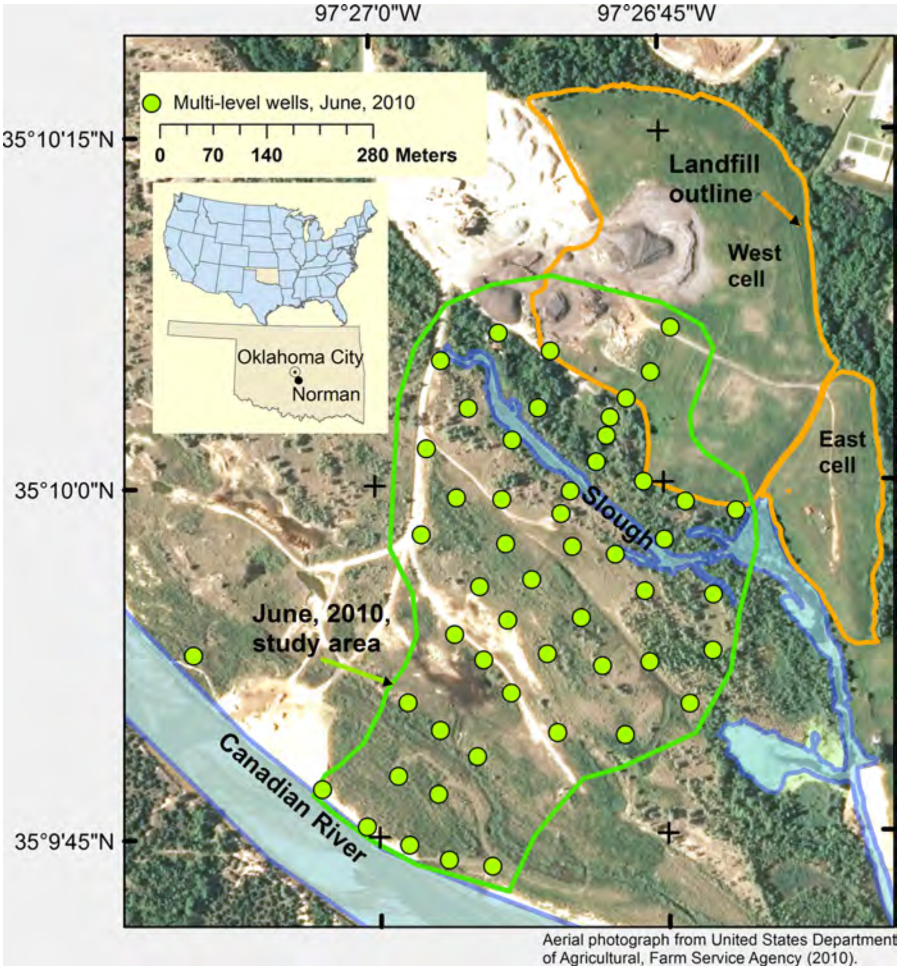

Aerial photograph from United States Department of Agricultural, Farm Service Agency (2010).

Fig. 1 Location of study area and monitoring well locations

USGS, other Federal agencies, and numerous universities have installed a large network of groundwater-sampling devices and instruments to investigate chemical, biological, and hydrologic processes in groundwater and surface water affected by the landfill leachate (http://ok.water.usgs.gov/projects/norlan/pubs.html).

The landfill began as an open dump in the early 1900s but became a sanitary landfill as regulatory controls increased in the 1960s through the 1980s. The landfill contains predominantly residential and commercial solid waste, with some reports indicating hazardous-waste disposal (Dixon 1992). In response to the passage of more stringent regulations in Subtitle D of the Resource Conservation and Recovery Act (RCRA), the landfill was closed in 1985, capped with local clay and silty sand, and sprigged with grassy vegetation. The capped landfill includes two cells, the east cell and the west cell, with the west cell the focus of most studies at this site (Fig. 1). The combined cells include 186,000 square meters (m^2) and rise 12 to 15 meters (m) above the alluvium. The total mass of buried waste has been estimated at 2.6 million tons (Dixon 1992).

The landfill adjoins the Canadian River flood plain and is about 600 m northeast of the river. The flood plain is relatively flat, with low sand dunes vegetated with small willow and cottonwood trees, shrubs, and native grasses. Average annual precipitation at the site is approximately 96 centimeters per year (cm/y) (Scholl et al. 2004). The water table in the Canadian River alluvium fluctuates in response to rainfall and seasonal evapotranspiration and has typically been less than 2 m below land surface near the landfill (Scholl et al. 2004). May and June typically have the most rainfall, with a secondary maximum in September and October (Jaeschke et al. 2011). Recharge estimated using chemical and physical methods averaged approximately 0.55 meters per year (m/y) (Scholl et al. 2004). A shallow stream with ponded wetland areas caused by beaver dams (subsequently referred to in this paper as the slough) has an average depth of about 0.75 m and runs parallel to and about 100 m from the southern edge of the landfill (Masoner et al. 2008) (Fig. 1). The slough serves both as a source and a sink for materials transported into the surficial alluvial aquifer (Eganhouse et al. 2001; Báez-Cazull et al. 2007; Lorah et al. 2009; Mendoza-Sanchez et al. 2013). The potentiometric-surface map prepared by Scholl and Christenson (1998), after the migration of the river channel, showed that regional groundwater flow was generally south from the landfill and under the slough toward the river.

The Canadian River alluvium that underlies the landfill is 10 to 12 m thick and consists of predominantly pale red, fine-to-medium-grained sand with interbedded, discontinuous layers of red-brown clayey silt and gravel. A high hydraulic conductivity layer containing coarse sand and gravel is near the base of the alluvium (Collins 2001). Low-permeability shale and siltstone in the Hennessey Group of Permian age act as a boundary to vertical groundwater flow beneath the alluvium. Sand layers of the alluvium are composed of quartz, illite/smectite clay minerals, feldspars, and minor calcite and dolomite; the mineralogy of the mud layer is similar but with greater amounts of clays that include illite/smectite, smectite, kaolinite, and chlorite (Breit et al. 2005). Hydraulic conductivity of this alluvium (excluding clay layers), which was measured by slug tests, ranged from 8.4×10^{-7} to 2.8×10^{-4} m/s, with a median value of 6.6×10^{-5} m/s; geometric mean 6.2×10^{-5} m/s (Scholl and Christenson 1998).

2 Monitoring Well Network

The monitoring well network at the site consisted of two types of multi-level well clusters, termed MLS for multi-level sampler, and PD for plume delineation. Each monitoring well had seven well screens that were set at the base of the alluvium and extended upward in 1.5 to 2.0 m increments to the water table.

The MLS wells were set along transects parallel to the groundwater-flow lines in which extensive geochemical studies were conducted (Cozzarelli et al. 2011). MLS wells were constructed out of 1.9-cm polyvinyl chloride (PVC) pipe. Each MLS well cluster had seven separate wells (1–7, with MLS-7 the deepest and MLS-1 the shallowest) with screens that were 12 cm long with 0.3-millimeter (mm) milled slots. The MLS well screens were set at different depths to intersect geochemical zones in the leachate plume (Cozzarelli et al. 2011).

The PD wells were installed approximately 75 to 100 m apart in a gridded pattern to delineate and monitor the leachate plume. PD wells were constructed out of 1.9-cm PVC pipe and 0.64-cm polyethylene tubing. Each PD well cluster had seven separate wells (1–7, with PD-7 the deepest and PD-1 the shallowest), with screens that were 12 cm long. The deepest well in the PD cluster was constructed using PVC pipe, and the other six wells were constructed using polyethylene tubing. The well screen for the deeper PVC well also was made of PVC with 0.3-mm milled slots. The well screens for the other six wells were made of stainless steel with 0.15-mm pore openings.

Water samples from wells were collected using a peristaltic pump and were then filtered through a 0.2-μm Nuclepore filter. Chloride concentrations were determined by ion-exchange chromatography with a Dionex 120 Ion Chromatograph with an ED50 electrochemical detector (Cozzarelli et al. 2011).

3 Methods of Plume Mapping

3.1 Mapping Spatial Extent of Leachate Plume in 1986

A substantial flood of the Canadian River on October 5, 1986 caused the active channel of the Canadian River to migrate from a position at the toe of the landfill to 600 m to the south and southwest (Fig. 2). Scanned and georeferenced historical aerial photos show the current (2012) river location and the river location in 1985 prior to the 1986 flood event that caused the river channel to migrate. Prior to the migration of the river, the leachate plume presumably would have extended 102 m and discharged into the active channel of the river. Based on the aerial photo, the spatial extent of the leachate plume in 1986 would have had an area of approximately 20,800 m^2. This likelihood of the plume extent encompassing the small area between the landfill and the river location in 1986 (Fig. 2.) is inferred retrospectively from knowledge that (1) the landfill is unlined with no leachate-collection system, (2) a previous study showed that the Canadian River is a discharge point for aquifer outflow at the Norman Landfill (Scholl and

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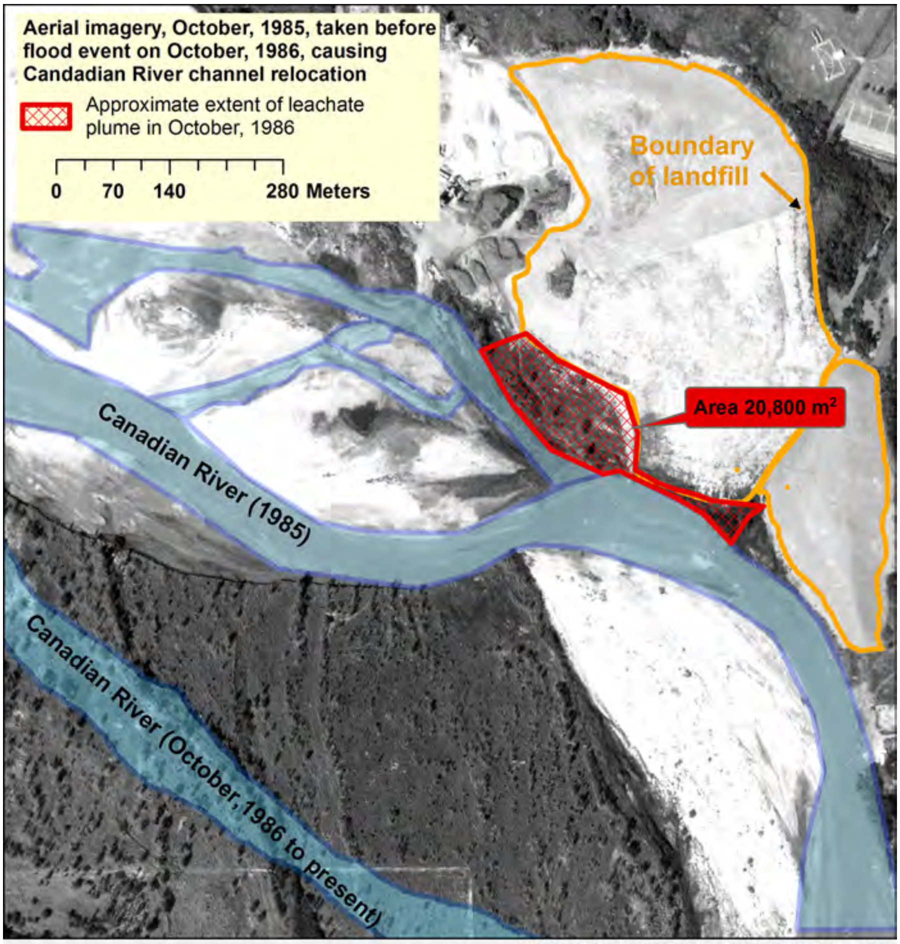

Aerial Photo from Ace Aerial Photography, Oklahoma City, Oklahoma.

Fig. 2 Location of Canadian River before and after flood event that relocated river channel 600 m south and southwest of the landfill, shown with extent approximate extent of leachate plume in 1986

Christenson 1998), (3) waste was disposed at its present location for over 50 years prior to closure (Dixon 1992), and (4) historical data collected during hundreds of measurements of alluvial properties described in previous studies at the site (Collins 2001; Becker 2002, and Breit et al. 2005).

3.2 Mapping Spatial Extent of Leachate Plume in 1996

To determine the approximate extent of the leachate plume in 1996, a geographic information system (GIS) was used to overlay maps (Figs. 12–15 in Becker 2002) that showed the horizontal and vertical distribution of specific conductance measurements made in 1995, 1996, and 1997 which were used to map areas in the alluvium affected by the plume. Additional point measurements of specific conductance measured in 1996 by a study described in Scholl and Christenson (1998) were included in GIS analysis to determine the approximate extent of the leachate plume in 1996. Based on specific conductance values greater than or equal to 2000 micro Siemens per centimeter (μS/cm) measured in 1996 and data from previous studies (Cozzarelli et al. 2011; Breit et al. 2005; Becker 2002; Collins 2001, and Scholl and Christenson 1998) of aquifer chemistry, plume geometry, and groundwater-flow direction, the approximate extent of the leachate plume in 1996 would have been about 92,200 m^2 (Fig. 3). The downgradient edge of the leachate plume would have migrated 366 m south and southwest toward

Fig. 3 Spatial extent of leachate plume in 1986, 1996, and 2010

the Canadian River over the 10-year interval from 1986 to 1996.

3.3 Mapping the Spatial Extent of Leachate Plume in 2010

Background chloride (Cl^-) concentrations have been well defined in the study area and ranged from 29 to 172 milligrams per liter (mg/L) from 1997 through 2008 (Table 1 in Cozzarelli et al. 2011). The 2010 Cl^- plume was delineated using dissolved Cl^- measurements collected in June 2010, from 52 multi-level wells with screens that represented top, middle, and bottom layers in the alluvium. GIS and inverse-distance weighting techniques were used to interpolate surface grids of Cl^- concentration for a 10-m cell size for top, middle, and bottom layers in the alluvium (Fig. 4a–c). Cl^- concentrations greater than or equal to 200 mg/L were used to designate areas in the alluvium affected by the plume. The top layer is defined as 0.5 to 1.5 m below the water table, the middle layer is 5 to 7 m below the water table, and the bottom layer is 11 to 12 m below the water table at the base of the alluvium.

GIS and inverse-distance weighting techniques also were used to interpolate a surface grid of maximum Cl^- concentrations to map the spatial extent of the leachate plume in June 2010 (Fig. 4a–c). The maximum Cl^- concentration for each multi-level well commonly occurred in the bottom layer. The only exception to this relation was between the landfill and the slough, near wells MLS35, 36, 37, 38, and 43 (Fig. 4a–c) where the vertical center of the leachate plume had not sunk to the base of alluvium. Using the maximum Cl^- value allowed delineation of the concentrated areas of the plume as it sank while migrating downgradient from the landfill into more permeable parts of the alluvium as

Table 1 Characteristics for the horizontal expansion of the leachate plume in 1986, 1996, and 2010

From date	To date	Area (m^2)	Pexp.[a] (m^2)	Pexp.[a] (days)	Pexp.[a] (years)	Pexp.[a] (rate m^2/y)	Pexp.[a] (rate m^2/day)	Percent increase in area[b]
	10/5/1986	20,800						
10/5/1986	1/1/1996	92,200	71,400	3326	9.1	7850	21.5	343
1/1/1996	6/10/2010	203,400	111,200	5199	14.2	7830	21.4	121
10/5/1986	6/10/2010	203,400	182,600	8525	23.4	7800	21.4	878

[a] Plume expansion

[b] Percent increase=Pexp./initial plume area × 100

described in Collins (2001). Based on maximum Cl^- concentrations greater than or equal to 200 mg/L, the spatial extent of the leachate plume in 2010 was approximately 203,400 m^2 and with the plume having migrated 223 m further south and southwest since 1996 to where it would have discharged into the Canadian River flow system (Figs. 3 and 4d).

4 Results and Discussion

4.1 Heterogeneous Vertical Distribution of Plume

Substantial differences were observed in June 2010 in the spatial distribution of the plume at different depths in the contaminated alluvium downgradient from the landfill. The mapped area of Cl^- concentration greater than or equal to 200 mg/L was 95,400 m^2 in the top layer, 142,360 m^2 in the middle layer, and 203,400 m^2 in the bottom layer. The distribution of Cl^- in the top layer of the alluvium near the water table (Fig. 4a) showed localized areas of high Cl^- concentrations ranging from 400 to 600 mg/L near the landfill cell at MLS40 and MLS41. Other localized areas of high Cl^- concentration in the top layer of the alluvium were measured in downgradient wells PD141, PD155, and in PD163, which is near the river. This top layer of the plume appeared shortened or truncated by interaction with uncontaminated water near the water table and surface water from the slough, because intersecting downgradient wells PD143, MLS88, PD153, and wells between the landfill and the slough (MLS36, for example) had Cl^- concentrations less than 200 mg/L.

Cl^- concentrations in the middle layer of the alluvium were greater and more laterally extensive than in the top layer; with concentrations greater than 600 mg/L being measured (Fig. 4b). The mapped area of Cl^- concentration that exceeded 200 mg/L increased from 95,400 m^2 in the top layer of the alluvium to 142,360 m^2 in the middle layer of the alluvium, an increase of 49.2 %. The mapped area of Cl^- concentration that exceeded 400 mg/L more than tripled from 27,450 m^2 in the top layer to 84,400 m^2 in the middle layer, an increase of 207 %. Localized areas of Cl^- concentrations greater than 600 mg/L were measured in wells MLS35, MLS55, PD137, PD138, and PD153; the lateral width of the plume was 210 m midway between the landfill and the river. The Cl^- plume in the middle layer of the alluvium was not as notably truncated as the top layer between the landfill and the slough. Water with lesser Cl^- concentrations in the middle layer appeared to dilute and truncate the plume between PD155 and wells near the river (PD162, for example). The wells near the river are assumed to be intersecting the plume in the middle of the alluvium because water samples had Cl^- concentrations >400 mg/L whereas background wells near the slough and river (PD132 and RBG2) had Cl^- concentrations of 29.2 and 14.7 mg/L, respectively (Fig. 4b). Historical Cl^- concentration in the river had been 124 mg/L (Table 2 in Schlottmann 2001).

The Cl^- plume in the bottom layer (Fig. 4c) of the alluvium was more laterally extensive than in the middle layer, with a width of about 340 m midway between the landfill and the river. This increase in width with depth indicates that the plume had migrated downward into the more permeable sediments at the base of the alluvium and has expanded laterally once in contact with the bedrock confining layer. The mapped area of Cl^- concentration exceeding 200 mg/L increased from 142,360 m^2 in the middle layer of the alluvium to 203,400 m^2 in the bottom layer, an increase of 42.9 %. The mapped area of Cl^- concentration exceeding 400 mg/L was similar in the middle and bottom layers of the alluvium at 84,400 m^2 and 84,370 m^2,

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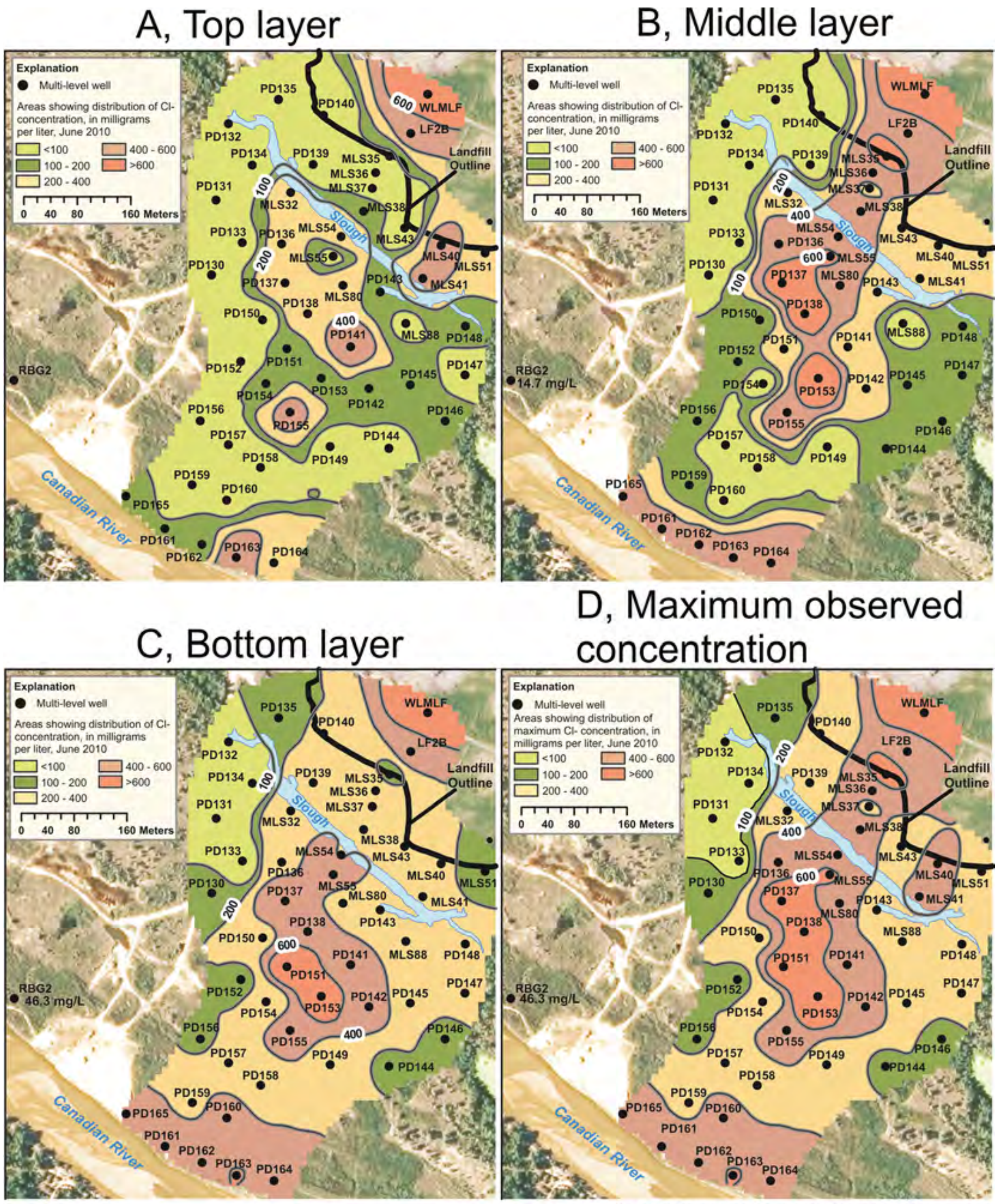

Aerial photograph from United States Department of Agricultural, Farm Service Agency (2010).

Fig. 4 Horizontal distribution of chloride concentrations (mg/L as Cl$^-$) downgradient from landfill in June 2010, for **a** top layer of alluvium, **b** middle layer of alluvium, **c** bottom layer of alluvium, and **d** maximum observed concentrations

respectively. Although the net area of Cl$^-$ concentration greater than 400 mg/L for the middle and bottom layers was similar, some locations between MLS35 and MLS54 (Fig. 4b and c) decreased in area and others increased in area. The changes in area in the bottom and middle layers are attributed to leachate discharging from beneath the landfill that had not yet sank to the base of the alluvium (Fig. 4a in Cozzarelli et al. 2011).

Wells near the river (at PD162, for example) that had Cl$^-$ concentrations ranging from 400 to 600 mg/L in the bottom layer could indicate the presence of a concentrated plume dipping beneath the deepest well screens

Table 2 Characteristics for the linear movement of the leading edge of leachate plume in 1986, 1996, and 2010

From date	To date	Pdis.[a] (length)	Pdis.[a] (days)	Pdis.[a] (years)	V[b] (m/y)	V[c] (cm/day)
	10/5/1986	102				
10/5/1986	1/1/1996	366	3326	9.1	40.2[d]	11.0[d]
1/1/1996	8/16/2001[d]	223	2025[d]	5.5[d]	40.2	11.0
1/1/1996	6/10/2010	223	5199	14.2	15.7[d]	4.3[d]
10/5/1986	6/10/2010	691	8525	23.4	29.5[d]	8.1[d]

[a] Travel distance of leading edge of plume

[b] Linear plume velocity (meters per year)

[c] Linear plume velocity (centimeters per day)

[d] Shaded in gray signifies calculated values

set at PD157, PD158, and PD159 before seeping upward and discharging into the river flow system (Fig. 4c). Another possible reason for the higher concentrated plume in wells near the river could be intersecting pulses of leachate with elevated Cl^- concentration released from the landfill into the groundwater-flow system during wet or dry periods. Such pulses may have caused the localized areas (hot spots) of increasing then decreasing Cl^- concentrations along groundwater-flow lines between the landfill and the river (Fig. 5) as seen in data from wells PD151 and PD153, where Cl^- concentrations greater than 600 mg/L were measured (Fig. 4c). The wells near the river are assumed to be affected by landfill leachate because water samples from those wells had Cl^- concentrations >400 mg/L; in contrast, water sampled from background wells (PD132 and RBG2) had Cl^- concentrations of 40.1 and 46.3 mg/L, respectively (Fig. 4c).

4.2 Temporal Migration of Leachate Plume

Lateral movement of the Canadian River channel in 1986 substantially increased the area of alluvium available for migration of the leachate plume. Over a 23.4-year period from 1986 to 2010, the horizontal plume area expanded from 20,800 m^2 in 1986 to 203,400 m^2 in 2010, an increase of 878 % or 182,600 m^2 (Table 1 and Fig. 3). From 1986 to 1996 the plume area expanded by 71,400 m^2, an increase of 343 %. From 1996 to 2010, the plume area expanded by 111,200 m^2, an increase of 121 %. The rate of plume expansion from 1986 to 2010 was 7800 m^2/y. The rate of expansion from 1986 to 1996 was similar to the rate from 1996 to 2010, 7850 m^2/y and 7830 m^2/y, respectively.

The June 2010 potentiometric-surface map (Fig. 5) shows a groundwater-flow line starting at the base of the landfill and extending to the edge of the river. The distances of individual groundwater flow-line segments that spanned the extent of the leachate plume in 1986, 1996, and 2010 were 102, 366, and 223 m, respectively (Fig. 3). A linear plume velocity was calculated by dividing the distance that the downgradient plume edge traveled by the elapsed time during the plume migration intervals (Table 2). From 1986 to 1996, the leading edge of the plume traveled 366 m and the calculated linear plume velocity was 40.2 m/y. The distance between the leading edge of the plume and the river in 1996 was 223 m. A linear groundwater velocity of 15.7 m/y was calculated based on a travel distance of 223 m and a time interval of 14.2 years from 1996 to 2010. This calculated velocity of 15.7 m/y during the 1996 to 2010 time interval is much less than the 40.2 m/y velocity estimated for the 1986 to 1996 time interval and indicates that the plume could have begun discharging to the river sometime before 2010. A plume arrival time of 5.5 years was calculated by dividing the 223 m travel distance by the linear velocity of 40.2 m/y calculated from the 1986 to 1996 time interval. Based on the calculated plume arrival time of 5.5 years from 1996, the leachate plume would have intersected and discharged to the Canadian River flow system during the middle of 2001 (Table 2).

A range of groundwater-seepage velocities were calculated using a measured porosity fraction of 0.4 (Scholl et al. 2004) and minimum, median, and maximum hydraulic conductivities (Scholl and Christenson 1998) and gradients (Cozzarelli et al. 2011) were calculated for the area between the landfill and the river (Table 3). Groundwater-seepage

Exhibit E

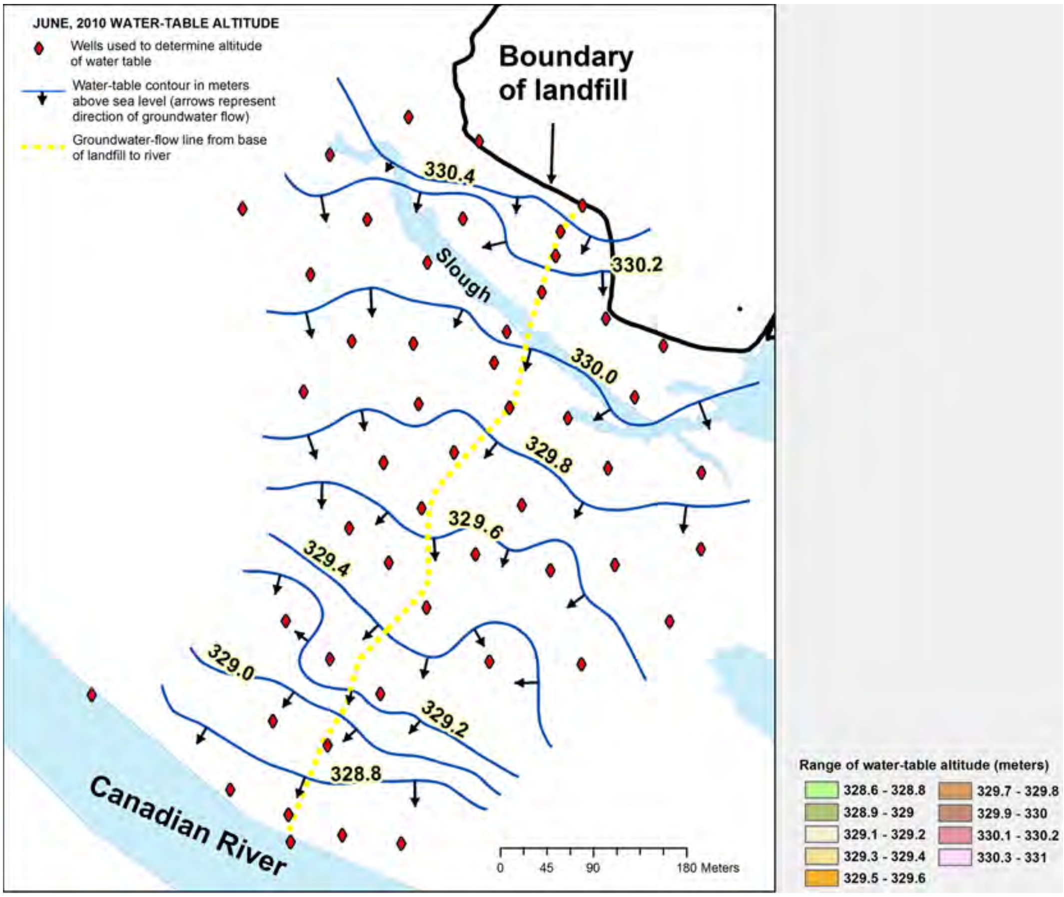

Fig. 5 Localized areas (hot spots) of increasing then decreasing Cl⁻ concentrations along groundwater-flow lines between the landfill and the river

velocities ranged from 4.5×10^{-2} m/y to 161 m/y (Table 3). A groundwater-seepage velocity of 55.2 m/y, which was calculated using a median hydraulic gradient and a maximum hydraulic conductivity, seems appropriate when delineating the leading edge of a non-reactive and soluble Cl^- plume. Conceptual models of permeability structure consistently show that the plume sinks downward into multiple stacked sequences of high permeability layers consisting of coarse sand and gravel deeper and at the base of the alluvium (Collins. 2001; Eganhouse et al. 2001; Cozzarelli et al. 2011). The linear plume velocity of 40.2 m/y calculated for the 1986 to 1996 interval is similar to the 55.2 m/y groundwater-seepage velocity calculated using median hydraulic gradient and maximum hydraulic conductivity measured at the site. Because of the high variability of hydraulic conductivity measured in the alluvium (Scholl and Christenson 1998), a linear plume velocity of 40.2 m/y was used to calculate a plume-scale hydraulic conductivity value that incorporated the volumetric average of hydraulic conductivity in alluvium, preferential groundwater flow, and the hydrogeological conditions in the alluvium. The calculated plume-scale hydraulic conductivity based on the linear plume velocity, porosity fraction of 0.4, and minimum, median, and maximum hydraulic gradients ranged from 7.0×10^{-5} to 7.5×10^{-4} m/s, with a median value of 2.0×10^{-4} m/s. This range of plume-scale hydraulic conductivity was substantially less than the range of field-measured hydraulic conductivity (8.4×10^{-7} to 2.8×10^{-4} m/s). There is no universally reliable method for determination of effective hydraulic conductivity from field measurements determined in sand-clay alluvium, with a common method being to use the median of field-measured hydraulic conductivity (Scholl 2000). At the North Bay Landfill in

Table 3 Range of groundwater-seepage velocities (m/y) for the area between the landfill and the Canadian River, calculated using minimum, median, and maximum hydraulic conductivities (*k*, meters per second) and gradients (dh/dl) and a porosity fraction of 0.4

	Minimum *k* (8.4×10^{-7})	Median *k* (6.6×10^{-5})	Maximum *k* (2.8×10^{-4})
Minimum dh/dl (6.8×10^{-4})	4.5×10^{-2}	3.5	15.0
Median dh/dl (3.1×10^{-3})	1.7×10^{-1}	13.0	55.2
Maximum dh/dl (7.3×10^{-3})	4.8×10^{-1}	38.0	161.1

Ontario Canada, more complex methods that included 3-D stochastic theory were used to calculate effective hydraulic conductivity that was similar to the geometric mean of measured hydraulic conductivity from cores (Sudicky et al. 2010). The median calculated plume-scale hydraulic conductivity (2.0×10^{-4} m/s) calculated in our study compared to the 95th percentile of the field-measured hydraulic conductivity (2.053×10^{-4} m/s) in Scholl and Christenson (1998). This comparison indicates when rates of plume-scale spreading, migration, and biodegradation are needed; the upper percentiles of field-measured hydraulic conductivity should be considered in heterogeneous alluvial aquifers.

4.3 Changing Annual Precipitation Patterns and Effect on Plume Migration and Concentration

The leachate plume is maintained by recharge that infiltrates through the landfill and moves toward downgradient discharge areas as part of the regional groundwater-flow system. The duration of below-normal precipitation (dry) or above-normal precipitation (wet) periods may have affected migration and concentration of chemical constituents in the leachate plume.

To determine dry and wet periods, monthly precipitation data were obtained from the NOAA NORMAN 3SSE site, 35.18 N, 97.43 W, and a normal precipitation period was defined as the mean of annual precipitation for the period from 1980 to 2011 (Oklahoma Climatological Survey 2011). Departures from normal precipitation were calculated to determine intervals of below-normal and above-normal precipitation. Mean-annual Cl^- concentrations were calculated from monthly water-quality samples collected in 2000 to 2011 from water-level monitoring at the landfill (WLMLF) well and from 1997 to 2010 from well middle layer in MLS35. The WLMLF and MLS35 wells were installed in the landfill and at the southern edge of the landfill (Fig. 4) along a defined flow path described in Cozzarelli et al. (2011). Mean-annual Cl^- concentrations were calculated and graphed with departures from normal precipitation to show patterns of changing Cl^- concentrations with mean-annual precipitation (Fig. 6). Although other investigators have shown that leachate strength decreases over time (Thomsen et al. 2012) at the Norman Landfill (Cozzarelli et al. 2011), showed that chloride concentrations did not decrease over time between 2000 and 2008. It is possible that a pattern of long-term trend of decreasing chloride concentrations in leachate might emerge if a longer data set were available.

Mean-annual Cl^- concentrations in water samples collected from well WLMLF increased during dry periods and decreased during wet periods. The Pearson's chi-square test was done to test for independence between two nominal variables determined from Cl^- concentrations during wet and dry periods (Pearson 1900). A nominal variable was determined that represents a 2-year increasing or decreasing trend for mean-annual Cl^- concentration. Mean-annual Cl^- concentration minus the previous mean-annual Cl^- concentration results in a positive or negative difference. A positive difference indicates that the current mean-annual Cl^- concentration was greater than the year before, an indication of a 2-year increasing trend in Cl^- concentration. A negative difference indicates a 2-year decreasing trend in Cl^- concentration. Positive and negative differences were coded to a nominal variable, "increasing" with a positive difference and "decreasing" with a negative response. Results from a contingency table indicated that the counts and proportions of increasing and decreasing responses were not the same during wet and dry periods (chi squared=5.1857, degrees of freedom=1, *p* value=0.0228). Increasing responses were significantly more abundant during dry periods than during wet periods, indicating a significantly greater mean-annual Cl^- concentration in water samples collected from well WLMLF during dry periods than during wet periods.

That pattern observed within the landfill at well WLMLF was not observed in water samples collected from the downgradient MLS35 well. Mean-annual

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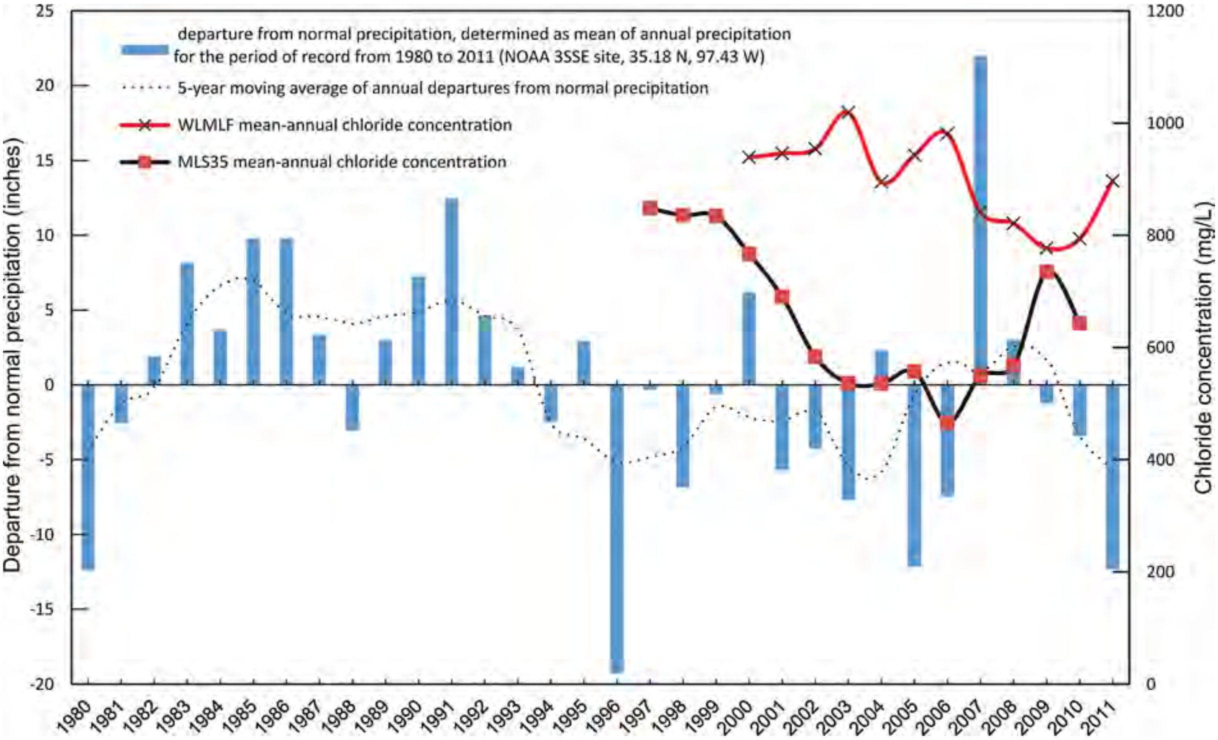

Fig. 6 Departure from mean-annual precipitation from 1980 to 2011 shown with mean-annual chloride concentrations for wells WLMLF and middle layer of MLS35 (locations shown on Fig. 4)

Cl^- concentrations generally decreased during dry periods and increased during wet periods (Fig. 6). Mean-annual Cl^- concentrations decreased in water sampled from well MLS35 during the dry period from 848 mg/L in 1997 to 466 mg/L in 2006. A wet period occurred in 2007 and 2008 with departures from normal precipitation of +22 and +3.0 in., respectively. Mean-annual Cl^- concentrations in water sampled from well MLS35 increased to 550 mg/L in 2007 and 568 mg/L in 2008. From 2006 to 2008, Cl^- concentrations increased by 22 % during the wet period. Cl^- concentrations continued to increase in 2009, with a mean-annual concentration of 735 mg/L, even though precipitation in 2009 was slightly below normal. This continued to increase in Cl^- concentration in 2009 provided evidence of a slight lag effect for leachate migration from the landfill. The lag effect is expected because well MLS35 is 100 m downgradient from well WLMLF, which is completed in the center of the landfill. A dry period started in 2009 and continued to 2012; mean-annual chloride concentrations in water sampled from well MLS35 decreased from 735 to 644 mg/L in 2010 (Fig. 6). Although mean-annual chloride concentrations in water sampled from well MLS35 decreased during dry periods and increased during wet periods, results from a contingency table indicated no significant difference (chi squared=0.6771, degrees of freedom=1, p value=0.4106) between increasing and decreasing responses for mean-annual Cl^- concentrations during wet and dry periods. This lack of significant difference in Cl^- concentrations in water sampled from well MLS35 may be due to lag effects like those observed in 2009 when Cl^- concentration continued to slightly increase during the start of a dry period. Previously, Harris et al. (1982) showed that leachate concentration in groundwater downgradient from landfills is positively correlated with high rainfall amounts.

Our findings of changing precipitation patterns affecting variability in leachate concentration in landfills are in agreement with observations reported in the literature. For example, an inverse correlation ($p<0.05$) was shown to exist between chemical properties and precipitation amounts in two landfills located in Tsuen Wan and Sai Kung, China (Chu et al. 1994); during wet periods, less concentrated leachate was generated; during dry periods, leachate concentration increased. In a study of temporal changes in leachate chemistry from a landfill in Florida, significant short-term variations in leachate concentration existed that were correlated to precipitation rather than fundamental changes to leachate composition (Statom et al. 2004). The study in Florida was unique in that data were collected before and after landfill closure. The Florida study showed that prior to capping the landfill, a positive correlation (leachate concentration increased during wet periods) existed between Cl^- concentration and precipitation, but after capping of the landfill, an inverse correlation (leachate concentration decreased during wet periods) between Cl^- and precipitation was measured.

The pattern of changing Cl^- concentrations during wet and dry periods contributes to understanding the influence of climate variability on plume concentration, composition, and migration, and provides knowledge that could affect or aid the design of sampling networks for monitoring the spatial and temporal migration of plumes. Recent research by Andrews et al. (2011) and Vidon et al. (2010) have shown hot spots and moments to be an important component of reactive-plume concentrations in alluvial settings, yet predictions of hot spots and moments remain uncertain because of their high spatial and temporal variability. The pattern of changing Cl^- concentrations along a defined flow path during wet and dry periods described in this study contributes to understanding the spatial and temporal variability of hot spots and moments from pulse releases from plume sources during wet periods. Such pulses may have caused the localized areas (hot spots) of increasing then decreasing Cl^- concentrations between the landfill and the river as described in this study.

5 Conclusions

Understanding the dynamics of leachate movement in space and time is essential for monitoring, planning and management, and assessment of risk to groundwater and surface-water resources. Spatial and temporal analysis of the Norman Landfill leachate plume showed that over a 23.4-year period, the plume area increased at a rate of 7800 m^2/y and expanded by 878 %. The increase in plume area with depth indicates the complex layering of low-permeable sediments throughout the alluvium does not limit plume migration into more permeable layers deeper in the alluvium. Analyses of field-measured and calculated plume-scale hydraulic conductivity distributions indicate that the upper percentile of field-measured values should be considered to evaluate rates of plume-scale migration, spreading, and biodegradation in heterogeneous alluvial aquifers, such as the Norman Landfill leachate plume.

Changing annual precipitation patterns show variability in leachate concentration in groundwater from the landfill and downgradient from the landfill. Cl^- concentrations in the landfill increased during dry periods and decreased during wet periods. The opposite condition was measured in groundwater sampled downgradient from the landfill; Cl^- concentrations downgradient from the landfill decreased during dry periods and increased during wet periods. This pattern of changing Cl^- concentrations in response to wet and dry periods indicates that the landfill retains, absorbs, or concentrates leachate during dry periods and discharges less concentrated leachate to the downgradient alluvium. During wet periods, leachate in the landfill is diluted but higher concentrated leachate seeps into the downgradient alluvium.

Unlined or leaky landfills sited in alluvial aquifers along river systems are likely to have different rates of plume expansion and migration than those measured at the Norman Landfill site due to differences in aquifer permeabilities and heterogeneity in hydrologic dynamics. At sites where landfill leachate plumes are in dynamic connection with a changing fluvial environment, understanding these connections, such as the pattern between variable precipitation amounts (i.e., during wet and dry periods) and changing leachate concentration in the landfill and in the downgradient alluvium, can provide increased understanding about the influence of climate variability on plume behavior and migration potential at other non-monitored landfill sites. To evaluate potential risk to environmental receptors, a thorough evaluation of the chemical variability of leachate plumes and a better understanding of the complex hydrogeologic and geochemical dynamics would be needed.

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descriptive purposes only and does not imply endorsement by the U.S. Government.

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Exhibit E

Migration of Landfill Leachate through Glacial Tills

by Keros Cartwright, Robert A. Griffin, and Robert H. Gilkeson[a]

ABSTRACT

To evaluate the potential of natural clay minerals for attenuating and preventing the pollution of water resources by landfill leachates, leachate was collected by anaerobic techniques from the 15-year old Du Page County sanitary landfill near Chicago, Illinois, and was passed through 44 laboratory columns that contained various mixtures of calcium-saturated clays and washed quartz sand. The columns were constructed to simulate slow, saturated, anaerobic flow, and manometers were placed at five locations in each column to measure any changes in hydraulic conductivity. Leachate was run through the columns for periods ranging from 6 to 10 months, during which time effluents were collected periodically and analyzed for 21 chemical constituents. The columns were then sectioned and the clays analyzed to determine the vertical distribution of the chemical constituents in each column. Sterilized landfill leachate was used in a duplicate set of columns to determine the effects of gross biological activity.

Chloride and certain organic compounds were relatively unattenuated by passage through the clay columns; monovalent cations, such as Na, K, and NH_4, were moderately attenuated; and heavy metals, such as Pb, Cd, and Zn, were attenuated by even small amounts of clay. Concentrations of Ca and Fe were much higher in the column effluents than they were in the original leachate. The increase in Ca in the column effluents was due to cation exchange with ions in the refuse leachate. The Fe increase probably resulted from reduction of the oxidized Fe on clay surfaces by anaerobic refuse leachate to more soluble reduced Fe.

Both biologically active and sterilized leachate reduced the hydraulic conductivity of the clay-mixture columns during the experiment. The active leachate reduced the hydraulic conductivity to a much greater degree than the sterile leachate.

Results of the laboratory data were compared with field data from the Du Page County sanitary landfill and from other existing landfills where detailed data are available. The field data show a "hardness halo" corresponding to the Ca release in the columns. The relative attenuation rates of some of the ions were also confirmed by the field data. The change in hydraulic conductivity was not as clearly shown.

Ion exchange capacity, hydraulic conductivity, and buffering capacity of the earth materials were all shown to be important in assessing the potential of landfills for water pollution.

INTRODUCTION

Land disposal of solid wastes, both domestic and industrial, has been practiced for many years, and the open burning dump has gradually been replaced by the sanitary landfill over the past 30 years. Garland and Mosher (1975) have estimated that there are about 14,000 landfills in the United States; Clark (1975) estimated that there are more than 2,000 known disposal sites in Illinois, although only about 240 are legally operating at this time. A reduction in the number of operating landfills is typical throughout the United States. This reduction in the number of disposal sites has effectively concentrated increasing volumes of refuse at fewer and fewer sites, especially near the urban centers.

There are only three media into which man can place his ever-increasing volume of waste—air, water, and land. The increasingly strict regulations governing the discharge of pollutants to the air and water

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[a] Illinois State Geological Survey, Urbana, Illinois 61801.

Discussion open until December 1, 1977.

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have placed new emphasis on land disposal. This restriction of waste discharge to one medium only serves to increase the stress upon that medium. Since there are interchanges between all the media, land disposal of waste ultimately discharges some of the waste products back to the water or air.

The environmental effects of land disposal are difficult to determine, inasmuch as the subsurface is complex and commonly insufficiently understood to monitor properly. The success of land disposal is judged primarily by the rate of return of the pollutants to the air or water; agricultural and biological scientists are just now beginning to study the uptake of some pollutants through biological systems.

There have been sufficient studies to show that leachate will form in sanitary landfills where there is enough moisture. This condition is met in all but the more arid regions of the nation. The pollutants thus leached from the refuse leave the site as a gas discharged to air or as a leachate discharged to the ground water or surface water. The migration of the pollutants in the subsurface is governed by geologic and hydraulic principles that have been delineated in a number of studies (for example, see Hughes *et al.*, 1971).

Most regulations in force today require either that refuse be placed in materials of sufficiently low hydraulic conductivity to prevent the leachate from entering a ground-water resource in quantities large enough to significantly degrade water quality, or that the disposal site be hydrologically controlled to prevent indiscriminant discharges of leachate. The low-conductivity material is usually a clayey material that either occurs there naturally or is placed there to prevent the escape of leachate that could cause ground-water pollution.

This paper reports some of the results of a laboratory study conducted at the Illinois State Geological Survey and supported in part by U.S. Environmental Protection Agency Contract 68-03-0211 (Cincinnati, Ohio). The purpose of the study was (a) to investigate and evaluate the attenuating properties of clay and the use of clay minerals as liners (natural or artificial) for sanitary landfills, and (b) to relate this laboratory work with the Geological Survey's ongoing program of field evaluation and research at sanitary landfill sites.

This paper relates two significant phenomena noted in the laboratory to field observations around sanitary landfills: The elution of large amounts of the calcium ion from the study columns (Griffin and Shimp, 1976) and the reductions in hydraulic conductivities that resulted from the introduction of leachate to the clay-sand mixtures. The applicability of laboratory studies to the complex field situation is necessary in order that the data may be used in designing the sanitary landfill. On the basis of these laboratory results, one can estimate the amounts of clay required to attenuate leachate as it passes through the clay liner. The results presented in this paper apply only to the leachate of the Old Du Page County landfill; the extent that these results may be generalized to other sites with leachate of different chemical composition is problematic.

EXPERIMENTAL

Laboratory Studies

The clays used in this study were kaolinite (1:1 lattice), montmorillonite (1:1 expanding lattice), and illite (2:1 nonexpanding lattice, mica type). These clay minerals were chosen for study because they are available in commercial quantities and it was felt that their compositions are more representative of natural materials used at landfills. The details of the clay mineralogy and chemistry and of the methods of study have been reported previously (Griffin and Shimp, 1976). The predominantly Ca-saturated $<2\ \mu m$ particle-size fraction of the three clays was then used in the column-leaching studies.

The leachate used in this study was collected from well MM63 at the Du Page County sanitary landfill near Chicago, Illinois. The site description and well location are given by Hughes *et al.* (1971). Details of the leachate collection, processing, and storage are described by Griffin and Shimp (1976). One drum was taken to the Argonne National Laboratories and sterilized by gamma-ray irradiation using a cobalt source that gave a dose of 3.36×10^6 rad at the center of the drum. The second drum was allowed to remain biologically active. Chemical analyses of both the sterilized and natural leachate used in the column-leaching study are given in Table 1.

The laboratory apparatus used in the study consisted of laboratory columns containing mixtures of clay minerals and washed quartz sand (Ottawa Silica Co.) through which leachate was passed (Figure 1). The columns and apparatus were constructed to simulate the slow (<2 pore volumes per month), saturated, anaerobic flow of leachate at the bottom of a landfill. More details of the column apparatus and design can be obtained from Griffin and Shimp (1975, 1976). The leachate was passed through the columns, and the effluents were collected in graduated cylinders for chemical analyses and the measurement of the flow rates.

Exhibit E

Table 1. Chemical Analyses of Landfill Leachate from Du Page County, Illinois

Analysis	Natural (ppm)	Sterilized (ppm)
	748.	744.
K	501.	491.
Ca	46.8	43.2
Mg	233.	230.
Cu	<0.1	<0.1
Zn	18.8	16.3
Pb	4.46	4.26
Cd	1.95	1.68
Ni	0.3	0.3
Hg	0.0008	0.37*
Cr	<0.10	<0.10
Fe	4.2	3.0
Mn	<0.1	<0.1
Al	<0.1	<0.1
NH_4	862.	773.
As	0.11	0.14
B	29.9	28.5
Si	14.9	15.0
Cl	3484.	3311.
SO_4	<0.01	<0.01
PO_4	<0.1	<0.1
COD	1340.	10,603.*
Organic acids	333.	290.
Carbonyls as acetophenone	57.6	90.1
Carbohydrates as dextrose	12.	11.
pH	6.9	7.2
Eh	+7 mv	+75 mv
E.C.	10.20 mmhos/cm	10.42 mmhos/cm

* Added during passage of sterilant gas.

SO_4 reduced to HS^-, H_2S

10,200 μmhos

The outflow tube was maintained above the top of the columns to ensure saturated flow. The level of the outflow tube was moved either up or down to maintain relatively constant flow rates throughout the experiment. The columns were constructed of two-inch acrylic tubing to which manometer outlets were fitted at five locations on the column. To simulate field conditions the leachate containers and columns were either painted black or masked with black tape; this blackening prevents growth of organisms such as algae or photosynthetic bacteria.

Except for the 32 percent and 64 percent montmorillonite-sand mixtures, which were packed in columns 30 cm deep, the clay minerals and sand were packed into columns 40 cm deep. The columns were packed to bulk densities within the range of densities of natural glacial tills (~1.8 g/cc; Manger, 1963). The sand grains were coated with the clays, according to the methods given by Grim and Cuthbert (1945), before packing. Table 2 lists some chemical and physical properties of the various columns. Field bulk densities were achieved, and the hydraulic conductivities for each particular clay content and bulk density agree with those given by Todd (1959) for natural materials The hydraulic conductivity (k) was computed using the relationship:

$$k = \frac{Q\,dL}{A\,dH}$$

where

Q = flow rate in cm^3/sec;
A = cross-sectional area of column in cm^2;
dL = length of the column in cm;
dH = head of water in cm (dL/dH = hydraulic gradient).

The experimental design used in the study is also given in Table 2, which gives the percentages, by weight, of clay mineral(s) in each column (to which pure quartz sand was added to total 100%). The experimental design includes 100 percent sand and a complete geometric progression of clay percentages from 2 percent to 64 percent of kaolinite and of montmorillonite. Since kaolinite and illite have very similar cation exchange and lattice expansion properties, a complete geometric array for illite was not included.

Leachate was passed through the columns for periods of time ranging from 6 to 10 months, depending on the hydraulic conductivity of the individual column. During this time, effluents from each column were collected periodically and

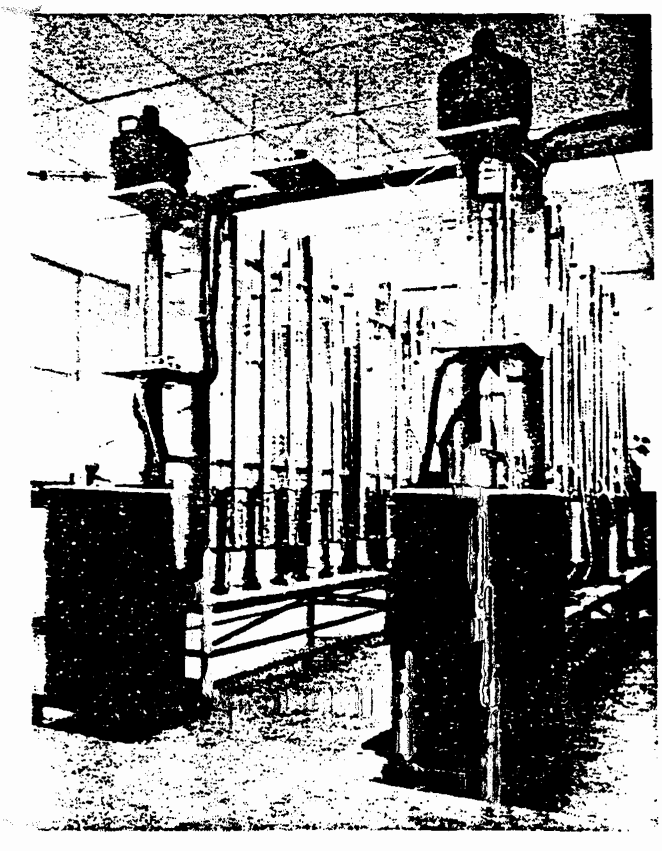

Fig. 1. The leaching apparatus. There are 44 columns controlled by two constant head inflow tanks and individually variable levels of outflow collection cylinders.

Table 2.

position
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32% M
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Table 2. Physical and Chemical Properties of Various Sand-Clay Columns

Composition of column	Cation exchange capacity (meq/100 g)		Bulk density (g/cc)		Initial hydraulic conductivity (k) (cm/sec)	
	Set A†	Set B†	Set A	Set B	Set A	Set B
100% sand	0.0	.1	1.71	1.71	$1.27 \cdot 10^{-3}$	$1.80 \cdot 10^{-3}$
Sand and						
2% M*	1.4	2.3	1.71	1.72	$9.45 \cdot 10^{-4}$	$7.93 \cdot 10^{-4}$
4% M	3.2	4.3	1.77	1.74	$4.34 \cdot 10^{-4}$	$3.47 \cdot 10^{-4}$
8% M	7.3	7.2	1.79	1.78	$4.70 \cdot 10^{-4}$	$2.61 \cdot 10^{-4}$
16% M	11.9	12.1	1.87	1.86	$1.22 \cdot 10^{-5}$	$1.44 \cdot 10^{-5}$
32% M	26.8	24.0	1.55	1.52	$1.27 \cdot 10^{-6}$	$2.17 \cdot 10^{-6}$
64% M	56.2	55.5	1.23	1.11	$3.05 \cdot 10^{-7}$	$6.83 \cdot 10^{-7}$
Sand and						
2% K*	0.7	0.4	1.68	1.70	$7.44 \cdot 10^{-4}$	$4.53 \cdot 10^{-4}$
4% K	1.1	0.8	1.76	1.74	$4.78 \cdot 10^{-5}$	$2.76 \cdot 10^{-5}$
8% K	1.5	1.4	1.80	1.77	$9.90 \cdot 10^{-4}$	$8.25 \cdot 10^{-4}$
16% K	1.8	2.5	1.87	1.90	$2.86 \cdot 10^{-5}$	$1.92 \cdot 10^{-4}$
32% K	3.8	3.4	1.66	1.55	$2.40 \cdot 10^{-6}$	$4.81 \cdot 10^{-6}$
64% K	9.6	8.5	1.22	1.32	$5.45 \cdot 10^{-7}$	$4.57 \cdot 10^{-7}$
Sand and						
4% I*	0.8	0.9	1.80	1.81	$8.17 \cdot 10^{-4}$	$7.16 \cdot 10^{-4}$
16% I	3.5	3.2	1.83	1.91	$2.68 \cdot 10^{-5}$	$2.19 \cdot 10^{-5}$

* M - montmorillonite, K - kaolinite, I - illite.
† Set A - natural leachate; set B - sterile leachate.

measurements were made for Na, K, Ca, Mg, Al, Zn, Pb, Cd, Hg, Fe, Mn, NH_4, B, Si, Cl, chemical oxygen demand (COD), Eh, pH, and hydraulic conductivity. Finally, after leaching of approximately 15 pore volumes was completed, the clay mineral columns were sectioned and the contents analyzed to determine the vertical distribution of chemical constituents in each column.

Duplicate sets of columns were used in the experiment; one set of columns was leached with natural effluent while the second set was leached with sterilized effluent. Sterilization was used to determine if gross biological activity would affect hydraulic conductivity of leachate through clay minerals used as liners. The results of the experiment were statistically analyzed using the students (paired) "t" test to determine whether there were significant differences in the attenuation of each chemical constituent between sterile and natural leachate, and between clay minerals. Linear regression and moving average analysis were also performed on the column effluent data to determine relationships between hydraulic conductivity, attenuation, and clay mineral properties.

RESULTS AND DISCUSSION

Ca Elution/Hardness Halo

Results of some analyses of calcium, iron, and manganese are shown in Figure 2 plotted as relative concentration versus pore fraction. Relative concentration is the ratio of the concentration of the effluent of the column divided by the concentration of the influent. Thus, the "breakthrough" point for a given element is where the concentration of effluent equals the concentration of influent and has a value of one. A pore volume of effluent is defined as the volume necessary to displace the volume of interstitial liquid in the pore spaces in the column. The pore fraction is then given as the cumulative volume of column effluent divided by the pore volume of the individual column (Griffin and Shimp, 1976).

A wide range of attenuation was observed for several of the elements in leachate as they passed through the various columns containing different percentages of clay. The amount of reduction in concentration of a given element as it passes through the columns is discussed by Griffin and Shimp (1975, 1976).

Figure 2 illustrates the negative attenuation, or elution, of Ca, Fe, and Mn from the columns containing 2 percent, 8 percent, and 16 percent

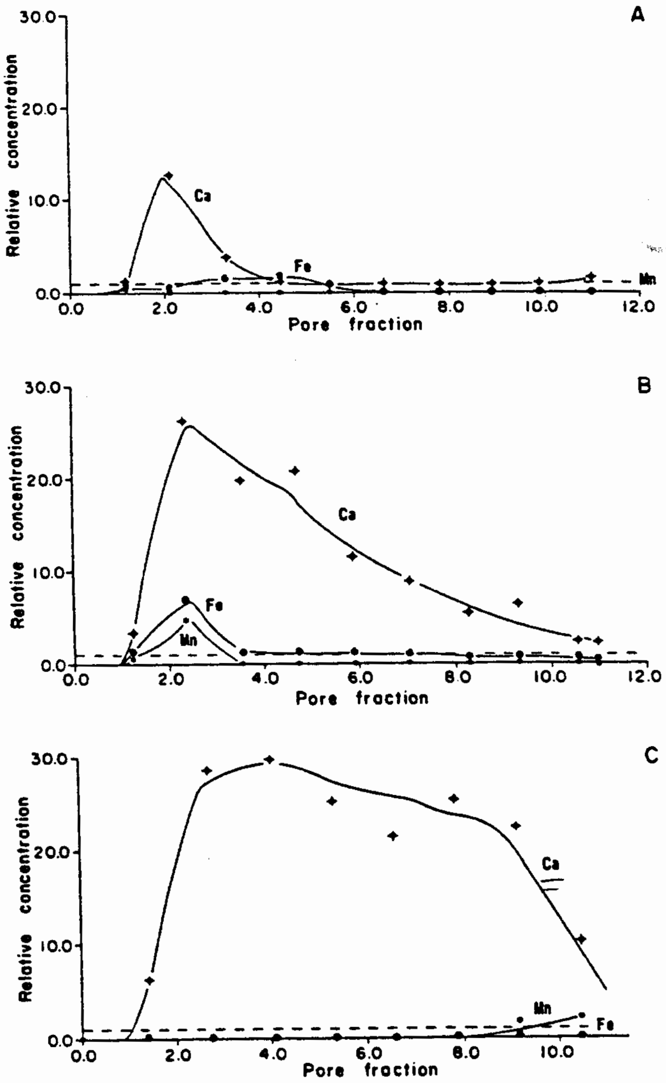

Fig. 2. Relative concentrations of Ca, Fe, and Mn as a function of pore fraction of leachate passed through columns containing (A) 2 percent montmorillonite clay, (B) 8 percent montmorillonite clay, and (C) 16 percent montmorillonite clay.

Exhibit E

montmorillonite clay in sand. The relative concentrations greater than 1 indicate that Ca, and to a lesser extent Fe and Mn, are emerging from column at much greater concentrations than those at which the influent leachate at various pore fractions. The area under the Ca curves can be seen to increase in proportion to the percentage of clay in the column. Griffin and Shimp (1976) quantified the observed attenuation represented by the area under each curve by integrating between pore fractions 1 and 11, and assigned a relative attenuation number (ATN) as shown in Table 3. Griffin and Shimp (1976) attributed the elution of Ca from the columns to an ion-exchange mechanism involving the replacing of the Ca bonded to the clays at their cation exchange positions by other ions in the leachate. The released Ca then passes onward with the ground water.

The unconsolidated surficial materials in much of Illinois are carbonate-rich, the clays generally having Ca in the cation exchange position and free carbonates in all except the leached zone. The presence of excessive hardness, reported as calcium carbonate, in the vicinity of sources of pollution has been noted in a number of articles, but its origin is rarely discussed. We have called this excessive hardness the "hardness halo." Examples of it are found in Du Page County, Illinois (Figure 3), as reported by Zeizel *et al.* (1962). There are two areas of the county where the hardness, indicated by $CaCO_3$, in the shallow carbonate aquifer exceeds 1,000 parts per million (ppm). The eastern area is a heavily developed residential area, where the glacial drift, which protects the aquifer from pollution, is relatively thin. No specific source can be attributed to the cause of the high hardness in this area; however, it is most likely due to a high concentration of home septic systems. The high hardness in the western area, near the town of West Chicago, is thought to have resulted from the discharge of large volumes of noncalcareous chemical waste to surface ponds (Walker, 1969). Further examples are reported in Anderson and Dornbush's (1967) study of a sanitary landfill in South Dakota and in Walker's (1969) discussion of ground-water pollution in Illinois. Most recently, Henning *et al.* (1975) found high calcium in monitoring wells very close to a landfill trench at Mentor, Ohio; the Ca concentrations decreased with distance from the fill and were lower in the refuse than in the closes wells.

Hughes *et al.* (1971) published the results of studies of five landfills in northeastern Illinois, including the Old Du Page County landfill, which was the source of the leachate used in this study. Monitoring of this landfill continued for three years after the completion of that report. Figure 4 was drawn using unpublished and published data

Table 3. Ranking of Chemical Constituents in Municipal Leachate According to Their Relative Mobility Through Clay Mineral Columns by Mean Attenuation Number (ATN) (from Griffin and Shimp, 1976)

most attenuated

Chemical constituent	ATN	Qualitative grouping
Pb	99.8	High
Zn	97.2	
Cd	97.0	
Hg	96.8	
Fe	58.4	Moderate
Si	54.7	
K	38.2	
NH_4	37.1	
Mg	29.3	
COD	21.3	Low
Na	15.4	
Cl	10.7	
B	-11.8	Negative (elution)
Mn	-95.4	
Ca	-656.7	

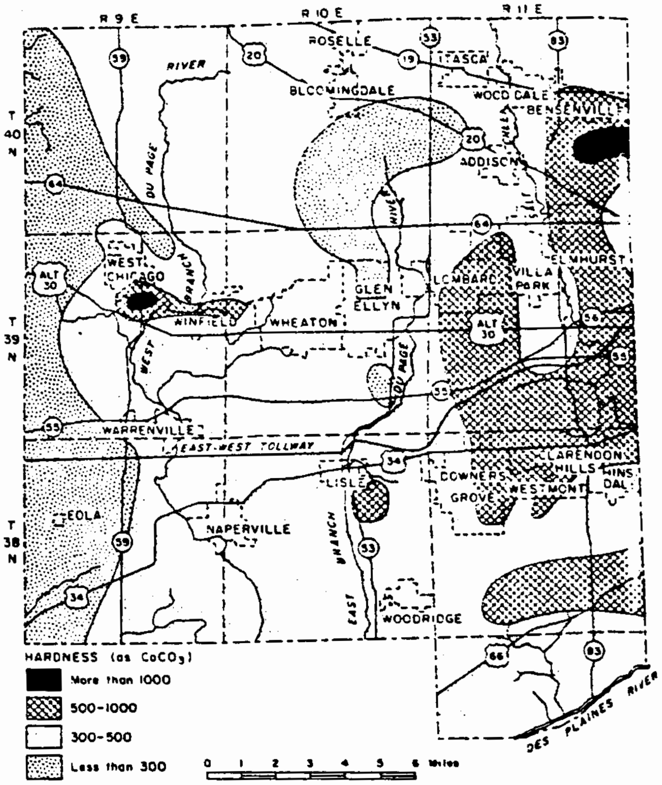

Fig. 3. Hardness of water, expressed as $CaCO_3$, in the Silurian dolomite aquifer in Du Page County, northeastern Illinois (after Zeizel *et al.*, 1962).

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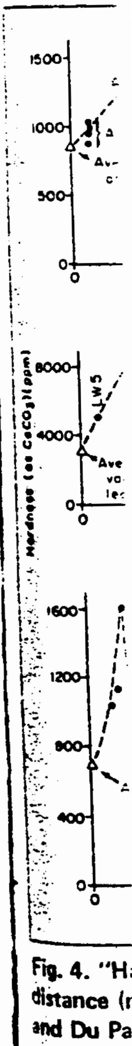

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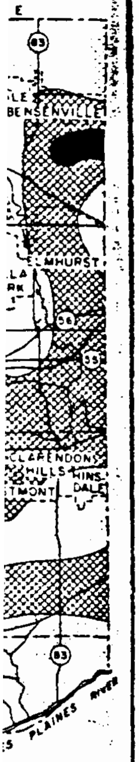

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from the Winnetka and the Old Du Page landfills. Distances of travel from the refuse are along the inferred flow paths given by Hughes *et al.*, 1971.

There is considerable scatter in the Winnetka data (top, Figure 4). This may in part be due to a mixture of points, some being in the fine-grained alluvium and the others in the glacial till, which has somewhat different properties. However, these data suggest that the hardness approaches background values within 12 to 18 meters of the refuse, which is somewhat less than the limit to which chloride traveled (Hughes *et al.*, 1971). Note that the four datum points from piezometer nest LW5 follow this pattern.

The till under the Old Du Page landfill clearly illustrates the increase followed by the decrease in hardness. This till is separated from the refuse by 1 to 1.5 meters of sand. The hardness returns to background values within about 1.5 meters of travel, which is about half the distance of the estimated travel of the chloride ion (Hughes *et al.*, 1971). Note, in particular, the values shown for piezometer nests LW5 and LW6. These data points are all for the younger, northern part of the fill; data from the older parts of the fill do not fit the same curve (all hardness concentration values were low).

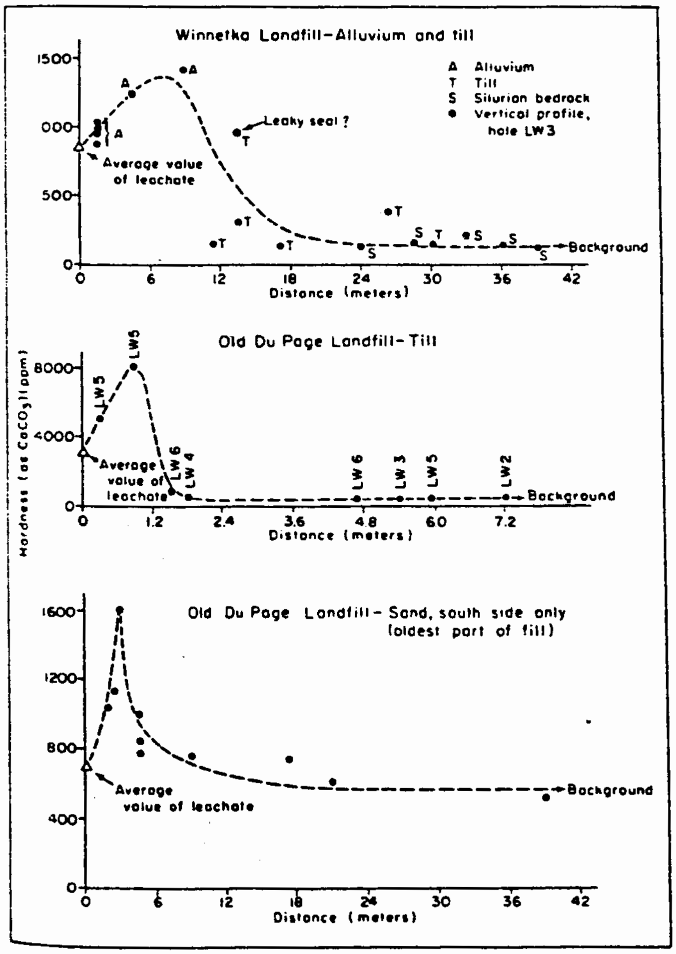

Fig. 4. "Hardness halo" effect shown as a function of distance (m) along the inferred flow path from the Winnetka and Du Page landfills in northeastern Illinois (after Hughes *et al.*, 1971).

The surficial sand (bottom, Figure 4) transmits leachate-contaminated water south from the older parts of the Du Page landfill and shows a hardness distribution similar to that of the north part of the fill. The hardness levels are much lower in the old refuse in this area, and all the values reflect that lower concentration. The hardness returns to background levels within 8 to 15 meters; however, the chloride ion has moved 240 to 300 meters in the permeable sand layer.

All these data clearly show that there is a "hardness halo" resulting from the movement of leachate into the surrounding till and sand, and that the rate of advance of the hardness front is less than that of the chloride ion. The chloride ion is probably the best tracer of this type of pollution in this environment. The distance of travel of the hardness front varied from slightly less than to approximately 10 percent of that of the chloride ion; this variation is probably controlled by the nature of the materials, cation exchange reactions, concentrations in the leachate, and ground-water flow rates. Nevertheless, all the data indicate that an increase in the chloride ion concentration followed by an increase in hardness of the water in the sediments over that in the leachate indicates that major pollution by the leachate plume will follow.

Hydraulic Conductivity

The results of initial hydraulic conductivity and bulk density measurements of the column contents are presented in Table 2. These data indicate that a wide range of hydraulic conductivities, with values in agreement with those expected under field conditions from similar materials (Todd, 1959), were observed. The relatively high bulk densities and slow flow rates used in this study closely simulate the conditions observed in the field. This procedure lends credence to the extrapolation of the results and conclusions of the laboratory studies to those obtained in the field.

During the initial stage of the experiment deionized water was circulated through the columns until hydraulic equilibrium was achieved. Hydraulic equilibrium was indicated by steady flow rates and relatively constant manometer readings from

Exhibit E

the five manometers located over the length of the column. The columns containing low percentages of clay reached hydraulic equilibrium relatively rapidly while the columns with high percentages of clay required circulation for more than a month to achieve steady manometer readings. When hydraulic equilibrium was achieved, the leachate was added to the columns.

Passage of leachate through the columns produced significant reductions of hydraulic conductivity. The natural leachate produced greater reduction than the sterile leachate. The changes in hydraulic conductivity that occurred in the kaolinite columns during the experiment have been reported previously (Griffin and Shimp, 1975). The results of hydraulic conductivity changes observed in columns containing montmorillonite, kaolinite, and illite clays are presented in Figures 5, 6, and 7. To more clearly show the trends in the data, the data presented in the Figures were statistically smoothed using the five-member moving average method. The change in hydraulic conductivity is expressed as units of the logarithmic scale. The raw data were statistically analyzed to determine whether significant differences in hydraulic conductivity existed between sterile and natural leachate. The data from the columns containing 4 percent kaolinite were rejected from the analysis when they were found to deviate by more than three standard deviations from the over-all mean change in hydraulic conductivity observed for all other columns. The manometer readings indicated that the outflow tubes were plugged. The reason that only the columns with 4 percent kaolinite showed this problem is not clear. The results of the statistical analysis indicated that columns leached with natural leachate had significantly (.05 level) greater reductions in hydraulic conductivity than those leached with sterile leachate. This result is illustrated clearly in Figures 5, 6, and 7. Furthermore, the statistical analysis indicated that columns containing montmorillonite had significantly greater average reductions in hydraulic conductivity than kaolinite or illite and that there was no significant difference in the reductions in hydraulic conductivity between kaolinite and illite. Considering that montmorillonite clay swells

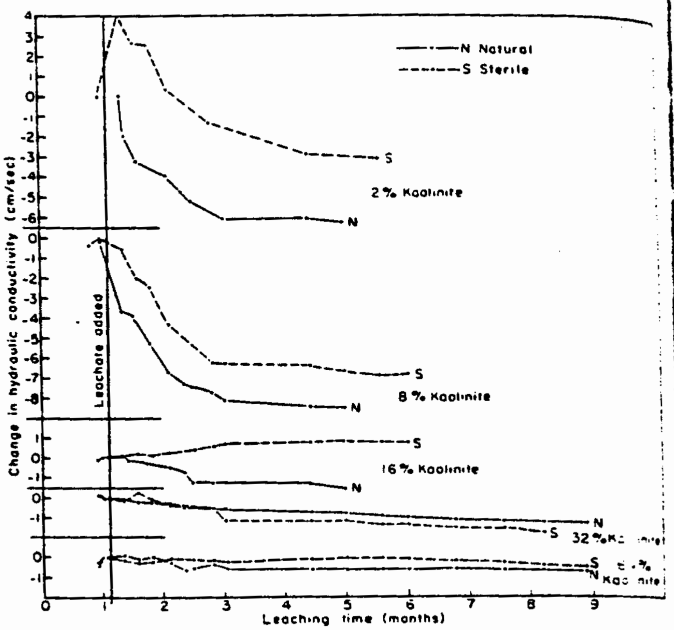

Fig. 6. Hydraulic conductivity of kaolinite-sand columns as a function of leaching time.

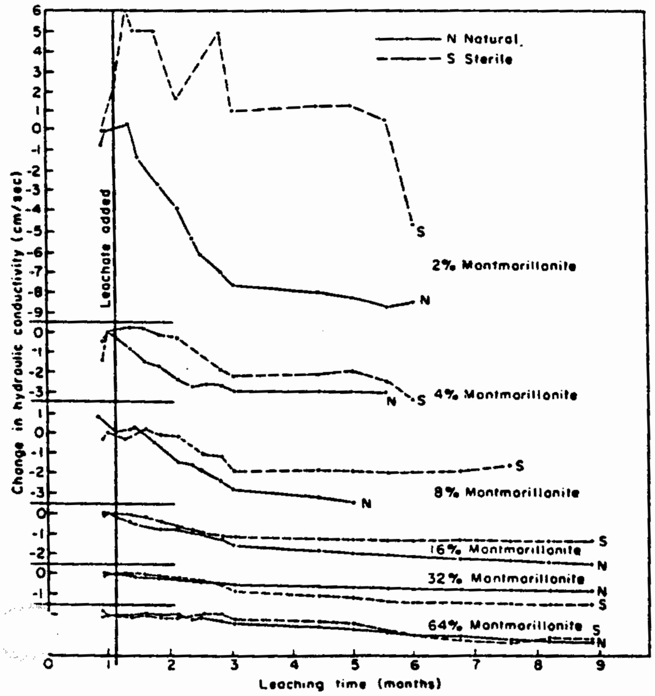

Fig. 5. Hydraulic conductivity of montmorillonite-sand columns as a function of leaching time.

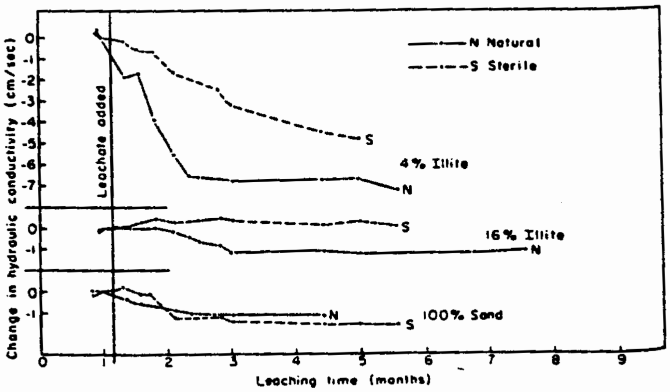

Fig. 7. Hydraulic conductivity of illite-sand columns as a function of leaching time.

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when it is wetted, this result is not surprising.

Field data to support the above laboratory observation are not as clear as the data were for the "hardness halo." There have been fewer field tests for hydraulic conductivities than chemical tests for water quality. In addition, field tests may only be accurate to approximately a half-order of magnitude.

At the Winnetka landfill, 23 hydraulic conductivity tests were conducted, 7 on refuse, 4 on alluvium, and 12 on till. The data for these are too scattered to show any significant differences with respect to distance from the refuse.

At the Old Du Page County landfill, 34 field hydraulic conductivity tests were made, 14 on refuse, 14 on sand, and 6 on till. The data on the hydraulic conductivity of the sand (all south of the fill) suggest some reduction in hydraulic conductivity. The tests (10) made on monitoring wells less than 6 meters from the fill, have a mean hydraulic conductivity of 2.00 × 10^{-4} cm/sec (range 5.0 × 10^{-4} to 1.9 × 10^{-7}; excluding a value of 1.9 × 10^{-3} obtained from a gravel lens), and those monitoring wells greater than 12 meters from the refuse (4 tests) have a mean conductivity of 2.59 × 10^{-3} cm/sec (range 7.6 × 10^{-3} to 9.5 × 10^{-4}). The data are not statistically significant, but they do seem to indicate a possible reduction of hydraulic conductivity similar to that noted in the laboratory.

The reductions in hydraulic conductivity observed in the experiment with the Du Page leachate are particularly significant inasmuch as the Du Page leachate is an old leachate, approximately 15 years (Hughes *et al.*, 1971), and contains a relatively low percentage of organic compounds which are readily degradable by microorganisms (Table 1). In addition, this leachate has a low nutrient status, both phosphate and sulfate being absent in detectable quantities. Much higher amounts of microbial growth and plugging might be expected from a younger leachate.

These results have led to the conclusion that if clay liners, either natural or man-made of similar composition to those used in this study are used in municipal landfills, significant reductions in hydraulic conductivity can be expected because of microbial growth. Furthermore, slightly higher reductions in hydraulic conductivity can be expected from montmorillonite clays, apparently because of their tendency to swell.

Attenuation of Leachate Pollutants

During the period of time from the collection of the leachate through the period that hydraulic equilibrium was being established, the leachate was stored under refrigeration (3° to 5° C) with either argon or sterilant gas being purged slowly over the top of each drum. During the 10-month period chemical analyses were performed weekly on the leachate to monitor possible changes in composition. The value reported in Table 1 for COD, and for all the other constituents, is the average of the 37 separate analyses performed during the 10-month period of leaching.

The process of determining the attenuation of chloride and the other major components of Du Page leachate has been described by Griffin and Shimp (1976). The results of this study indicated that there was an average 6 percent greater attenuation of chloride in the columns leached with sterile leachate than those leached with the natural leachate. This greater attenuation is attributed to the reaction of chloride with the ethylene oxide to form ethylene chlorohydrin. Other than the slight increase in chloride attenuation, no other significant difference was apparently due to the increase in COD in the sterile leachate as compared to the natural leachate.

There were, however, other significant differences between the sterile and natural leachate treatments that were not attributed to the higher COD of the sterile leachate. Figure 8 illustrates the difference observed in Mn elution from the columns. The negative attenuation numbers indicate that more Mn eluted from the column than was present in the influent leachate. It can be seen that much higher levels of Mn were found in effluents from the columns leached with natural leachate. Griffin and Shimp (1976) concluded that the elution of Mn was due to reduction of surface coatings of Mn oxides on the clays by the anaerobic leachates. This conclusion is further verified by the difference in Mn elutions from the natural and sterile leachate treatment. This difference is attributed to the stronger anaerobic environment provided by the active microorganisms present in natural leachate. Inspection of the data in Table 2 shows that the average Eh (oxidation potential) reading of the natural leachate was an order of magnitude lower than the sterile leachate, even though both were in the anaerobic range (Eh readings less than 197 m.v. are considered to reflect anaerobic conditions). A similar result was obtained for Fe in that significantly (.05 level) greater mobility of Fe was found in columns leached with natural leachate than in those leached with sterile leachate. A mechanism similar to that for Mn elution is postulated as the reason for the

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observed differences between the natural and sterile leachate.

Those chemical constituents for which no significant difference in attenuation between the normal and sterile leachate was found were Ca, Mg, Na, K, NH_4, Pb, Hg, Zn, and Cd. The constituents Al, Cu, Ni, Cr, As, S, and PO_4 were found in such low concentrations in the Du Page leachate that no attenuation order could be determined. Table 4 lists the constituents of the Du Page leachate and the hazard index determined by Griffin and Shimp (1976). They defined the hazard index of a leachate as the product of the Toxicity Index and the Mobility Index (see Table 4); it indicates the relative environmental hazard associated with individual ions.

Design of a Landfill

The design of a landfill should take into account three factors: the hydrologic system governing direction of pollutant travel;
the geochemistry of the water-sediment system; and the release rate of unattenuated pollutants to surface or ground waters. The first factor has been the subject of a number of papers and will not be discussed here.

Current landfill design and engineering practice ilizes thick liners, either natural or artificial, containing high percentages of clay. The motive is to create relatively impermeable liners that will contain the leachate and therefore protect the ground-water resources. This approach creates difficulties in humid climates where infiltration exceeds the capacity of the liner to dissipate the leachate. This causes what is referred to as the "bathtub" effect wherein the relatively impermeable clay liner fills with leachate and then overflows. The overflow manifests itself in the form of leachate springs on the surface and results in surface-water pollution instead of ground-water pollution. Neither form of pollution is necessary if proper design features are utilized in the construction of the sanitary landfill.

The results of a chemical attenuation study reported by Griffin and Shimp (1976) have indicated that most of the toxic constituents found in municipal leachates are moderately to highly attenuated by passage through laboratory columns containing relatively low percentages of clay minerals. If it is assumed that the "bathtub" effect is an undesirable feature of clay liners, then it follows that it is desirable to determine the point of "optimal" attenuation, that is, the percentage of clay in a liner which gives maximum attenuation balanced with maximum hydraulic conductivity. The data presented in Figure 9 represent examples of the percentage of montmorillonite necessary for "optimal" attenuation as determined for Cl, NH_4, and Pb. Figure 9 is a dual-scaled graph with the initial hydraulic conductivity (k) of the montmorillonite columns

Table 4. Chemical Constituents Contained in Du Page Leachate Ranked by Pollution Hazard Index [See Griffin and Shimp (1976) for the Definition and Derivation of Each Term]

Chemical constituent	Effective concentration / D. W. Standard	Toxicity Index[1]	Mobility Index[2]	Hazard Index[3]
NH_4	962/0.5	1724.	62.9	108 .40.
B	(29.9 + 3.5)/1.0	33.4	111.8	[illegible]
COD	1340/50	26.8	78.7	2,109.
Hg	0.87/.002	435.	3.2	1,392.
Cl	3484/250	13.9	89.3	1,241.
Ca	(46.8 + 307.3)/250*	1.42	756.7	1,072.
Cd	1.95/.01	195.	3.0	585.
Fe	4.2/0.3	14.0	41.6	582.
Na	748/270	2.77	84.6	234.
Mn	(0.02 + 0.02)/.05	0.78	195.4	153.
K	501/250*	2.00	61.8	123.
Mg	233/250*	0.93	70.7	55.7
Pb	4.46/.05	89.2	0.2	7.8
Zn	18.8/5.0	3.76	2.8	0.5
Si	14.9/250*	0.06	45.3	2.7

[1] Toxicity Index = $\frac{\text{Effective concentration}}{\text{Drinking water standard}}$

[2] Mobility Index = (100 - attenuation number)

[3] Hazard Index = Toxicity Index × Mobility Index

* Actual value not established by EPA, therefore assumed to be the same as chloride.

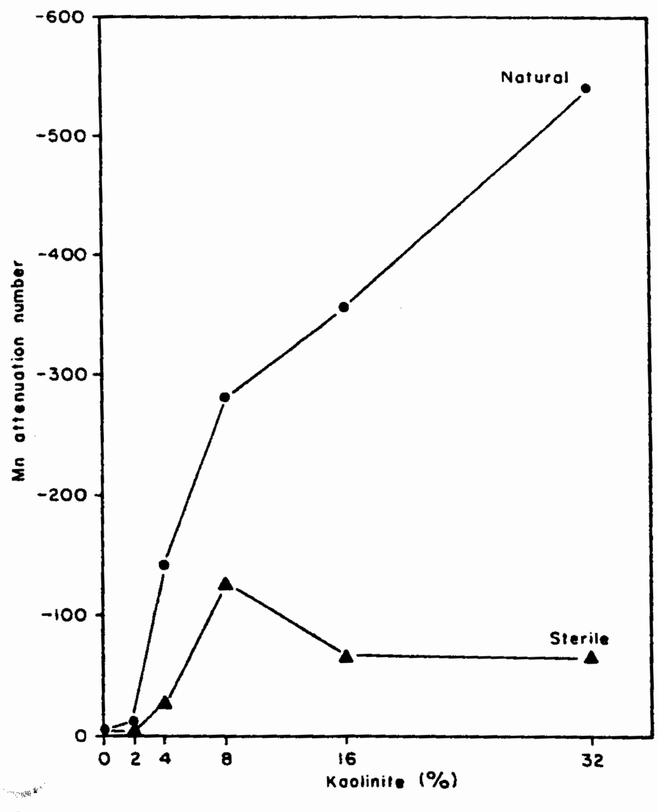

Fig. 8. Mn elution related to percentage of kaolinite leached with natural and sterile leachate.

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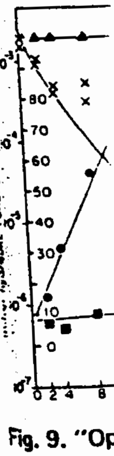

Fig. 9. "Op
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given in Table 2 plotted as a function of percentage of montmorillonite. The other scale is the attenuation number for the chemical constituent of interest also plotted as a function of the percentage of montmorillonite. The attenuation numbers, as reported by Griffin and Shimp (1976), are the percentage of removal of the element from the leachate upon passage through 10 pore fractions of the clay-sand mixture. The attenuation scale is given as 0 at the point of minimum hydraulic conductivity and 100 at the point of maximum hydraulic conductivity. The point where the attenuation curve and the hydraulic conductivity curve cross is taken to be the "optimal" percentage of montmorillonite which gives highest attenuation and permeability.

For the heavy metals, for example Pb, even small amounts of clay gave almost total removal. The heavy metals, even though toxic, thus represent a minimal pollution hazard in municipal leachates because they are attenuated very strongly. Therefore, they can usually be ignored from consideration as far as determination of the optimal clay liner for a given leachate. At the other extreme are the relatively noninteracting constituents represented by Cl. Cl as shown in Figure 9 is relatively unattenuated by even large amounts of clay, which suggests that in order to prevent chloride migration, relatively impermeable clay liners would be necessary. Because of the nontoxic nature of the chloride ion, it also ranks low along with the heavy metals in the pollution "hazard index" (Table 4). In view of the problems associated with the "bathtub" effect, it seems unwise to design clay liners to optimize chloride attenuation. Rather, it seems prudent to design clay liners for optimum attenuation of the most hazardous constituents found in a particular leachate. In the case of the Du Page leachate used in this study, the pollution hazard index ranks NH_4 as 30 times more of a pollution hazard than any other constituent found in this leachate. It therefore seems reasonable to design a clay liner for Du Page leachate that gives optimal attenuation of NH_4. With such a liner all the other constituents should also be attenuated to relatively safe levels for minimal pollution of the ground waters adjacent to the landfill site.

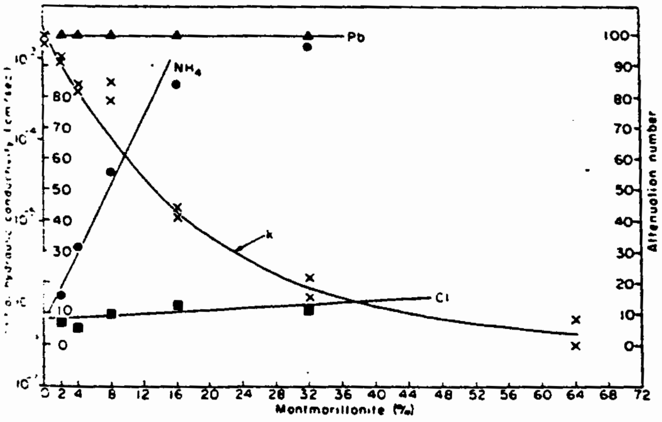

Fig. 9. "Optimal" montmorillonite percentages for attenuation of Pb, NH_4, and Cl, and the hydraulic conductivity (k) of the clay-sand mixtures.

Table 5. Estimated Thickness of Landfill Liner for Total Attenuation of Leachate for Each Meter Thickness of Overlying Refuse During a 20-Year Fill Life*

Constituent	Initial Concentration†		Cation exchange capacity (meq/100 g)					
			10		20		30	
	Ave. (ppm)	Max. (ppm)	Ave. (cm)	Max. (cm)	Ave. (cm)	Max. (cm)	Ave. (cm)	Max. (cm)
NH_4	379 (830)	1,106	32	92	16	46	11	31
Na	755 (740)	7,700	118	1,208	59	604	39	403
K	763 (530)	3,770	51	252	26	126	17	84
Mg	1,609 (240)	15,600	226	2,191	113	1,096	75	730

* Assumptions: Bulk density = 1.8 g/cc; 100 liters of leachate generated per m^3 of refuse per yr; initial concentration decreases linearly to zero at 20 yr; removal efficiencies for each constituent were estimated using the average values given by Griffin and Shimp (1976): NH_4 = 37.1%, Na = 15.4%, K = 38.2%, Mg = 29.3%.

† Concentrations taken from the 20 leachate analyses reported by EPA (1974); those in parentheses are the values of Old Du Page landfill leachate used in this study.

For the case of NH_4 (shown in Figure 9) the optimal attenuation is achieved by approximately 10 percent montmorillonite. If one extrapolates the curve, it is apparent that 18 to 20 percent montmorillonite would give nearly total removal of the NH_4 from the leachate, but would result in very low hydraulic conductivities. The ratio of the optimal percentage to the percentage necessary for nearly total removal indicates that if the liner with 10 percent of montmorillonite is doubled in thickness from the 40 cm used in this study to 80 cm, it will contain enough montmorillonite to give nearly total removal of the NH_4 in 10 pore volumes of leachate and will still retain the relatively high hydraulic conductivity of 6×10^{-5} cm/sec.

The thicknesses of mixtures of sand and clay of different cation exchange capacity (CEC) that would achieve total attenuation of selected relatively mobile ions are shown in Table 5. The removal efficiency will differ in leachates, depending upon the relative strength of ions. The efficiencies used in Table 5 are based on the Du Page leachate used in this study. There is direct relationship between the liner thickness and total attenuation; a thick liner with low CEC will have the same attenuation capacity as a thin liner with a high

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CEC. Increasing cation exchange capacity generally reflects increasing clay content of the liner. Thus, a thicker liner with greater hydraulic conductivity and lower CEC may be the optimal liner for attenuation.

Determining the release rate to aquifers or surface waters of contaminants that are not attenuated or are poorly attenuated by clay liners (natural or man-made) is necessary for proper design of landfills. In designing a landfill, a decision must be made to determine which ions should be totally attenuated and which ions eventually may be released to the environment. The chloride ion, which moves essentially unattenuated and is not noxious at low concentrations, is the most obvious example of the latter type.

The calculation of release rate of leachate from the bottom and sides of a landfill and the flow path it will take is a complex problem. At present, there are several models, existing and under development, which use the high-speed digital computer to predict the rate and path of fluids from a landfill (for example, Elzy *et al.*, 1974). These models are quite accurate and will provide very good estimates of the quantities desired. They are, of course, dependent upon the accuracy of the physical data input—infiltration rates, hydraulic conductivities, and geologic description.

Preliminary estimates of leakage can also be made by simply using Darcy's equation as suggested by Hughes *et al.* (1971):

$$Q = kA\frac{dH}{dL}$$

where:

Q = flow rate in cm^3/sec;

k = hydraulic conductivity;

A = area of the landfill in cm^2;

dL = thickness of the liner in cm;

dH = head of water across the liner in cm.

This equation is subject to some of the same limitations as the computer-solved models. Either representative or measured values of hydraulic conductivity can be used. However, the presence of a landfill generally changes the hydraulic gradient. In addition, the gradient will differ with changing hydraulic conductivities. Hughes *et al.* (1971) observed gradients as high as 1 cm/cm in glacial till with a hydraulic conductivity of about 4×10^{-7} cm/sec, and a 0.02 cm/cm gradient in dirty, surficial sand with a hydraulic conductivity of 1×10^{-3} cm/sec. Thus, one must estimate the gradient from experience.

The leakage thus calculated must then be compared in volume to the receiving waters. In the case of a surface-water body receiving the pollutant discharge, the calculation is relatively straightforward. For instance, Hughes *et al.* (1971) calculated that the Elgin landfill, located in highly permeable gravel, increased the total dissolved solids of the Fox River by 0.30 parts per million.

The leakage to aquifers is more difficult to estimate, and the computer models have considerable advantage. However, one may calculate the volume of water passing below the landfill in a simplistic way similar to the way the leakage was calculated; "A" in the equation becomes the cross-sectional area of the aquifer. However, groundwater flow is laminar, and dispersion becomes the only mechanism for dilution into the total volume of water; thus the calculation represents a total value for the receiving aquifer, and not a spot value. Nevertheless, these two simple calculations can be informative before one proceeds to more detailed hydrogeologic analyses.

Table 6 shows some representative estimates of increased ion concentration in some surface-water streams and aquifers. The Table was calculated assuming an aquifer 30 meters thick, a hydraulic conductivity of 1×10^{-2} cm/sec, and a small stream with a discharge of 1 cubic meter per second. The salinity of the discharge is assumed to be 2,000 ppm as found at the Elgin landfill by Hughes *et al.* (1971).

CONCLUSIONS

The results of this study raise some basic questions about landfill design and monitoring. The results indicate that use of hydraulic conductivity information and the pollution hazard

Table 6. Increase in Salinity of an Aquifer or Small Stream from Leakage of Landfill Leachate*

Liner (Hydraulic conductivity, cm/sec)	Increase in aquifer salinity (ppm)	Increase in stream salinity (ppm)
1×10^{-8}	0.8	0.002
1×10^{-6}	7.7	0.02
1×10^{-4}	77.	0.2
1×10^{-2}	769.	2.0

* Assumptions:

1)

	Hydraulic conductivity (cm/sec)	Gradient (cm/cm)
Aquifer	1×10^{-2}	1/1000
Liner	1×10^{-8}	1/1
Liner	1×10^{-6}	1/10
Liner	1×10^{-4}	1/100
Liner	1×10^{-2}	1/1000

2) 10^4 square meters of refuse

3) Aquifer 30 m thick

4) Leachate salinity 2000 ppm (Hughes et al., 1971)

5) Stream discharge 1 m^3/sec

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ating for a given leachate or waste stream can allow different approach to landfill design from the prevalent "containment" policy. The data suggest hat over-all pollution would be decreased if andfill liners were designed to achieve higher permeability and to selectively attenuate the most toxic pollutants from the leachate. The ground waters could then dilute the nontoxic components, which can be tolerated at much higher concentrations without deleterious effects. Thus, stabilization and use of the landfill for other productive purposes can be achieved at much faster rates than can at present be achieved by containment liners.

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EPA-600/2-78-157
August 1978

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Research and Development

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Attenuation of Pollutants in Municipal Landfill Leachate by Clay Minerals

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EPA-600/2-78-157
August 1978

ATTENUATION OF POLLUTANTS IN MUNICIPAL LANDFILL LEACHATE BY CLAY MINERALS

by

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Illinois State Geological Survey
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Contract No. 68-03-0211

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OFFICE OF RESEARCH AND DEVELOPMENT
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DISCLAIMER

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FOREWORD

The Environmental Protection Agency was created because of increasing public and government concern about the dangers of pollution to the health and welfare of the American people. Noxious air, foul water, and spoiled land are tragic testimony to the deterioration of our natural environment. The complexity of that environment and the interplay between its components require a concentrated and integrated attack on the problem.

Research and development, that necessary first step in solving a problem, involves defining the problem, measuring its impact, and searching for solutions. The Municipal Environmental Research Laboratory develops new and improved technology and systems to prevent, treat, and manage wastewater and solid and hazardous waste pollutant discharges from municipal and community sources, to preserve and treat public drinking water supplies, and to minimize the adverse economic, social, health, and aesthetic effects of pollution. This publication is one of the products of that research; it is a most vital communications link between the researcher and the community.

This report presents results from laboratory investigation of the capacity of clay minerals to remove pollutants from municipal landfill leachates. These results are applicable to the design of clay mineral liners for sanitary landfills and to the land disposal of municipal and hazardous wastes.

Francis T. Mayo, Director
Municipal Environmental Research
Laboratory

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ABSTRACT

The first part of this project was a laboratory column study to evaluate the potential of mixtures of sand and calcium-saturated clay minerals for attenuating and preventing pollution of water resources by pollutants in municipal solid waste landfill leachate. Chloride, Na, and water-soluble organic compounds (COD) were relatively unattenuated by passage through the clay-sand columns; K, NH_4, Mg, Si, and Fe were moderately attenuated; and heavy metals -- such as Pb, Cd, Hg, and Zn -- were strongly attenuated by even small amounts of clay. Concentrations of Ca, B, and Mn in the column effluents increased markedly over the original leachate concentrations.

Montmorillonite was found to have the highest attenuation capability, followed by illite and then kaolinite. Precipitation, with resultant accumulation in the surface layers of the columns, was found to be the principal attenuation mechanism for the heavy metals Pb, Cd, Hg, and Zn. The cation exchange capacity of the clay minerals was concluded to be the dominant attenuation mechanism responsible for removal of other substances from the leachate.

The second part of the project involved batch studies of adsorption of Cr, Cu, Pb, Cd, Hg, and Zn by montmorillonite and kaolinite from water solutions and from landfill leachate. The adsorption in leachate proved to be 50 to 90% lower in most cases than the clays' adsorption capacity for the metal ions in pure aqueous solutions. The adsorption of the cations Cr(III), Cu, Pb, Cd, Hg, and Zn increased with increasing pH while the anions Cr(VI), As, and Se decreased with increasing pH. At pH values greater than about 5.3, precipitation of the heavy metal cations was found to be an important attenuation mechanism while adsorption was the principal mechanism for the anions over the entire pH range studied.

Pollutant adsorption by clay minerals (and hence the mobility of pollutants in clays and clay soils) was significantly affected by other, non-hazardous solutes in the leachates. This effect was so pronounced that information on movement of pollutants in one landfill leachate cannot be directly applied to predicting the movement of the same pollutants present at the same concentrations in a different landfill leachate.

To evaluate the relative pollution hazard for municipal leachates, a ranking system was developed. Results of the study are applicable to the use of clay minerals as liners for sanitary landfills and to the land disposal of municipal and hazardous wastes.

This report was submitted in fulfillment of Contract Number 68-03-0211, by the Illinois State Geological Survey, under the partial sponsorship of the Environmental Protection Agency. Work was completed as of August 1975.

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SECTION 1

INTRODUCTION

During the past 30 years, the landfill method for disposal of municipal and industrial waste has been widely used in the United States. More than 90% of our nation's wastes are now placed on the land for ultimate disposal at the approximately 14,000 landfills throughout the nation (Garland and Mosher, 1975). These 14,000 landfills accept more than 360 million tons of household, commercial, industrial, and municipal solid waste per day, at a cost of more than 4.5 billion dollars annually (Black et al., 1968). As industry in the United States complies with the Clean Air Act and the Federal Water Pollution Control Act, the volume of industrial solid wastes, sludges, and liquid concentrates of pollutants is expected to double in the next 10 years. The disposal of such huge volumes of solid waste by landfilling is not without its environmental impact. When refuse buried in a landfill comes in contact with water, then leachate, a mineralized liquid high in organic substances, is produced and may move out of the fill and pollute the ground water.

Garland and Mosher (1975) have cited several examples of pollution by leachates migrating from landfills. An example of severe economic damage incurred by pollution of a drinking water aquifer by leachate from a landfill occurred in New Castle County, Delaware (Apgar and Satterthwaite, 1975). Leachate from the landfill migrated more than 800 feet and contaminated the Potomac drinking water aquifer 4 years after the landfill site had been closed. The drinking water was contaminated with such high levels of organic compounds and metal ions that it was no longer potable. To date, this problem has cost the county $800,000 for interim solutions and, if the dump must be moved to completely remedy the situation, the cost may reach as high as 20 million dollars. In addition to the monetary costs, the county estimates that it will take 10 years to restore full use of the aquifer.

In another case, reported by Garland and Mosher (1975), contamination of ground water by selenium was found to extend more than 2 miles from a dump site in Long Island. In this case as elsewhere, heavy-metal contamination may impart no odor or color to indicate that the water is contaminated.

The solid waste problem is most acute in the metropolitan areas, where competition for the available land is intense. A city of 2 million inhabitants generates 5000 tons of solid waste per day (Wirenius and Sloan, 1973), which rapidly fills the conveniently situated landfill locations. The problem of finding environmentally acceptable sites close to metropolitan areas is compounded by urban sprawl and persistent opposition from citizen and environmental groups. The rapid increase in problems and the costs associated

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with transporting refuse for long distances now make it prudent to consider sites that were previously unacceptable because they failed to meet certain geologic and hydrologic critera. As of January 1975, Illinois had 2,040 waste disposal sites recorded with the Illinois State Environmental Protection Agency. Since 1965, the management of refuse disposal in Illinois has greatly improved, owing to passage of the Illinois Refuse Disposal Act, which assigned the regulation of solid waste disposal to the Department of Public Health. More comprehensive regulation was provided in 1970 with the creation of the Environmental Protection Agency by passage of the Environmental Protection Act (HB3788). Regulations were passed that were designed to insure that solid waste disposal facilities are located at such sites and operated in such a manner as will protect the physical environment and public health. These regulations have been enforced for the past 10 years. During this time, the Illinois State Geological Survey has assisted the regulatory agencies by evaluating the hydrogeologic conditions at proposed or operating waste disposal sites. During the past 8 years, the Survey has appraised at about 100 sites annually the conditions relative to pollution hazard. Some sites were not approved for geologic reasons, including locations in floodplains or gravel pits, on fractured rock over aquifers, on steep grades, or in areas of special environmental significance. Other sites were approved but were never put into operation because of persistent opposition from citizen and environmental groups or for other reasons.

The future of landfill disposal is clear. Acceptable disposal sites will be difficult to find, their location will be approved only after certain geologic and hydrologic criteria are met, and greater care will be required in their operation. The relative unavailability of geologically acceptable sites in close proximity to metropolitan areas and the rapidly escalating costs associated with transportation of waste materials across long distances now make it economically feasible to consider physically modifying geologically unacceptable sites that may be ideal in other respects. The Illinois State Geological Survey has conducted extensive studies of the movements of pollutants through various geologic strata and in a variety of hydrologic settings at several landfill sites in northeastern Illinois (Hughes et al., 1971). Cartwright and McComas (1968) also conducted geophysical investigations at the same sites. The above studies, and others by Apgar and Langmuir (1971) and Emrich (1972), have indicated that pollutants in leachate can be detected at variable distances from a landfill, depending on the clay content of the soil or the hydraulic conductivity of the soil strata. It has therefore been suggested that a clay liner in the bottom of previously unacceptable sites, such as gravel pits or old quarries, could make them acceptable for disposal of municipal and/or industrial wastes. However, no sound evidence existed to indicate how thick such a layer must be or what types of clay minerals were best suited for removal of toxic metals in the presence of municipal leachate.

This paper reports the results of a study (1) to investigate and evaluate the attenuating properties of several clay minerals for the pollutants contained in leachates from municipal solid waste, and (2) to determine the capacity of the two major clay mineral types for removing the heavy metals -- Cr, Cu, Pb, Cd, Hg, As, Se, and Zn -- from solution and the effect municipal leachates have on this capacity at various pH values. The study was also de-

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signed to provide insight into the mechanisms responsible for attenuation of heavy metals as well as to evaluate the potential use of clay minerals as liners for waste disposal sites. Such liners would be used to prevent or mitigate pollution of ground and surface waters by liquid effluents.

It is clear that, based on their intrinsic properties alone, municipal leachates are noxious waste streams that pose a potential threat to public health (Hanks, 1967; Peterson, 1974). To assess the magnitude of the pollution hazard of such a stream is a difficult problem and was the subject of the U. S. Environmental Protection Agency (1973) decision model for screening, selecting, and ranking hazardous wastes streams. Use of the priority ranking formulation requires evaluation of the "critical product" (pollution hazard). At present, no actual waste-stream data for municipal leachates is available. Therefore, one goal of this study was to provide waste-stream data that could be used to determine the mobility index of several of the major pollutants found in municipal leachates that had passed through simulated clay mineral landfill liners. The mobility index thus derived could be used to compute the pollution hazard for most of the chemical constituents found in municipal leachate.

This report is presented in separate chapters that describe different aspects of the work that was performed. For the convenience of the reader, each chapter includes its own abstract. The column leaching studies (Sections 5 and 6) used "natural" landfill leachate as described in the Experimental section (Section 4). Sections 7 through 11 report equilibrium adsorption "batch" studies using small amounts of clays mixed with aqueous solutions of metal salts and landfill leachates that had been "spiked" with metal salts. The results of these investigations will also find application in the land disposal of industrial and energy production wastes.

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SECTION 2

CONCLUSIONS

The results from the column leaching and adsorption studies have yielded complementary data that have allowed us to make predictions as to the expected magnitude of the reduction in concentration or attenuation in soil for most of the common chemical constituents found in landfill leachates. The data also indicate that several mechanisms may be responsible for attenuation of the various pollutants under differing environmental conditions.

Strong evidence is presented supporting the conclusion that the cation exchange capacity is the principal chemical property of a clay mineral to effect attenuation. Of the three clays used in this study, montmorillonite was found to have the highest attenuation capability, followed by illite and then kaolinite. This order was concluded to be a result of their respective cation exchange capacities.

The pH of the leachate was found to significantly affect the amount of attenuation. It was concluded that the heavy metal cations -- Pb, Cd, Cu, Cr(III), Hg, and Zn -- were attenuated primarily by an exchange-adsorption mechanism which was affected by pH and competition from other cations. However, at pH values between 5 and 6, a large increase in removal can be expected due to increased adsorption of metal complex ions and to formation of insoluble heavy metal hydroxide and carbonate compounds. It was therefore concluded that at high pH the primary mechanism of attenuation for these ions was precipitation. The effect of pH on the attenuation of the heavy metal anions Cr(VI), As, and Se was found to be the opposite of the cations and it was concluded that precipitation was not an important attenuation mechanism. Rather, the adsorption of the anions was found to correlate well with the distribution of certain ionic species in solution. It was concluded that $HCrO_4^-$ was the species adsorbing in this study, since Cr(VI) adsorption became zero as the pH was raised to 8.4, corresponding to the disappearance of $HCrO_4^-$ from solution in favor of the $CrO_4^=$ ion. The adsorption of Cr(VI) was also found to start to decrease as the pH was lowered past 2, corresponding to the decrease in $HCrO_4^-$ ion in favor of H_2CrO_4. Likewise, As and Se adsorption were also found to correspond to the distribution of $H_2AsO_4^-$ and $HSeO_3^-$ species in solution. These results led to the conclusion that the principal attenuation mechanism for the heavy metal anions was adsorption of the monovalent species from solution. It was also concluded that at higher pH values the heavy metal anions would be significantly more mobile than the cations.

The relative mobilities of the heavy metals, as determined from equilibrium adsorption data from pure solutions of the metals at pH 5, were:

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Cr(III) < Cu < Pb < Zn < Cd < As(V) < As(III) < Se < Cr(VI)

The cationic heavy metals are generally adsorbed to a greater degree than are the anionic heavy metals. However, this ranking is dependent on pH and ionic competition and therefore changes somewhat in different leachates.

A significant point shown in the ranking is the importance of the valence state of an element to the amount of that element removed from solution by clay minerals. Cr(III) species were removed to a much greater extent than Cr(VI), and more As(V) was removed than As(III). These data suggested that safer disposal of certain elements may be achieved if the element were converted to the form most strongly attenuated prior to disposal.

The formation of Pb and Cd organic complexes in leachates was measured, and their effect was determined to be of secondary importance to adsorption and precipitation. This seemed to be due to competition from high concentrations of other cations present in leachates. Due to the complex interactions between inorganic, organic, and volatile forms of Hg, the mobility and relative importance of organic Hg complexes could not be accurately assessed.

The results of this study have led to the conclusion that passage of leachate through a Ca-saturated clay material will result in high attenuation of the heavy metals; in moderate attenuation of K, NH_4, Mg, and Si; and in relatively low attenuation of Cl, Na, and water-soluble organic compounds (COD). It was further concluded that the oxidation-reduction potential of the leachate controlled the attenuation of Fe and Mn. Under strongly anaerobic conditions, Fe and Mn will probably not be attenuated and may even elute in substantial concentrations due to the dissolution of oxide coatings on the clay surfaces. However, under mildly anaerobic conditions, substantial attenuation can occur.

Substantial concentrations of Ca were eluted from the columns. Since a very highly significant linear regression ($r = 0.97$) was obtained for the amount of Ca eluted versus the cation exchange capacity of the clay, and since the sum of the amount of K, NH_4, Na, and Mg removed from the leachate agreed within about 3% with the amount of Ca eluted, it was concluded that Ca elution was due to exchange with the other cations present in the leachate. It was also concluded that this Ca elution observed in the laboratory experiment corresponded to the "hardness halo" effect observed in field monitoring wells around sanitary landfill sites.

Significant reductions in hydraulic conductivity were observed when landfill leachate was passed through the columns. It was concluded that microbial action is primarily responsible for the observed reductions and that hydraulic activity of clay-sand liners placed in the bottom of a landfill will decrease after a period of leaching with municipal effluent. It was further concluded that montmorillonite clays will decrease in permeability to a greater extent than the other clays. This was assumed to be due to its tendency to swell to a much greater extent than other types of clay.

A pollution hazard ranking system was developed. Using this system, it was concluded that NH_4^+ was a 30 times greater pollution hazard than any other

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constituent found in the DuPage leachate. It was also concluded that in a fresh, young leachate, COD or Fe most likely would present the highest pollution hazard and that the characteristics of each leachate and earth material must be considered when evaluating their potential for pollution. The well known variability in composition of municipal landfill leachates (Garland and Mosher, 1975) and the difficulty in predicting leachate composition before landfilling is begun will make it difficult to apply this hazard-ranking system. Nevertheless, the ranking system has the advantage of quantifying the expected pollution hazard of a given leachate and allows comparisons of the pollution hazards of one leachate with another. The ranking system also aids regulators, landfill designers, and researchers by focusing attention on those chemical constituents in the leachate with the highest potential for serious pollution.

The mobility of a given leachate constituent, and hence the thickness of a clay liner necessary to attenuate the constituent, depends to a large degree on the element and the form of the element, the adsorption capacity of the earth material, the cations present initially on the exchange complex, the chemical composition of the leachate, and the pH of the leachate. The adsorption capacity of the clay minerals and the reversible nature of exchange-adsorption reactions have important environmental consequences. Industrial wastes containing heavy metals placed in sanitary landfills could alter the ionic composition and/or pH of the leachate. A change in pH may release large amounts of potentially toxic heavy metals into the aqueous phase, especially in places where precipitates may have accumulated. Other ions in the waste compete with the heavy metals and may exchange with them, thus allowing metal ions to come into solution. These multiple interactions must be considered when a disposal site is designed and when the environmental impact of adding heavy-metal wastes to municipal landfills is assessed.

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SECTION 3

RECOMMENDATIONS

This study dealt specifically with attenuation of the inorganic constituents of leachate, but, because leachates contain high concentrations of organic compounds, also needed is a laboratory investigation dealing with the attenuation of the specific organic compounds in leachate. The results of our study, using COD as an indicator of organic-compound movement, showed poor attenuation of organics. At the same time, the pollution hazard index indicates that the organic fraction of leachate poses a serious pollution hazard, especially for young leachates. It is therefore recommended that an attenuation study be initiated, involving a comprehensive organic analysis to determine removal of specific organics by passage through clay liners and/or soils.

The results of this study also illustrated the important role that the pH of the leachate or waste stream plays in pollutant removal by clay minerals. It is therefore recommended that, in conjunction with the organic removal studies, further studies be carried out to determine techniques which will allow the pH to be manipulated to enhance and economically optimize pollutant (organic and inorganic) removal by earth materials. Also, landfill disposal of anionic forms of heavy metals such as Cr(VI), As, and Se should be closely scrutinized because of their relatively high mobility and the fact that manipulation of pH conditions to enhance removal of cationic heavy metals such as Pb, Cd, Zn, Cu, and Cr(III) may actually increase the mobility of the anionic metal ions.

Due to the relatively high toxicity of Hg and the complex interactions between inorganic, organic, and volatile forms of the element, much more research is necessary to determine the environmental impact of Hg in landfill environments. In conjunction with the study of Hg, Pt has also been reported to be methylated in aquatic systems, thus establishing a previously unknown mechanism of transfer. The major source of potential redistribution of complexed forms of Pt is expected to come from the disposal into landfills of spent catalysts from catalytic-converter-equipped automobiles. Thus, it is recommended that Hg and Pt be studied to quantitatively determine the adsorption capacity of clays and soils for the inorganic and organic forms of Hg and Pt. It is also important to determine the magnitude and role of microorganisms in the methylation of Hg and Pt to volatile forms under the conditions found in municipal landfills.

A major task still before us is the utilization of quantitative soil chemistry data to make predictions of pollutant migration beneath landfills.

Exhibit E

It is therefore recommended that further studies be carried out that involve a cooperative effort between soil chemists, groundwater hydrologists, and modelers for the computer implementation of the prediction process and to identify possible gaps in knowledge that may still bar the successful prediction of long-term pollutant migration from disposal sites.

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SECTION 4

EXPERIMENTAL

The clays used in this study were the purified clay minerals kaolinite (1:1 lattice type), montmorillonite (2:1 expanding lattice), and illite (2:1 nonexpanding lattice, mica type). These clay minerals were chosen for study because they are the most common clay minerals in earth materials that would be used individually or in combinations for landfill sites. Earth materials containing one or more of these clay minerals can generally be obtained locally for landfill liners.

The clays were brought to the laboratory, where they were crushed, ground, and purified by sedimentation techniques to obtain the <2 µm particle fraction that contained essentially pure clay minerals. Chemical analyses of the three clays are given in Table 1. Details of the methods used and results of X-ray diffraction analyses of the clays are given in the appendix. The predominantly Ca-saturated, <2 µm fractions of the clays were then used in the column leaching and heavy metal adsorption studies.

The municipal landfill-leachates used in this study were collected from the DuPage County landfill (well MM 63) and from the monitoring well located on the Blackwell Forest Preserve landfill. The details of the site descriptions and well locations are given by Hughes et al. (1971). The leachate was collected by using a tubing pump and large plastic containers that were equipped with valves to allow continuous purging of high-purity CO_2 or argon gas to maintain anaerobic conditions. The DuPage leachate collected initially for use in the column leaching study was stored under argon. Both the DuPage and Blackwell leachates collected at a later date for use in the heavy metal adsorption studies were stored under CO_2. Purging with CO_2, a naturally occurring landfill gas, was found to be a more satisfactory method than argon purging since it permitted the leachates to be stored in the laboratory for longer periods of time without significant changes in pH. The leachate used in the column study was collected with a tubing pump and was split into two 53-gallon plastic closed-head drums. One drum was taken to the Argonne National Laboratories and sterilized by gamma ray irradiation using a cobalt source which gave a dose of 3.36×10^6 rad at the center of the drum. Both the sterile and natural drums were stored under refrigeration with the temperature maintained at 3 to 5° C. The drum containing the microbially active leachate was stored with argon purged over the top of the leachate, while the sterilized drum was stored over a 12% ethylene oxide/88% freon gas mixture which maintained both sterility and an anaerobic environment. Mercuric nitrate salt was later added to the drum (Table 2) to maintain sterility. Plate counts were performed on both leachate drums using potato dextrose

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TABLE 1. CHEMICAL CHARACTERIZATION OF THE CLAY MINERALS USED IN ATTENUATION STUDIES OF LEACHATE POLLUTANTS

	Kaolinite (Pike County, Illinois) (ppm)		Montmorillonite (American Colloid Co. southern bentonite) (ppm)		Illite (Minerva Co. Mine) (ppm)	
Element	Exch.*	Total	Exch.*	Total	Exch.*	Total
Ca	2,592.	3,700	13,120.	22,300	5,248	23,350.
Mg	76.8	1,800	680.	25,500	800.	10,430.
Na	43.2	929	24.0	178	115.2	1,050.
K	87.2	8,200	240.	1,100	800.	56,270.
NH_4	13.0	40	43.	38	50.	62.5
Fe	<2.0	6,600	<2.0	25,500	<2.0	28,730.
Mn	0.06	29	0.02	25	0.37	<390.
Pb	<2.0	46	<2.0	<15	<2.0	93.8
Cd	<0.2	<3	<0.2	<3	<0.3	18.8
Zn	0.80	20	1.00	40	2.5	37.5
B	-	46	-	3	-	43.8
Al	-	221,800	-	95,600	-	130,100.
Si	-	217,700	-	284,800	-	226,500.
Ti	-	14,700	-	1,300	-	4,010.
Carbon (%)						
Total		0.54		0.93		2.19
Organic		0.51		0.92		1.81
Inorganic		0.03		0.01		0.38
CEC (meq/100g)		15.1		79.5		20.5
Surface area (m^2/g)		34.2		86.0		64.6

*Exchangeable

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TABLE 2. SUMMARY OF CHEMICAL CHARACTERISTICS OF LANDFILL LEACHATES

Component	Range of all values given by Garland and Mosher (1975) (mg/l)	Blackwell Forest Preserve leachate (Hughes, 1971b) (mg/l)	DuPage leachate used in sorption study (mg/l)	DuPage leachate used in column study (mg/l)	
				Natural	Sterile
COD	40 - 89,520	39,680.	1,362.	1,340.	10,603.*
BOD	9 - 54,610	54,610.	-	-	-
TOC	256 - 28,000	-	-	-	-
Organic acids	-	-	333.	333.	290.
Carbonyls as acetophenone	-	-	57.6	57.6	90.1
Carbohydrates as dextrose	-	-	12.	12.	11.
pH	4 - 9	7.10	6.79	6.9	7.2
Eh (m.v.)	-	-180.	-155.	+7.	+75.
TS	0 - 59,200	-	-	-	-
TDS	0 - 42,276	19,144.	5,910.	-	-
TSS	6 - 2,685	-	-	-	-
E.C. (mmhos/cm)	3 - 17	10.90	7.20	10.20	10.42
Alkalinity ($CaCO_3$)	0 - 20,850	3,255.	4,220.	-	-
Hardness ($CaCO_3$)	0 - 22,800	7,830.	1,100.	-	-
Total P	0 - 154	6.	<0.1	<0.1	<0.1
Ortho P	6 - 85	-	-	-	-
NH_4-N	0 - 1,106	-	809.	862.	773.
NO_3+NO_2-N	0 - 1,300	1.70	-	-	-
Al	-	2.20	<0.1	<0.1	<0.1
As	-	4.31	0.11	0.11	0.14
B	-	-	33.	29.9	28.5
Ca	5 - 4,080	-	49.	46.8	43.2
Cl	34 - 2,800	1,697.	1,070.	3,484.	3,311.
Na	0 - 7,700	900.	822.	748.	744.
K	3 - 3,770	-	516.	501.	491.
Sulfate	1 - 1,826	680.	<0.01	<0.01	<0.01
Mn	0 - 1,400	1.66	<0.1	<0.1	<0.1
Mg	16 - 15,600	-	204.	233.	230.
Fe	0 - 5,500	5,500.	4.40	4.2	3.0
Cr	-	0.20	<0.1	<0.1	<0.1
Hg	-	-	0.0008	0.0008	0.87*
Ni	-	-	0.3	0.3	0.3
Si	-	-	15.1	14.9	15.0
Zn	0 - 1,000	-	0.03	18.8	16.3
Cu	0 - 10	0.05	<0.1	<0.1	<0.1
Cd	0 - 17	<0.05	<0.01	1.95	1.88
Pb	0 - 5	-	<0.1	4.46	4.26

*Added as a result of sterilization maintenance

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agar media. No growth occurred on plates inoculated with the sterilized leachate while active growth of microbial colonies was observed on plates inoculated with the natural leachate, thus indicating that sterility had been achieved.

The results of chemical analysis of the leachates are presented in Table 2. Chemical procedures used are given in the appendix. For comparison, Table 2 also contains a summary of the range of leachate characteristics found for more than 20 other leachates as given by Garland and Mosher (1975). It is useful to note that the two leachates used in this study have widely different chemical compositions. The DuPage leachate is approximately 15 years old and has a lower total salt, phosphate, and sulfate content than the Blackwell. In addition, the organic matter of the DuPage leachate consists mainly of microbially resistant compounds, which have been found to be more mobile in soils than are biodegradable compounds (Hughes et al., 1971, Gowler, 1970). The Blackwell leachate, on the other hand, is younger and ranks among the most concentrated ever reported, especially with regard to BOD and Fe.

The laboratory apparatus used in the leaching study consisted of laboratory columns containing mixtures of clay minerals and washed quartz sand through which leachate was passed. A diagram of the column apparatus design appears in Figure 1. The columns and apparatus were constructed to simulate the slow (<2 pore volumes per month), saturated, anaerobic flow of leachate as it is thought to occur at the bottom of a landfill.

$$\text{Pore Volume} \cong \left[1 - \left(\frac{\text{Bulk Density}}{\text{Particle Density}}\right)\right] \times \text{Volume of Column} \qquad \{1\}$$

The entire column leaching system was maintained under an argon atmosphere to maintain anaerobic conditions. A tubing pump lifted the leachate to a 5-gallon plastic carboy which acted as both a constant head device (Marriot bottle) and a temperature equilibration reservoir. The leachate was then passed through the columns and the effluents were collected in graduated cylinders, which also allowed measurement of the flow rates. The outflow tube was maintained above the top of the columns to insure saturated flow. The level of the outflow tube was moved either up or down to maintain relatively constant flow rates throughout the experiment.

The columns were constructed of 2-inch acrylic tubing, to which manometer outlets were fitted vertically on the column at five locations. To simulate field conditions, the leachate containers and columns were either painted black or masked with black tape to prevent growth of organisms, such as algae or photosynthetic bacteria, which are not indigenous to deep refuse leachate.

The sand grains were coated with the clays, according to the methods given by Grim and Cuthbert (1945). The clay minerals and sand were then uniformly packed in the columns to a depth of 40 cm, except for the 32% and 64% montmorillonite columns, which were 30 cm thick. The columns were packed to bulk densities approximating those of naturally occurring glacial tills (~1.8 g/cc; Manger, 1963). Table 3 gives some chemical and physical properties of the column contents. The hydraulic conductivities for each particular

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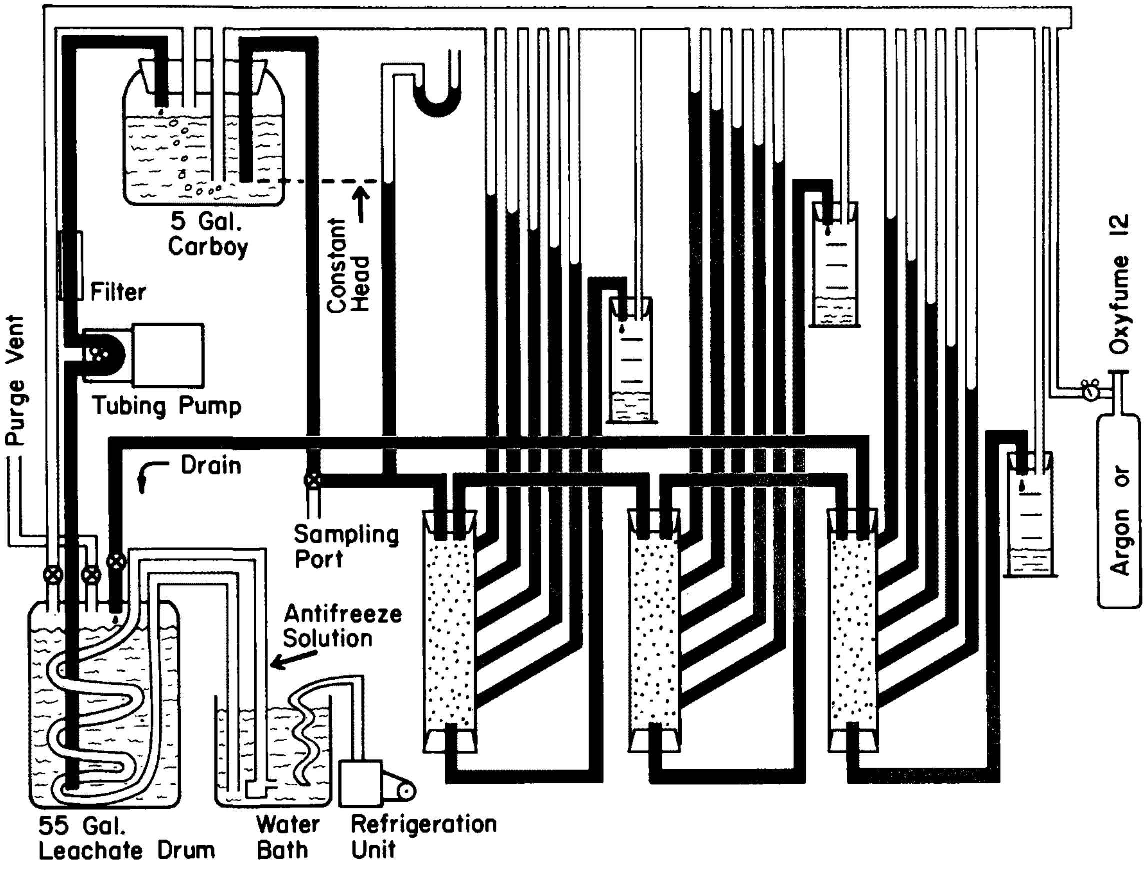

Figure 1. Diagram of column apparatus used in leachate study.

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TABLE 3. DESIGN OF EXPERIMENT AND SOME PHYSICAL AND CHEMICAL PROPERTIES OF THE COLUMN CONTENTS

Natural Leachate Treatment	Cation Exchange Capacity (meq./100g)		Bulk density (g/cc)		Initial hydraulic conductivity (cm/sec)	
	Set A*	Set B†	Set A	Set B	Set A	Set B
100 Sand	0.0	.1	1.71	1.71	$1.27.10^{-3}$	$1.80.10^{-3}$
2 M††	1.4	2.3	1.71	1.72	$9.45.10^{-4}$	$7.93.10^{-4}$
4 M	3.2	4.3	1.77	1.74	$4.34.10^{-4}$	$3.47.10^{-4}$
8 M	7.3	7.2	1.79	1.78	$4.70.10^{-4}$	$2.61.10^{-4}$
16 M	11.9	12.1	1.87	1.86	$1.22.10^{-5}$	$1.44.10^{-5}$
32 M	26.8	24.0	1.55	1.52	$1.27.10^{-6}$	$2.17.10^{-6}$
64 M	56.2	55.5	1.23	1.11	$3.05.10^{-7}$	$6.83.10^{-7}$
2 K††	0.7	0.4	1.68	1.70	$7.44.10^{-4}$	$4.53.10^{-4}$
4 K	1.1	0.8	1.76	1.74	$4.78.10^{-5}$	$2.76.10^{-5}$
8 K	1.5	1.4	1.80	1.77	$9.90.10^{-4}$	$8.25.10^{-4}$
16 K	1.8	2.5	1.87	1.90	$2.86.10^{-5}$	$1.92.10^{-6}$
32 K	3.8	3.4	1.66	1.55	$2.40.10^{-6}$	$4.81.10^{-6}$
64 K	9.6	8.5	1.22	1.32	$5.45.10^{-7}$	$4.57.10^{-7}$
4 I††	0.8	0.9	1.80	1.81	$8.17.10^{-4}$	$7.16.10^{-4}$
16 I	3.5	3.2	1.83	1.91	$2.68.10^{-5}$	$2.19.10^{-5}$
8K + 8I	2.4	2.3	1.90	1.98	$1.48.10^{-6}$	$1.68.10^{-6}$
8M + 8K + 8I	8.8	8.5	1.64	1.69	$8.08.10^{-6}$	$9.43.10^{-6}$

*Set A - Natural leachate

†Set B - Sterile leachate

††M = Montmorillonite, I = Illite, K = Kaolinite

clay content and bulk density agree with those given by Todd (1959) for natural materials. The experimental design used in the study is also shown in Table 3, which gives the percentages of clay mineral(s) in each column (to which pure quartz sand was added to total 100%). The experimental design includes a complete geometric progression of clay percentages from 2% to 64% kaolinite and montmorillonite and two mixtures of clays as given in Table 3. A 100% sand column was also included. Only 4 and 16 percentages of illite were included because kaolinite and illite have very similar cation exchange and lattice expansion properties, and thus a complete geometric array for illite was not considered necessary.

After the leachate and the column contents were characterized, the leachate was passed through the columns for periods of between 6 and 10 months, depending on the hydraulic conductivity of the individual column. The hydraulic conductivity (K) was computed using the relationship:

$$K = \frac{QdL}{AdH} \qquad \{2\}$$

where Q = flow rate in cm^3/sec
A = cross sectional area of column in cm^2
dL = length of the column in cm
dH = head of water in cm.

During this time effluents from each column were collected periodically and measurements were made for Na, K, Ca, Mg, Al, Zn, Pb, Cd, Hg, Fe, Mn, NH_4, B, Si, Cl, chemical oxygen demand (COD), Eh, pH, and hydraulic conductivity. Finally, after approximately 15 pore volumes were leached, the clay mineral columns were sectioned and the contents analyzed to determine the vertical distribution of chemical constituents in each column.

Duplicate sets of columns were used in the experiment; one set of columns was leached with natural effluent, another with sterilized effluent. The sterilized treatment was used to determine how gross biological activity might affect hydraulic conductivity of leachate through clay minerals used as liners. The results of the experiment were statistically analyzed using the paired t statistic to determine if there were significant differences in the attenuation of each chemical constituent between sterile and natural leachate and between clay mineral types. Linear regression and moving average analysis were also performed on the column effluent data to determine relationships between hydraulic conductivity, attenuation, and clay mineral properties.

In addition to the column leaching study, a series of separate equilibrium studies on the capacity of clays to adsorb eight potentially hazardous elements -- Pb, Cd, Zn, Cu, Cr, As, Se, and Hg -- were performed. From these studies, adsorption isotherms for kaolinite and montmorillonite were constructed to determine the adsorption capacities as a function of concentration, pH, and ionic competition. The details of the experimental procedures used for each element are included in the section of the report dealing with that particular element.

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SECTION 5

COLUMN LEACHING STUDY[1]

ABSTRACT

To evaluate the potential of clay minerals for attenuating the various chemical constituents of landfill leachate, leachate was collected by anaerobic techniques from the 15-year old DuPage County sanitary landfill near Chicago, Illinois, and passed through laboratory columns that contained various mixtures of calcium-saturated clays and washed quartz sand. The columns were constructed to simulate slow, saturated, anaerobic flow of leachate through earth materials outside the landfill. Manometers were placed in each column to measure any changes in permeability. Leachates were run through the columns for periods of up to 10 months, during which time effluents were periodically collected and analyzed for 16 chemical constituents. The column contents were then cut into sections and analyzed to determine the vertical distribution of chemical constituents in each column.

Chloride, Na, and water-soluble organic compounds (COD) were relatively unattenuated by passage through the clay columns; K, NH_4, Mg, Si, and Fe were moderately attenuated; and heavy metals, such as Pb, Cd, Hg, and Zn, were strongly attenuated by even small amounts of clay. Concentrations of Ca, B, and Mn in the column effluents increased markedly over the original leachate concentrations. The increase in Ca was due to cation exchange with ions in the leachate. The amount of Ca eluted from the columns was found, by mass balances, to agree within 3% with the sum of Na, K, NH_4, and Mg removed from solution. The Mn increase probably resulted from a reduction of the oxidized Mn on clay surfaces by the anaerobic leachate to more soluble ionic species.

Of the three clays used in the study, montmorillonite had the highest attenuation capability, followed by illite and then kaolinite. This order correlates well with the cation exchange capacities of the three clay minerals, which appear to be the dominant attenuation mechanism in these clays. The principal attenuation mechanism for the heavy metals Pb, Cd, Hg, and Zn was found to be precipitation, with resultant accumulation of the metals in the surface layers of the columns.

A ranking system was developed for evaluating the relative pollution hazard for municipal leachates. The new ranking method overcomes the problems and objections found in evaluation of the critical product parameter for

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municipal leachates by a method previously proposed to the U. S. EPA for hazardous wastes.

Results of the study are applicable to the use of clay minerals as liners for sanitary landfills and to the disposal of industrial and power plant wastes in landfills and mines.

INTRODUCTION

The following results and discussion consider data from the columns leached with normal leachate and do not include results from the sterilized leachate. Details of the effect of sterile leachate on hydraulic conductivity and chemical constituent attenuation will be the subject of Section 6. However, for those chemical constituents for which no significant difference in attenuation between the normal and sterile leachate treatment was found, the results were pooled to give added statistical significance to analysis of clay-type effects. Those constituents for which no significant difference was observed were Ca, Mg, Na, K, NH_4, Pb, Hg, Zn, and Cd.

COLUMN LEACHING STUDIES

Hydraulic conductivity and bulk density measurements of the column contents are presented in Table 3. A wide range of hydraulic conductivities, with values in agreement with those expected under field conditions from similar materials (Todd, 1959), was observed. The relatively high bulk densities and slow flow rates used in this study closely simulate the conditions observed in the field, which lends credence to the extrapolation of the results and conclusions presented here to field applications using clay liners of similar composition.

Results of some column effluent analyses are shown in Figures 2 and 3 plotted as relative concentration versus pore fraction. Relative concentration is the ratio of the column effluent concentration divided by the influent concentration. Thus the "breakthrough" point for a given element is where the column effluent concentration equals the influent concentration and has a value of one. A pore volume of effluent is defined as the volume necessary to displace the volume of interstitial liquid in the pore spaces in the column. The pore fraction is then given as the cumulative volume of column effluent divided by the pore volume of the individual column.

Figures 2 and 3 illustrate the wide range of attenuation observed for several elements contained in the leachate as it passed through columns containing 2, 8, and 16% montmorillonite clay. The amount of reduction in concentration of a given element as it passes through the columns is reflected by the shift of the curves toward higher pore volumes. The results shown in Figure 2 for Cl, Na, NH_4, and K are qualitatively in excellent agreement with the results reported by Farquhar and Rovers (1975), who used soils in their tests. The attenuation order also follows the general order of cation replaceability given by Grim (1968).

Figure 3 illustrates the negative attenuation or elution of Ca from the columns. The relative concentrations greater than 1 indicate that Ca, and to

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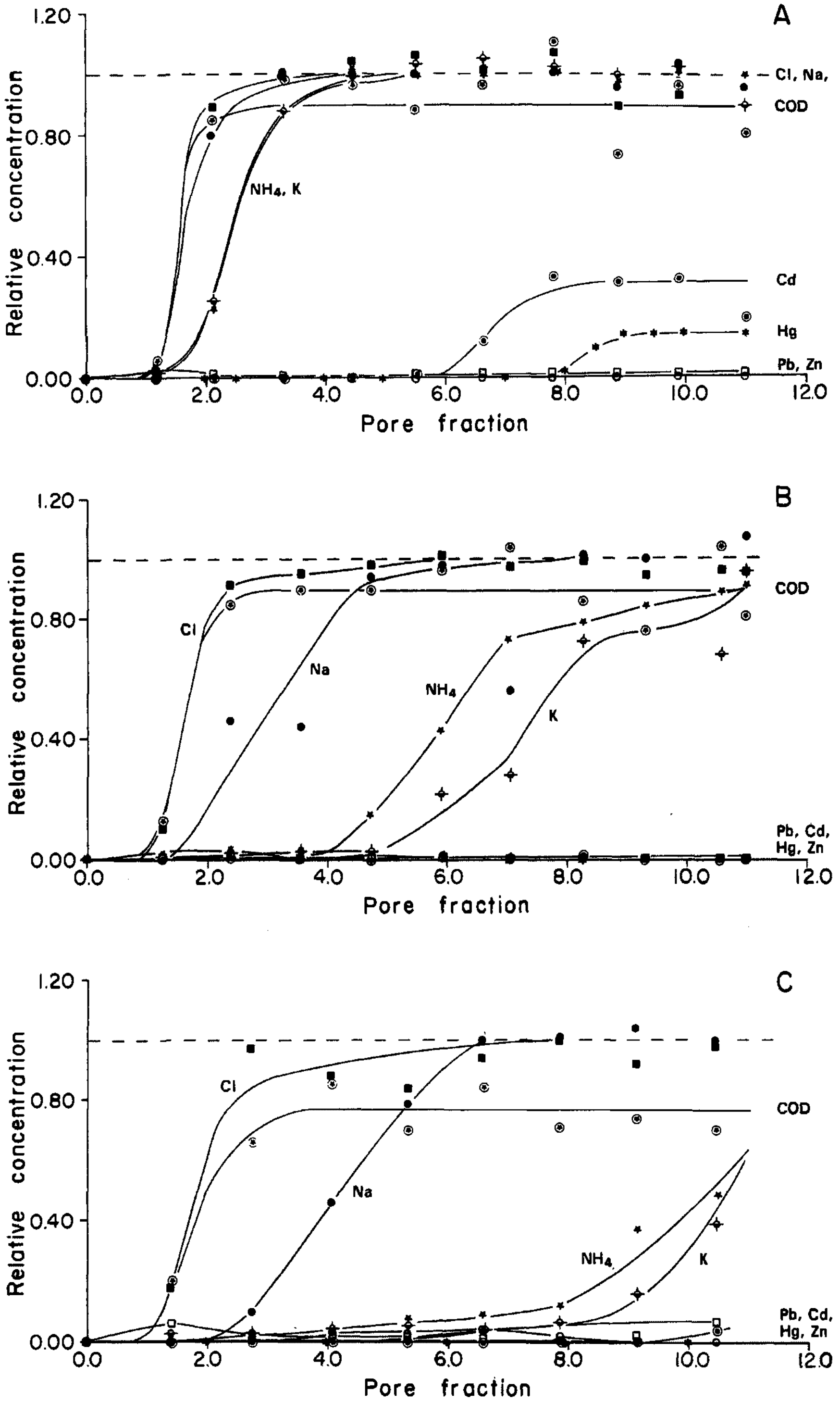

Figure 2. Relative column effluent concentrations for several elements as a function of pore fraction of leachate passed through columns containing (a) 2% montmorillonite, (b) 8% montmorillonite, and (c) 16% montmorillonite clay.

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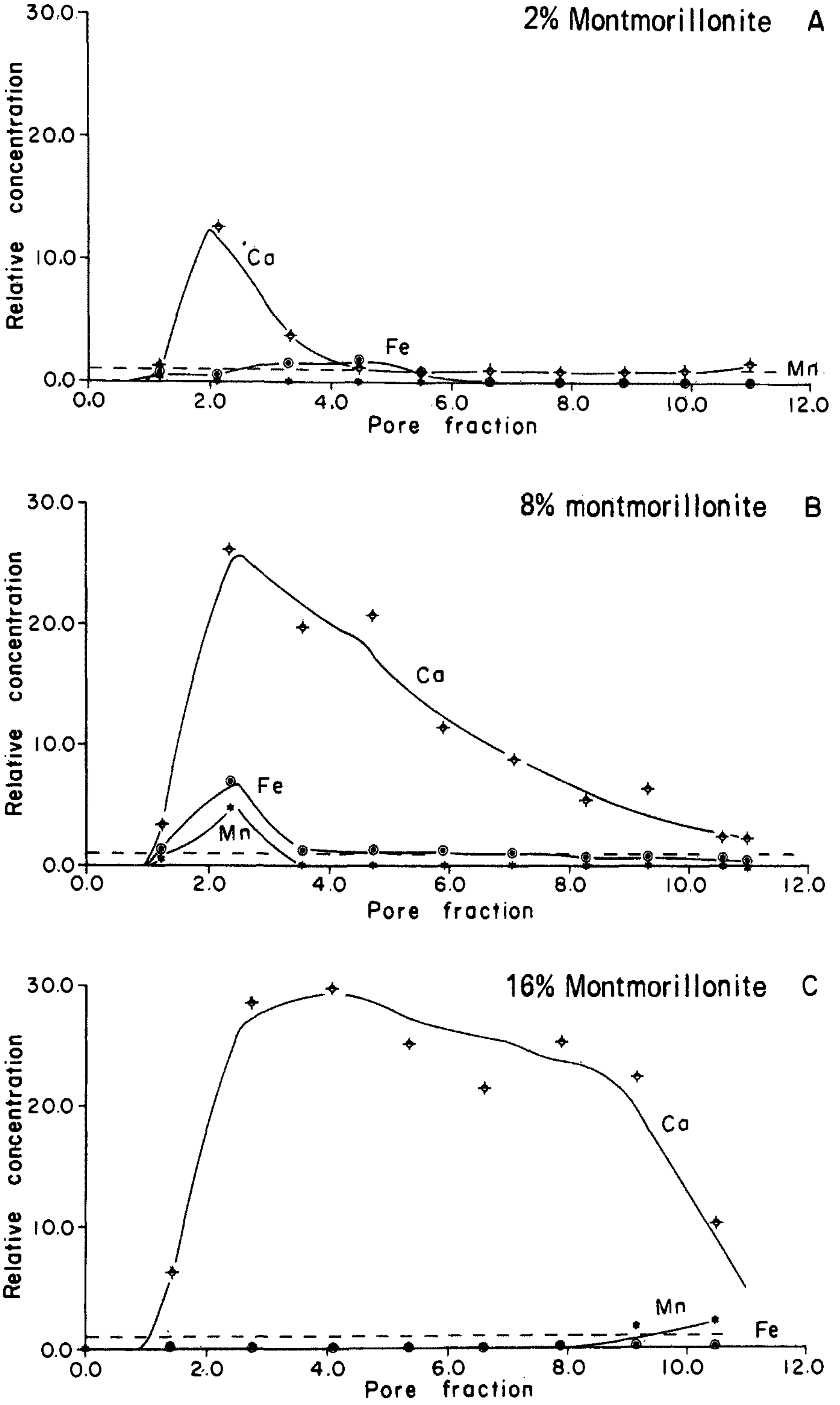

Figure 3. Relative column effluent concentrations for several elements as a function of pore fraction of leachate passed through columns containing (a) 2% montmorillonite, (b) 8% montmorillonite, and (c) 16% montmorillonite clay.

a lesser extent Fe and Mn, are eluting from the columns at much higher concentrations than the influent leachate at various pore fractions. The area under the Ca curves in Figure 3 increases in proportion to the percentage of clay in the column.

To quantify the observed attenuation, the area under each curve was integrated between pore fractions 1 and 11. The area between 0 and 1 pore fraction was not included because it was merely the displacement of the deionized water initially present in the column. The total area was that bounded by 10 pore volumes and relative concentrations between 0 and 1. The relative attenuation number (ATN) was then obtained by subtracting the area under the curve in each case from the total area and was expressed as a percentage. The ATN numbers are unique for each element and each clay and express the relative mobilities of each element through each particular clay or clay mixture column.

The attenuation number was computed for all columns and each chemical constituent studied. The mean attenuation number for each chemical constituent was used to rank the constituents according to their relative mobility through the clay columns and is reported in Table 4. The constituents Al, Cu, Ni, Cr, As, S, and PO_4 were found in such low concentrations in the DuPage leachate that no attenuation order could be determined. The results showed that greater amounts of the heavy metals Pb, Zn, Cd, and Hg than any other element were removed from leachate, yielding an average of about 97% attenuation for 10 pore volumes leached. The data for 2% montmorillonite (Fig. 2a) show that Cd and Hg were the most mobile of the heavy metals studied. Measurable amounts of Cd and Hg appeared in the effluents of the 2% clay column after about 6 pore volumes were leached. Only traces of Cd and Hg appeared in the effluents of the 8% and 16% clay treatments (Fig. 2b, 2c). Removals of Pb and Zn were very high in all columns.

Results obtained from chemical analysis of sectioned columns revealed large accumulations of all four heavy metals in the surface layers of each column, including the 100% sand column. These removals could be attributed to cation exchange replaceability, but a precipitation and/or filtration mechanism appears a more plausible cause. Precipitation could involve formation of heavy-metal hydroxides or carbonates, brought about by the relatively high pH found in the column effluents. The average pH of the influent leachate was 6.9, while the average pH of the column effluents rose to values of 7.3-7.9. The increase in pH could result in precipitation of the heavy metals from solution in the columns. The precipitation mechanism is given further credence by the measurements of the effluent concentrations from the sand columns, which have no cation exchange capacity and an average effluent pH of 7.8. No Pb and markedly reduced concentrations of Zn, Cd, and Hg eluted from the sand columns. These data, along with the high accumulations of the metals in the surface layers of the sand columns, indicate that precipitation of heavy-metal hydroxides and carbonates can be an important attenuation mechanism. This conclusion has been further verified by our equilibrium studies of the effect of pH on heavy-metal removal by clay reported in Sections 7, 8, 9, 10, and 11 of this report.

Filtration of particulate material in the leachate by the earth

Exhibit E

TABLE 4. RANK OF CHEMICAL CONSTITUENTS IN MUNICIPAL LEACHATE ACCORDING TO THEIR RELATIVE MOBILITY THROUGH CLAY MINERAL COLUMNS

Chemical constituent	Mean attenuation number	Principal attenuation mechanism	Relative mobility
Pb	99.8	Precipitation/Exchange	Low
Zn	97.2	Precipitation/Exchange	
Cd	97.0	Precipitation/Exchange	
Hg	96.8	Precipitation/Exchange	
Fe	58.4	Oxidation-Reduction	Moderate
Si	54.7	--	
K	38.2	Cation Exchange	
NH_4	37.1	Cation Exchange	
Mg	29.3	Cation Exchange	
COD	21.3	Microbial Degradation	High
Na	15.4	Cation Exchange	
Cl	10.7	Dispersion	
B	-11.8	Artifact?	More Eluted Than Applied
Mn	-95.4	Elution from Clay	
Ca	-656.7	Exchanged from Clay	

Exhibit E

materials is also a possible attenuation mechanism. Experiments in which the DuPage leachate was filtered through 0.45 µm pore size membranes indicated that only relatively small amounts of metals were retained on the membrane. It was therefore concluded that filtration was not an important attenuation mechanism for the heavy metals in this study but may be an important mechanism for many other leachates.

Moderate attenuation was observed for the leachate constituents Fe, Si, K, NH_4, and Mg, which had values ranging between 58.4% and 29.3% attenuation. Little attenuation was found for COD, Na, and Cl, values for which ranged between 21.3% and 10.7% attenuation. The elements Ca, Mn, and B were not attenuated by the clays, but, rather, were found in substantially higher concentrations in the column effluents than in the influent leachate.

To determine what mechanisms were responsible for the observed differences in attenuation for each leachate constituent, the effect of clay type was investigated. The mean attenuation obtained for each clay and chemical constituent is tabulated in Table 5. The results show that no significant difference in attenuation for the three clay minerals was observed for the heavy metals (Pb, Cd, Hg, Fe, and Zn) or for B or Cl. Illite and kaolinite attenuated Si significantly better than montmorillonite. Kaolinite was found to elute Mn in significantly higher amounts than either montmorillonite or illite. No significant difference in COD attenuation between montmorillonite and illite was found, and both attenuated COD significantly better than kaolinite. Montmorillonite was found to attenuate the cations Na, K, NH_4, and Mg and to elute Ca to a significantly greater degree than illite and kaolinite.

A precipitation mechanism for the four heavy metals (Pb, Cd, Hg, and Zn), as discussed above, is consistent with the fact that no differences in attenuation were found among the three clays. Because these four metals exist in solution as cations, a significant clay-type effect would be expected if cation exchange were the attenuation mechanism. No clay-type effect was observed, which is taken as additional evidence that the primary attenuation mechanism for these four heavy metals is precipitation.

To determine whether the higher attenuation of the cations Na, K, NH_4^+, and Mg and elution of Ca by montmorillonite was due to its higher cation exchange capacity, the attenuation numbers were plotted as a function of CEC for the three clay minerals. The results are shown in Figures 4 and 5. The very highly significant linear regression of attenuation numbers as a function of CEC led to the conclusion that the principal attenuation mechanism for Na, K, NH_4, and Mg was the cation exchange of these constituents for Ca.

Ca was the predominant exchangeable cation present on these clays at the beginning of leaching (Table 1). To further confirm that this mechanism was responsible, a mass balance for these five cations was computed for data presented in Figure 2. The sums of the amounts of Na, K, NH_4, and Mg removed from the leachate agreed within 3% with the amount of Ca eluted. Increases in the concentration of alkaline earth metals in groundwater preceding a leachate plume have been observed in the field during monitoring of the groundwater chemistry around landfill sites. Such increases, termed the "hardness

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TABLE 5. MEAN ATTENUATION NUMBER (ATN) OF SOME CHEMICAL CONSTITUENTS FOUND IN MUNICIPAL LEACHATES FOR THREE CLAY MINERALS

	Mean ATN			
Chemical constituent	Montmorillonite	Illite	Kaolinite	All columns
Pb	99.6*	100.0	99.9	99.8
Zn	97.7	98.6	98.1	97.2
Cd	96.7	100.0	97.5	97.0
Hg	98.4	98.1	95.2	96.8
Fe	34.8	82.8	67.6	58.4
Si	39.2	81.6	71.2	54.7
K	58.9	31.0	23.2	38.2
NH_4	54.8	31.0	25.1	37.1
Mg	48.2	19.7	18.1	29.3
COD	24.6	23.2	16.2	21.3
Na	20.6	16.4	9.7	15.4
Cl	9.3	13.5	14.3	10.7
B	-16.1†	-12.8	-11.5	-11.8
Mn	-73.2	-6.4	-266.2	-95.4
Ca	-885.5	-233.3	-190.2	-656.7

*Underlined means are not significantly different (0.05).
†Minus numbers indicate elution.

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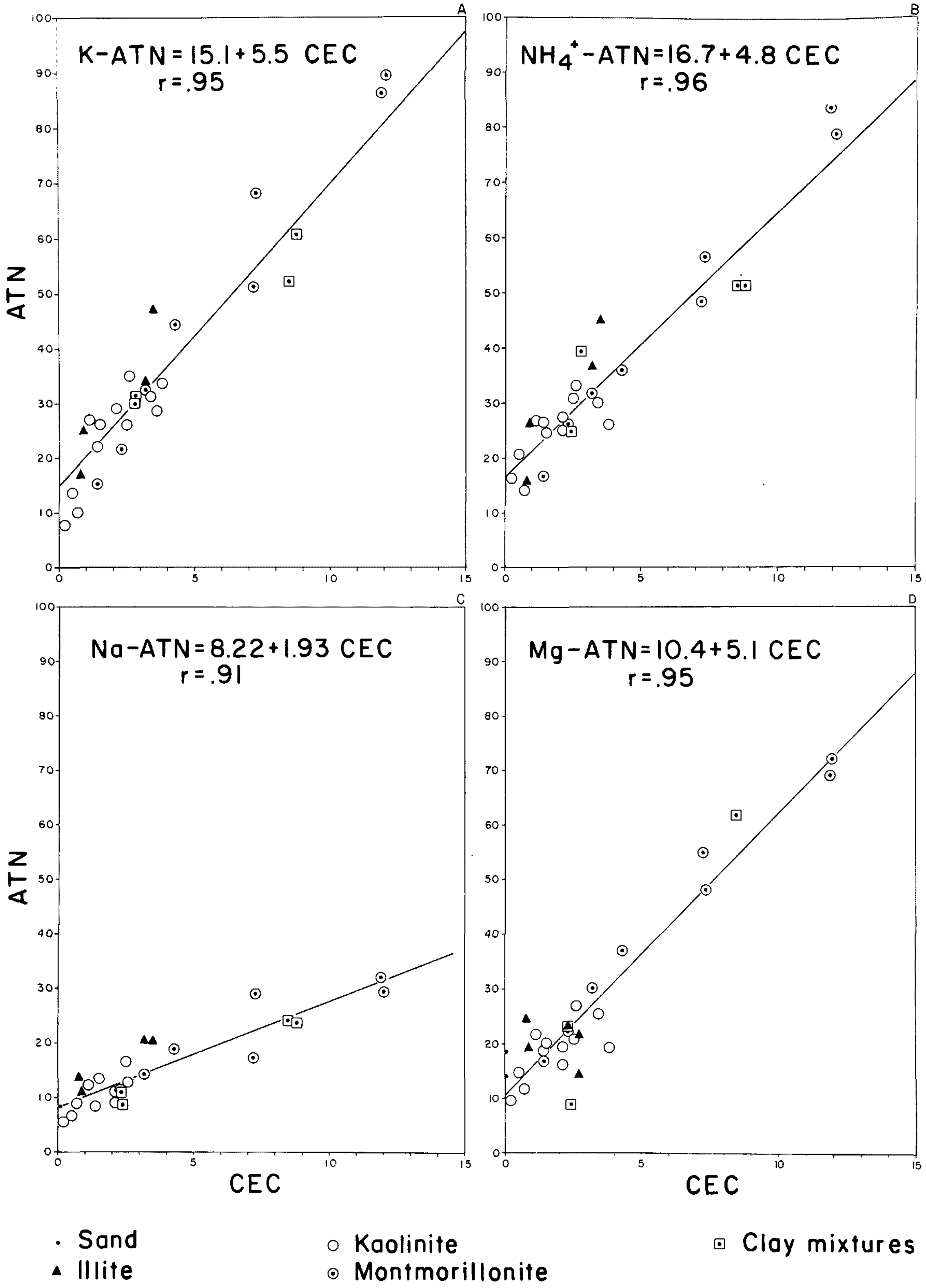

Figure 4. The attenuation number related to cation exchange capacity (a) K, (b) NH_4^+, (c) Na, and (d) Mg.

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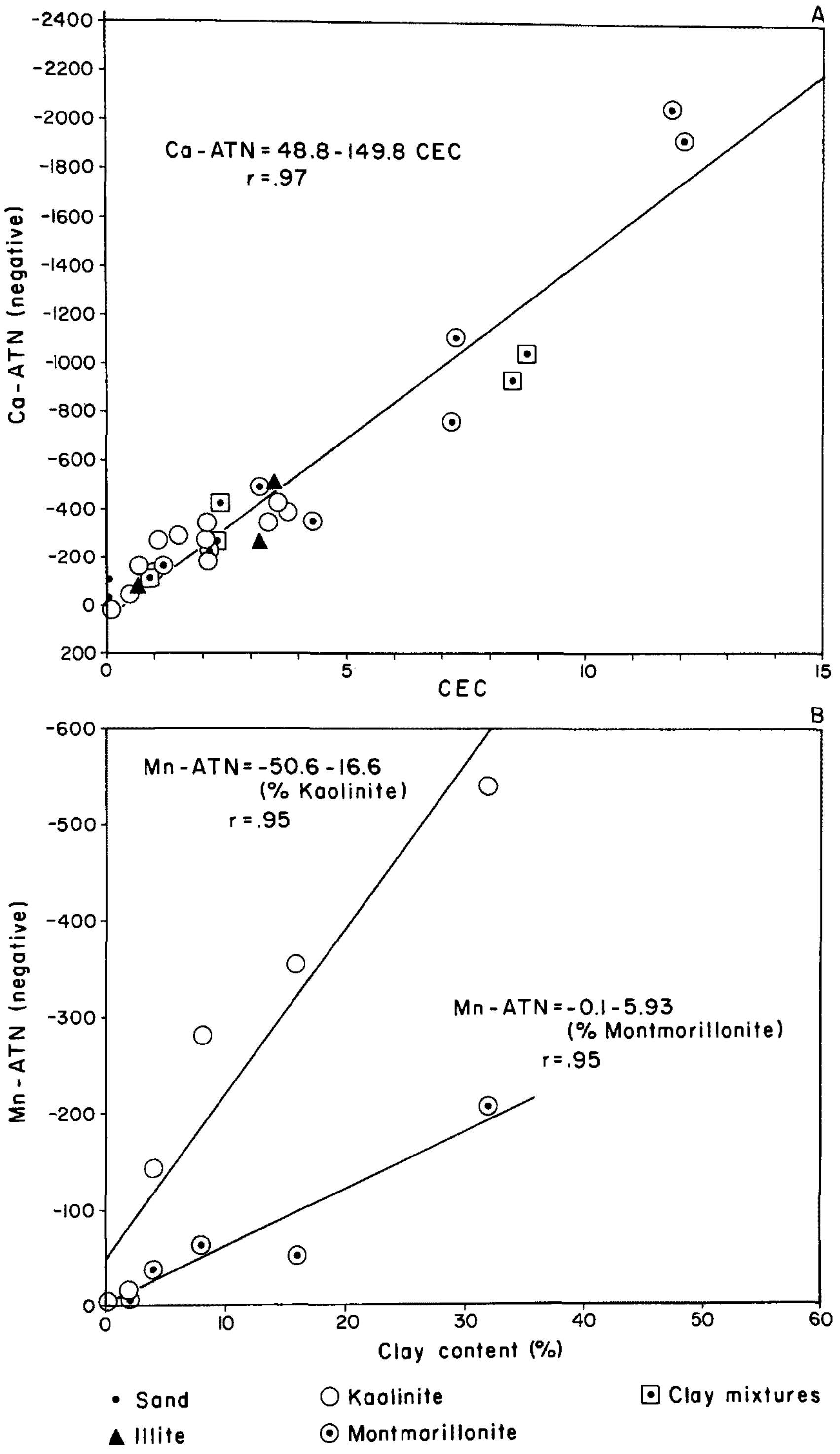

Figure 5. (a) Ca attenuation number related to cation exchange capacity.
(b) Mn attenuation number related to clay percentage.

Exhibit E

halo," are likely due to the same mechanism responsible for the Ca elution from the columns in this study. This is discussed further in Section 6.

No significant linear regression of attenuation as a function of either CEC or clay percentage was obtained for Fe, Si, COD, Cl, B, or Mn, except for a very highly significant linear regression obtained for Mn elution and clay percentage. The results of the regression of Mn elution as the percentage of kaolinite and montmorillonite increased are presented in Figure 5b. No significant linear regression could be obtained with illitic clay because only two illite columns were used. The data illustrated in Figure 5b show that approximately three times as much Mn eluted from the kaolinite-containing columns as from the montmorillonite columns. The data presented in Table 1 indicate that kaolinite contains only slightly more total Mn than montmorillonite. However, surface Mn is three times more abundant on kaolinite than on montmorillonite and corresponds to the increased elution from the kaolinite columns. No correlation of Mn elution was observed with CEC, and the amounts of surface-extractable Mn correlate with the amounts eluted from the various columns. These facts, along with the anaerobic conditions in the columns, have led to the conclusion that Mn elution is due to the reduction of surface coatings of Mn compounds on the clays to more soluble reduced ionic species. The increase in Mn elution from kaolinite columns is proportional to, and apparently due to, the larger amount of Mn on the surface, where it is readily available for reduction and solubilization by the anaerobic leachate.

The behavior of Fe is similar to that of Mn; however, it is more sensitive than Mn to the oxidation potential in the leachate. During the early stages of leaching, Fe was also solubilized and eluted from the columns, as is shown in Figure 3. However, unlike Mn, Fe showed a net attenuation of 58.4% when the entire 10 pore volumes leached were considered. The results of this study, therefore, indicate that Fe may be either eluted or not attenuated by clay liners if the leachate is strongly anaerobic, or it may be strongly attenuated under weakly anaerobic conditions.

Other data from this study indicate that attenuation of COD was relatively low after passage of DuPage leachate through clay columns. This result is in agreement with those of Urioste (1971), who reported poor removal of COD when leachate was ponded on soils. The lack of a strong clay effect and of a significant correlation of attenuation of COD with either clay percentage or CEC indicate that the observed attenuation was probably the result of microbial degradation of the organic compounds. The fact that the leachate is relatively old probably accounts for the relatively low reduction in COD. It has only a small percentage of readily degradable organics and a low nutrient status, owing to the lack of PO_4 (Table 2).

Chloride attenuation was also relatively low, only 10.7%. This low attenuation is not surprising, because Cl is considered as a mobile non-interacting anion in soil systems. The low Cl attenuation was not a function of the type or amount of clay mineral present and is attributed to physical dispersion in the porous column media, with perhaps a small amount of interaction at anion exchange sites on the clay, or to other chemical reactions.

Since Cl is a negative ion, it would be attracted only by the positive charge at the edge of the clay minerals. Oxygen and OH are the negative ions of the lattice, and any other negative ion would have to be nearly the same size as the oxygen ion in order to coordinate with and continue or substitute for the oxygen. Because the chloride ion is about two and one half times the volume of the oxygen ion, it is too large to replace or coordinate with the oxygen and hydroxyl ions, although fluorine can do so because it is about the same size as the oxygen and hydroxyl ions.

No attenuation of B was observed in this study; rather, a small elution of boron from the columns took place throughout the leaching experiment. This may be interpreted as a slight solubilization of B from the clay minerals or sand in the columns. However, no effect of type or percentage of clay and no changes in elution with leaching time were found during the study. These facts have led to the conclusion that the B results may be an artifact of the experiment. It has been suggested that B may be dissolving from the borosilicate glass tubing used throughout the apparatus. More importantly, B may be solubilized from the spun glass wool used as a filter to keep sand and clay from migrating into each of the five manometers and the outflow tubing (Fig. 1). The high surface area of the spun glass and the neutral pH of the leachate make it plausible that the boron elution may be due to contamination. In any case, no attenuation of boron was observed in this study.

The results presented in Figure 4 and Table 5 permit the three clay minerals to be ranked, according to their overall attenuating ability for the chemical constituents found in municipal leachate, as follows:

montmorillonite > illite > kaolinite.

The montmorillonite used in this study has properties similar to those of smectites produced by weathering of micas, chlorites, and other crystalline minerals. The cation exchange capacity is lower than that for montmorillonite produced from weathering of volcanic ash and basaltic rocks.

The montmorillonite used produces clay material (e.g., Porter's Creek Clay) that have much higher permeabilities than those from Wyoming-type montmorillonite. Such high permeability should make this montmorillonite more useful than some other types of montmorillonite in making landfill liners in humid climates. With its high cation exchange capacity, it would adsorb more of the cations in the leachate than either illite or kaolinite. With its greater permeability, it allows more water to pass through the liner than do many other types of montmorillonite. The low permeabilities of other montmorillonite types would probably increase the hazard of lateral seepage from the sides of the landfill in humid climates.

Some sodium montmorillonites tend to shrink when sodium is exchanged for divalent and trivalent cations or when salt concentrations are high. This shrinkage sets up tension, which in turn produces cracks called syneresis cracks. Syneresis cracks were common in irrigation ditches in Colorado that were lined with sodium montmorillonite (personal communication, R. D. Dirmeyer, Jr., 1961). Shrinkage could be reduced considerably by using calcium montmorillonites and mixing them with other earth materials (e.g., 16 to 32% montmorillonite and 68 to 84% sand).

Exhibit E

The kaolinite used in this study is a fine-grained material in which the crystallinity of the kaolinite crystals is poor. It has a high cation exchange capacity compared with other kaolinites. Well crystallized kaolinites with large crystals have a cation exchange capacity of 1 to 5 meq/100 g. The kaolinite used in this study would be better suited than most kaolinites for landfill liners. The permeability of this kaolinite is lower than that of well crystallized kaolinite with large crystals. The kaolinite in most sediments has a cation exchange capacity and permeability between those of the kaolinite used and the well crystallized kaolinites.

The illite used is similar in cation exchange capacity and permeability to the illite found in most sediments. The sediment from which the experimental illite was taken contained only one clay mineral -- the illite -- whereas most sediments that contain illite also contain other clay minerals.

It was concluded that the attenuation order was due principally to the cation exchange capacity of each of the three clays.

Attenuation of Leachate

During the period of time from collection of the leachate through the establishment of hydraulic equilibrium, the leachate was stored in a refrigerated (3 to 5^{o} C) condition with either argon or sterilant gas being purged slowly over the top of each respective drum. Chemical analyses were performed weekly on the leachate to monitor possible changes in composition. As a result of this monitoring, it was determined that the COD of the sterile drum was steadily rising. It was determined that the active component of the sterilant gas, ethylene oxide, was able to react with the chloride ion present in the leachate which acted as a nucleophile to produce ethylene chlorohydrin (Rosenkranz and Wibdkowski, 1974). When it was discovered that the COD was rapidly rising, the use of the sterilant gas was discontinued. Argon was then used as the purge gas for both drums and mercuric nitrate salt was added to the sterile drum to maintain sterility. Further monitoring of both drums was continued at approximately 1 week intervals during the 10 month period during which leaching of the columns occurred. The COD values were found to remain constant at the value obtained when purging of sterilant gas was discontinued. The value reported in Table 2 for COD, and for all the other constituents, is the average of the 37 separate analyses performed during the 10 month period of leaching.

Determination of the attenuation of chloride and the other major components of DuPage leachate has been described in Section 5. The results of this study indicated that there was an average 6% greater attenuation of chloride in the columns leached with sterile leachate than those leached with the natural leachate. This greater attenuation is attributed to the reaction of chloride with the ethylene oxide to form ethylene chlorohydrin. Other than the slight increase in chloride attenuation, no other significant difference was apparently due to the increase in COD in the sterile leachate as compared to the natural leachate.

There were, however, other significant differences between the sterile and natural leachate treatments which were not attributed to the higher COD

Exhibit E

of the sterile leachate. Figure 6 illustrates the difference observed in Mn elution from the colums. It should be noted that a negative attenuation number indicates that more Mn eluted from the column than was present in the influent leachate. It can be seen that much higher levels of Mn were found in effluents from the columns leached with natural leachate. It was concluded in Section 5 that this elution was due to reduction of surface coatings of Mn oxides on the clays by the anaerobic leachates. This conclusion is further verified by the difference in Mn elution between the natural and sterile leachate treatment. This difference is attributed to the stronger anaerobic environment provided by the active microorganisms present in natural leachate. Inspection of the data in Table 2 shows that the average Eh (oxidation potential) reading of the natural leachate was 10 times lower than the sterile leachate, even though both were well in the anaerobic range (Eh readings less than 197 m.v. are considered to reflect anaerobic conditions). A similar result was obtained for Fe in that significantly (.05 level) greater mobility of Fe was found in columns leached with natural leachate as compared to those leached with sterile leachate. A mechanism similar to that for Mn is postulated as the reason for the observed differences between the natural and sterile leachate.

Those chemical constituents for which no significant difference in attenuation between the normal and sterile leachate was found were Ca, Mg, Na, K, NH_4, Pb, Hg, Zn, and Cd.

POLLUTION HAZARD OF LEACHATE

In addition to determining the relative mobilities of the various chemical constituents of leachate through clays (liner materials), their relative pollution hazard should be evaluated. Ranking wastes in terms of their existing or potential threats to public health and/or the environment has been the subject of the "Priority Ranking System" suggested for development by the U.S.-EPA (1973).

The priority ranking formula is:

$$R = \dot{Q}/CP \qquad \{3\}$$

where R = ranking factor,
Q = annual production quantity for the waste being ranked, and
CP = critical product for the waste being ranked.

A critical product is the lowest concentration at which any of the hazards of concern become manifest in a given environment, multiplied by an index representative of the waste's mobility into that environment. Thus, for a municipal leachate that would be discharged through a clay liner or soil into an aquifer used for drinking water, the toxicity factor could be the public water supply limits for the given element, and the mobility index could be the attenuation numbers derived above.

Evaluation of the critical product for municipal leachates moving through soils or clay liners by the U.S.-EPA (1973) formula proved to be awkward and unsatisfactory for several reasons. The first problem encountered

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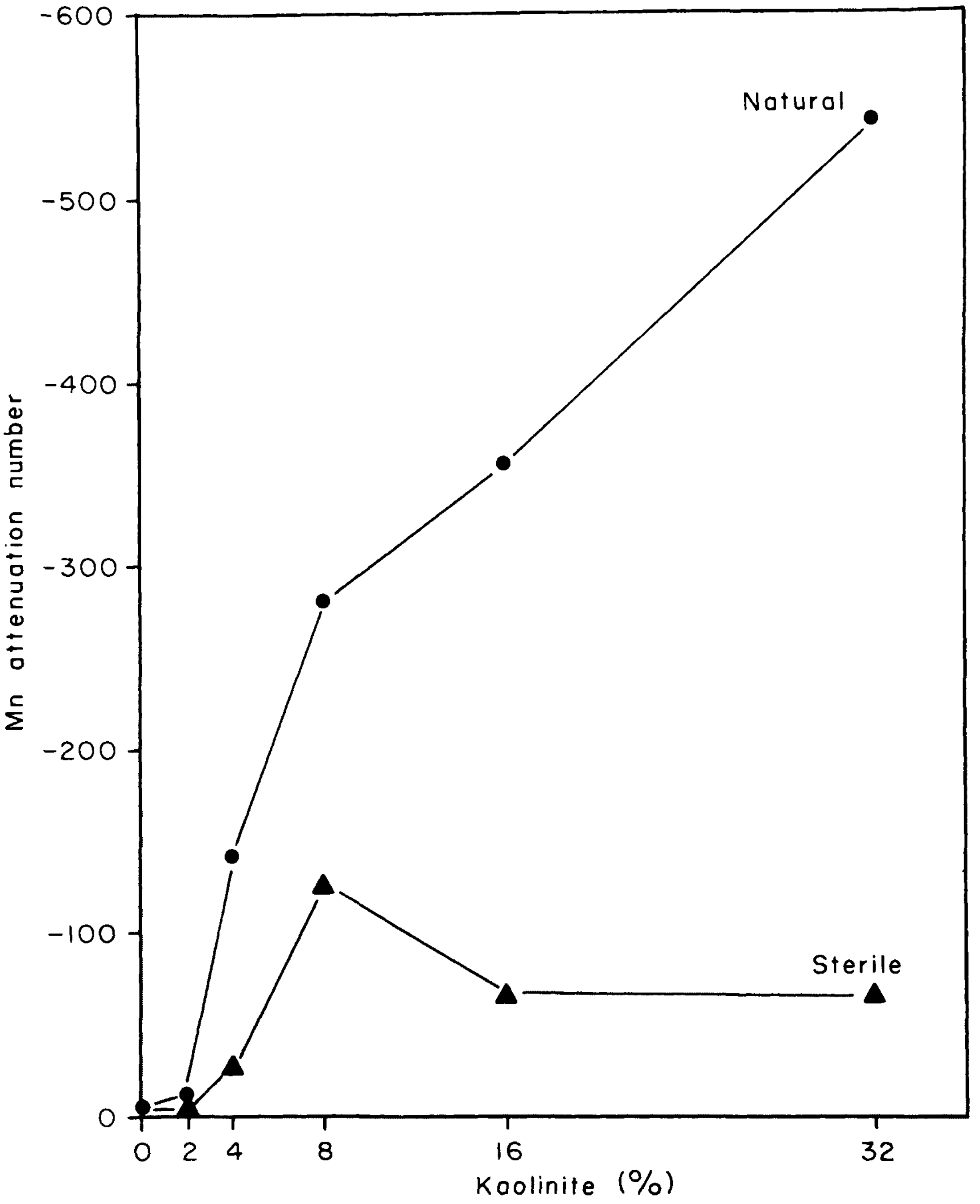

Figure 6. Manganese elution related to percentage of kaolinite leached with natural and sterile leachate.

was that negative attenuation numbers, such as those obtained for calcium, were not accounted for by the formula. A transformation of the data would be necessary to express the negative numbers in a manner that could be used in the CP formulation.

The second problem encountered was evaluation of the CP for the four heavy metals. An upper boundary on the attenuation number, such as the 100% removal, used to express the heavy metal removed from leachate is not allowed conceptually by the formula. Instead, what is required is the actual attenuation as determined by leaching until "breakthrough" of the particular element is achieved. For Pb, an estimated 300 pore volumes would have to be leached through an average column to achieve breakthrough. It was deemed impractical to actually measure the breakthrough of the heavy metals, and estimating their breakthrough required additional analytical data that could cause errors in estimating the pollution hazard.

A third problem with evaluating the pollution hazard by using the CP was that it was not specific for the waste being evaluated in that the concentration of the element of interest in the waste did not enter into the evaluation of the hazard. That this is a serious fault can be illustrated by simple examples: an element with a relatively high toxicity and mobility index could get a high hazard rating, even though only a trace was present in the waste; conversely, an element with a relatively low toxicity and mobility could receive a low hazard rating even though it was present in very high concentrations.

A fourth criticism of the CP rating was that it was conceptually illogical because large CP values indicated a low pollution hazard and, conversely, a very small number represented a very high hazard. It was considered more logical to express high pollution hazards as large numbers when a relative scale was used or when pollution potentials were evaluated.

To overcome these objections to the CP formulation of a pollution hazard index for municipal leachates, the ranking equation was changed as follows:

$$R = (Q)\ (HI) \qquad \{4\}$$

where R and Q are as previously defined and
HI = the pollution hazard index for the waste.

The pollution hazard index (HI) is a toxicity index for the element within a given leachate, multiplied by a mobility index for the element in a particular leachate-clay system. The pollution hazard for the whole leachate is that for the constituent with the highest hazard within the particular leachate.

$$HI = \left(\frac{C}{DWS}\right) (100 - ATN) \qquad \{5\}$$

where C = the effective concentration of the chemical constituent,
DWS = the drinking water standard (U.S.-EPA, 1972), and
ATN = the attenuation number for the given element.

Exhibit E

The effective concentration is defined as the concentration of the chemical constituent in the leachate plus the concentration of the constituent that may be leached from the soil or clay. When attenuation is occurring, the effective concentration is merely the concentration of the constituent in the influent leachate. When elution from the columns is occurring, as it did for the three elements B, Ca, and Mn, the effective concentration is the leachate concentration plus the concentration eluted from the column. Table 6 presents the 15 chemical constituents for which ATN values are available, ranked according to their pollution hazard, as determined by equation 5.

The results in Table 6 give a reasonable ranking of the chemical constituents in terms of what would be expected from a gross overview of the data. The ranking system has the advantage of quantifying the expected pollution hazard of a given leachate and allows comparisons of the pollution hazards of one leachate with another. The ranking system also focuses attention on the chemical constituent with the highest pollution potential. In the case of DuPage leachate, NH_4^+ was found to have the highest pollution hazard. In a fresh leachate, COD might be expected to have the highest pollution potential. However, in the DuPage leachate the hazard index clearly indicates that NH_4^+ is a pollution hazard about 30 times greater than any other constituent found in this particular leachate.

We feel that the proposed pollution hazard ranking system for municipal leachates (equation 5) overcomes the objections posed previously for the CP component of the Priority Ranking System. The toxicity index can in most cases be computed readily from a chemical analysis of the leachate.

The evaluation of the toxicity index is flexible in that drinking water standards need not be the criteria. LD_{50} values, or some other toxicity evaluation, can be used in place of drinking water standards. What we think is important is the computation of the ratio of the actual waste concentration relative to whichever toxicity evaluator is used. The mobility index, however, must be determined experimentally or estimated from the data presented in this paper. The results of this study indicate that the mobility index will be a function of the CEC of the earth material, the cations present initially on the exchange complex, the chemical composition of the leachate, and the pH of the leachate.

Exhibit E

TABLE 6. CHEMICAL CONSTITUENTS IN DUPAGE LEACHATE, RANKED ACCORDING TO POLLUTION HAZARD

Chemical constituent	Effective concentration / D. W. standard	Toxicity index	Mobility index	Hazard index
NH_4	862/0.5	1724.	62.9	108,440.
B	(29.9 + 3.5)/1.0	33.4	111.8	3,734.
COD	1340/50	26.8	78.7	2,109.
Hg	0.87/0.002	435.	3.2	1,392.
Cl	3484/250	13.9	89.3	1,241.
Ca	(46.8 + 307.3)/250*	1.42	756.7	1,072.
Cd	1.95/0.01	195.	3.0	585.
Fe	4.2/0.3	14.0	41.6	582.
Na	748/270	2.77	84.6	234.
Mn	(0.02 + 0.02)/0.05	0.78	195.4	153.
K	501/250*	2.00	61.8	123.
Mg	233/250*	0.93	70.7	65.7
Pb	4.46/0.05	89.2	0.2	17.8
Zn	18.8/5.0	3.76	2.8	10.5
Si	14.9/250*	0.06	45.3	2.7

*Actual value not established by EPA; therefore it was assumed to be the same as chloride.

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SECTION 6

CONFIRMATION OF LABORATORY COLUMN STUDIES BY COMPARISON WITH FIELD DATA[1]

ABSTRACT

The results of the laboratory column leaching experiments were checked at the DuPage County sanitary landfill and at other existing landfills where detailed field data are available. These field data clearly show a "hardness halo" corresponding to the Ca release observed in the column experiments. The relative attenuation rates of some of the ions are also confirmed by the field data.

Laboratory results show that the leachate reduced the hydraulic conductivity of the columns during the experiment. Although similar change in field hydraulic conductivity was not clearly demonstrated, the field data suggest that it took place.

These results suggest that overall pollution from landfill leachate would be reduced by designing earth material landfill liners for higher permeability. Properly designed liners would selectively attenuate the toxic pollutants from the leachate and allow the ground water to dilute the non-toxic components which can be tolerated at much higher concentrations without harmful effects. The study raises some basic questions on monitoring systems and landfill design which should be addressed by regulatory agencies responsible for environmental quality.

INTRODUCTION

This paper principally relates two phenomena noted in the laboratory to field observations around sanitary landfills: the elution of large amounts of the calcium ion from the study columns (Fig. 3) and the reductions in hydraulic conductivities which resulted from the introduction of leachate to the clay-sand mixtures. It is felt that the testing of laboratory results in field situations is necessary before the data may be used in sanitary landfill design.

RESULTS AND DISCUSSION

Hardness Halo

Figure 3 (Section 5) illustrates the negative attenuation or elution of

[1] Authors: K. Cartwright, R. A. Griffin, and R. H. Gilkeson.

Exhibit E

Ca, Fe, and Mn from the columns containing 2, 8, and 16% montmorillonite clay in sand. The relative concentrations greater than 1 indicate that Ca and to a lesser extent Fe and Mn are eluting from the column at much greater concentration than the influent leachate at various pore fractions. The area under the Ca curves can be seen to increase in proportion to the percentage of clay in the column, was quantified in Section 5 by integrating between pore fraction 1 and 11, and was assigned a relative attenuation number (ATN) as shown in Table 4 (Section 5).

The elution of Ca from the columns was attributed to an ion-exchange mechanism; the replacing of the Ca bonded to the clays at their cation exchange positions by other ions in the leachate.

Soils in much of Illinois are carbonate rich, with the clays generally having Ca in the cation exchange position, and have free carbonates in all except the leached zone of the soils. The presence of excessive hardness in the vicinity of sources of pollution has appeared in a number of articles, but is rarely discussed as to its origin. An example is found in a DuPage County study (Fig. 7, from Zeizel et al., 1962). There are two areas of the county where the hardness, as $CaCO_3$, in the shallow carbonate aquifer exceeds 1000 parts per million (ppm). The eastern area is a fairly heavily developed residential area and the glacial drift, which protects the aquifer from pollution, is relatively thin. No specific source of the high hardness can be established; however, it is most likely due to a high concentration of home septic systems. The western area of high hardness near West Chicago is thought to have resulted from the discharge of large volumes of waste chemical salts to surface ponds.

Other examples can be found in Anderson and Dornbush's (1967) study of a sanitary landfill in South Dakota, and Walker's (1969) discussion of groundwater pollution in Illinois. Most recently, Henning et al. (1975) showed high calcium in monitoring wells very close to a landfill trench at Mentor, Ohio; the Ca concentrations both decreased with distance from the fill and were lower in the refuse than in the closest wells.

Hughes et al. (1971) published the results of studies of five landfills in northeastern Illinois, including the Old DuPage County landfill from which the leachate was taken for this study. Monitoring continued for three years following the completion of that report. Figure 8 was drawn, using data from the Winnetka and Old DuPage landfills.

The Winnetka data (top, Fig. 8) shows considerable scatter. This may be partly due to a mixture of points, some in the fine-grained alluvium and some in the glacial till which have somewhat different properties. However, these data suggest that the hardness approaches background within 9 to 15 meters of the refuse which is somewhat less than the distance that the chloride ion travelled (Hughes et al., 1971). Note that the four data points from piezometer nest LW3 follow this pattern.

The till under the Old DuPage landfill clearly illustrates the increase, then decrease in hardness. The till is separated from the refuse by 1 to 1.5 meters of sand. The hardness returns to background within about 1.5 meters of

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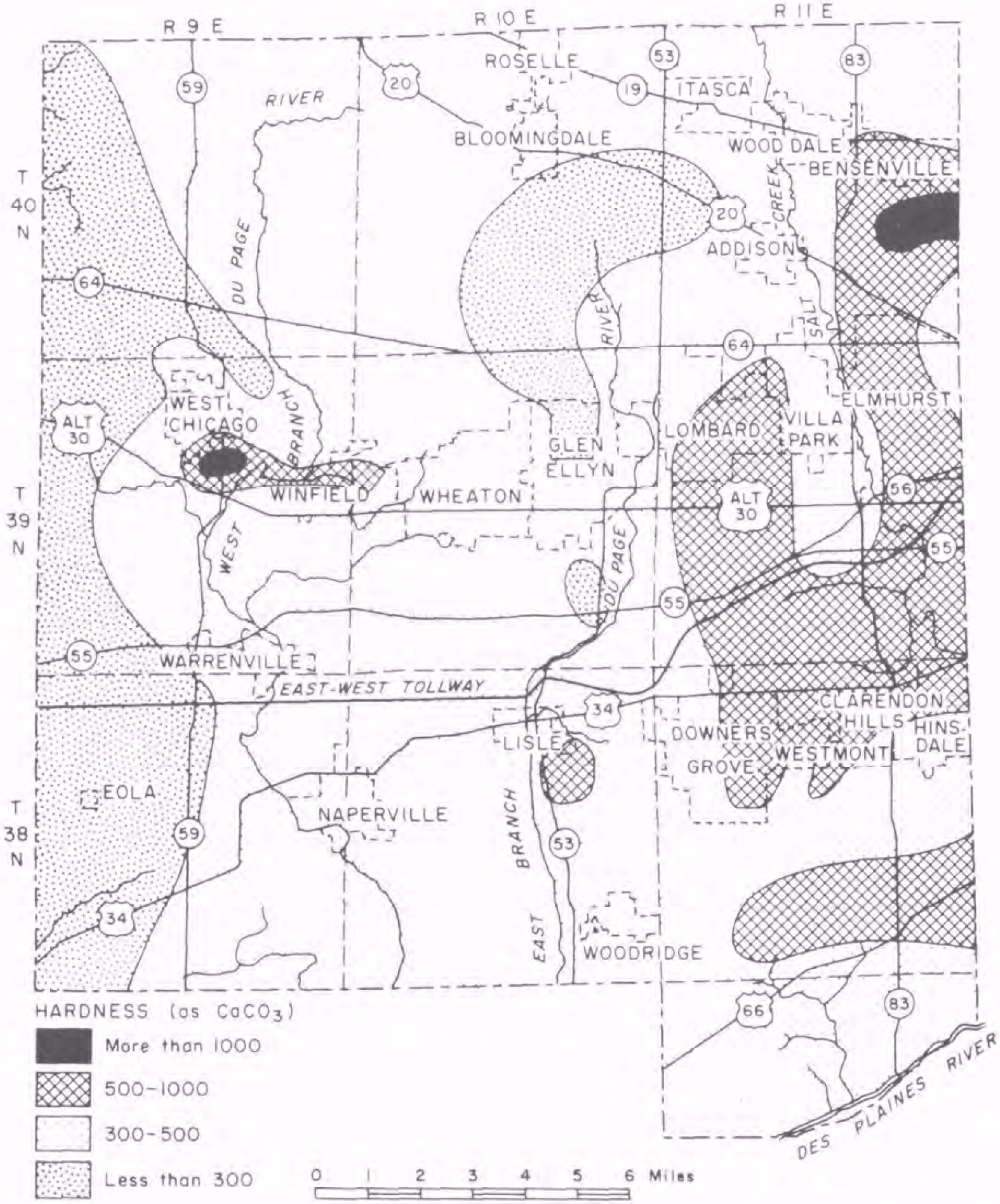

Figure 7. Hardness of water, expressed as $CaCO_3$, in the Silurian Dolomite aquifer in DuPage County, northeastern Illinois (from Zeizel et al., 1962).

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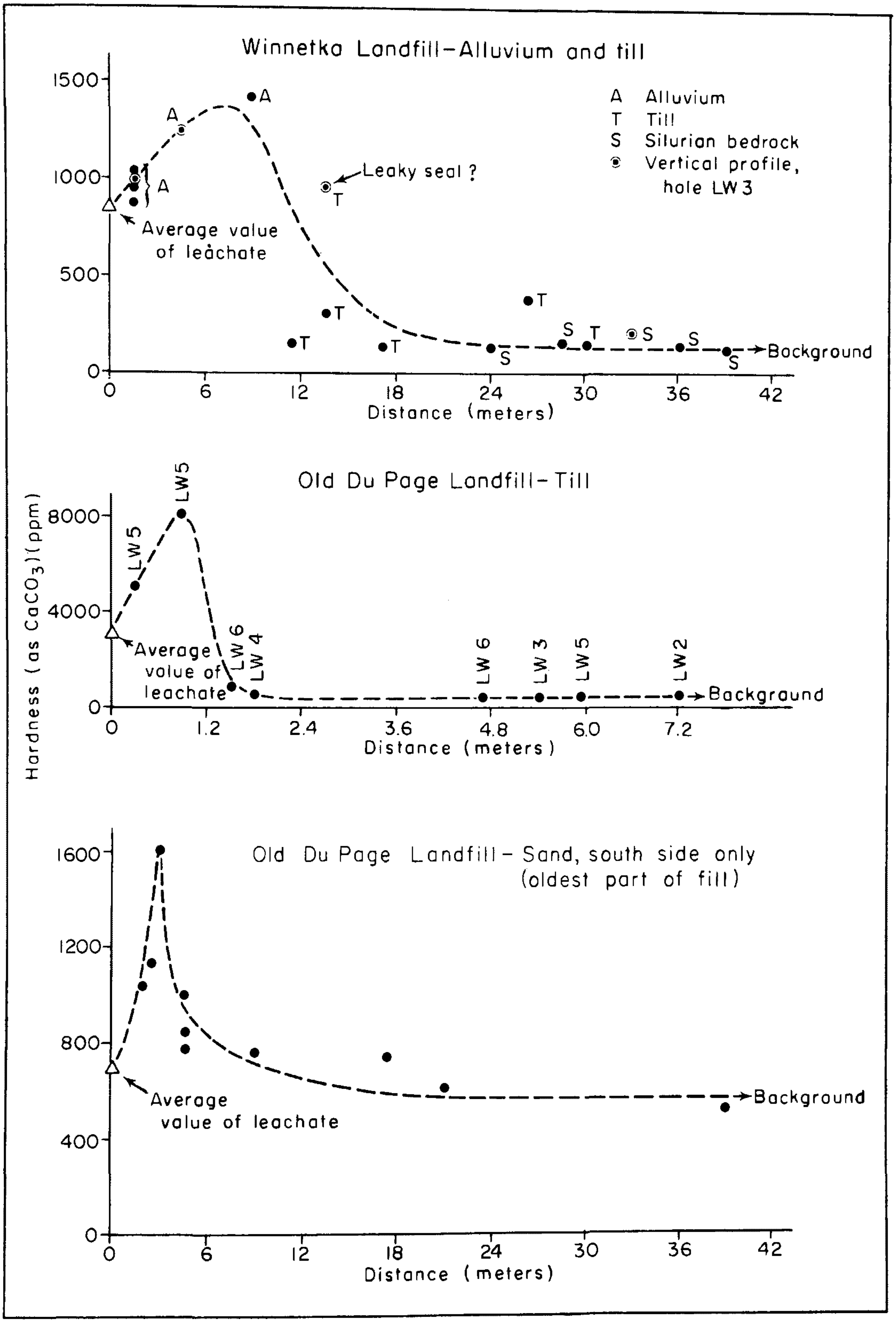

Figure 8. "Hardness halo" effect shown as a function of distance (m) from the Winnetka and DuPage landfills in northeastern Illinois.

travel, about half the distance of the estimated travel of the chloride ion (Hughes et al., 1971). Note, in particular, the values shown for piezometer nests LW5 and LW6. These data points are all for the younger, northern part of the fill; data from the older parts of the fill do not fit the same curve (all hardness concentrations fall too low).

The surficial sand transmits leachate-contaminated water south from the older parts of the DuPage landfill and shows a similar hardness distribution. The hardness levels are much lower in the old refuse in this area, and all the values reflect that lower concentration. The hardness returns to background levels within 9 to 15 meters; however, chloride ion has moved 240 to 300 meters in the permeable sand layer.

All these data clearly show the presence of the "hardness halo" resulting from the movement of leachate into the surrounding till and sands, and that the rate of the hardness front is less than that of the chloride ion. The chloride ion is probably the best tracer of this type of pollution in this environment. The distance of travel varied from slightly less to approximately 10% of that of the chloride ion; this probably is controlled by the nature of the materials, cation exchange reactions, concentrations in the leachate, and ground-water flow rates. Nevertheless, all the data show an increase in the hardness of the water in the sediments over that in the leachate.

Hydraulic Conductivity

The results of initial hydraulic conductivity and bulk density measurements of the column contents in the laboratory study are presented in Table 3. These data indicate that a wide range of hydraulic conductivities, with values in agreement with those expected under field conditions from similar materials (Todd, 1959) were observed. The relatively high bulk densities and slow flow rates used in this study closely simulate the conditions observed in the field. This lends credence to the extrapolation of the results and conclusions of the laboratory studies to those obtained in the field.

During the initial stage of the experiment, the columns were leached with deionized water until steady state conditions were achieved. The columns containing low percentages of clay reached hydraulic equilibrium relatively rapidly while the high percentage clay columns required leaching for well over a month to achieve steady manometer readings. When hydraulic equilibrium was achieved, as indicated by steady flow rates and relatively constant manometer readings from the five manometers located over the entire length of each column, the leachate was added to the columns.

Significant reductions in hydraulic conductivity and significant differences in the reductions between natural and sterile leachate were observed. The results of hydraulic conductivity changes observed in columns containing montmorillonite, kaolinite and illite clays are presented in Figures 9, 10, and 11. The data presented in these figures were statistically smoothed using the five-member moving-average method to show more clearly the trends in the data. The raw data were statistically analyzed to determine whether significant differences in hydraulic conductivity occurred between

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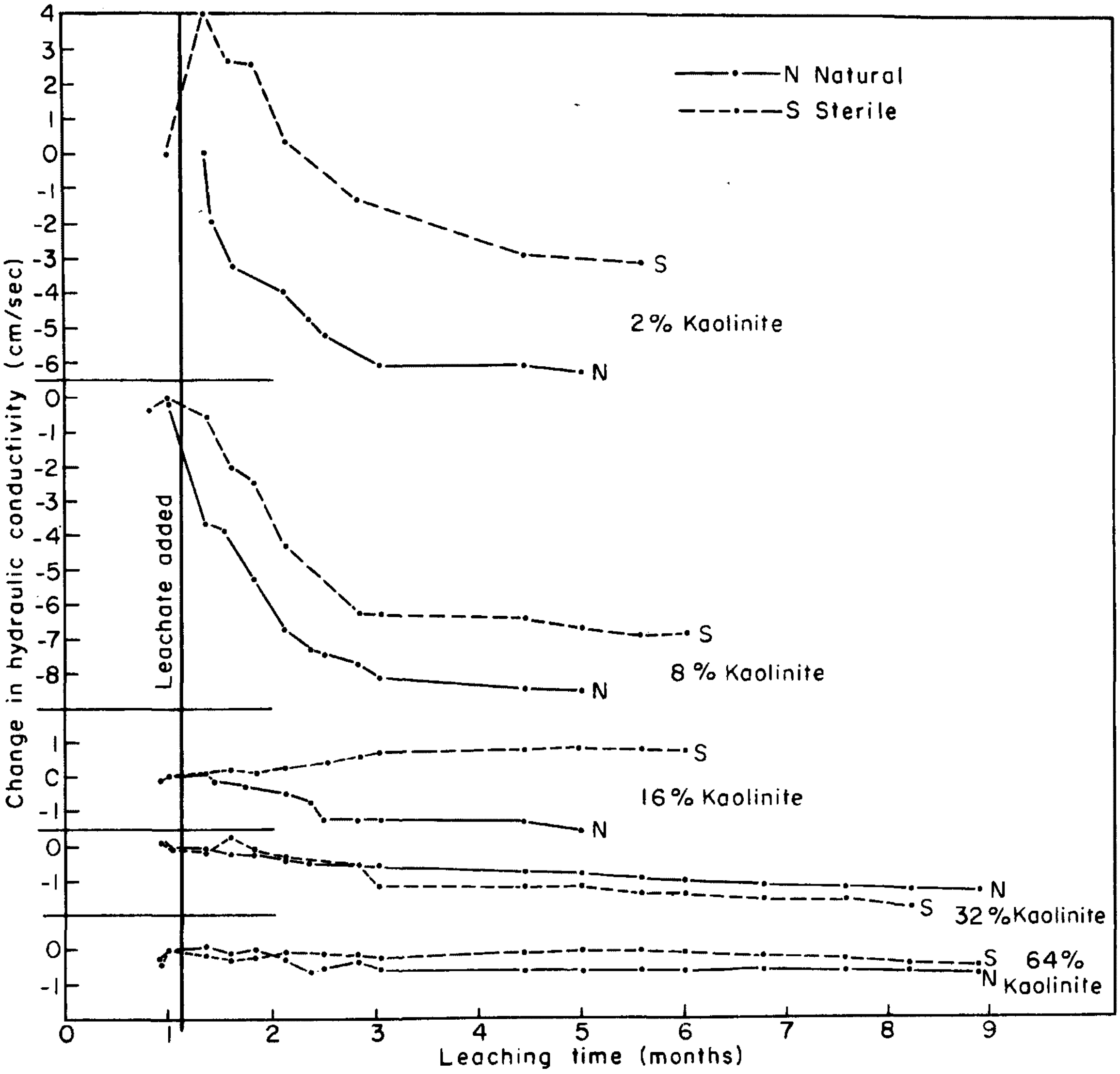

Figure 9. Hydraulic conductivity of kaolinite-sand columns as a function of leaching time.

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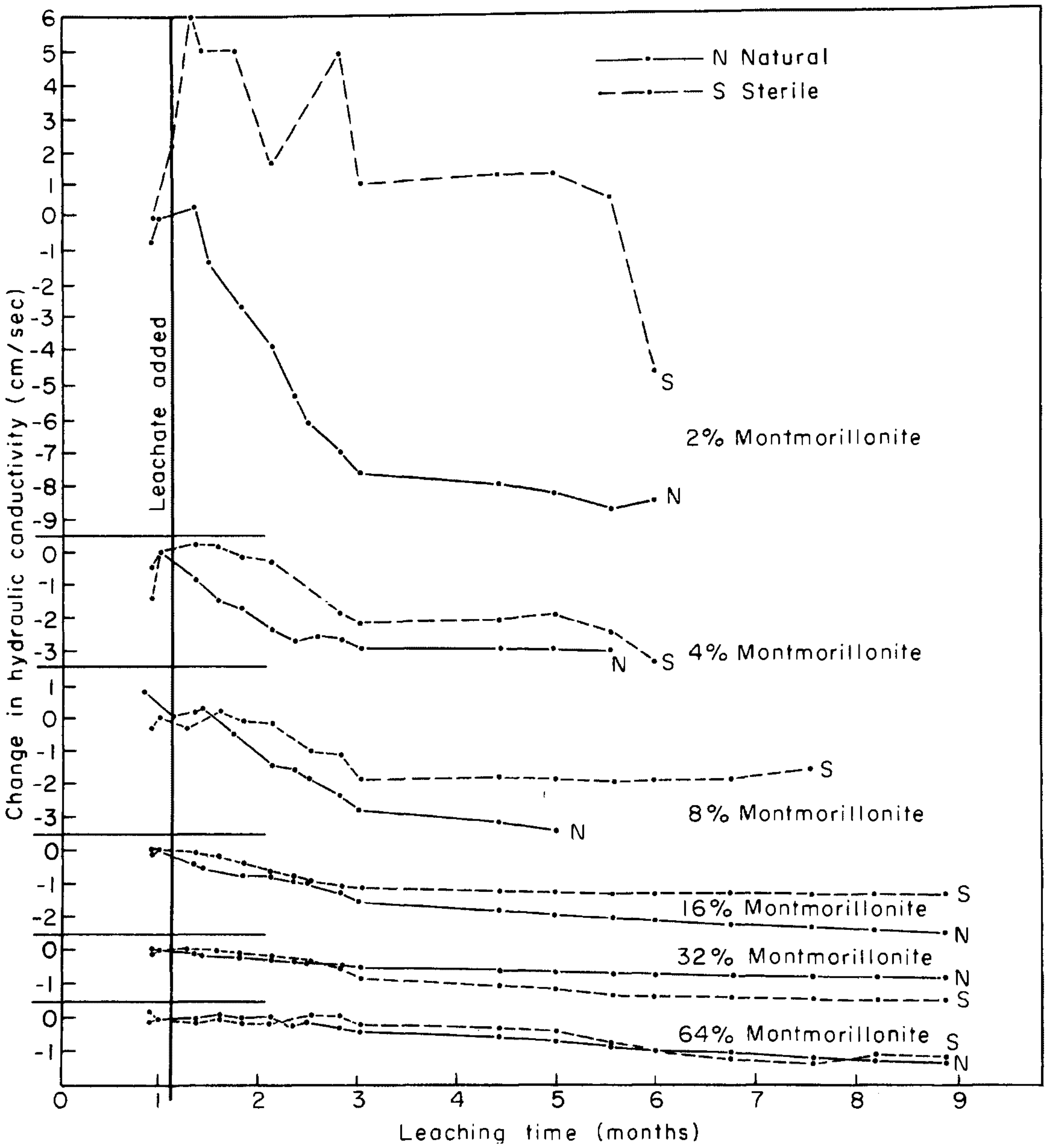

Figure 10. Hydraulic conductivity of montmorillonite-sand columns as a function of leaching time.

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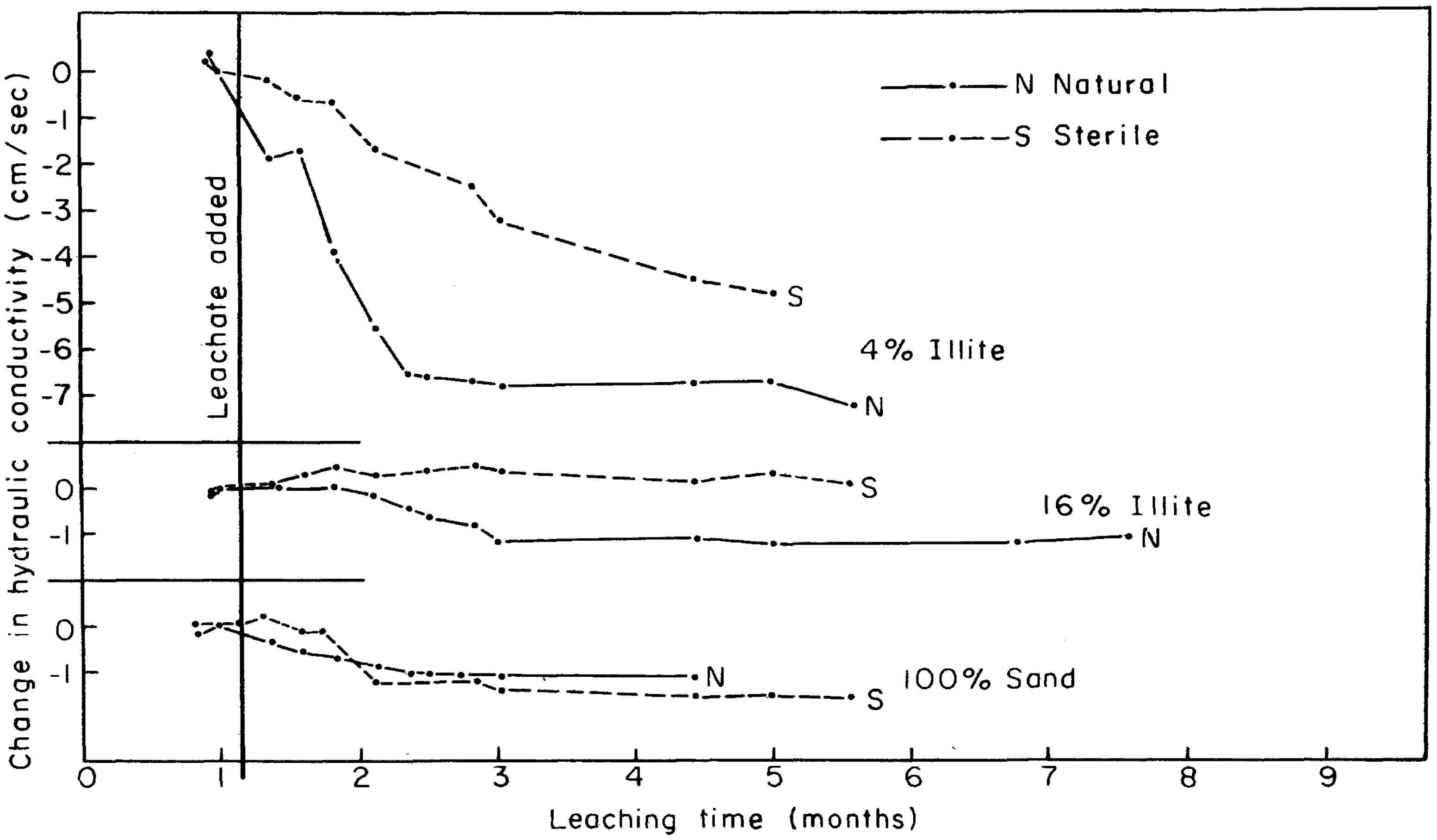

Figure 11. Hydraulic conductivity of illite-sand columns as a function of leaching time.

Exhibit E

sterile and natural leachate. The data from the columns containing 4% kaolinite were rejected from the analysis when they were found to deviate by more than 3 standard deviations from the overall mean change in hydraulic conductivity observed for all other columns. The manometer readings indicated that the outflow tubes were plugged. The reason why only 4% kaolinite treatments had this problem is not clear.

The results of the statistical analysis indicated that columns leached with natural leachate had significantly (.05 level) greater reductions in hydraulic conductivity than those leached with sterile leachate. This result is illustrated clearly in Figures 9, 10, and 11. Furthermore, the statistical analysis showed that columns containing montmorillonite had significantly greater average reductions in permeability than kaolinite or illite and that there was no significant difference between kaolinite and illite. This result is consistent with the swelling nature of montmorillonite clay and is not surprising.

Field data to support this conclusion are not as clear as for the "hardness halo." Fewer field tests have been made for hydraulic conductivities than chemical tests for water quality. In addition, field tests may be accurate only to approximately a half-order of magnitude.

At the Winnetka landfill (Hughes et al., 1971), 23 hydraulic conductivity tests were conducted, 7 on refuse, 4 on alluvium, and 7 on till. These data are too scattered to show any significant differences with distance from the refuse.

At the Old DuPage County landfill, 34 field hydraulic conductivity tests were made, 14 on refuse, 14 on sand, and 6 on till. The data on the hydraulic conductivity of the sand (all south of the fill) suggest some reduction in hydraulic conductivity. The 10 tests made on monitoring wells less than 6 meters from the fill have a mean hydraulic conductivity of 4.32×10^{-4} cm/sec (range 1.9×10^{-3} to 1.9×10^{-7}), and those monitoring wells greater than 12 meters from the refuse (4 tests) have a mean conductivity of 2.59×10^{-3} cm/sec (range 7.6×10^{-3} to 9.5×10^{-4}). The data are not statistically significant, but they do suggest a hydraulic conductivity reduction similar to that noted in the laboratory.

The reductions in hydraulic conductivity observed in the laboratory study with the DuPage leachate seem particularly significant. This is due to the fact that the DuPage leachate is approximately 15 years old (Hughes et al., 1971) and contains a relatively low percentage of organic compounds which are readily degradable by microorganisms (Table 2). In addition, this leachate has a low nutrient status with both phosphate and sulfate being absent in detectable quantities. Much higher amounts of microbial growth and plugging might be expected from a younger leachate.

The results have led to the conclusion that if clay liners, natural or man-made, of similar composition to those used in this study are used in municipal landfills, significant reductions in hydraulic conductivity can be expected due to microbial growth. Further, slightly higher reductions in hydraulic conductivity can be expected from montmorillonite clays, apparently

Exhibit E

due to their swelling tendency. It was also concluded that Mn and/or Fe may be leached from clay surfaces in substantial amounts under highly anaerobic conditions but may not be leached under mildly anaerobic conditions.

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SECTION 7

EFFECT OF pH ON EXCHANGE-ADSORPTION OR PRECIPITATION OF LEAD FROM MUNICIPAL LEACHATES BY CLAY MINERALS[1]

ABSTRACT

The capacity of kaolinite and montmorillonite clay minerals to remove Pb from municipal landfill leachates and the mechanisms by which removal is achieved were studied to evaluate the potential usefulness of clay minerals as liners for waste disposal sites under conditions of varying pH and ionic competition.

Montmorillonite was found to remove as much as 5 times more Pb from various solutions than did kaolinite. Results indicated that Pb removal was reduced as much as 85% by leachate when compared to the amounts removed from pure $Pb(NO_3)_2$ solutions. A precipitate was found to form in leachates at pH values above 5 and was identified as $PbCO_3$. The complexing capacity of DuPage leachate for Pb was measured and the extent of complexation was found to be 11%. The higher-ionic-strength Blackwell leachate had no measurable complexing capacity for Pb. Increased adsorption of $Pb(NO_3)_2$ was found to correspond to the appearance of Pb-hydroxyl species in solution.

It was concluded that Pb removal from solution is primarily a cation exchange-adsorption reaction that is affected by pH and ionic competition. It was also concluded that formation of Pb-organic complexes are of secondary importance in landfill leachates due to competition from high concentrations of other cations. At pH values above 6, a large increase in Pb removal from solution by clay can be expected, due to either increased adsorption of Pb-hydroxyl complexes or formation of $PbCO_3$ in landfill leachates.

The thickness of clay liners necessary to remove Pb from solutions of $Pb(NO_3)$, 0.1 M NaCl, and landfill leachates at concentrations ranging between 10 and 1000 ppm Pb and at pH values from 3 to 8 were computed. Some undesirable environmental consequences of the reversible Pb exchange-adsorption reaction with clay may ensue where pH and ionic competition are unfavorable.

INTRODUCTION

This section reports the results of an investigation, the purpose of which was to determine the capacity of the two major clay mineral types for removing Pb from solution and the effect municipal leachates have on this capacity at various pH values. Another purpose of the investigation was to

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[1] Authors: R. A. Griffin and N. F. Shimp.

gain insight into the mechanisms responsible for attenuation of Pb as well as to evaluate the potential use of clay minerals as liners for waste disposal sites.

Lead was chosen for study because documented evidence shows that low Pb levels in drinking water can cause death to humans. In one case in Australia, 94 adults died of chronic lead poisoning because throughout childhood they drank water collected from roofs of houses painted with lead-pigmented paint (Henderson, 1955). There is also evidence (Broadbent and Ott, 1957) that organic chelates form with hydrolyzable metals and that they may make Pb more mobile in soils or clay liners when municipal leachates are present than in effluents that do not contain high concentrations of organic compounds.

EXPERIMENTAL

The Pb removal studies were conducted by placing a known weight of clay, between 0.100 and 1.000 g, into a 125 ml Erlenmeyer flask. The weight of clay used was chosen to give an estimated 20 to 50% change in the Pb concentration of the solution at equilibrium. A 50 ml aliquot of either deionized water, 0.1 M NaCl solution, or leachate and then a 2 ml aliquot of a $Pb(NO_3)_2$ solution were pipetted into the flask. The pH of the solutions were adjusted with either HNO_3 or NaOH over the pH range of interest, and the volumes of acid or base added were recorded. The volumes added were usually less than 1 ml. The flasks were tightly stoppered, and as a result the CO_2 liberated from the leachate solutions caused a slight positive pressure in the flask, which aided in maintaining anaerobic conditions during equilibration. (For a period of time after addition of acid, the stoppers were removed to relieve excessive pressure, and then the flasks were restoppered.) The results of rate studies indicated that 4 hours were necessary for Pb in leachate to equilibrate with kaolinite. This result is in agreement with Beevers (1966), who found that $Pb(NO_3)_2$ solutions equilibrated in from 1 to 12 hours, depending on the clay mineral. The samples in this study were shaken for at least 24 hours in a constant temperature bath at 25 ± 0.5° C to insure equilibration. The equilibrium pH was recorded, the samples were centrifuged, and the solutions were analyzed for their Pb concentration by atomic absorption. The difference between the initial concentration and the equilibrium concentration was used to compute the amount of Pb removed from the solution at the particular pH by a given clay mineral. This procedure was carried out for a range of initial Pb concentrations that varied between 10 and 1,000 ppm.

The resulting data were plotted as amount of Pb removed from solution per gram of clay versus pH. The resulting family of curves allowed construction of adsorption isotherms for any individual pH value of interest throughout the pH range 3 to 6. Representative adsorption isotherms and plots of the data according to the Langmuir (1918) adsorption equation were constructed at various pH values to determine the maximum amount of Pb that could be adsorbed from the various solutions by the two clay minerals and to try to gain insight into the mechanisms of adsorption. The Langmuir (1918) equation in its linear form is:

$$\frac{C}{x/m} = \frac{1}{kb} + \frac{C}{b} \qquad \{6\}$$

Exhibit E

where C is the equilibrium concentration of Pb, x/m is the amount of Pb adsorbed per unit mass of clay, 1/b is the slope where b is the adsorption maximum for Pb, and k equals the slope/intercept where k is a term relating to the energy of adsorption.

The ability of the two municipal leachates to complex metal ions, in particular Pb, was studied. The leachates were centrifuged at 1000 rpm for 10 minutes and then filtered through a 0.45 μm pore-size Millipore membrane held in an anaerobic bacteria filter holder under argon pressure. The leachate obtained after centrifugation and filtration was considered to contain only soluble organics and was used in the complexation studies. Successive aliquots of Pb were added to the leachate and equilibrated for several hours. The concentration of free and complexed lead ions in solutions were determined from pulse polarographic wave heights using the methods and equipment described by Gadde and Laitinen (1973a).

Lead was removed from leachate solutions as a white precipitate at pH values greater than 6. The precipitate was separated from solution on a 0.45 μm Millipore membrane, washed with deionized water and dried at room temperature. The chemical compound was then identified from its X-ray diffraction pattern.

RESULTS

The results of Pb removal from 25° C solutions of DuPage leachate by kaolinite and montmorillonite clay minerals were plotted as a function of pH in Figures 12 and 13, respectively. Similar results obtained for Pb removal from Blackwell leachate by kaolinite are shown in Figure 14.

The data presented indicate that Pb removal from landfill leachate increases with increasing pH values and with increasing concentration of Pb in solution. Increasing Pb concentration is indicated on the figures by increasing alphabetical order, and the initial Pb concentration, weight of clay used, micrograms of Pb added, and volume of solution that correspond to the alphabetical designations are given in Table 7. A blank (no clay) solution of leachate with Pb added was carried along through the experiment and the results of these also appear on the figures.

Data for Pb removal from leachate plotted as a family of curves of increasing concentration have the advantage that sorption isotherms may be constructed from the plot, by using the information given in Table 7, for any desired pH value from pH 3 to pH 6.

Pb sorption isotherms can be constructed from these plots by first placing a vertical line across the family of curves at the pH of interest. The amount of Pb removed from solution is found on the graph at the points where the vertical pH line intersects each curve. The equilibrium Pb concentrations that correspond to the chosen pH value are then computed from the amounts of Pb removed at each concentration, as determined from the graph and the information for each Pb curve given in Table 7 by using the following relation:

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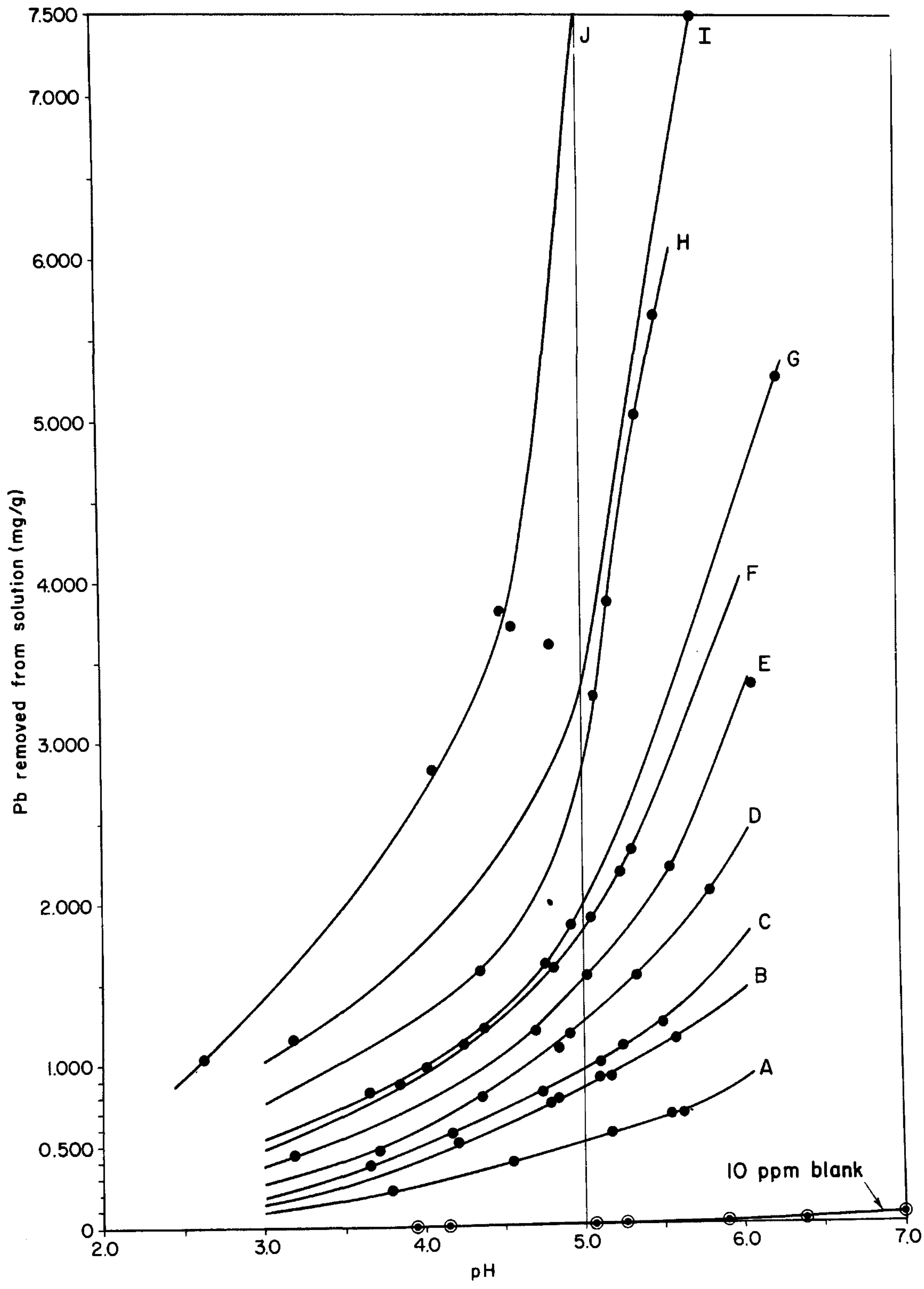

Figure 12. The amount of Pb removed from DuPage leachate by kaolinite at 25° C plotted as a function of pH.

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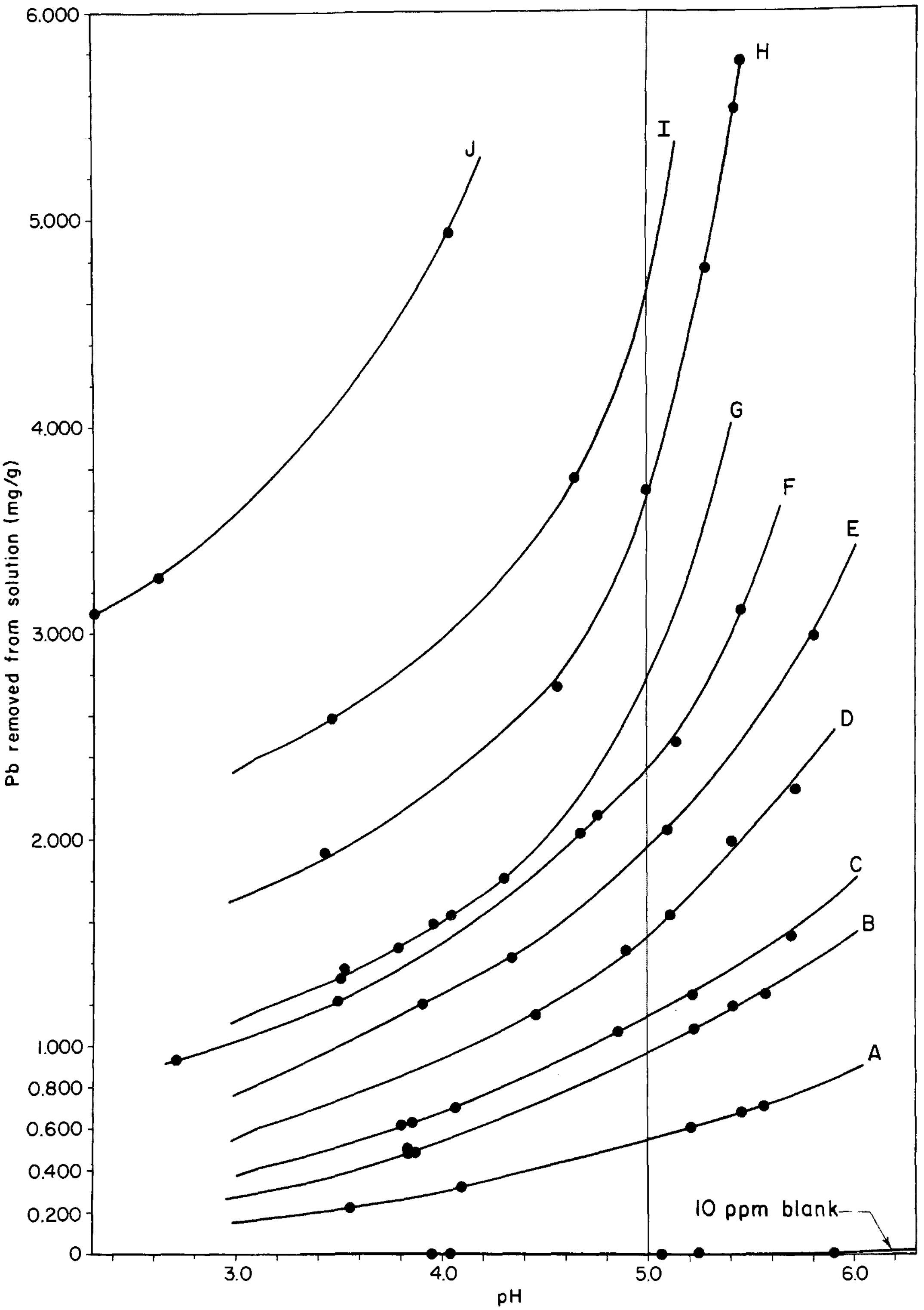

Figure 13. The amount of Pb removed from DuPage leachate by montmorillonite at 25^{o} C plotted as a function of pH.

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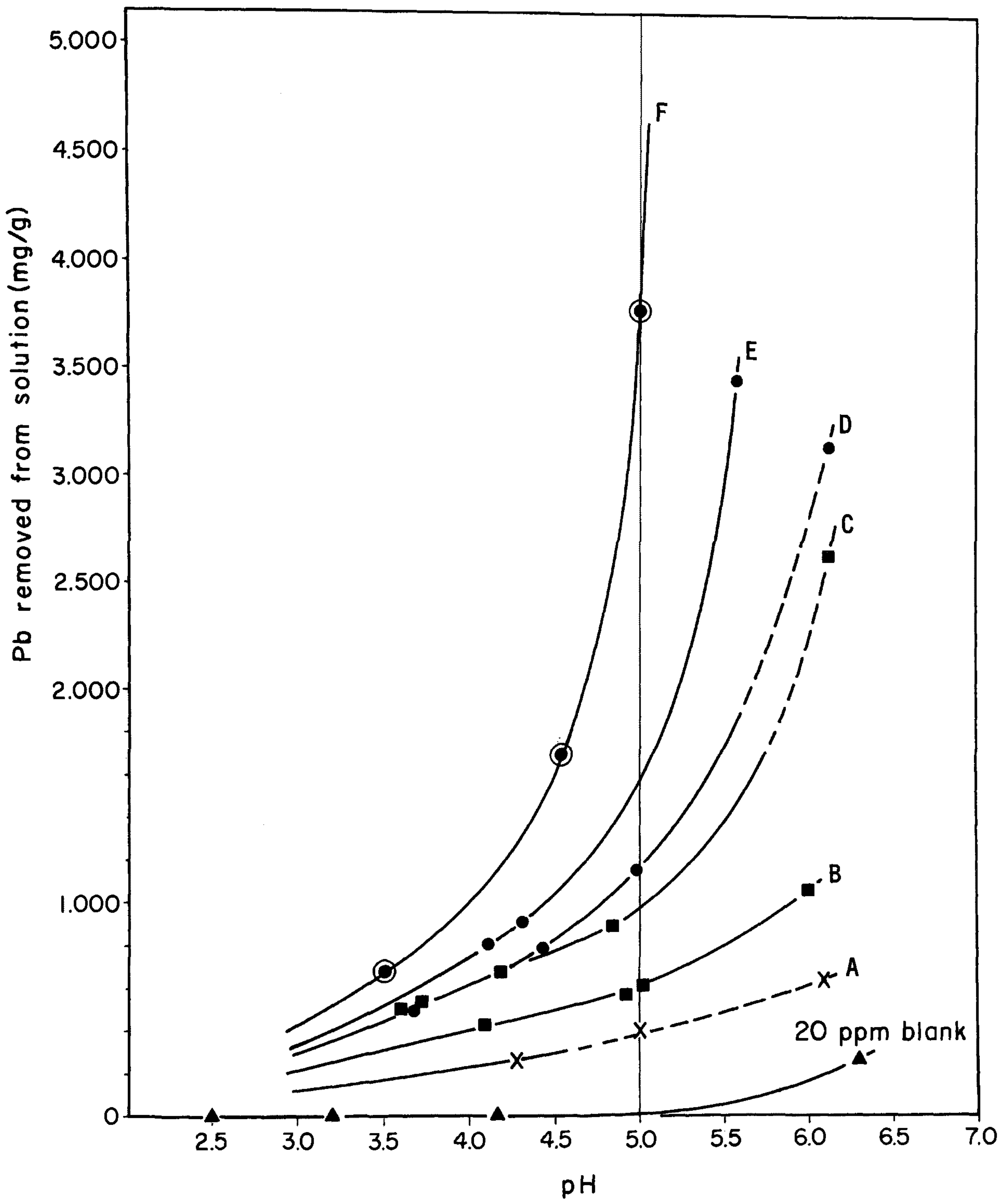

Figure 14. The amount of Pb removed from Blackwell leachate by kaolinite at 25° C plotted as a function of pH.

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TABLE 7. Pb REMOVAL PARAMETERS USED TO COMPUTE SORPTION ISOTHERMS FROM 52 ml REACTION VOLUMES

	Curve	Initial Pb concentration (ppm)	Pb added (micrograms)	Clay weight (grams)
DuPage leachate - kaolinite (Fig. 2)	A	9.62	500	0.500
	B	19.23	1,000	0.500
	C	38.46	2,000	1.000
	D	57.69	3,000	1.000
	E	76.92	4,000	1.000
	F	96.15	5,000	1.000
	G	115.38	6,000	1.000
	H	153.85	8,000	1.000
	I	192.31	10,000	1.000
	J	384.62	20,000	1.000
DuPage leachate - montmorillonite	A	9.62	500	0.500
	B	19.23	1,000	0.500
	C	38.46	2,000	1.000
	D	57.69	3,000	1.000
	E	76.92	4,000	1.000
	F	96.15	5,000	1.000
	G	115.38	6,000	1.000
	H	153.85	8,000	1.000
	I	192.31	10,000	1.000
	J	384.62	20,000	1.000
Blackwell leachate - kaolinite (Fig. 4)	A	19.23	1,000	1.000
	B	38.46	2,000	1.000
	C	76.92	4,000	1.000
	D	96.15	5,000	1.000
	E	192.31	10,000	1.000
	F	288.46	15,000	1.000

Exhibit E

$$\text{Equil. Pb} = \frac{\text{Pb added } (\mu g) - (\text{Pb removed } (\mu/g) \times \text{wt. clay}}{\text{sample volume}}$$

Pb sorption curves were constructed by this method for several pH values from the plots given in Figures 12, 13, and 14. Representative curves are presented in Figure 15 along with sorption isotherms obtained at pH 5.0 and 25° C for Pb sorption from $Pb(NO_3)_2$ solutions and 0.1 M NaCl solutions, followed by the DuPage and Blackwell leachates, respectively.

The sorption curves for the two leachates show a sharp upswing occurring at equilibrium concentrations of approximately 200 ppm Pb. Qualitatively identical curves, also with a sharp upswing at about 200 ppm Pb, were obtained by using montmorillonite clay. The data presented in Figure 13 may be used to verify this finding. Sorption isotherms computed from Figures 12, 13, and 14 at pH 3.0 or 4.0 did not exhibit the sharp upswing. A sharp upswing in a sorption isotherm at higher concentrations is generally viewed as initiation of precipitation of an insoluble compound. The fact that the sharp rise in Pb removal occurred at about 200 ppm Pb under the CO_2 partial pressures in the flasks, while at pH 4.0 no sharp increase was observed, is consistent with solubility computation which assume a mechanism of $PbCO_3$ formation.

To predict the maximum amounts of Pb that could be sorbed by the two clays from the various solutions, the kaolinite sorption data plotted in Figure 15 and the sorption data obtained for montmorillonite were plotted according to the Langmuir adsorption isotherm equation. The results are illustrated in Figure 16.

The Langmuir equation was found to describe the data obtained for $Pb(NO_3)_2$ sorption by both kaolinite and montmorillonite and for Pb sorption from 0.1 M NaCl solutions by kaolinite over the entire concentration range studied. The results obtained for the leachates, however, were somewhat different. The Langmuir equation was found to describe the sorption up to concentrations between 30 and 40 ppm, at which point a sharp change in slope occurred, giving two distinct linear regions to the isotherms. The adsorption maximums computed from the slopes of the lines shown in Figure 16 are given in Table 8. From the values in Table 8 a quantitative estimate of the sorption differences noted in Figure 15 and a comparison of the sorption capacities of the two clays can be made. In $Pb(NO_3)_2$ solution, montmorillonite sorbed approximately five times more Pb than kaolinite, while in DuPage leachate it sorbed less than twice as much as kaolinite. This result indicates that the competitive ions contained in landfill leachate affect the relative sorption affinity of Pb for the montmorillonite; i.e., leachate reduced Pb sorption by montmorillonite proportionately more than it reduced Pb sorption by kaolinite.

DISCUSSION

The data presented above suggest that several mechanisms are responsible for removal of Pb from solutions of varying ionic composition and pH.

Precipitation was found to be an important mechanism in landfill leachates, as is shown by the removal of Pb from the blank solutions, which con-

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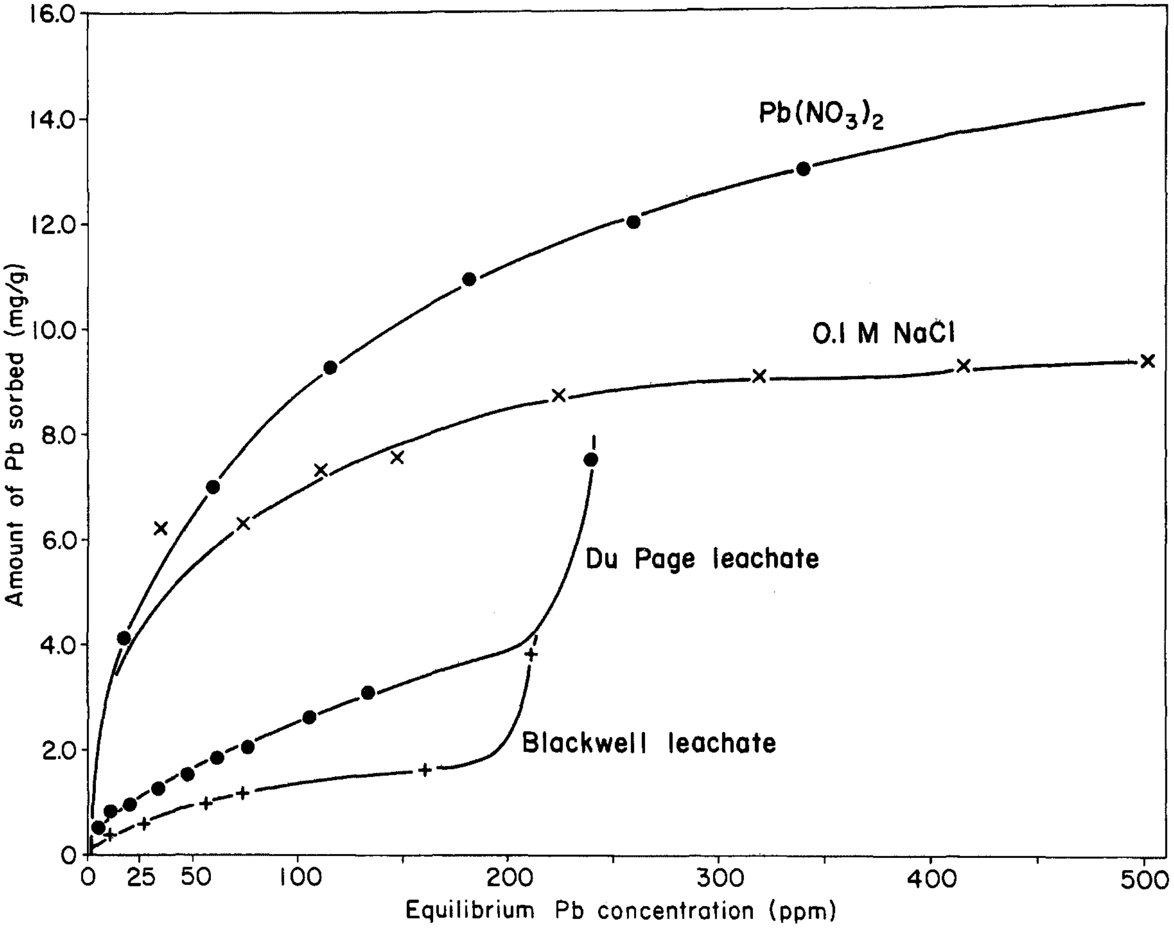

Figure 15. The amount of Pb sorbed per gram of kaolinite at pH 5.0 and 25° C plotted as a function of the equilibrium Pb concentration.

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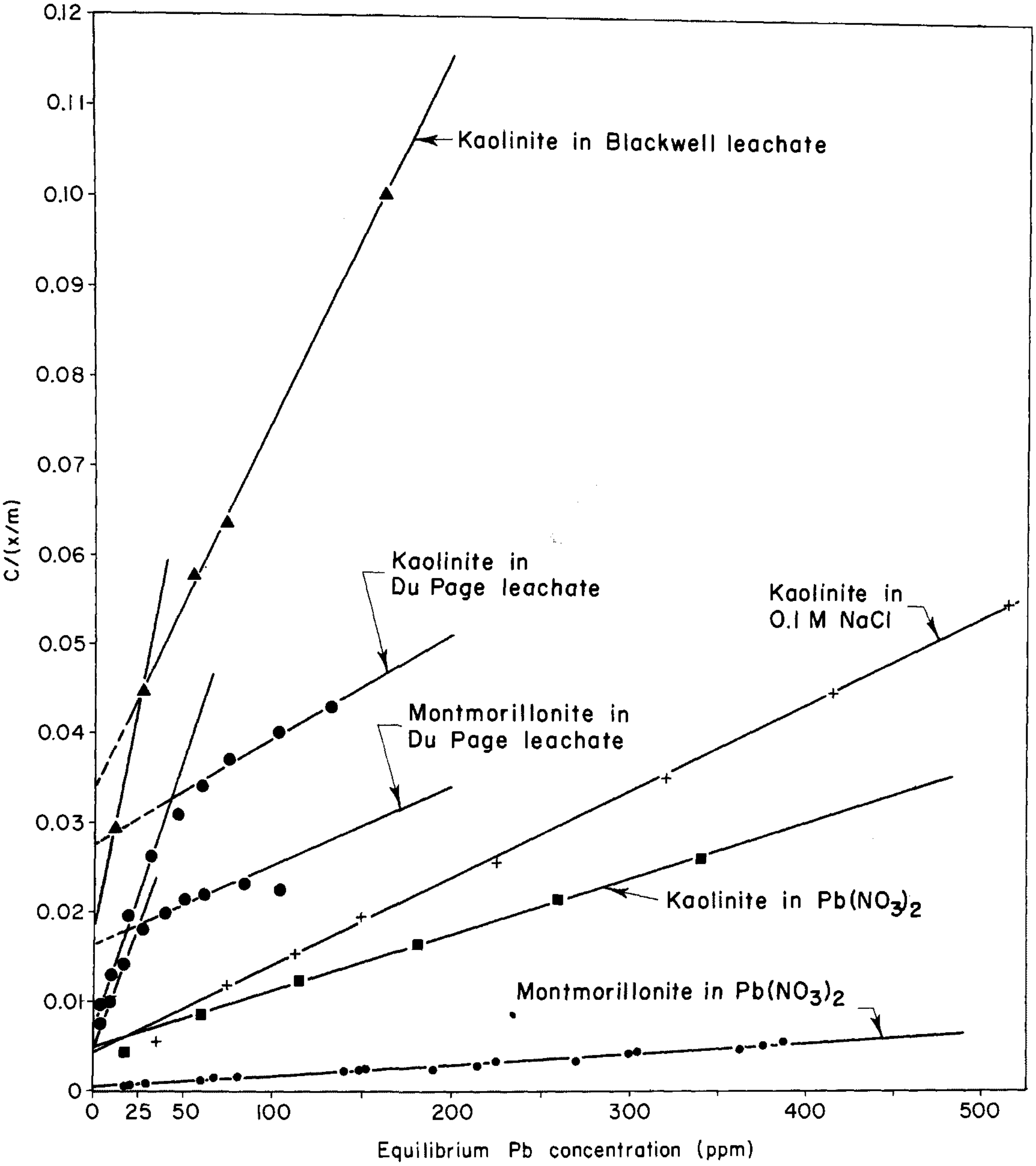

Figure 16. Pb sorption data for kaolinite and montmorillonite at pH 5.0 and 25° C plotted according to the Langmuir isotherm equation.

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TABLE 8. MAXIMUM REMOVAL OF Pb FROM pH 5.0 and 25° C SOLUTIONS COMPUTED USING THE LANGMUIR EQUATION

	Micrograms/g		Meq Pb^{++}/100 g clay	
	Region 1	Region 2	Region 1	Region 2
KAOLINITE				
$Pb(NO_3)_2$	--	15,914	--	15.36
0.1 M NaCl	--	10,240	--	9.88
DuPage leachate	1,680	8,530	1.62	8.23
Blackwell leachate	986	2,401	0.95	2.32
MONTMORILLONITE				
$Pb(NO_3)_2$	--	82,428	--	79.56
DuPage leachate	1,811	11,133	1.75	10.75

tained no clay (Figures 12, 13, and 14). Losses of Pb from the DuPage leachate were observed at pH values greater than about 6 and in Blackwell leachate at pH values above 5. A white precipitate was observed forming in the leachate solutions at pH values greater than 6. It was filtered out, and the chemical compound was identified by its X-ray diffraction pattern as a highly crystalline $PbCO_3$. The peaks were sharply defined, and no peaks other than those attributed to $PbCO_3$ were observed. This is offered as evidence that $PbCO_3$ formation was the compound responsible for Pb removal from leachate solutions at the higher pH values, and it is presumed to be the cause of the apparent formation of a precipitate at concentrations of Pb greater than 200 ppm observed in the sorption isotherms (Figure 15).

Stumm and Morgan (1962) showed that the occurrence of metal hydroxyl species can affect the sorption of hydrolizable metal ions. They found that the pH at which metal hydroxyl species formed corresponded to the pH at which metal ion sorption became significant. To check the role of hydrolysis of the Pb ion on its sorption by clay at various pH values and in solutions where precipitate formation did not effect Pb removal, the distribution of various hydroxyl species in a 4×10^{-4} M $Pb(NO_3)_2$ solution in the pH range 3 to 8 was obtained from Gadde and Laitinen (1973b), who computed the species distribution by using the constants given by Olin (1960). The distribution of Pb hydroxyl species, along with data obtained for sorption by kaolinite from a solution with an initial concentration of 4×10^{-4} M Pb as $Pb(NO_3)_2$, is illustrated in Figure 17.

It is evident from the plots in Figure 17 that species other than Pb^{++} are relatively insignificant (<1%) at pH values less than 6. Sorption at pH values below 6 are not related to the hydroxyl species of Pb, but rather to Pb^{++} ion. The decrease in Pb sorption at low pH values is apparently due to an increase in competition for sorption sites, with H^+ and its related competitive effects on Pb sorption caused by the dissolution of Al^{+++} ions from the clay crystal lattice (Grim, 1968). At pH values above 6, a sharp rise in Pb sorption occurred coincident with the formation of hydroxyl Pb species. It therefore seems likely that at least a portion of the observed increase in Pb sorption with decreasing pH and the rapid increase in the amount of Pb sorbed coincident to the formation of monovalent Pb-hydroxyl species are consistent with a cation exchange mechanism for Pb removal from solution by clay minerals. Table 8 exhibits further evidence that cation exchange is the principal mechanism for Pb removal by clay minerals.

The sorption maximums for $Pb(NO_3)_2$ solutions, computed from the slope of the Langmuir plots, for kaolinite and montmorillonite are 15.36 and 79.56 meq Pb^{++}/100 g clay, respectively. These values can be compared to the cation exchange capacity (CEC) values of 15.1 for kaolinite and 79.5 meq/100 g for montmorillonite that were determined by the ammonium acetate method and reported in Table 1. The CEC values are within 2% of the Pb sorption maximums computed from the Langmuir equation; i.e., Pb^{++} sorption is merely another method of measuring the cation exchange capacity of a clay.

Further evidence of a cation exchange mechanism is the reduction in Pb sorption in solutions containing 0.1 M NaCl and also as the total salt content of the two leachates studied increases. The decrease in Pb sorption is

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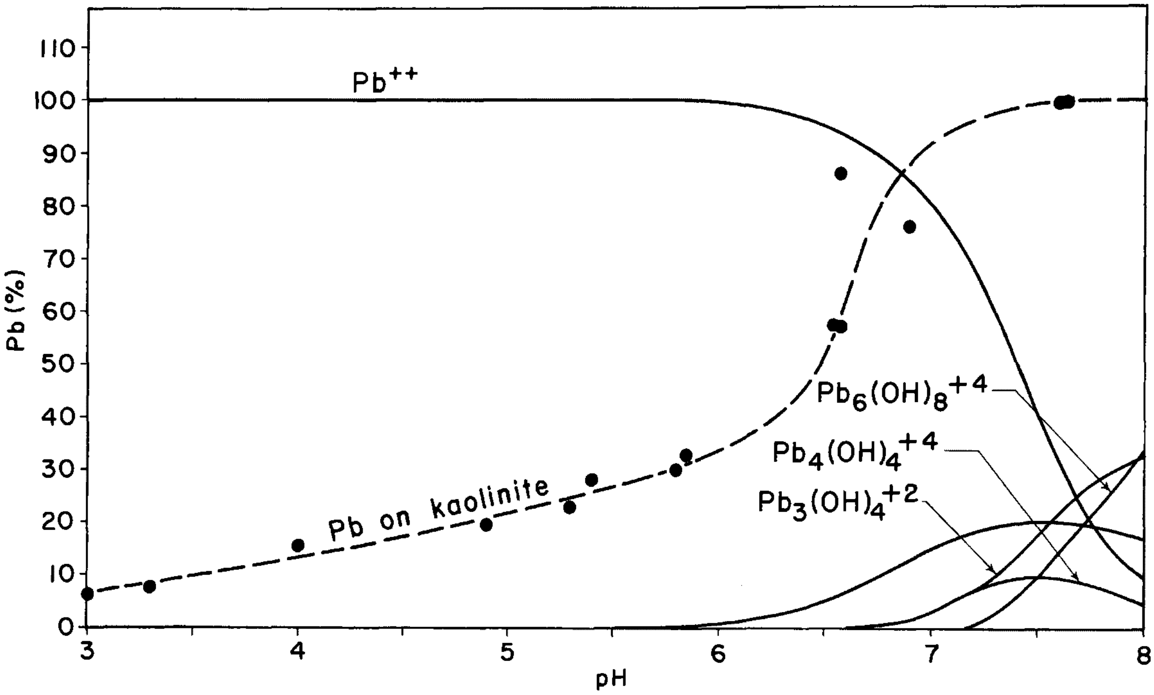

Figure 17. Distribution of Pb (II) species in 4 x 10^{-4} M $Pb(NO_3)_2$ and uptake by 0.1 g kaolinite from 60 ml of solution.

attributed to increasing competition for cation exchange sites by Na^+ in the 0.1 M NaCl solutions and to an increase in the divalent cation competition in the two leachates. For example, the Blackwell leachate contains much more Fe in solution than the DuPage leachate (Table 2). Such high levels of competing ions could account for the large reductions in Pb sorption observed in the presence of landfill leachate compared to the sorption in pure $Pb(NO_3)_2$ solutions.

The results for Pb sorption from leachate, plotted according to the Langmuir adsorption equation, show a distinct two-slope character. This shape of curve has been attributed to adsorption at sites of distinctly different energy (Griffin and Burau, 1974; Griffin and Jurinak, 1973). However, in the present study competition from other cations in solution seems to be responsible for the change in slope, because it was observed only in the multicomponent cation systems. Solutions of $Pb(NO_3)_2$ or NaCl did not exhibit the sharp change in slope for Pb sorption that was observed for the leachates.

One of the assumptions of the Langmuir equation is that the adsorbent surface is homogeneous with respect to the energy of the adsorption sites. However, in a multicomponent cation system the sites are occupied by cations with various retention energies relative to Pb; i.e., Pb can displace certain cations, such as Na^+, much more easily than it can replace cations such as Ca^{++}. This reaction is postulated to affect the shape of the adsorption isotherm by filling the lower energy sites preferentially; i.e., Pb first exchanges with a cation, or a group of cations, of similar exchange energy. This phase of the sorption is attributed to the initial slope of the Langmuir plot. As the concentration of Pb in solution is increased, the chemical potential gradient is increased until it is sufficient to initiate exchange of the cation, or group of cations, with the next highest energy of retention relative to Pb. This second energy level of exchange is postulated to produce the sharp change in slope of the Langmuir plots in the leachate solutions.

An explanation, other than competition for cation exchange sites, for the observed reductions in over-all Pb sorption is the tendency of Pb to form metal-organic complexes with the organic compounds present in landfill leachate. These organic-metal complexes can lower the activity of the Pb in solution, thus reducing the chemical potential gradient for sorption. Gadde and Laitinen (1973a) showed that Pb forms stable complexes with organic compounds found in soils and that these compounds were able to solubilize Pb present in different forms in the solid phase.

To determine the role of Pb-organic complexes in the observed Pb sorption reductions in leachates, the complexing capacity of Pb in the two leachates was measured.

In the DuPage leachate, the extent of complexation (ppm complexed) was found to be 22 ppm at a Pb concentration of 200 ppm. It is clear from the above data that only about 11% Pb is complexed, while it would take more than 50% complexation to explain the reduction in Pb sorption by an organic complexing mechanism.

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The fact that formation of a Pb-organic complex cannot be used to explain more than a small fraction of the observed reduction in Pb sorption is emphasized by the results obtained from using Blackwell leachate. In this study it was found that addition of successive aliquots of Pb to the leachate gave approximately the same incremental response (μA-current) in the wave for free lead ion. Apparently up to 80 ppm total Pb, no complexation of Pb was observed. It was noted that Fe^{++} or its weak complex with leachate is presumed to have produced the large increase in polarographic current observed at a potential ~1.4 V. From the results of this study, it appears that Pb^{++} is either unable to compete with Fe^{++} or other cations present in large amounts in Blackwell leachate, or the leachate has little or no complexing capacity. The former explanation appears to be the more plausible.

The results of the above studies have led to the conclusion that Pb removal from solution is primarily an exchange-adsorption reaction that is affected by pH and ionic competition. The formation of Pb-organic complexes was concluded to be of secondary importance in landfill leachates due to competition from high concentrations of other cations. At pH values above 6, removal of Pb from solution by clay can be expected to increase substantially, owing either to increased adsorption of Pb-hydroxyl complexes or to formation of $PbCO_3$ in landfill leachates.

Disposal Site Design Application

An example of how the data from the study can be used is its application to the question posed at the beginning of the paper -- how thick a proposed clay liner must be to remove all Pb from landfill leachates, from industrial waste streams of similar ionic strength to the leachates (0.1 M NaCl), or $Pb(NO_3)_2$ solutions at various pH values and Pb concentrations. The results of the computations are presented in Table 9.

The table gives the thickness of a square meter of a 30% clay liner, packed to a bulk density of 1.60 g/cc, that contains enough clay to remove all the Pb from 762 liters (201 gal) of solution. This particular volume is the amount generated from a typical sanitary landfill containing municipal solid waste placed 3 meters (10 feet) deep and having an annual net infiltration of 254 mm (10 inches) (U.S.-EPA, 1974). The thicknesses of the clay liner given in the table, therefore, effect total removal of Pb for a year by a square meter of liner at the given concentrations of Pb and pH values. They are, of course, the minimum thickness possible since they represent an idealized situation. The actual thickness necessary in a field application will be somewhat greater to allow for non-equilibrium conditions, physical dispersion, diffusion, and the normal engineering safety factors.

The information compiled in Table 9 indicates that only relatively thin layers of clay, especially montmorillonite, are necessary for removal of Pb unless the pH values are very acid and the Pb concentrations are high. The high sorption capacity of clay minerals and the reversible nature of exchange adsorption reactions have important environmental consequences. Soils and surface waters may change in ionic composition or pH as environmental conditions change. A sudden decrease in pH may release large amounts of potentially toxic Pb into the aqueous phase, especially in places where $PbCO_3$ has

Exhibit E

TABLE 9. THICKNESS (cm) OF A SQUARE METER OF A 30% CLAY LINER NEEDED TO REMOVE Pb FROM 762 LITERS (201 gallons) OF SOLUTION PER YEAR

	Pb Concentration								
	10 ppm			100 ppm			1000 ppm		
	at pH			at pH			at pH		
	3	5	8	3	5	8	3	5	8
KAOLINITE									
$Pb(NO_3)_2$	--	<1	--	5.3	1.8	<1	--	10.0	--
0.1 M NaCl	--	<1	--	--	2.3	--	--	15.5	--
DuPage	15.9	2.1	*	28.9	6.4	*	79.4	*	*
Blackwell	19.8	4.0	*	49.6	11.3	*	264.6	*	*
MONTMORILLONITE									
$Pb(NO_3)_2$	--	<1	--	--	<1	--	--	1.93	--
DuPage	9.9	1.8	*	13.2	3.7	*	18.0	*	*

*Precipitation as $PbCO_3$

Exhibit E

accumulated. Cations, especially di- and tri-valent, compete with Pb and may exchange with it, thus allowing Pb to come into solution. These multiple interactions must be considered when a disposal site is designed and the environmental impact of Pb assessed.

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SECTION 8

EXCHANGE-ADSORPTION OF Cu, Zn, AND Cd FROM DEIONIZED WATER AND LEACHATE SOLUTIONS BY CLAY MINERALS[1]

ABSTRACT

The effect of pH on the removal (exchange-adsorption by kaolinite and montmorillonite clay minerals plus precipitation) of copper, zinc, and cadmium in deionized water (pH range 4 to 6) and municipal leachate (pH range 2 to 8) solutions was studied. Solutions contained up to 1000 ppm Cu, Zn, or Cd. Families of removal versus pH curves were obtained that can be used to construct removal isotherms for specific pH values. With certain exceptions, very significant increases in the amounts removed from both solutions were observed as the pH rose in the pH ranges studied. Precipitation contributes significantly to removal of Cu from leachate above pH 5, Zn above 7, and Cd above 6.

Three different pH 5.0 removal isotherms are presented for deionized water solutions. These isotherms were constructed from removal curves obtained by different experimental methods which were shown to influence the interpretation of the results. The differences in the three isotherms are resolved by use of a Langmuir-type isotherm equation that was derived to express the simultaneous competitive adsorption of two cations. The equation reveals that, under certain conditions, the amount of exchange adsorption of a cation should be independent of its solution concentration. This proved to be true for the exchange adsorption of Cu, Zn, and Cd from deionized water solutions by the clay minerals at pH 5.0.

Isotherms of leachate removal at pH 5.0 were constructed and compared with the deionized water isotherms for the same pH. The amount of removal at pH 5.0 from leachate is significantly lower than it is from deionized water solutions because of competition from the other cations present in the leachate. Competition prevents the amount of exchange-adsorption at low concentrations from becoming independent of concentration. The leachate isotherms are specific for the leachate used and may not approximate the exchange-adsorption from another leachate of different ionic strength and composition.

The mobility of Cu, Zn, and Cd in soils or clay minerals is dependent upon the pH and ionic strength of the solution as well as on the CEC of the soils or clay minerals. The CEC value is of little importance at sufficiently

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[1] Authors: R. R. Frost and R. A. Griffin

Exhibit E

high (above 7) pH values because precipitation is then more important than cation exchange in the removal of Cu, Zn, or Cd from solution.

INTRODUCTION

The results of chemical analyses of 20 municipal leachates have been reported by the U. S. Environmental Protection Agency (EPA, 1974). These analyses showed that leachate was similar to sewage sludge effluent with respect to its high content of organic matter, nitrogen, phosphorus, and potassium and also indicated levels as high as 10 ppm for Cu, 1000 ppm for Zn, and 17 ppm for Cd. The accumulation of these potentially toxic heavy metals in soils makes long-term application of municipal leachates to the land hazardous because Cu, Zn, and Cd enter the human food chain by accumulating in plants. However, a lack of basic data on the reactions of these metal ions with soil colloids in the presence of a complex solution matrix, such as leachate, hampers efforts to determine what levels of application can be tolerated without degradation or loss of the soil resource to food crop production.

The original purpose of this study was to measure the adsorption of Cu, Zn, and Cd by kaolinite and montmorillonite clay minerals from a landfill leachate at pH 5.0. However, the study was later expanded to investigate the adsorption of low concentrations of heavy metal ions by earth materials from deionized water solutions and their removal (adsorption plus precipitation) from a leachate in the pH range 2.0 to 8.0. The results of this study give insights into the mobility of Cu, Zn, and Cd in soils irrigated with leachates and can be applied to the design of clay liners for municipal and industrial waste disposal sites.

THEORETICAL

In any adsorption study, the amount adsorbed is usually measured as a function of adsorbate concentration in the medium surrounding the adsorbent. It is generally desirable to be able to fit the adsorption data to an adsorption isotherm equation so that "parameters" associated with the adsorption isotherm can be calculated for comparisons and correlation with other data.

The Langmuir (1918) equation is given as:

$$x/m = \frac{KbC}{1 + KC} \tag*{\{7\}}$$

where x/m = amount of adsorbate adsorbed per gram of adsorbent, C = the equilibrium ion concentration in solution, b = the adsorption maximum, and K = a constant related to the bonding-energy of the adsorbate to the adsorbent. This equation has been used extensively in studies of adsorption of ions from solution by soils and clay minerals. Eq. {7} can be rearranged into a linear form, where:

$$C/(x/m) = 1/(Kb) + C/b. \tag*{\{8\}}$$

The application of Eq. {8} to experimental data for Zn adsorption by soils (Shuman, 1975) has produced two linear portions of the plot. Following

Exhibit E

the lead of Syers et al. (1973), Shuman (1975) attributed this result to two types of adsorption sites. However, the adsorption model upon which Eq. {7} is based assumes that the surface of the adsorbent contains only one type of adsorption site. Therefore, there is no justification for arguing the existence of two sites on an adsorbent surface when a one-site model equation has been applied to the experimental data. Also, inspection of Eq. {7} shows that, at low concentrations, it reduces to:

$$x/m = KbC. \qquad \{9\}$$

Therefore, Eq. {8} has no significance at low concentrations, even though C/(x/m) values can be calculated and plotted. If a two-site adsorption model is to be discussed, then the following equation should be applied to the experimental data:

$$(x/m)_{\text{total}} = \alpha \frac{K_1 b_1 C}{1 + K_1 C} + (1-\alpha) \frac{K_2 b_2 C}{1 + K_2 C} \qquad \{10\}$$

where α = fraction of sites with bonding-energy coefficient K_1. In practice, Eq. {10} would be almost impossible to apply to experimental data.

The linear form of the Langmuir equation (Eq. {8}) holds best for the plateau region of the adsorption isotherm (high concentrations). This is true regardless of the equilibrium concentrations because the deviations from the linear plot occur as the equilibrium concentration approaches zero. A close look at Eq. {8} confirms this point. At, or near, the plateau region of the adsorption isotherm, (x/m) is about constant and, hence, the real plot is (C/constant) versus C, which must be a straight line. But at low concentrations, where (x/m) is increasing as C is increasing, values of C/(x/m) can change at a faster rate than they do at higher concentrations at which C is the only variable changing to an appreciable extent. Therefore, all Langmuir plots (Eq. {8}) will probably show two or more straightline segments if data points are obtained at sufficiently low and high concentrations.

The most important point ignored by the application of Eq. {7} to adsorption of cations from solution by soils and clay minerals is that the adsorption process is primarily one of cation exchange, and for every cation adsorbed one or more cations must be desorbed. The latter can then compete for adsorption sites. Boyd, Shubert, and Adamson (1947) developed an adsorption equation for the simultaneous competitive adsorption of two equally charged cations, A and B. By formal analogy with the Langmuir (1918) equation for adsorption from a binary gaseous mixture the following equation is obtained:

$$(x/m)_A = \frac{b\ K_A/K_B\ (C_A/C_B)}{1 + K_A/K_B\ (C_A/C_B)} \qquad \{11\}$$

The linear form of Eq. {11} is

Exhibit E

$$\frac{C_A/C_B}{(x/m)_A} = \frac{K_B}{K_A\, b} + \frac{1}{b}\,\frac{C_A}{C_B}. \qquad \{12\}$$

Where the concentration of A is small compared to the concentration of B, so that adsorption of A does not produce a detectable change in the concentration of B (e.g., adsorption on a Ca-saturated clay from solutions with high Ca content), a plot of $C_A/(x/m)_A$ versus C_A should be linear. The plot should also be linear when $(x/m)_A$ approaches the cation exchange capacity (CEC), because C_B would then become a constant value and would not change as C_A changes. From Eq. {11} it can be seen that the amount adsorbed, $(x/m)_A$, must depend upon the ratio of the equilibrium concentrations of the exchanging cations and not upon the actual concentrations in solution. Where $C_B >> C_A$, $(x/m)_A$ will become a linear function of C_A, and when $C_A >> C_B$, $(x/m)_A$ will become a constant and independent of the concentration of A.

Equation {11} demonstrates that, under appropriate experimental conditions, the amount of exchange-adsorption should be independent of the solution concentration of the cation adsorbed. If it is desirable to study the migration of a cation through soils or clays by measuring its adsorption from a pure solution, then a fixed weight of soil sample and a fixed solution volume should be maintained throughout the concentration range being studied. However, it is not sufficient to measure the exchange-adsorption from pure cation solutions. For example, to determine how far the Cu, Zn, or Cd in 250 ml of 200 ppm deionized water solutions will migrate down a clay column the following procedure should be followed. One gram of clay is placed in the 250 ml of solution (initial concentration, C); adsorption will occur to give an equilibrium concentration, C_1. In the process, $(200-C_1) \times 0.25$ mg of cation is adsorbed and an equivalent number of moles of exchangeable cations on the clay will be desorbed. Hence, the solution phase will now contain a mixture of cations from which the amount of exchange-adsorption measured from a pure solution with a concentration of C_1. This process should be carried out stepwise, C to C_1, C_1 to C_2, ... , C_{n-1} to C_n, until $C_n \to 0$. Thus, the amount of adsorption from solution concentration C_1 will be dependent upon the initial concentration of the solution from which C_1 was derived.

EXPERIMENTAL

After pH adjustment, all clay-leachate or clay-deionized water suspensions in this study were shaken in a constant temperature bath at 25 ± 0.5^{o} for at least 24 hours to insure complete equilibration. The equilibrium pH values of the clay suspensions were measured, the clay suspensions centrifuged, and the supernatant solutions were analyzed by atomic absorption spectroscopy for their Cu, Zn, or Cd concentrations. Blanks (i.e., no clay) of spiked leachate or deionized water solutions that had been prepared along with the clay suspensions also were analyzed to determine the initial Cu, Zn, or Cd concentrations present in the solutions. The amount of Cu, Zn, or Cd removed from solution by a given clay at a particular pH was calculated as the (initial equilibrium concentration) x (solution volume/sample weight) / 1000. The amount of Cu, Zn, or Cd removed from solution was plotted as a function of pH.

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Three types of experiments were conducted on the removal of Cu, Zn, and Cd by the clay minerals from deionized water solutions of Cu, Zn, or Cd nitrates. In the first, 1.000 g of kaolinite or montmorillonite and 50-ml aliquots of the appropriate nitrate solution were placed into 125-ml Erlenmeyer flasks. The approximate concentrations chosen were: 25, 50, 100, and 200 ppm Cu and 10, 40, 200, and 400 ppm Zn for both kaolinite and montmorillonite; 100, 200, and 500 ppm Cd for kaolinite; and 100, 500, and 1000 ppm Cd for montmorillonite.

Three or four replicate clay suspensions were prepared for each concentration of Cu, Zn, or Cd. The pH values of the replicate clay suspensions were adjusted to various values in the pH range 4 to 6 with dilute HNO_3 or dilute NaOH solutions. The use of NaOH was avoided if possible because Na ions can compete for adsorption sites.

In the second type of experiment, the weight of the clay sample and/or the volume of solution were chosen so that the total amount of Cu, Zn, or Cd in solution per gram of clay would be a constant. The following quantities were used: about 12.5 mg of Cu/g of kaolinite (i.e., 250 ml at 25 ppm Cu/0.5g) at 10, 25, 125, 200, and 500 ppm Cu; about 62.5 mg of Cu/g of montmorillonite (i.e., 250 ml at 25 ppm Cu/0.10g) at 25, 125, and 500 ppm Cu; about 20.0 mg of Zn/g of kaolinite (i.e., 50 ml at 40 ppm Zn/0.10g) at 10, 40, 200, and 400 ppm Zn; about 100 mg of Zn/g of montmorillonite (i.e., 250 ml at 40 ppm Zn/0.10g) at 10, 40, 200, and 400 ppm Zn; about 25.0 mg Cd/g of kaolinite (i.e., 50 ml at 50 ppm Cd/0.10g) at 20, 50, 200, and 500 ppm Cd; about 125.0 mg Cd/g of montmorillonite (i.e., 250 ml at 50 ppm Cd/0.10g) at 50, 100, 200, and 1000 ppm Cd. Three or four replicate suspensions were prepared for each concentration of Cu, Zn, or Cd. The pH values of the replicate clay suspensions were adjusted to various values in the pH range 4 to 6.

In the third type of experiment, stepwise removal of Cu, Zn, or Cd from solution was studied. Some of the second type of experiment that used 250-ml solutions were taken as the first step in the third type of experiment. For the second step, the supernatant solutions from replicate clay suspensions in the first step were sampled for analysis and then mixed together. The combined solution was used with fresh clay samples to prepare three replicate clay suspensions which were adjusted to various pH values in the pH range 4 to 6. The supernatant solutions from the second step were used in a third step, etc.

Experiments on the removal of Cu, Zn, or Cd from leachate were carried out by pipeting 50-ml aliquots of leachate into 125-ml Erlenmeyer flasks. Either the leachate had been spiked with Cu, Zn, or Cd nitrates to give the desired concentration prior to the previous step, or 2.0 ml of an appropriate stock solution was pipeted into the flasks containing the 50-ml aliquots of non-spiked leachate. Several replicates were prepared for each concentration of Cu, Zn, or Cd used. The pH values of the replicate spiked leachate solutions were adjusted to various values throughout the pH range 2 to 8. Appropriately sized samples of either kaolinite or montmorillonite, were then weighed out and transferred to the flasks. The weight of clay used was chosen so that the amount of Cu, Zn, or Cd removed from the leachate solutions could be determined with some precision from the difference between the initial and final solution concentrations.

It was discovered during preliminary experiments that, when the pH of a clay-leachate suspension was adjusted to a particular value, the pH of the suspension would rise on shaking and that the removal of Cu, Zn, or Cd increased with increasing pH. Thus, addition of the clay to the spiked leachate solutions after pH adjustments have been made avoids such potential problems as the possible irreversible removal of Cu, Zn, or Cd. The irreversible removal could occur if the pH of the prepared clay-spiked leachate suspension was high and the pH of the suspension was then adjusted to a much lower value. The experimental procedure used should produce true equilibrium removal data.

Several individual experiments also were carried out in which clay samples were placed in a mixture of 50-ml aliquots of pH 5 leachate or deionized water and 2-ml aliquots of different stock solutions. The pH of the resulting suspensions was repeatedly adjusted to 5.0 until equilibrium was obtained.

RESULTS AND DISCUSSION

The amount of Cu, Zn, or Cd removed from deionized water solutions was plotted versus pH. Except in certain cases, very significant increases in the amounts removed were observed as the pH rose in the range 4 to 6. The initial concentration of Cu, Zn, or Cd in solution, the weight of clay used, the final solution volume after pH adjustments, and the removal versus pH curves themselves can be used to construct "adsorption" or "removal" (adsorption plus precipitation) isotherms at different pH values by use of the following equation:

$$\text{Equilibrium concentration (ppm)} = \text{initial concentration (ppm)} - \frac{\text{Amount removed (mg/g)} \times \text{wt. clay (g)} \times 1000}{\text{Final solution volume (ml)}}. \qquad \{13\}$$

Isotherms were calculated from the data recorded for the deionized water solutions at pH 5.0, and the results are shown as isotherm types I, II, and III in Figures 18 and 19.

The type I isotherms (Figs. 18 and 19) are those obtained when 1.00 g of kaolinite or montmorillonite was placed in about 50 ml of Cu, Zn, or Cd solutions. The total amounts of Cu, Zn, or Cd present in 50 ml of solution at different concentrations are given in Table 10. For kaolinite (CEC 15.1 meq/100 g), 75.5 μmoles of a divalent cation/g would be required for complete exchange; for montmorillonite (CEC 79.5 meq/100 g), 397.5 μmoles/g would be required for complete exchange. Thus, as indicated in Table 10, at low concentrations of Cu, Zn, or Cd, insufficient cations are present in 50 ml of solution for complete exchange of 1.00 g of clay (especially montmorillonite). The amount of Cu, Zn, or Cd that can be adsorbed is therefore necessarily limited by the number of Cu, Zn, or Cd ions initially present in solution. The number of Cu, Zn, or Cd ions actually adsorbed will depend on how well the desorbing Ca ions compete with the Cu, Zn, or Cd ions remaining in solution. The type I isotherms in Figures 18 and 19 specifically represent the

Exhibit E

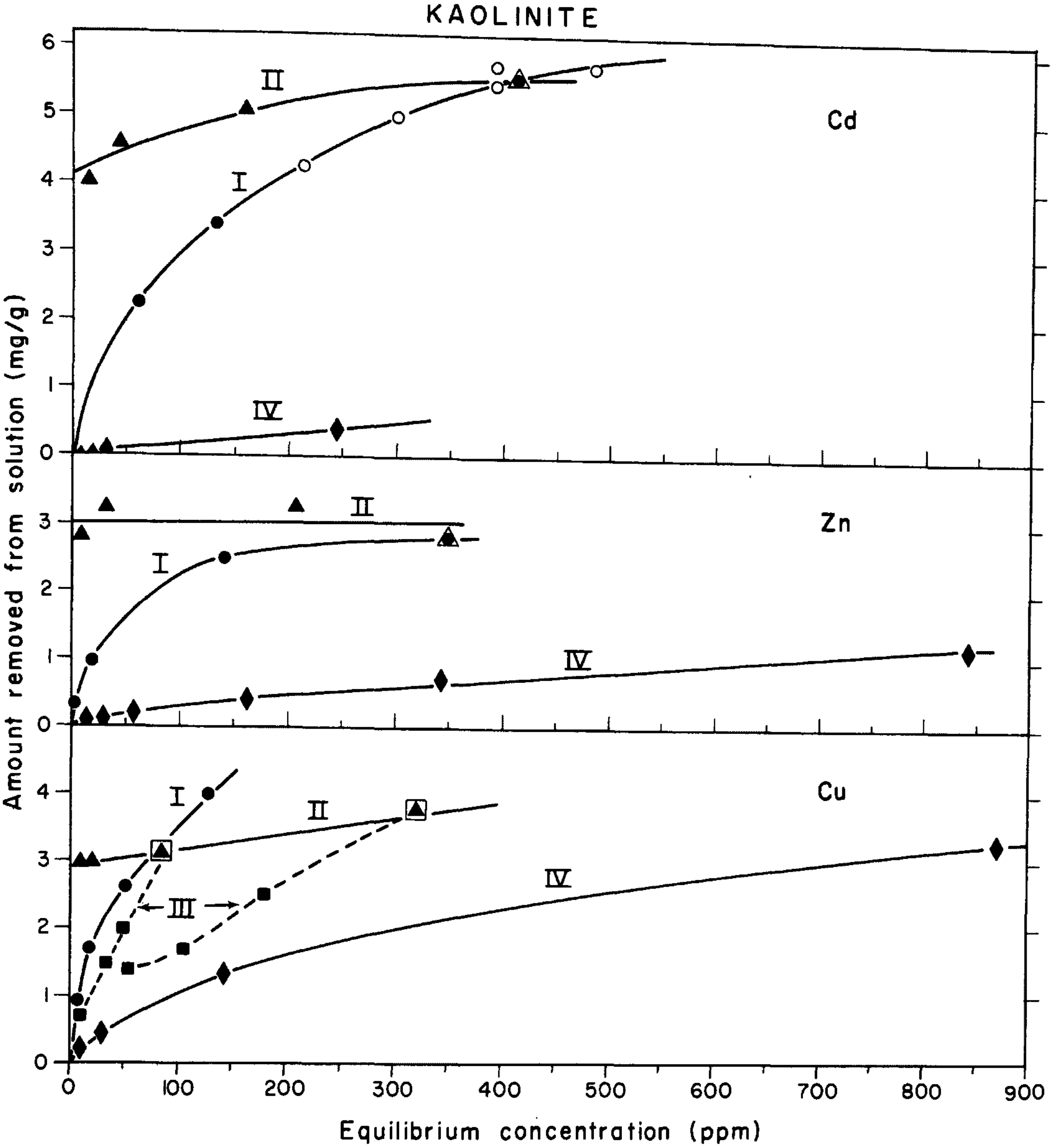

Figure 18. The amount of Cu, Zn, or Cd removed from solution per gram of kaolinite at pH 5.0 and 25° C, plotted as a function of the equilibrium concentration. Curve I - fixed weight clay/fixed solution volume; Curve II - total amount of clay exchangeable ions/total amount of Cu, Zn, or Cd ions in solution held about constant; Curve III - stepwise isotherms; Curve IV - DuPage leachate isotherms. Open symbol data points were obtained from clay suspensions adjusted several times to pH 5.0 instead of being calculated from removal curves at pH 5.0.

Exhibit E

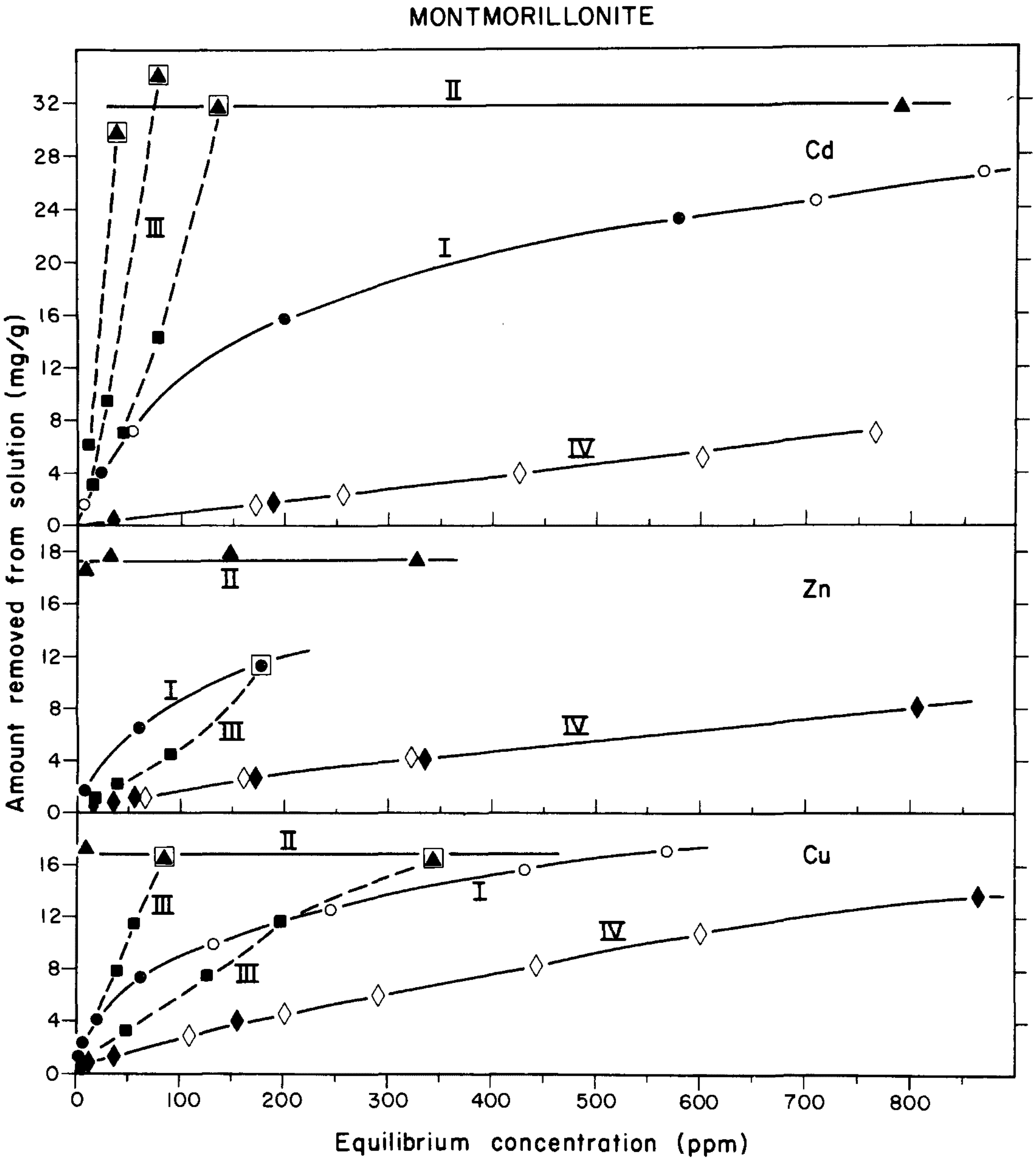

Figure 19. The amount of Cu, Zn, or Cd removed from solution per gram of montmorillonite at pH 5.0 and 25° C, plotted as a function of the equilibrium concentration. The labels I - IV and the open symbols have same meaning as in Fig. 18.

Exhibit E

TABLE 10. TOTAL CONTENT OF Cu, Zn, OR Cd IN 50 ml OF SOLUTION

Initial concentration in solution	Cu	Zn	Cd
ppm	µmoles in 50 ml solution volumes		
4	3.15	3.06	1.78
10	7.87	7.15	4.45
25	19.7	17.9	11.1
40	31.5	30.6	17.8
50	39.4	38.2	22.2
100	78.7	76.5	44.5
200	157.4	153.0	89.0
400	314.8	306.0	178.0
500	393.4	382.5	222.5
1000	786.9	765.0	445.0

Exhibit E

amount of Cu, Zn, or Cd adsorption by 1.00 g of clay from about 50 ml of solution.

The type II isotherms in Figures 18 and 19 were obtained when the weight of clay samples and/or solution volumes were adjusted so that the ratios (total number of Cu, Zn, or Cd ions)/(number of exchangeable cations on the clay samples) were held about constant (at least 2/1) and independent of the concentrations in the initial solution. Although, at equilibrium, the equilibrium concentration of Cu, Zn, or Cd (C_A) could not be considered to be much greater than the concentration of desorbing Ca ions (C_B), the ratio of C_A/C_B should be a constant and, hence, Eq. {11} says that $(x/m)_A$ should be constant and independent of C_A. This is shown by the type II isotherms in Figures 18 and 19. The "scatter" in the experimental data points for the type II isotherms is attributed to experimental errors due primarily to problems in measuring accurately the small changes in concentration that are due to adsorption. These errors must then be multiplied by large factors to compute the amount of metal removed per gram of clay.

The type I and II isotherms plotted according to the linear form (Eq. {8}) of the Langmuir equation (Eq. {7}) are shown in Figures 20 and 21. The Langmuir plots for the type I isotherms (1.00 g clay/50-ml solution) show a definite two-slope character (except the plot for Zn-kaolinite); in fact, three linear segments of the Langmuir plot appear to exist for the Cu-montmorillonite plot. The Langmuir plots (Fig. 21) of the type II isotherms for montmorillonite (Fig. 19; the total amount of Cu, Zn, or Cd initially present in solution /g clay was held about constant) show only a one-slope character throughout the concentration range investigated. The $C/(x/m)$ values definitely approach zero as the equilibrium concentration approaches zero. This is precisely what should occur if the competitive Langmuir equation (Eq. {11}) is valid, because Eq. {11} says that, if the equilibrium ratio C_A/C_B is constant, $(x/m)_A$ is independent of the actual concentration, and, therefore, as C_A approaches zero, $C_A/(x/m)_A$ must approach zero.

The Langmuir plots (Fig. 20) for the Cu and Cd type II isotherms with kaolinite (Fig. 18) do show a two-slope character. It was observed during the Cu adsorption experiments that the pH of the Cu-kaolinite suspensions in deionized water decreased when the flask was shaken, thereby indicating that hydrolysis of the Cu^{+2} ion was occurring in solution (i.e., $Cu^{+2} + H_2O = CuOH^+ + H^+$, etc.). Data on hydrolysis of cations that were assembled by Mesmer and Baes (1974) show that no appreciable concentrations of $CuOH^+$ or $Cu_2(OH)_2^{+2}$ will exist in solutions of low Cu concentration below pH 7, but, in the pH range 5 to 6, precipitation can occur from solutions of about 400 ppm Cu. Thus, precipitation is a reasonable explanation for the occurrence of the second slope in the Langmuir plot for Cu-kaolinite. Although similar arguments could be advanced for the Cd-kaolinite Langmuir plot, it appears from Mesmer and Baes (1974) that, in the range of Cd-concentrations used, hydrolysis and precipitation cannot be considered to be contributing factors to the "adsorption" of Cd by kaolinite around pH 5.0.

Shuman (1975) obtained two-slope Langmuir plots when he plotted Zn adsorption by Georgia soils data according to Eq. {8}. John (1972) found no significant correlation between the CEC values and Cd Langmuir adsorption

Exhibit E

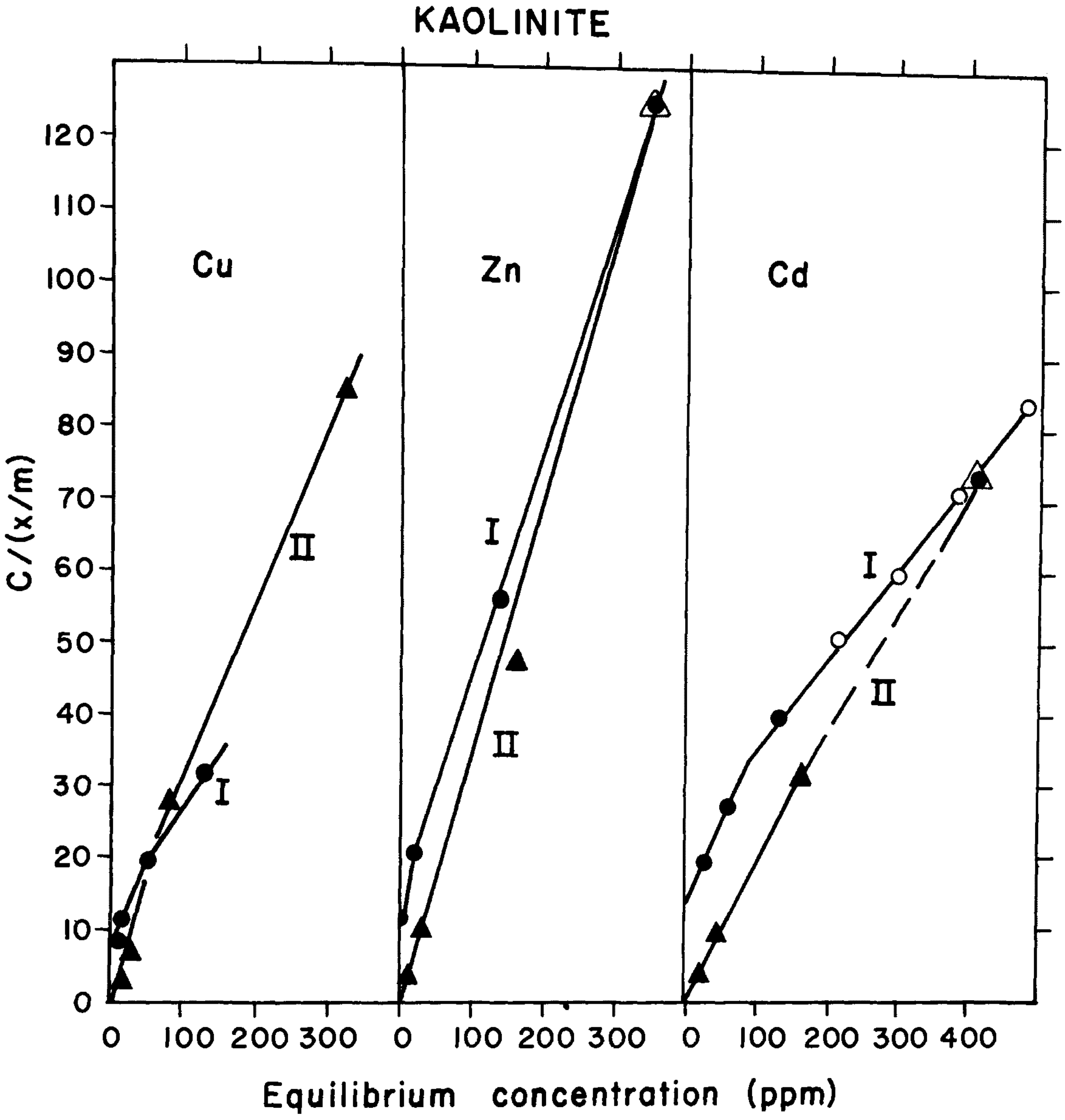

Figure 20. Cu, Zn, and Cd removal data for kaolinite in deionized water solutions at pH 5.0 and 25° C, plotted according to the Langmuir equation (Eq. 8). The roman numerals beside the plots indicate the corresponding isotherm in Fig. 18.

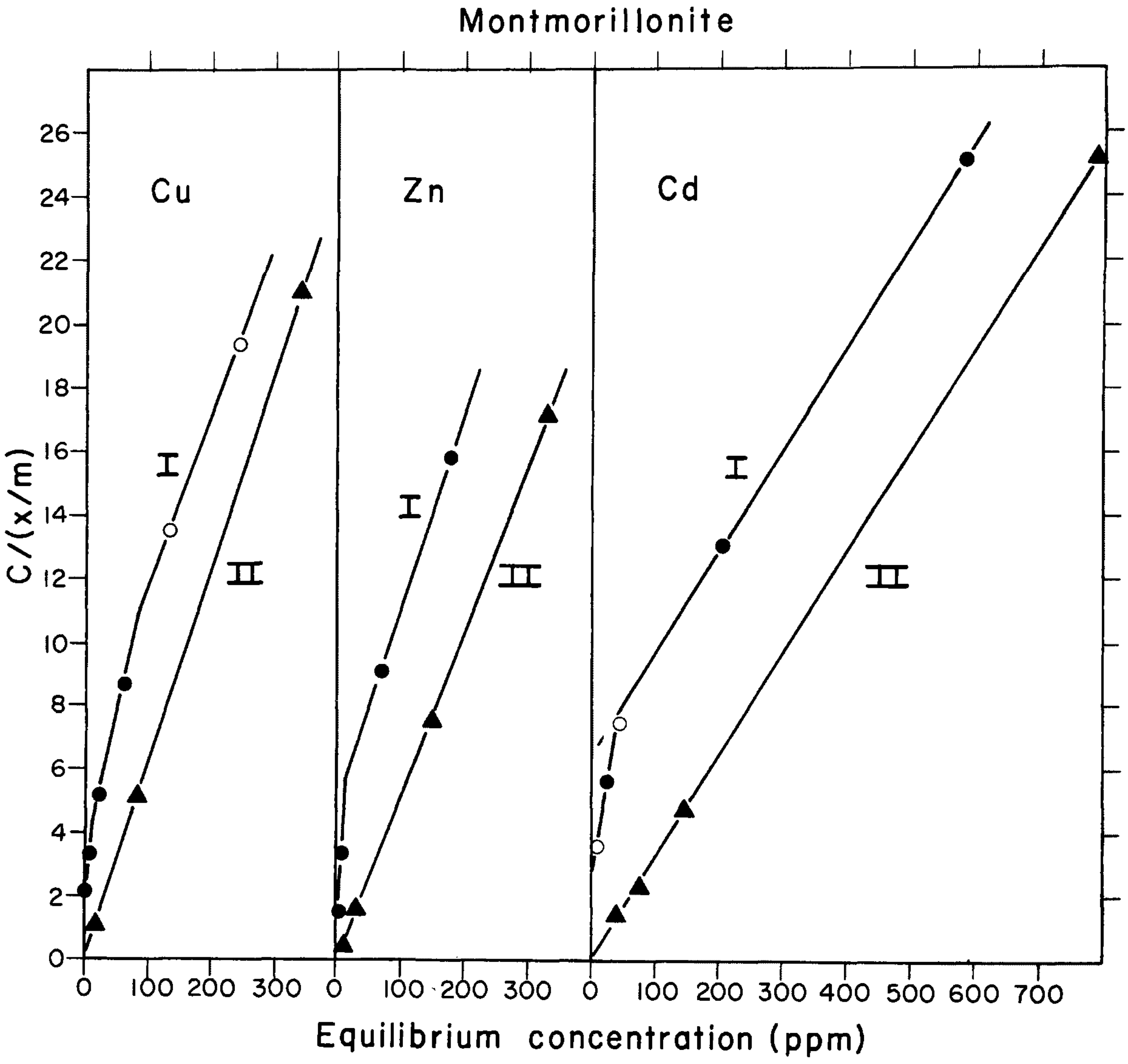

Figure 21. Cu, Zn, and Cd removal data for montmorillonite in deionized water solutions at pH 5.0 and 25° C, plotted according to the Langmuir equation. Numerals indicate corresponding isotherms in Fig. 19.

maximums for 30 different soil samples. Both Shuman (1974) and John (1972) used a fixed weight of soil and a fixed volume of solution in their adsorption measurements. The results of this study indicate that both Shuman (1974) and John (1972) would have obtained somewhat different results and conclusions if they had equilibrated their soil samples with sufficient solution volumes of low-Zn or Cd concentration so that the total Zn or Cd content of the solutions would exceed the CEC values of their respective soil samples. The appropriate solution volumes will necessarily depend on the CEC values of the soil samples (the larger the CEC, the larger the solution volume required) and what kind of exchangeable cations are present on the soil samples.

The type III isotherms in Figures 18 and 19 are "stepwise" isotherms. These isotherms show the competitive effect of the desorbing exchangeable cations initially present on the clay minerals on the removal of other heavy metal cations from solution. Thus, the type I and II isotherms in Figures 18 and 19 do not provide sufficient information to predict the migration of Cu, Zn, or Cd in pure solutions through soils or clays.

The adsorption data plotted by using the linear form (Eq. {12}) of the competitive Langmuir equation (Eq. {11}) are shown in Figures 22 and 23. It was assumed that the number of ions (presumed to be all Ca, which is more reasonable for kaolinite than for montmorillonite) desorbed from the clays into solution equals the amount of Cu, Zn, or Cd adsorbed from solution. It can be shown that C_A (ppm)/ΔC_A (ppm) = C_A(moles/l)/C_{Ca}(moles/l), where C_A = equilibrium concentration of Cu, Zn, or Cd and $\Delta C_A = C_{Initial} - C_A$, so that $(C_A/\Delta C_A)/(x/m)_A$ versus $(C_A/\Delta C_A)$ was plotted in Figures 22 and 23. For stepwise isotherms, the ΔC_A used included the ΔC_A values from previous steps. Although there is appreciable scatter to the data, reasonably straight lines (except for Cd-kaolinite), can be drawn through most of the data points, which include all data plotted for deionized-water solution isotherms I, II, and III in Figures 18 and 19. Some data points lie above the line drawn through the data points. At these data points, $C/\Delta C$ is generally small and the number of ions adsorbed (x/m) is limited by the total number of ions initially present in solution. Negative deviations from the main linear region can occur when Eq. {8} is used at low concentrations. Positive deviations from the main linear region can occur when Eq. {12} is used for small values of $C/\Delta C$.

The adsorption maximums calculated from the type II Langmuir plots in Figures 20 and 21 and the competitive-Langmuir plots in Figures 22 and 23 are given in Table 11.

The question arises as to why there is such poor correlation between the adsorption maximums calculated from the CEC values and the experimental adsorption maximums if cation exchange is the primary adsorption mechanism. Bittel and Miller (1974) have determined the selectivity coefficients for Cd/Ca on kaolinite and montmorillonite to be about one (i.e., Ca and Cd ions compete on about an equal basis for adsorption sites), but they do not specify a pH for their experimental measurements. The data obtained in this study indicate that the selectivity coefficients for Cu, Zn, and Cd on Ca-saturated kaolinite and montmorillonite are less than one at pH 5 and ap-

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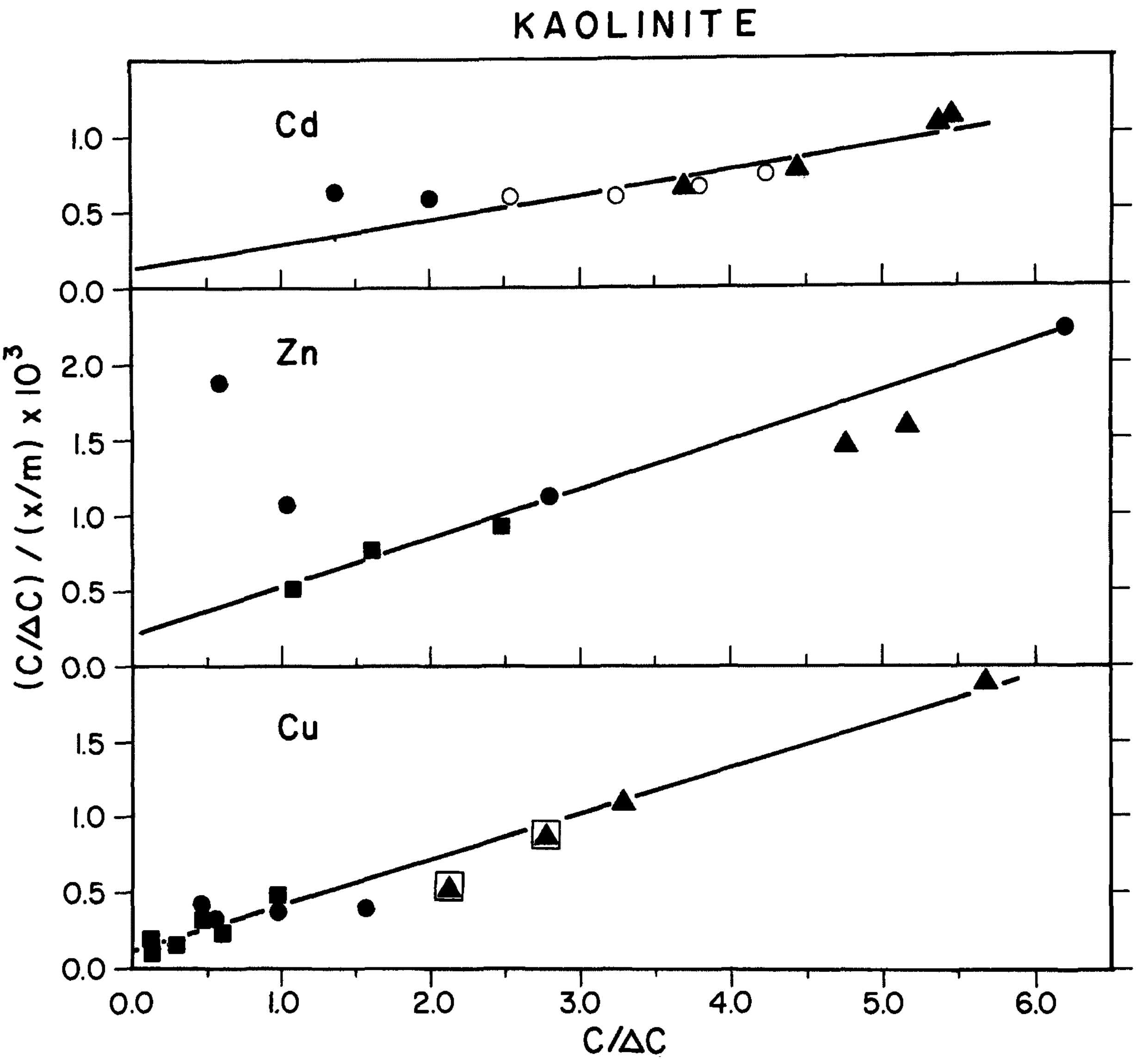

Figure 22. Cu, Zn, and Cd removal data for kaolinite in deionized water solutions at pH 5.0 and 25° C, plotted according to the competitive Langmuir equation (Eq. 12). The data point symbols correspond to those used in Fig. 18.

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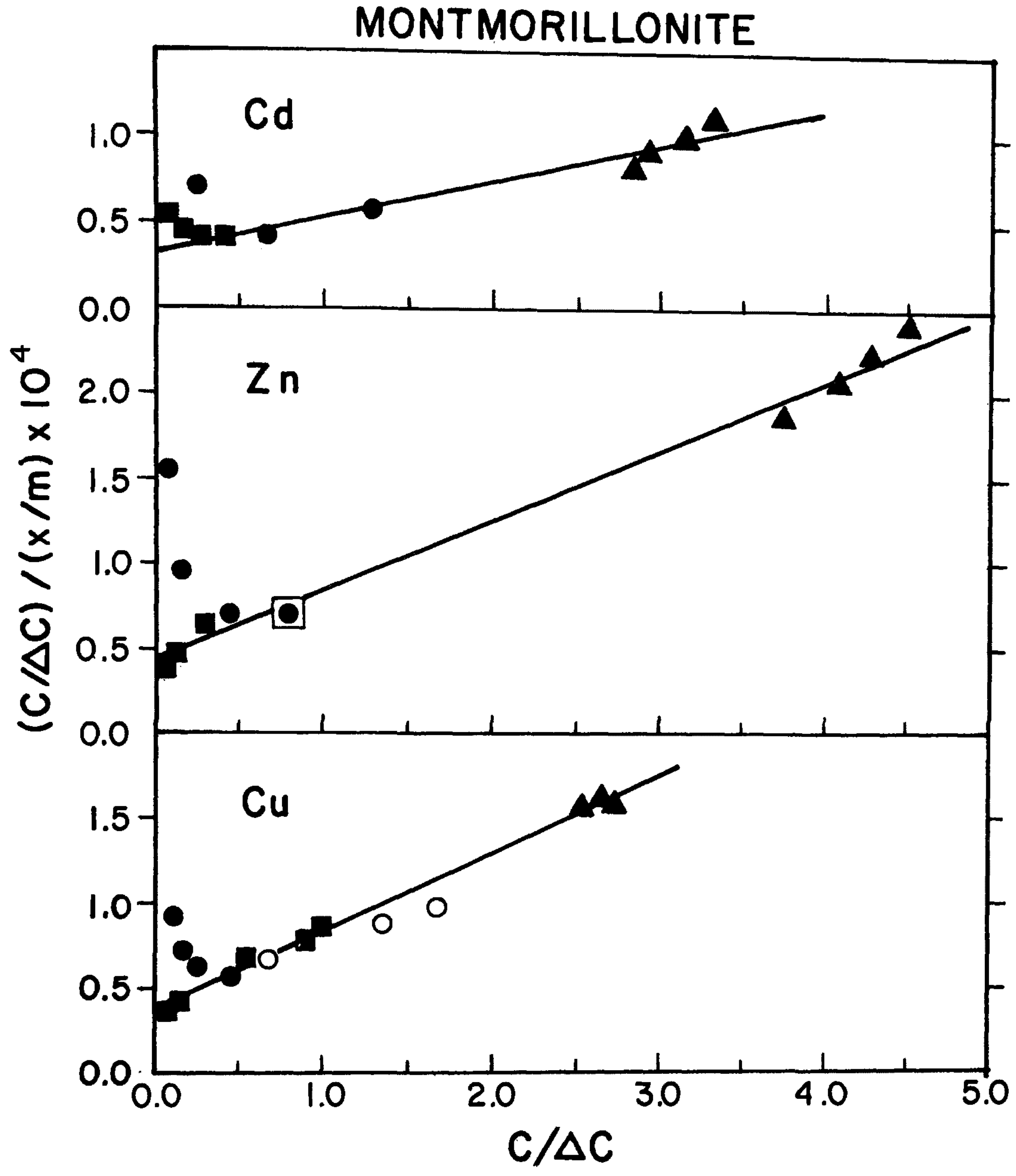

Figure 23. Cu, Zn, and Cd removal data for montmorillonite in deionized water solutions at pH 5.0 and 25° C, plotted according to the competitive Langmuir equation (Eq. 12). The data point symbols correspond to those used in Fig. 19.

TABLE 11. COMPARISON OF LANGMUIR ADSORPTION MAXIMUMS IN DEIONIZED WATER WITH CEC VALUES

Source	Cu		Zn		Cd	
	K*	M†	K	M	K	M
	mg/g					
II - Langmuir plots (Figs. 21 and 22)	3.08	18.5	2.86	19.2	5.0	31.2
Langmuir plots (Figs. 23 and 24)	3.33	21.0	3.00	23.6	-	50.0
Calc. from CEC values - Table 1	4.80	25.3	4.94	26.0	8.45	44.8

*Kaolinite
†Montmorillonite

Exhibit E

proach one at higher pH. Therefore, the experimental adsorption maximums for Cu, Zn, or Cd would not approach the CEC values until the equilibrium ratio C/C_{Ca} was larger than was the case in any of our experiments. Because the adsorption of Cu, Zn, or Cd is pH-dependent, the adsorption maximums will, of course, show definite pH-dependence. Prior to the onset of precipitation, which is dependent on both concentration and pH, decreasing competition from H^+ and increasing concentration of hydrolyzed ions (e.g., $Cu_2(OH_4)^{+2}$, $ZnOH^+$, and $CdOH^+$) are possible reasons for the "adsorption" to increase as pH increases.

Curves for pH versus the removal of Cu, Zn, or Cd from leachate by kaolinite and montmorillonite are shown in Figures 24 and 25, respectively. The data listed beside each curve and in the figure captions were used in Eq. {13} to calculate the type IV isotherms at pH 5.0, which are shown in Figures 18 and 19. This was done so that direct comparisons could be made with the deionized-water isotherms. Figures 18 and 19 show that the removal from leachate is appreciably lower than the removal from deionized-water solutions. Boyd, Shubert, and Adamson (1947) gave a general expression for the exchange adsorption of a cation, A, from a mixture of equally charged cations in solution, which is as follows:

$$(x/m)_A = \frac{b\,K_A\,C_A}{1 + \sum_{\text{all}_j} K_j\,C_j}. \qquad \{14\}$$

Equation {14} says that the exchange adsorption of any one cationic species at constant concentration will decrease as the concentrations of other cationic species increase. Thus, from solutions of constant ionic strength, in which the total ionic content is large compared to the total number of exchangeable cation on any soil or clay mineral sample placed in that solution, the amount of Cu, Zn, or Cd removal cannot approach the CEC of the soil or clay mineral at low concentrations, as is true in the case of exchange-adsorption from deionized water (i.e., increasing solution volume will usually not affect the equilibrium concentration ratio of the cation of interest to the other cations in solution to any appreciable extent). Only when the concentrations of Cu, Zn, or Cd in solution exceed the combined concentrations of all other cationic species in solution will the amount of exchange-adsorption of Cu, Zn, or Cd approach the CEC of the soil or clay mineral sample being tested. In practice, except at very low pH, precipitation of Cu, Zn, Cd and other heavy metal ions as hydroxides and/or carbonates will occur at moderate concentrations so that precipitation rather than cation exchange adsorption can become the principal mechanism for the removal of heavy metal ions from solution.

The sharply rising portions of the removal curves shown in Figures 24 and 25 can easily be interpreted, with the aid of information assembled by Mesmer and Baes (1974), as being caused primarily by precipitation of Cu, Zn, or Cd carbonates, hydroxides, or hydroxide-carbonates. Removal of Zn and Cd from the leachate by both kaolinite and montmorillonite is greatly reduced compared to their removal from deionized water solutions at pH 5.0. The amount of Zn and Cd removed is reduced proportionally about the same for both

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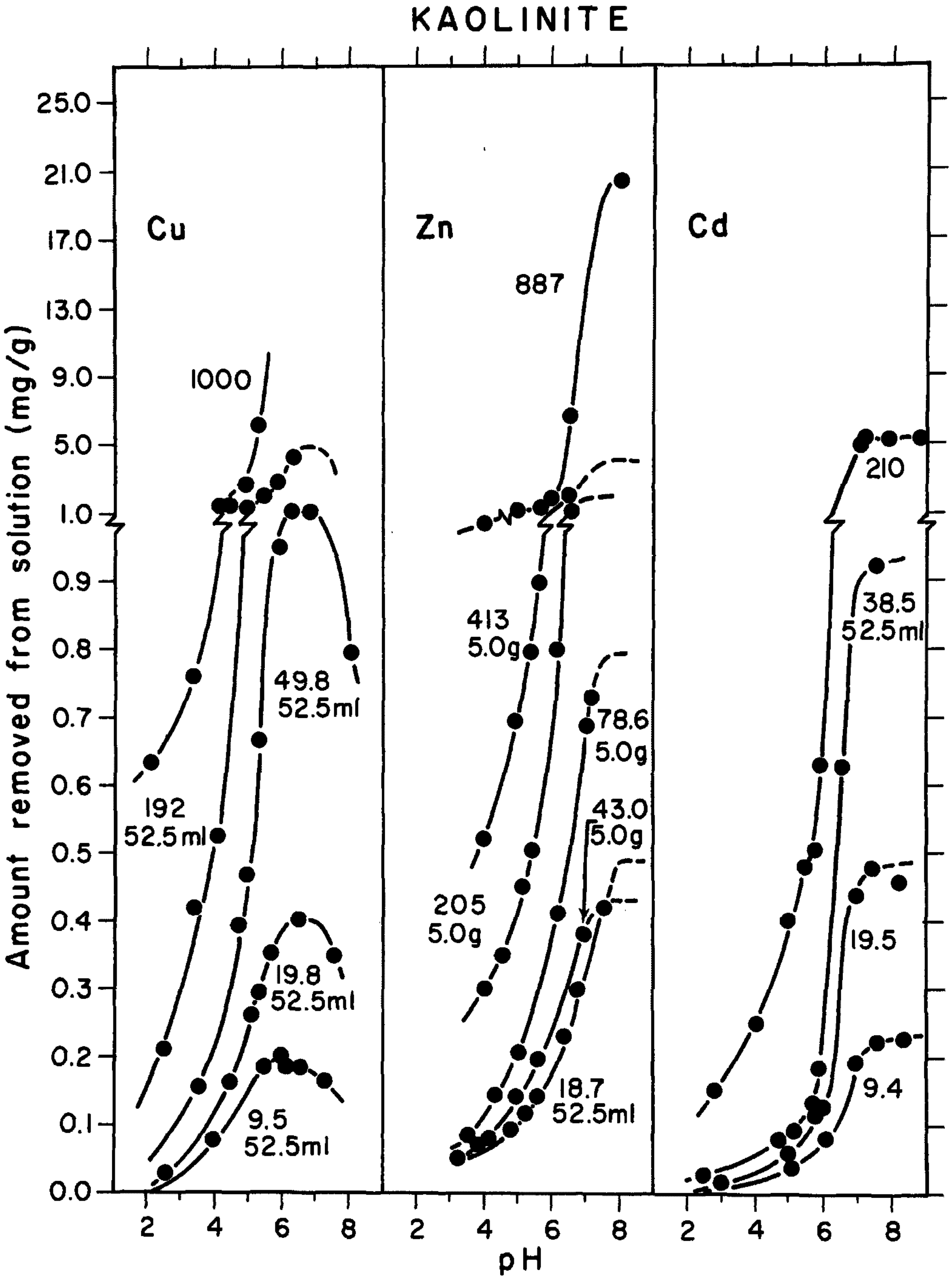

Figure 24. The amount of Cu, Zn, or Cd removed from DuPage leachate solutions by kaolinite at 25° C, plotted as a function of pH. The plots are labeled with the initial solution concentration (ppm) of Cu, Zn, or Cd from which each plot was obtained. Unless otherwise indicated, 2.0 g of clay and a total leachate solution volume of 50.5 ml were used to obtain each data point.

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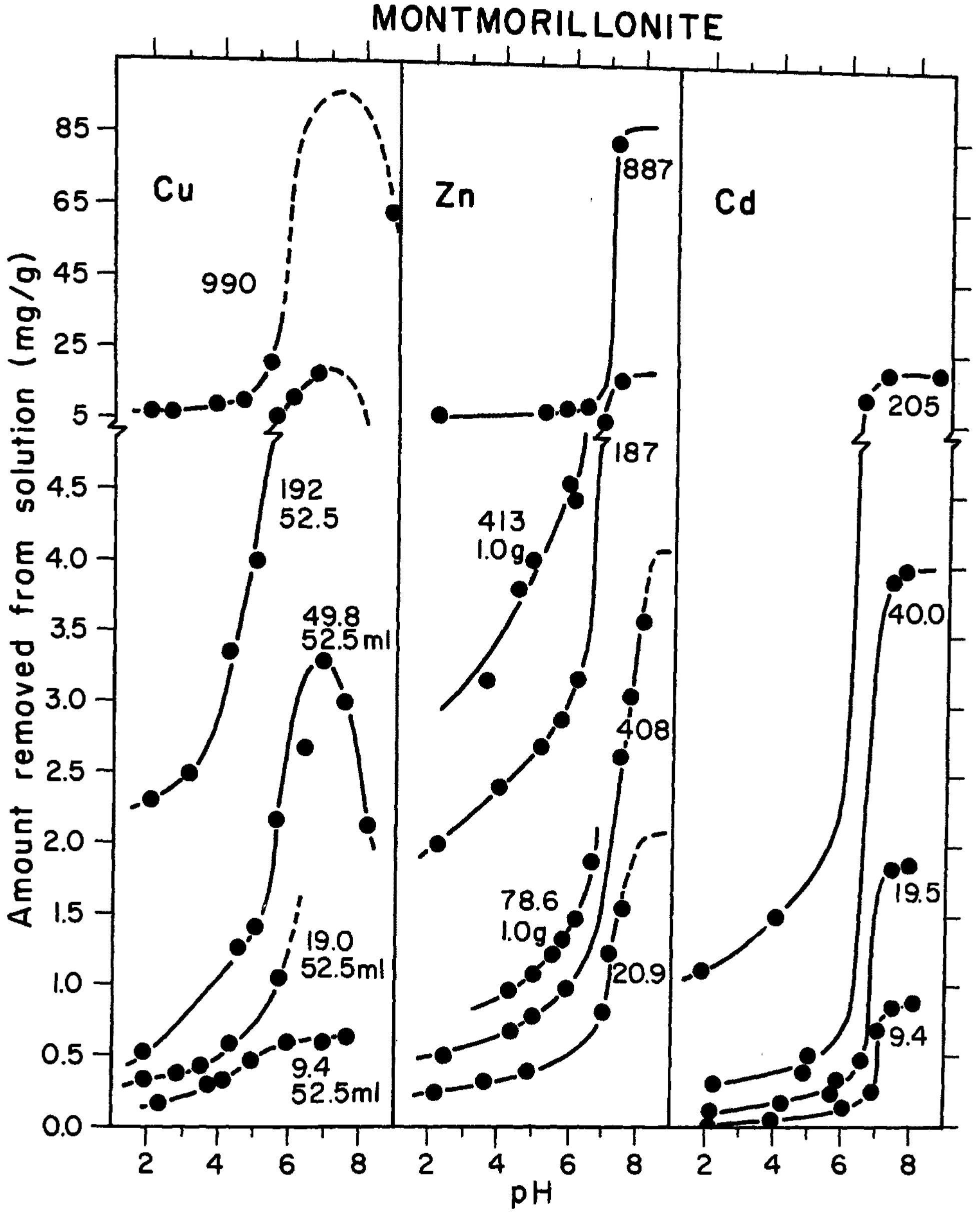

Figure 25. The amount of Cu, Zn, or Cd removed from DuPage leachate solutions by montmorillonite at 25° C, plotted as a function of pH. The plots are labeled with the initial solution concentration (ppm) of Cu, Zn, or Cd from which each plot was obtained. Unless otherwise indicated, 0.5 g of clay and a total leachate solution volume of 50.5 ml were used to obtain each data point.

kaolinite and montmorillonite, but the reduction in the amount of Cu removed from the leachate is appreciably greater for montmorillonite than for kaolinite. This can readily be explained on the basis that the Cu-leachate isotherms represents a combination of exchange-adsorption and precipitation. The amount of Cu removed by precipitation, for example 1 mg/g, will be about the same for leachate solutions at pH 5, whether kaolinite or montmorillonite is present in solution. However, the 1 mg/g represents about 20% of the CEC for kaolinite, while it represents only about 4% of the CEC for montmorillonite. The decrease in removal from leachate, therefore, appears much greater for montmorillonite than for kaolinite. The actual decrease in Cu exchange-adsorption is probably proportionally the same for both clays. The removal of Cu from leachate reaches a maximum about pH 7 (Figs. 24 and 25) and then decreases for pH values above 7. This behavior is due to the amphoteric character of $Cu(OH)_2$ precipitates, which redissolve in basic solutions by forming $Cu(OH)_3^-$, etc. ions.

The amount of Cu, Zn, or Cd removed from leachate has no significant apparent dependence on leachate volume, as can be seen from the leachate isotherms (Figs. 18 and 19), on which data points obtained for different clay sample weights but constant leachate volumes have been plotted on one isotherm curve. However, the amount removed could become dependent on the leachate volume if the clay sample is very large.

Equation {14} implies that at some given ionic strength, where

$$\sum_{\text{all}_j} K_j \, C_j$$

is about constant and large compared to one, $(x/m)_A$ = Constant x C_A. The isotherms for Cd (Figs. 18 and 19) are linear to quite high concentrations.

The isotherms for Cu, Zn, or Cd removal from leachate were <u>not</u> plotted according to the linear form of a Langmuir adsorption isotherm equation, although, most assuredly, straight line plots would have been obtained and "adsorption" maximums could be calculated. The reasons for not plotting them were, first, none of the leachate isotherm plots have really reached the plateau region in the concentration range studied (up to 1000 ppm). Second, any adsorption maximums calculated from the Langmuir plots would be somewhat meaningless because the amount of exchange-adsorption from leachate is limited by competition, owing to the high ionic strength of the leachate and not because all the adsorption sites have been occupied by Cu, Zn, or Cd ions, as is implied with a Langmuir adsorption maximum. Third, if an adsorption maximum is calculated from the rising part of an isotherm, it represents the amount adsorbed at some higher hypothetical concentration that may or may not lie on the real adsorption isotherm. Finally, our purpose was to determine the maximum amount of Cu, Zn, or Cd that can be removed by kaolinite or montmorillonite from leachate at any particular concentration up to approximately 1000 ppm. As we have seen for removal from deionized water, with appropriate experimental conditions, the amount removed is independent of concentration and is proportional to the CEC values of the clays. It would presumably approach the CEC at higher (volume)/(weight of clay) ratios. But, with leach-

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ate, the ionic strength is not a variable to be adjusted and the conditions cannot be created where at low concentrations of Cu, Zn, or Cd the ratio of the (equilibrium concentration of Cu, Zn, or Cd)/(concentration of other cations) is large. The maximum amount removed must then be a function of the ionic strength of the leachate, the CEC of the clay sample, and pH of the leachate. Therefore, the maximum amount removed at any concentration and pH from leachate (or for that matter any solution) is simply the value read from the removal isotherm itself at the concentration of interest.

SUMMARY AND CONCLUSIONS

Under appropriate experimental conditions, the amount of Cu, Zn, or Cd exchange-adsorbed from deionized water by purified kaolinite and montmorillonite clay minerals is independent of the equilibrium concentration of Cu, Zn, or Cd. However, the maximum amount of Cu, Zn, or Cd adsorbed in our experiments was related to, but not equal to, the CEC values of the clay minerals, probably because the desorbing Ca ions effectively competed with the Cu, Zn, or Cd ions present in solution. If cation-exchange adsorption experiments are carried out at constant (solution volume)/(sample weight) ratios for Cu, Zn, or Cd in deionized water, the amount of adsorption is necessarily limited by the total amount of Cu, Zn, or Cd that was initially present in solution at low concentrations. Therefore, the isotherm obtained is really a plot of the amount of Cu, Zn, or Cd removed by a fixed weight of sample from a fixed volume of solution versus concentration. At low concentrations a different isotherm can be obtained simply by using a different constant (solution volume)/(sample weight) ratio in the experiments. To properly simulate field conditions, soil samples must be equilibrated with sufficient solution volumes so that the total metal ion content of the solutions exceeds the adsorption capacity (CEC values) of the respective soil samples. The appropriate solution volumes will necessarily depend on the CEC of the soils and the kind of exchangeable cations present on the soil samples.

If it is desirable to study the migration of Cu, Zn, or Cd from deionized water through soils or clays by means of batch experiments, the experiments can be carried out stepwise (i.e., repeated treatments of a solution with new soil or clay samples) for each initial solution concentration tested. That is necessary because of the increasing concentration of exchangeable cations in solution as exchange-adsorption of an individual cation from solution occurs stepwise towards zero. This is not a particular problem in high ionic strength solutions such as landfill leachate as discussed below.

The three different types of isotherms obtained for the same range of Cu, Zn, or Cd concentration are easily interpreted in terms of a cation exchange-adsorption mechanism. Also, the correct "Langmuir" isotherm equation to apply to exchange adsorption data is Eq. {11}, which covers the simultaneous competitive adsorption of two cations, and not Eq. {7}, which is for a single cation. Although strict application of Eq. {11} requires the exchangeable cations on the adsorbent to be homoionic, the principal conclusion that "under appropriate conditions" the amount of exchange-adsorption is independent of concentration will apply, regardless of the number of exchangeable cations on the adsorbent.

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The adsorption of Cu, Zn, or Cd from leachate by kaolinite and montmorillonite clay minerals is presumed to occur via a cation exchange mechanism, but, because the high ionic strength of the leachate is relatively unvariable in the adsorption experiments, the amount adsorbed does not become independent of the concentration of Cu, Zn, or Cd in the leachate. Thus, there is no way to predict the maximum amount of Cu, Zn, or Cd that will be adsorbed from a given leachate by a given soil or clay mineral, at a given pH and at some concentration without actually measuring it. At pH 5.0, precipitation of Cu as a hydroxide-carbonate makes a very significant contribution to the total amount of Cu removed by kaolinite but, because montmorillonite has a higher amount of exchange-adsorption, the contribution of precipitation to the total amount of Cu removed by montmorillonite is less significant. If the pH of the leachate is lower than about 6.5, precipitation does not make a significant contribution to the total amount of Zn and Cd removed by kaolinite and montmorillonite.

The mobility of Cu, Zn, and Cd in soils or clay minerals is similar to Pb and is dependent upon solution pH and ionic strength as well as on the CEC of the soils or clay minerals. This is of little importance at sufficiently high (above 7) pH values, because precipitation is then more important than cation exchange in the removal of Cu, Zn, or Cd from solution. However, the mobility of Cu would apparently reach a minimum at pH 7 and would subsequently increase at pH values above 7. At pH 5, Cu, Zn, and Cd in leachate will be quite mobile in soils or clay minerals with low CEC values, especially when the ionic strength of the leachate is high. Thus, if adsorption data at pH 5.0 is obtained either from a leachate very high in ionic strength or from a low CEC soil or clay mineral, and the mobility of Cu, Zn, or Cd is calculated, it can be stated that for higher pH values, for higher CEC values, and/or for leachates low in ionic strength, the mobility would be less than it is at pH 5.0. These facts add a built-in safety factor to estimations of adsorption and/or mobility.

Treatment of a soil with a waste stream or leachate will alter the exchangeable cation distribution of the soil; for example, a high Ca soil will become a high Na soil if treated with a high Na-content waste stream or leachate. Thus, other potential problems may be created that must be evaluated in addition to the problem of heavy metal toxicity to plants or heavy metal accumulation in the food chain when waste streams or leachates are disposed of on agricultural land.

Exhibit E

SECTION 9

EFFECT OF pH ON CHROMIUM ADSORPTION FROM LANDFILL LEACHATE BY CLAY MINERALS[1]

ABSTRACT

The adsorption of Cr(VI) and Cr(III) species by kaolinite and montmorillonite clay minerals was found to be highly dependent upon the pH of the clay suspensions and the physical-chemical properties of the clay minerals. Solution ionic strength was found to be of secondary importance to estimations of Cr(VI) and Cr(III) adsorption.

No precipitation of Cr(VI) was detected in the pH range 1.0 to 9.0. Precipitation of Cr(III) as an amorphous hydrated hydroxide starts to occur above pH 4.5.

The adsorption of Cr(VI) from a given solution decreased as pH increased. The Cr(VI) species distribution indicated that the $HCrO_4^-$ ion was the Cr(VI) species predominantly adsorbed. Montmorillonite adsorbed about four times more Cr(VI) than kaolinite under similar conditions of pH and ionic competition. Contrary to expectations, less Cr(VI) was adsorbed from pure K_2CrO_4 solutions than from leachate solutions.

The adsorption of Cr(III) increased as the pH of the suspensions increased. At pH 2.5, the amounts of Cr(III) adsorbed were consistent with a cation exchange mechanism involving Cr^{3+} ions. As the pH is raised to 4.0, the amounts adsorbed correspond to cation exchange adsorption of the hydrolized Cr(III) species, $Cr(OH)_2^+$ and $Cr_6(OH)_{15}^{3+}$. The adsorption of Cr(III) is 3% to 14% lower in leachate than in pure $Cr(NO_3)_3$ solutions.

For a given type of clay, about 30 to 300 times more Cr(III) than Cr(VI) is adsorbed depending upon pH and the ionic competition in solution. The results of the study suggest that landfill disposal of Cr(VI) wastes represents a potential pollution hazard due to its high mobility in earth materials and that safe disposal may require conversion of Cr(VI) wastes to Cr(III) before disposal in landfills.

INTRODUCTION

Efforts to effectively dispose of most industrial heavy metal wastes without polluting the environment have thus far proved unfruitful. Traditionally, rivers or lakes have been used for the disposal of these potentially

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[1] Authors: R. A. Griffin, Anna K. Au, and R. R. Frost

Exhibit E

hazardous discharges. Industrial plants have also disposed of their wastes through recharge basins or diffusion wells (Welsch, 1955), and into sewer systems (Nassau County, N. Y., Department of Public Works Sewer Regulations, 1955). All of these disposal methods can contribute to contamination of surface and ground water (Davids and Lieber, 1951). To minimize the problems caused by heavy metal wastes in sewage treatment, laws have been enacted in some northern Illinois counties forbidding the disposal of such wastes into sanitary sewers. That prohibition has increased the pressure for permission to dispose of these wastes in the available sanitary landfill sites. However, unless specially designed, sanitary landfills also are a potential source of surface and ground-water pollution (Walker, 1969). For that reason a demand has arisen for information about the capacity of earth materials to adsorb heavy metals from landfill leachates (Fuller, 1975).

Chromium compounds are widely used in the leather, textile, chemical manufacturing, metal finishing, and other industries. Approximately 30,000 tons of chromium-bearing wastes are discharged annually from the metal finishing industries alone (U.S.-EPA, 1973), and problems of environmental pollution have arisen. Chromium (VI) contamination of the village wells in Douglas, Michigan, was reported in 1947 (Davids and Lieber, 1951), and as early as 1952 chromium was found in high concentration in the ground water of Nassau County, New York (Welsch, 1955).

In trace amounts, chromium is an essential element in the diet of some animals and, presumably, human beings. However, at sufficiently high concentrations, all compounds of chromium are toxic (Smith, 1972). The valence state of chromium has a considerable influence on its toxicity. It is well established that Cr(VI) compounds are the most toxic and are usually irritating and poisonous to all tissues (Baetjer, 1956).

Thus far, the distribution and impact of chromium on aquatic ecological systems have not received extensive study, so that relatively little is known about the transfer of the metal from waste streams to earth materials and then to living systems. Because knowledge of the chromium-leachate system is scant, the present study was conducted to investigate the effect pH has on Cr(VI) and Cr(III) adsorption by clay minerals plus precipitation in deionized water and municipal leachate solutions. It was also desired to gain insight into the factors that affect the mobility of chromium as it passes through soils or clay-mineral layers. These soil or clay layers may be potentially useful as liners for waste disposal sites.

EXPERIMENTAL

Various concentrations of Cr(VI) in deionized water and DuPage leachate were prepared using potassium chromate (K_2CrO_4), and 50-ml aliquots were pipetted into Erlenmeyer flasks containing either 3 g of montmorillonite or 5 g of kaolinite. The weight of clay used was chosen so that the amount of Cr removed from the solutions could be determined with some precision from the difference between the initial and final solution concentrations. Several replicate suspensions for each concentration were prepared, and their pH values were adjusted with either HNO_3 or NaOH to various values in the pH range 1.0 to 9.0.

In preliminary experiments, the amount of Cr(VI) adsorption was found to decrease as pH increased, and pH values of the Cr(VI)-clay suspensions rose when the flasks were shaken. Also, apparent irreversible Cr(VI) adsorption occurred if the Cr(VI)-clay suspensions had been equilibrated at one pH value and again equilibrated at a higher pH value. Therefore, the flasks were shaken for about 2 weeks in a constant temperature bath at 25 ± 0.5° C; the pH values of the clay suspensions were measured each day, and acid or base was added when necessary to maintain the initial pH value. At least one day after the final pH adjustment, the pH values were recorded and the suspensions were centrifuged. The supernatant solutions were then decanted into plastic bottles and their pH adjusted to 2.0 to prevent any Cr adsorption by the container. The equilibrium Cr concentrations C_{Eq} (ppm) in the supernatant solutions were determined by atomic absorption spectroscopy. The initial Cr concentration (C_I) in ppm was determined by analyses of blank sample, i.e., sample without clay, prepared at the same time as the clay suspensions. In our experiments, C_I concentrations ranging from 5 to 300 ppm Cr as Cr(VI) were used.

The amount of Cr(VI) adsorbed (x/m) in mg/g clay at a given pH was calculated as $(C_I - C_{Eq}) \times V_E/1000$ where V_E = final solution volume (ml)/weight of clay sample (g). The amount of Cr(VI) adsorbed by a fixed amount of clay from a given C_I solution at various pH values was plotted against the pH values to obtain an adsorption-pH curve.

The experimental procedures for the Cr(III) adsorption studies were similar to those used in the Cr(VI) experiments. It was determined that 0.100 g of the clay minerals would give the desired precision in determining the change in Cr(III) concentrations at equilibrium. Chromium (III) nitrate ($Cr(NO_3)_3 \cdot 9H_2O$) was used as a source of Cr(III). The study of Cr(III) adsorption was generally limited to the pH range of 1.5 to 4.5 because of Cr(III) precipitation around pH 5. Because of the precipitation, the pH of the leachate was adjusted to about 4 prior to "spiking" with Cr(III). An initial Cr(III) concentration range of 30 to 800 ppm was chosen for the experiments.

RESULTS AND DISCUSSION

Adsorption isotherms can be calculated from a family of adsorption-pH curves at different pH values. The amount of Cr adsorbed (x/m) in mg/g clay at a particular pH value is read from an adsorption-pH curve for a particular C_I and the equilibrium concentration, C_{Eq}, in ppm is calculated from the following equation:

$$C_{Eq}\ (\text{ppm}) = C_I\ (\text{ppm}) - \frac{(x/m) \cdot 1000}{V_E} \qquad \{15\}$$

where all the parameters are as previously defined.

Interpretation of the adsorption data was aided by application of the Langmuir equation (1918). In the derivation of the Langmuir equation it is assumed that (a) the surface is energetically homogeneous, (b) the adsorbate-adsorbate interaction on the surface is negligible, and (c) the adsorbed molecules do not influence neighboring sites. The Langmuir adsorption equation in its linear form is:

$$\frac{C}{x/m} = \frac{1}{kb} + \frac{C}{b} \qquad \{16\}$$

where C is the equilibrium concentration of the ion, x is the amount adsorbed, m is the mass of adsorbent, b is the adsorption maximum, and k is a constant that relates to the energy of adsorption.

Chromium (VI) Adsorption

No precipitation of Cr(VI) was observed in the pH range 1.0 to 9.0. Families of Cr(VI) adsorption-pH curves are presented in Figures 26 and 27. Several characteristics of Cr(VI) adsorption by the clays appear. First, the adsorption of Cr(VI) decreases as pH increases. Second, Cr(VI) is not adsorbed by the clays near pH 8.5 and above. Third, the amounts of Cr(VI) adsorbed are small compared to the amounts of exchangeable cations on the clay samples.

Diagrams showing the distribution of Cr(VI) species covering the experimental concentration range are presented in Figure 28 and were calculated by using the constants given in Butler (1964). Noteworthy is the rapid decrease in the fractions of $HCrO_4^-$ and $Cr_2O_7^{2-}$ species above pH 5 and the corresponding increase in the fraction of CrO_4^{2-} species, which become the principal species present in solution at about pH 8.5 (Fig. 28). Below pH 2 the fraction of $HCrO_4^-$ ions decrease rapidly as the fraction of H_2CrO_4 species increases.

The behavior of the Cr(VI) adsorption-pH curves in Figures 26 and 27 implies that the $HCrO_4^-$ ion is the principal ion being adsorbed by the clay minerals. Conversely, the lack of adsorption at pH values above 8.5 indicates that the CrO_4^{2-} ion is not adsorbed at all by either of the two clays. The mechanism of Cr(VI) adsorption by these clay minerals apparently cannot neutralize the two negative charges present on the CrO_4^{2-} ion. On the other hand, $Cr_2O_7^{2-}$ ions may be adsorbed at low pH values because of its more open structure, $CrO_3^- - O - CrO_3^-$, which places the two negative charges an appreciable distance apart, as opposed to charges on adjacent oxygens that occur in the CrO_4^{2-} structure. The charge separation on the $Cr_2O_7^{2-}$ ion may allow it to act essentially as two monovalent ions, with each negative charge fulfilling an adsorption site or one negative charge fulfilling an adsorption site and the other negative charge being neutralized by a cation in solution. If the distribution of Cr(VI) species in solution is the only factor governing adsorption of Cr(VI) over the pH range 2 to 5, a plateau should be observed in the Cr(VI) adsorption-pH curves; however, the adsorption of Cr(VI) continues to rise with decreasing pH to a pH value around 2. Therefore, in the low pH range the pH probably modifies the structures of the clay minerals to permit increased Cr(VI) adsorption to occur. Dissolution of clay minerals is known to occur at low pH levels (Hofmann et al., 1956). This can alter the surface structure and surface area of the clays, resulting in changes in their adsorption characteristics as the pH is lowered.

Adsorption isotherms were constructed from the Cr(VI) adsorption-pH

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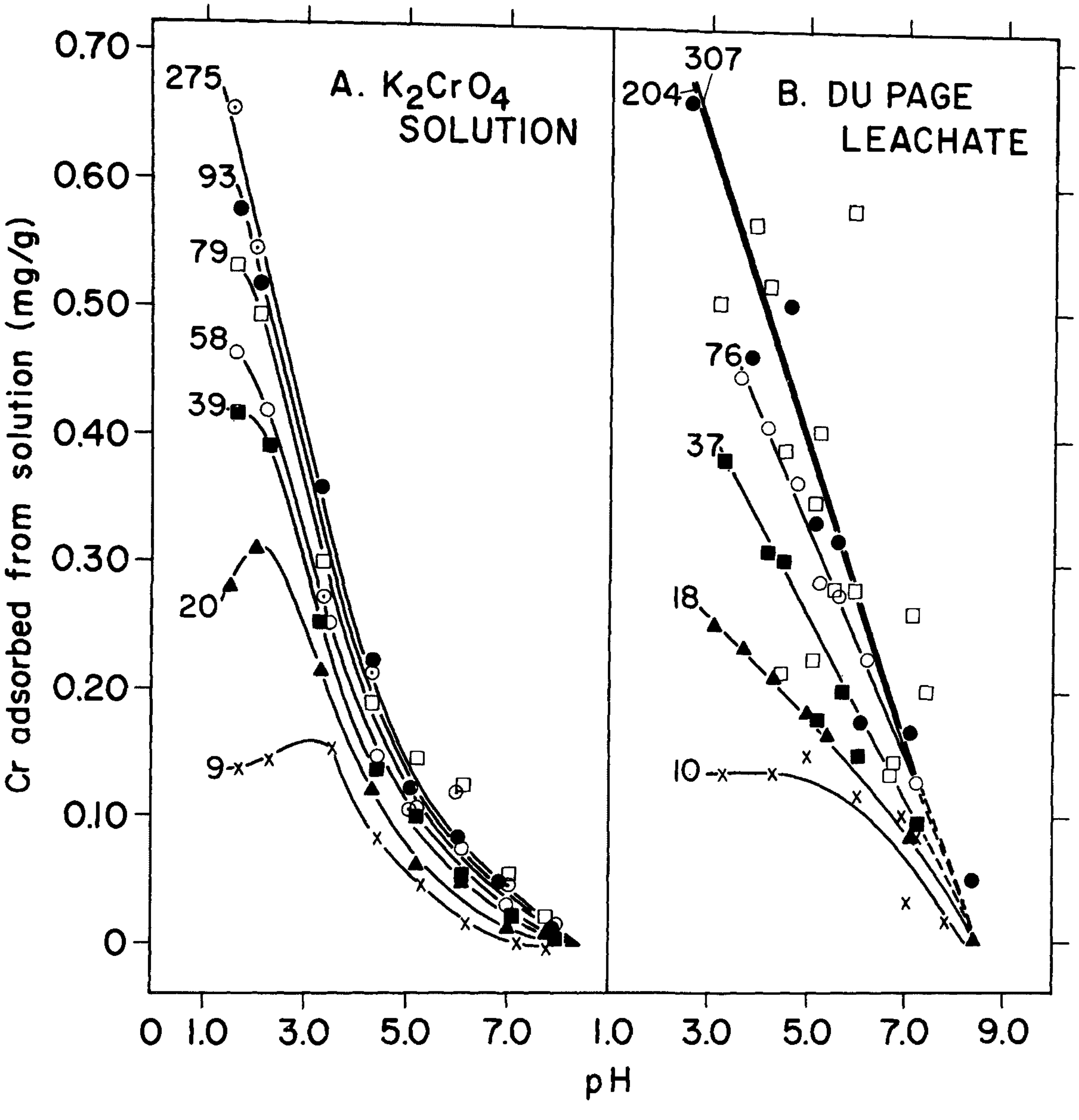

Figure 26. Chromium (VI) adsorption-pH curves for montmorillonite at 25° C. Initial Cr(VI) concentrations (ppm) are indicated beside each curve, and the equivalence volume for each curve is 16.7 ml/g montmorillonite.

Exhibit E

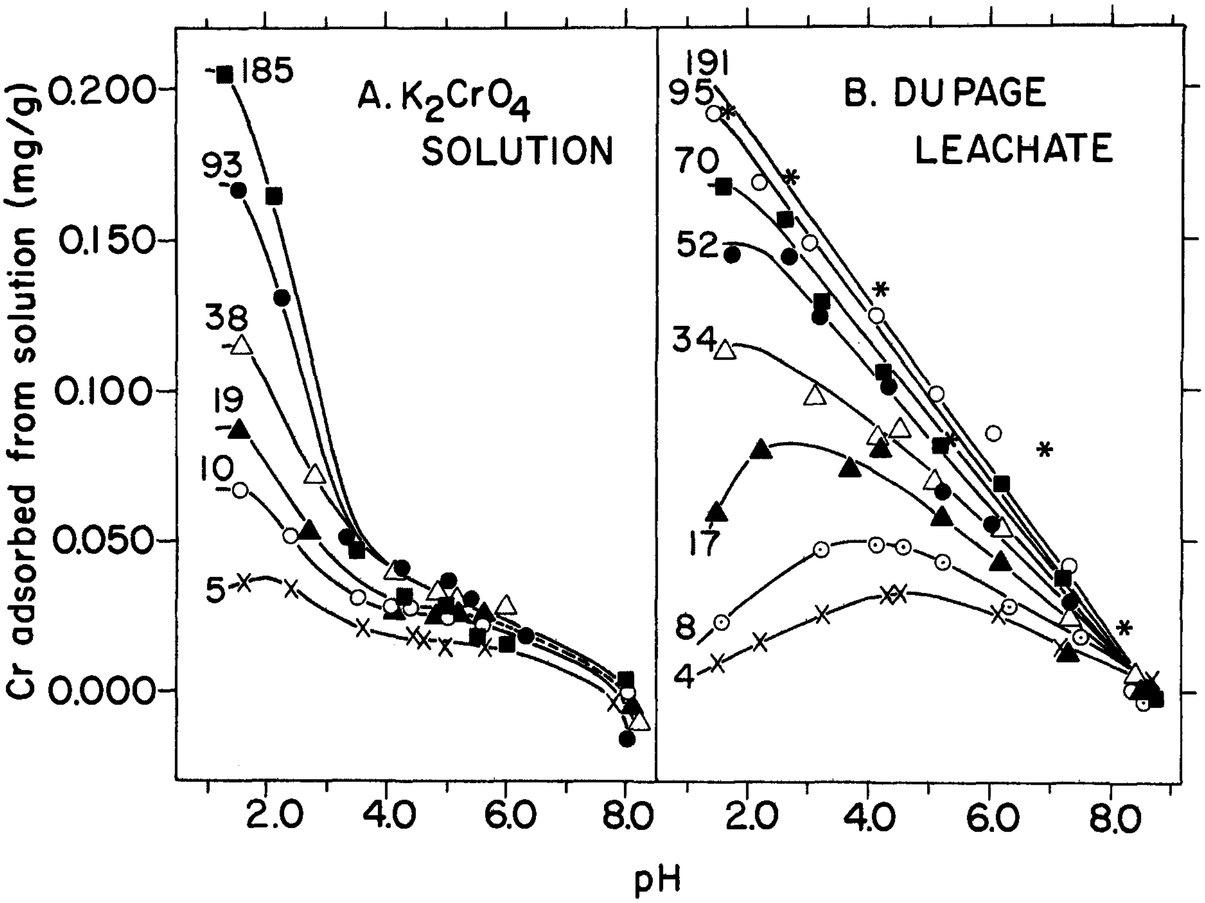

Figure 27. Chromium (VI) adsorption-pH curves for kaolinite at 25° C. Initial Cr(VI) concentrations (ppm) are indicated beside each curve and the equivalence volume for each curve is 10.0 ml/g kaolinite.

Exhibit E

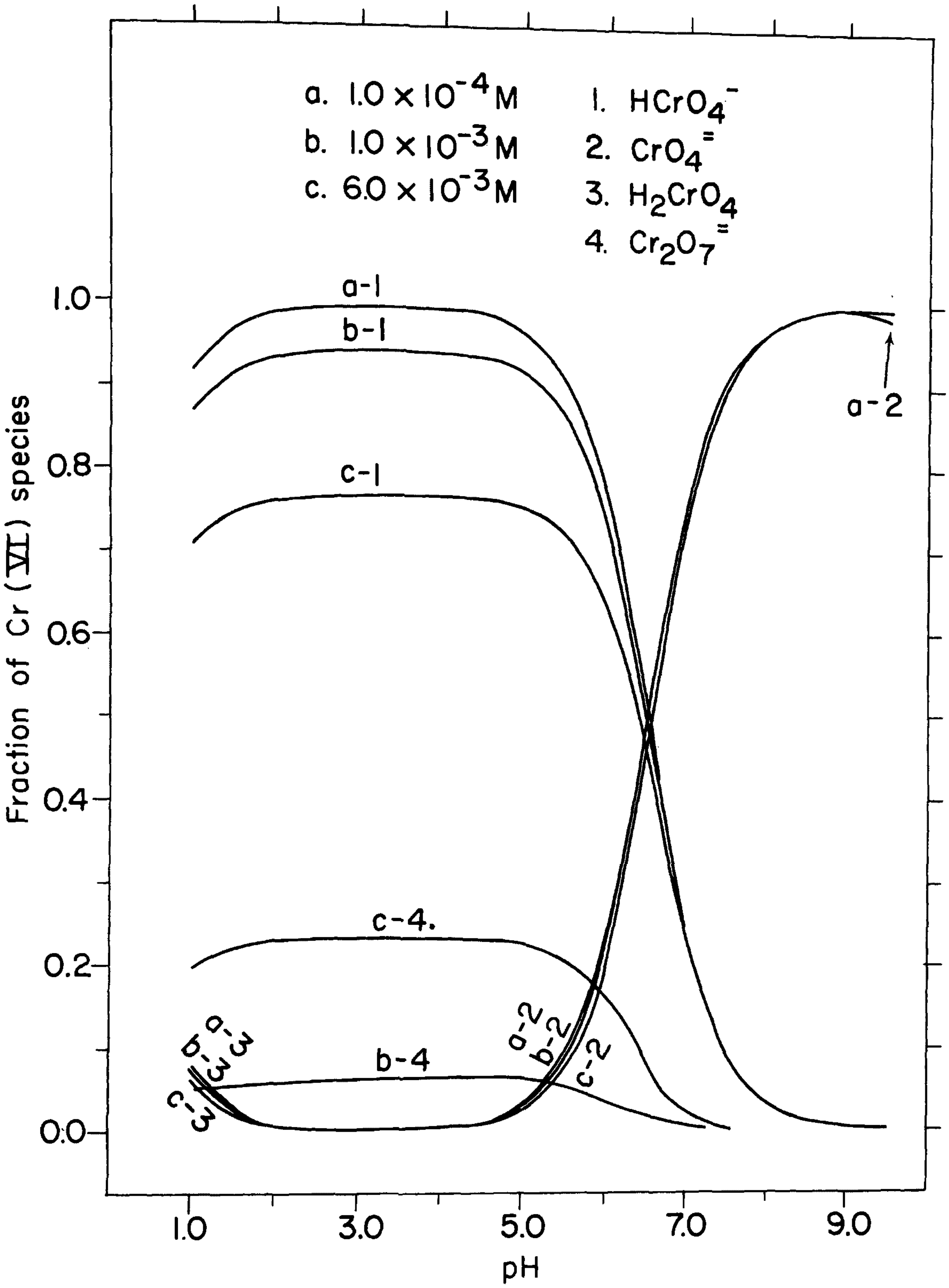

Figure 28. Distribution of Cr(VI) species for various Cr(VI) concentrations.

Exhibit E

curves in Figures 26 and 27 using Equation {16} at pH values 3.0, 4.0, 5.0, and 7.0. Sample adsorption isotherms, constructed at pH 4.0, are shown in Figure 29. For both clay minerals, more Cr(VI) was adsorbed from DuPage leachate solutions than from pure K_2CrO_4 solutions throughout the pH range 3.0 to 7.0. This result is contrary to that which was expected. Evidently, anions (e.g., Cl^- and HCO_3^-) in the leachate do not compete favorably with $HCrO_4^-$ ions, or adsorption would have decreased.

The effect of the Cl^- ion on the adsorption of Cr(VI) by clay was determined by adsorption experiments carried out with 20 ppm Cr(VI) in deionized water with and without 1000 ppm of Cl^- added as NaCl. No appreciable change in the adsorption of Cr(VI) was caused by the Cl^- ion. That more Cr(VI) was adsorbed from DuPage leachate than from pure K_2CrO_4 solutions may be the result of formation of polynuclear complexes in the leachate solutions, organic or inorganic in nature, which can be adsorbed by the clay. The high ionic strength of the leachate may also contribute to higher adsorption of Cr(VI) species by a depression of the diffuse double-layer surrounding the clay particles (van Olphen, 1963), which allows more ions to approach the clay surface and be adsorbed.

The adsorption isotherms for Cr(VI) at pH values of 3.0, 4.0, 5.0, and 7.0 were plotted according to the linear form of the Langmuir equation (Equation 16). All the Langmuir plots gave linear regression r^2 values 0.99. The Langmuir plots at pH 4.0 are shown in Figure 30. From the slopes of the Langmuir plots, adsorption maxima were calculated and are presented in Table 12. The difference in the calculated adsorption maxima of montmorillonite and kaolinite reflects the difference in the probable number of available adsorption sites, based on comparison of the structural differences and the surface areas of the two clay minerals (Table 1). The precise mechanism for anion adsorption by clay minerals is uncertain, but we assume, as have others, that anion exchange plays an important role in the adsorption process. However, the adsorption maxima presented in Table 12 represent the maximum amount of Cr(VI) ions adsorbed at some sufficiently high concentration of Cr(VI) ions in solution, whereas the adsorption isotherms in Figure 29 represent the maximum amount of Cr(VI) ions that can be adsorbed at any given concentration of Cr(VI) ions in solution.

Chromium (III) Adsorption

During preliminary experiments on Cr(III) adsorption by kaolinite, the removal curves shown in Figure 31 were obtained. The curve labeled "blank" in Figure 31, representing removal of Cr(III) from a solution containing no clay, shows that precipitation becomes a very important mechanism of Cr(III) removal near pH 5.0. The precipitate formed was blue-gray, and X-ray diffraction patterns of the precipitate showed no definite crystalline structure. Because only HNO_3 and NaOH were used to adjust the pH of the $Cr(NO_3)_3$ solution, it is reasonable to believe that the precipitate formed is a chromic hydroxide. Murray (1956) stated that chromic hydroxide is a hydrous oxide ($Cr_2O_3 \cdot nH_2O$) of indefinite composition that is blue-gray when its water content is high. It was therefore concluded that chromic hydroxide was the precipitate of our experiments.

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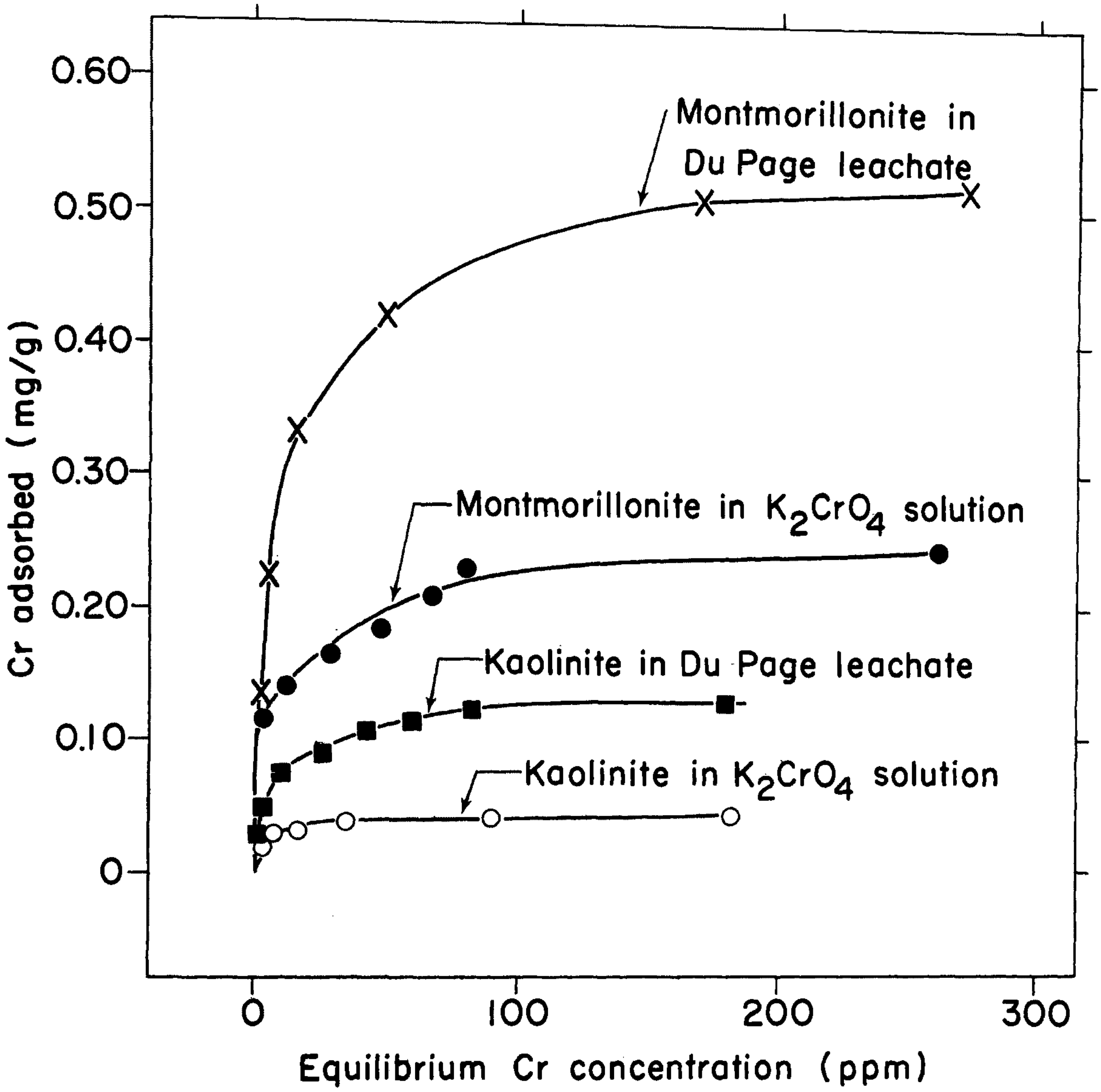

Figure 29. Adsorption isotherms for Cr(VI) at pH 4.0 and 25° C.

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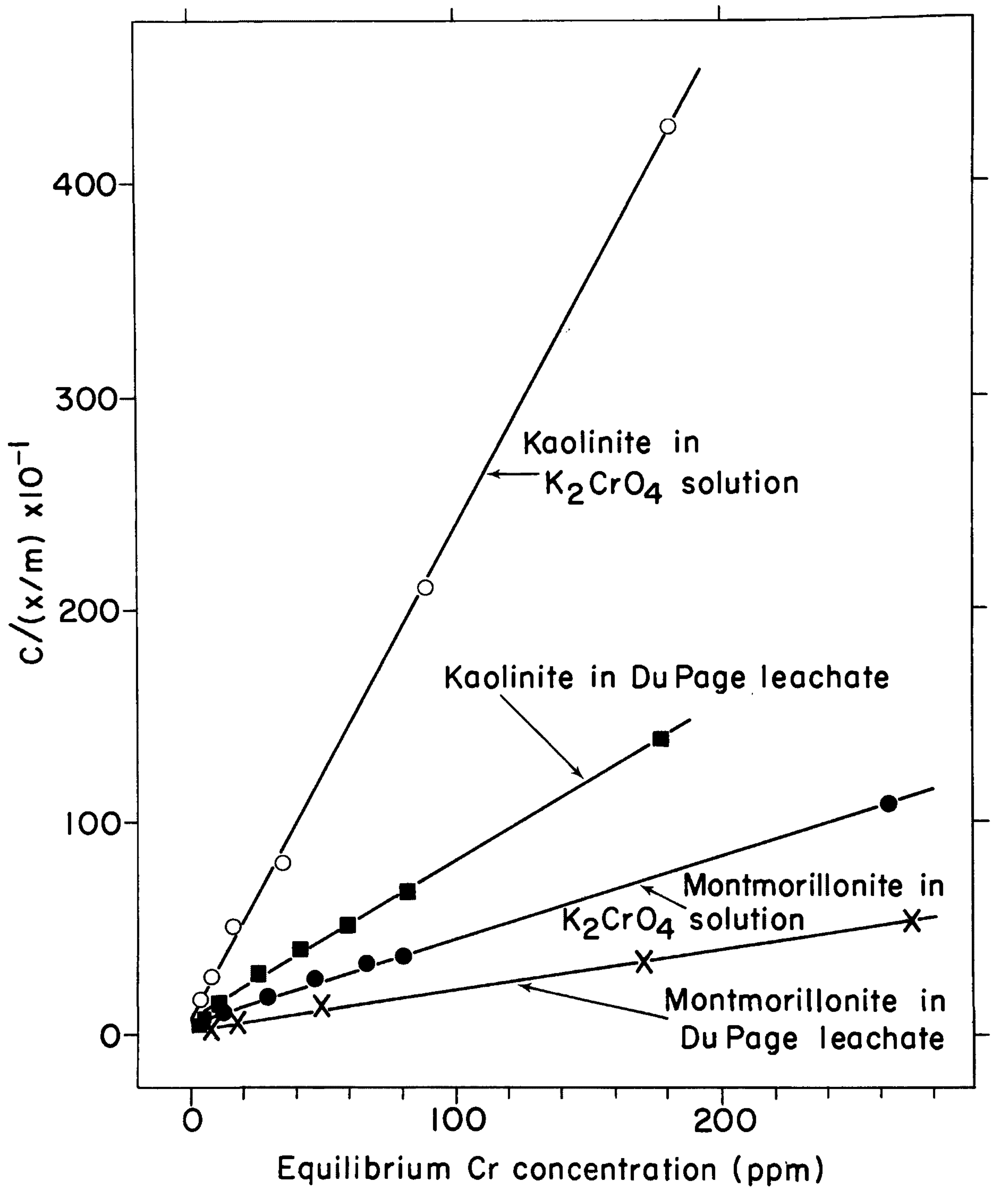

Figure 30. Langmuir plots of Cr(VI) adsorption data at pH 4.0 and 25° C.

Exhibit E

TABLE 12. ADSORPTION MAXIMA FOR Cr(VI) BY MONTMORILLONITE AND KAOLINITE AT 25° C FOR VARIOUS pH VALUES

pH	mg/g Pure Solution	mg/g DuPage Leachate Solution
	Montmorillonite	
3.0	0.400	0.667
4.0	0.256	0.526
5.0	0.147	0.417
7.0	0.052	0.169
	Kaolinite	
3.0	0.093	0.189
4.0	0.044	0.130
5.0	0.032	0.115
7.0	0.015	0.051

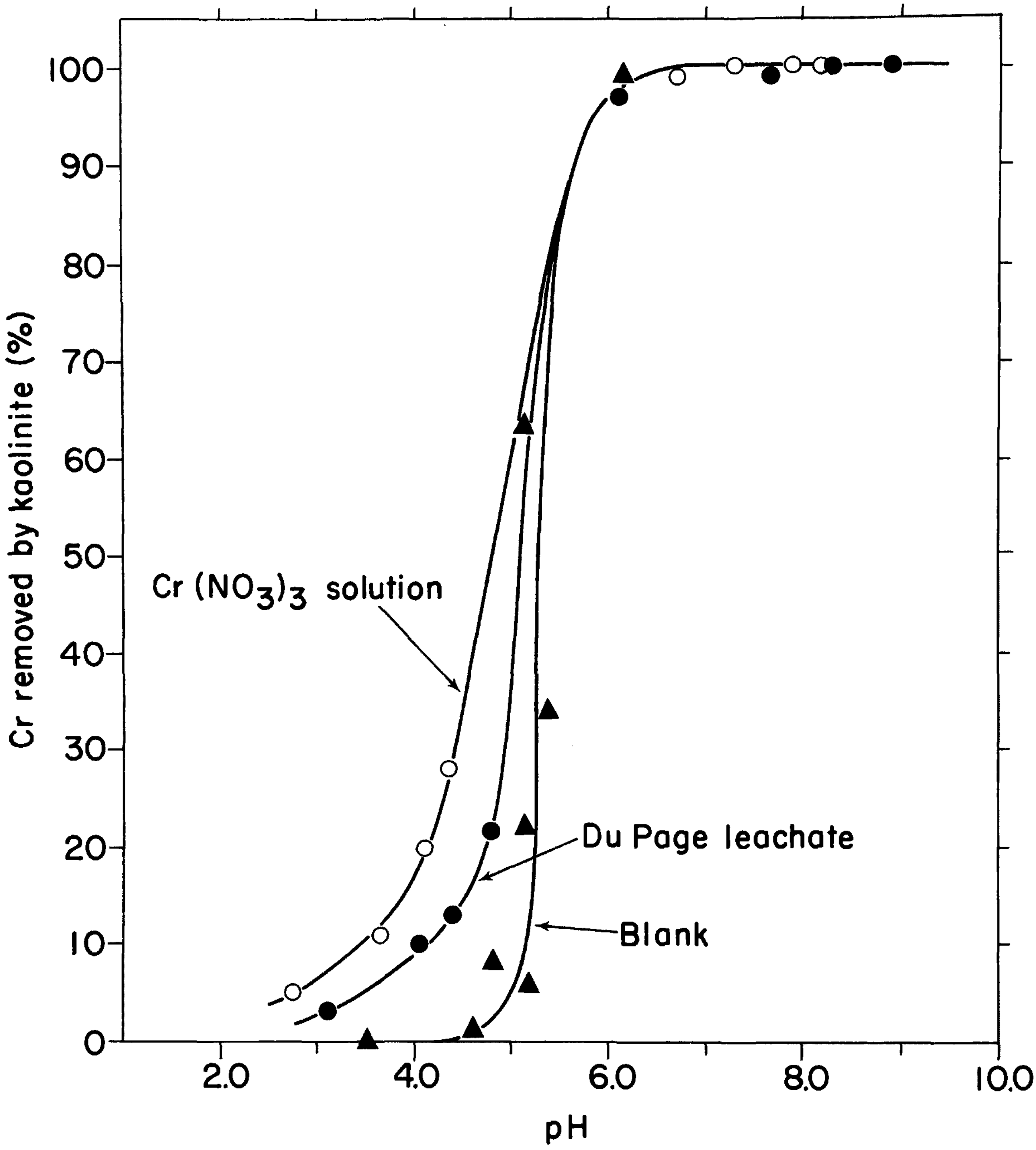

Figure 31. Removal of Cr(III) from solution by kaolinite. The curve labeled "Blank" represents $Cr(NO_3)_3$ solution without kaolinite.

Exhibit E

Families of Cr(III) adsorption-pH curves for the pH range 1.5 to 4.5 are presented in Figure 32. Cation exchange is generally accepted as the principal mechanism for cation adsorption by soils and clay minerals. Chromium (III) is known (Rollinson, 1956) to be extensively hydrolyzed in acid solutions to species such as $Cr(OH)^{2+}$, $Cr(OH)_2^{1+}$ or $Cr_2(OH)_4^{2+}$ or $Cr_2(OH_{12})^{6+}$, and $Cr_6(OH)_{15}^{3+}$. Therefore, the increasing adsorption of Cr(III) as pH increases can, in part, be attributed to exchange-adsorption of hydrolyzed Cr(III) species other than Cr^{3+} ions.

Adsorption isotherms were constructed from the adsorption-pH curves (Fig. 32) by using Equation {15} at pH values 2.5, 3.0, and 4.0. The isotherms constructed for pH 4.0 are shown in Figure 33. As was expected, the adsorption of Cr(III) by the clay minerals is lower in DuPage leachate than in pure $Cr(NO_3)_3$ solutions. However, significantly less reduction in adsorption of Cr(III) from DuPage leachate (3% to 14%) took place than observed in tests of Pb, Cu, Zn, and Cd adsorption from DuPage leachate by the same clay minerals. The Cr(III) species existing in solution are so strongly adsorbed that the cations present in the DuPage leachate do not effectively compete with the Cr(III) species for exchange-adsorption sites.

The adsorption isotherm data for Cr(III) at pH values 2.5, 3.0, and 4.0 were plotted according to the Langmuir equation (Equation {16}) and the Langmuir plots for the pH 4.0 adsorption isotherms are shown in Figure 34. Adsorption maxima calculated from the slopes of the Langmuir plots in Figure 34 are presented in Table 13. The amounts of the various hydrolyzed Cr(III) species that could be adsorbed via a cation exchange mechanism by the montmorillonite and kaolinite clay minerals that had CEC values of 79.5 meq/100 g and 15.1 meq/100 g, respectively, are presented in Table 13, because, if cation exchange is the principal adsorption mechanism, the ratio of the adsorption maxima should be about equal to the ratio of the CEC values for the two clay minerals.

At pH 2.5 the adsorption maximum ratio is close to the CEC ratio (Table 13), but the adsorption maxima themselves are higher than those based on exchange adsorption of Cr^{3+} ions. This implies that some hydrolyzed Cr(III) species are being adsorbed even at pH 2.5. The question arises, however, as to the validity of using CEC values obtained from NH_4^+ ion exchange at pH 7.0 to calculate the expected adsorption maxima at pH 2.5. However, as there is a general relative correlation between the adsorption maxima and CEC values, it is reasonable to use adsorption maxima calculated from CEC values for comparison purposes. At pH 4.0, the ratio of the adsorption maxima increases to about 13, and the amount of Cr(III) adsorbed by montmorillonite is even larger than would be expected from the exchange adsorption of the $Cr_6(OH)_{15}^{3+}$ ion.

The high adsorption maximum ratio at pH 4.0 is the result of the large adsorption maximum obtained for montmorillonite, which appears to be indirectly caused by our experimental procedure. The rates of some of the Cr(III) hydrolysis reactions are very slow, and, in one reported case (Laswick and Plane, 1959), about 107 days were required for Cr(III) solutions, even at elevated temperatures, to reach equilibrium. In our Cr(III) experiments, the clay mineral suspensions were adjusted to a particular pH value,

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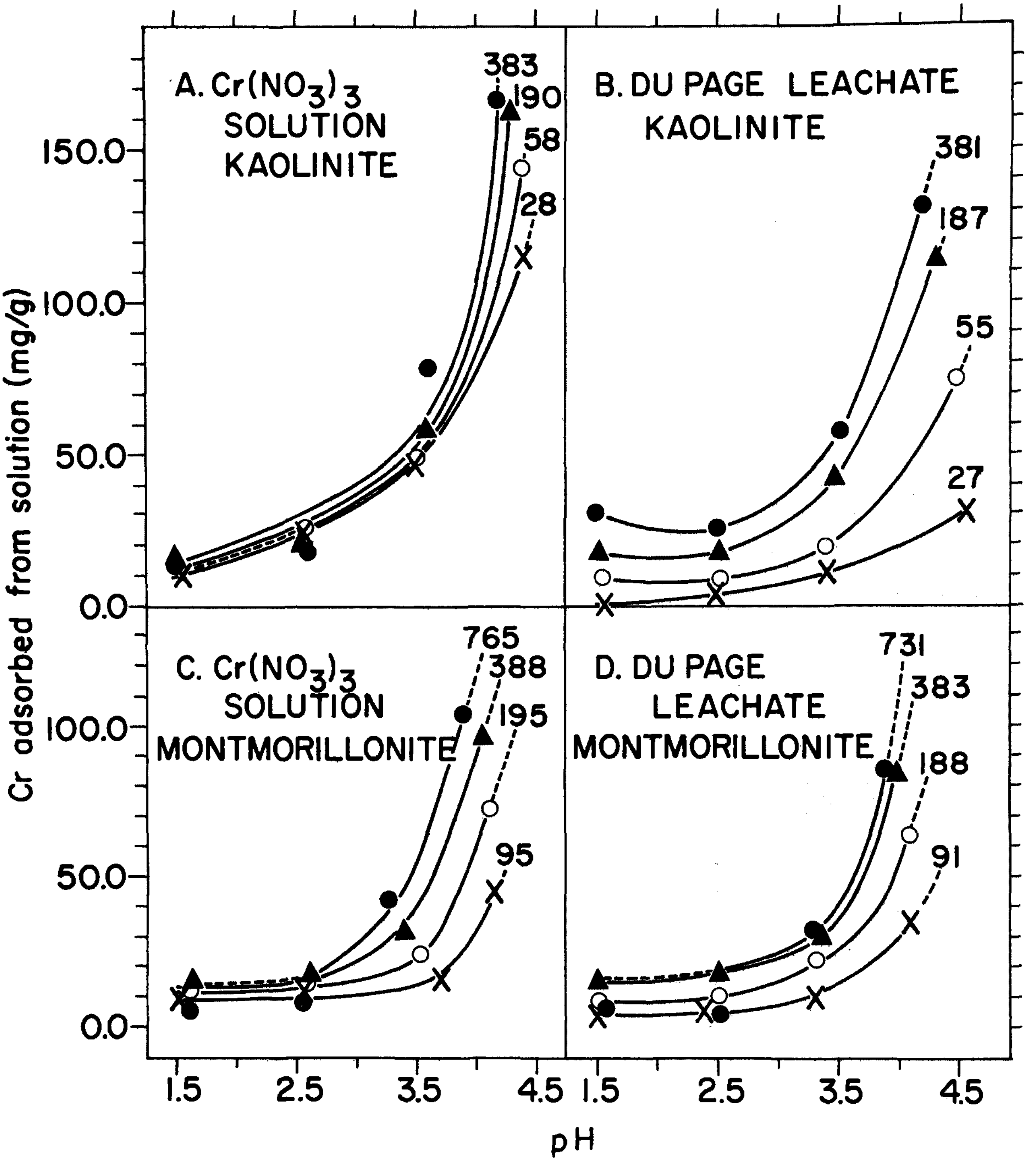

Figure 32. Chromium (III) adsorption-pH curves at 25° C. Initial Cr(III) concentrations (ppm) are indicated beside each removal curve, and the equivalence volume for each curve is 500.0 ml/g kaolinite.

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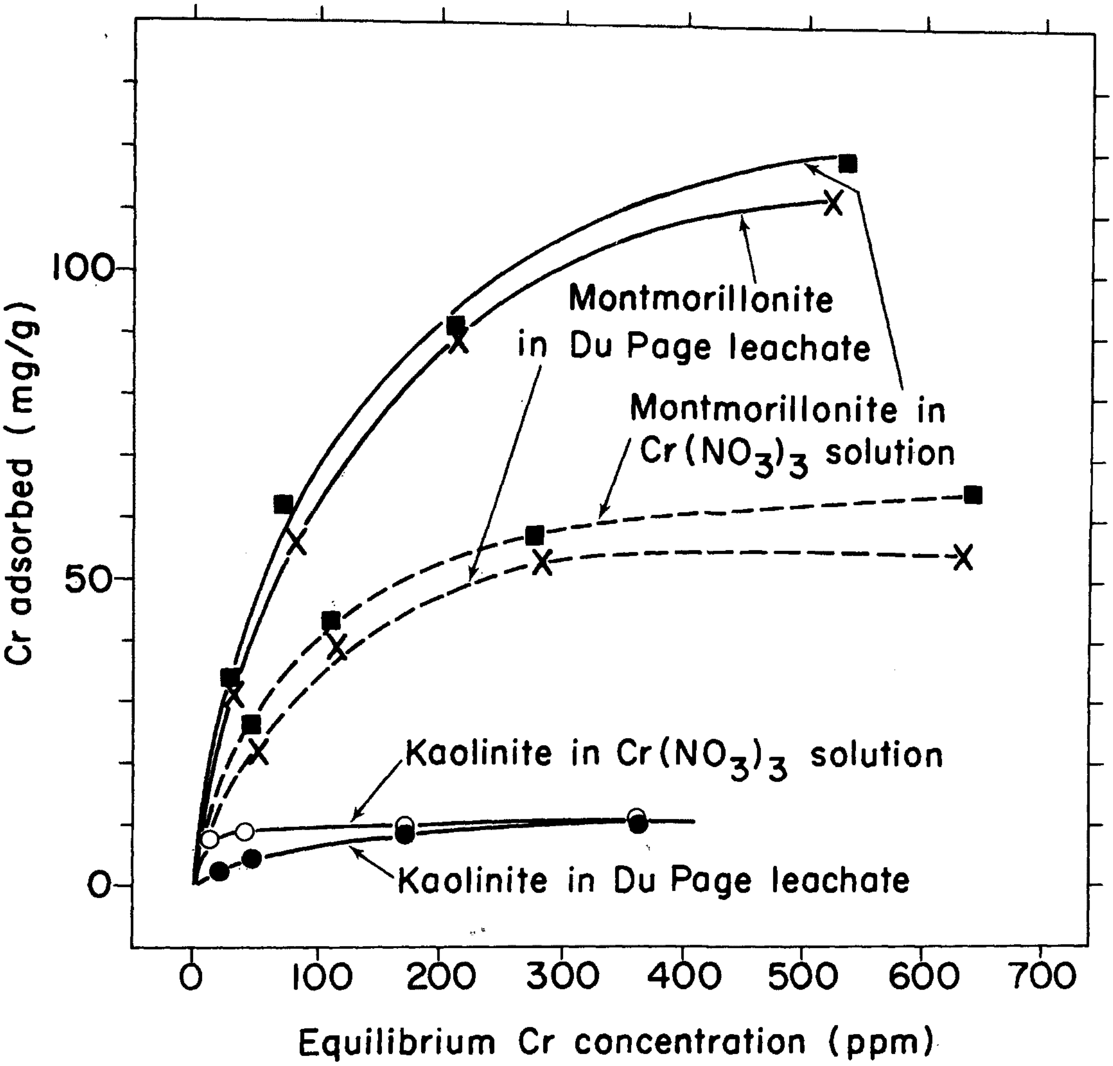

Figure 33. Chromium (III) adsorption isotherms at pH 4.0 and 25° C. The plots shown in dotted lines were obtained from the "corrected" adsorption-pH curves.

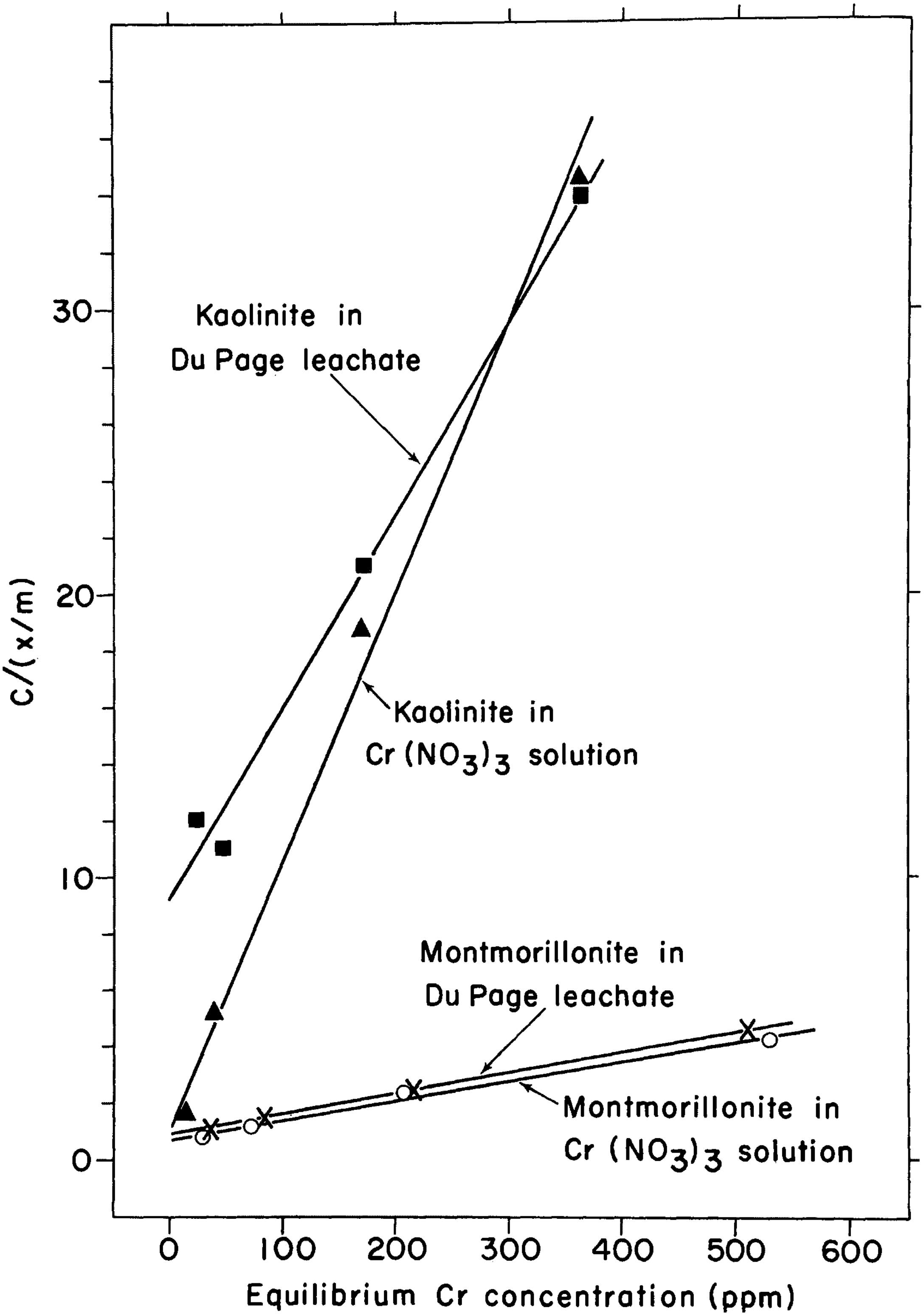

Figure 34. Langmuir plots of Cr(III) adsorption data at pH 4.0 and 25° C.

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TABLE 13. ADSORPTION MAXIMA FOR Cr(III) BY MONTMORILLONITE AND KAOLINITE AT 25° C FOR VARIOUS pH VALUES

(mg/g)									
pH 2.5		pH 3.0		pH 4.0		Values Based on CEC for Different Species			
P[a]	L[b]	P	L	P	L	Cr^{+3}	$Cr(OH)^{2+}$	$Cr(OH)_2^+$	$Cr_6(OH)_{15}^{3+}$
Montmorillonite									
17.9	--	33.7	32.8	139.6	136.1	13.8	20.7	41.4	82.7
Kaolinite									
3.3	--	5.0	5.0	10.7	14.7	2.6	3.9	7.8	15.6
Ratio of Adsorption Maxima									
5.4	--	6.5	6.6	13.0	9.3	5.3	5.3	5.3	5.3

[a] Pure solutions, [b] DuPage leachate solutions

such as 4.5. After a few hours, hydrolysis caused the pH of the suspensions to drop. The pH of the suspensions were readjusted to 4.5, but the pH again dropped because of hydrolysis. The pH of the suspensions were all readjusted to the desired pH value several times during a period of two weeks. They were then shaken for 2 days before a final pH value was measured, and the suspensions were centrifuged. What appears to occur in the pH range 3.5 to 4.5 is as follows. Adsorption plus possible precipitation of Cr(III) takes place at the higher initial pH values to which the suspensions had been adjusted. But, when the pH of the suspensions drops due to hydrolysis, desorption of Cr(III) species from the clay mineral or dissolution of any precipitate formed apparently does not occur at rates fast enough to achieve true equilibrium in the clay suspension. The pH values of the montmorillonite suspensions showed larger decreases in pH than the kaolinite suspensions; this apparently produces much larger differences between the calculated and true equilibrium adsorption maxima for montmorillonite than for kaolinite.

The adsorption-pH curves shown in Figure 32 were replotted as the amount of Cr(III) adsorbed versus the highest pH values to which the clay suspensions were adjusted. The adsorption isotherms were calculated from the "corrected" adsorption-pH curves at pH 4.0 and are shown as the dotted isotherms for montmorillonite in Figure 33. The "corrected" adsorption isotherms for kaolinite are almost superimposable on the isotherms shown in Figure 33, and, therefore, were omitted. Adsorption maxima from pure $Cr(NO_3)_3$ solutions, calculated by Langmuir plots of the "corrected" isotherms at pH 4.0, are 72.2 mg/g for kaolinite. Thus, the "corrected" adsorption maxima agree with an exchange-adsorption mechanism involving hydrolyzed Cr(III) species. We have learned, as Laswick and Plane (1959) pointed out, that the changes that Cr(III) species undergo are generally quite slow, which makes the interpretation of the experiments difficult.

CONCLUSIONS

The results of this study indicated that Cr(III) yielded the strongest attenuation of all the heavy metals studied. This suggests that landfill disposal of Cr(III) wastes would exhibit low mobility and probably would initiate fewer pollution problems than would the other heavy metals. Above pH 6, Cr(III) should be immobile because of precipitation. Below pH 4, Cr(III) species were strongly adsorbed by both kaolinite and montmorillonite and would have a relatively low mobility through soils or clay minerals used as landfill liners. Between pH 4 and 6, the combination of adsorption and precipitation should render Cr(III) quite immobile.

In the pH range 1.5 to 4.0, 30 to 300 times more Cr(III) than Cr(VI) was adsorbed by the clay minerals; and at higher pH values the ratio (Cr(III) removed)/(Cr(IV) removed) became even larger because of increased Cr(III) removal and decreasing adsorption of Cr(VI). The adsorption of Cr(VI) was low relative to Cr(III), even at very low pH values where Cr(VI) adsorption was strongest. Cr(VI) adsorption was the weakest of the heavy metals studied and was markedly reduced as the pH was raised into the alkaline range. Thus, it would become very mobile at high pH. Since Cr(VI) is the most toxic and mobile form of Cr, landfill disposal of Cr(VI) wastes can potentially cause serious pollution problems even if the landfill has a thick clay liner. The results of this study suggest that a conversion of Cr(VI) wastes to Cr(III) by a process such as that devised by Shiga (1975) would greatly reduce the hazard to water resources from Cr(VI) wastes disposed of in landfills.

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SECTION 10

EFFECT OF pH ON ADSORPTION OF As AND Se FROM LANDFILL-LEACHATE BY CLAY MINERALS[1]

ABSTRACT

The effect of pH and ionic competition on arsenate (As(V)), arsenite (As(III)), and selenite (Se(IV)) adsorption by kaolinite and montmorillonite clay minerals from municipal landfill-leachate solutions were determined.

The results showed that pH had a strong influence on the amounts adsorbed of all three of the elemental forms studied. Montmorillonite clay was found to adsorb about twice as much As or Se as kaolinite. Leachate was found to have little effect on the adsorption of As(V) or Se(IV), while As(III) adsorption was reduced 30 to 50%. It was concluded that the principal adsorption mechanism was anion exchange of the monovalent species of each elemental form.

The results of the study suggest that land disposal of As and Se wastes under alkaline conditions represents a potentially high pollution hazard.

INTRODUCTION

As and Se are quite toxic (U.S.-EPA, 1972) and, therefore, they have a high potential to produce pollution problems. The U. S. Environmental Protection Agency (EPA) cites several examples of instances where land disposal of arsenic wastes have resulted in the poisoning of drinking water wells (U.S.-EPA, 1973) and selenium has been reported to have polluted ground water as far as two miles from a dump on Long Island (Garland and Mosher, 1975). As and Se waste streams may be liquids, suspensions, or sludges. Sample waste streams from copper, lead, and zinc smelting, from duplicating and photo equipment manufacturing, and from pharmaceutical industries have been measured and reported to contain from 1,000 to 30,000 ppm As and from 3,000 to 50,000 ppm Se (Lehman, 1973). These waste streams may be disposed of on land in lagoons, in landfills, or by spreading. Land spreading of municipal wastewater effluents (U.S.-EPA, 1975) and sewage sludges which may contain low concentrations of As and Se is now being considered as a viable alternative to treatment.

The purpose of this study was to provide some basic data regarding the effect of pH on the removal of As and Se from landfill-leachate by kaolinite and montmorillonite, which are common clay minerals found in soils. The re-

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[1] Authors: R. R. Frost and R. A. Griffin

Exhibit E

sults of the present study give insights into whether or not As and Se waste streams can be safely disposed of in properly designed landfills for municipal solid waste. The results of the study also provide basic information on the mobilities of As and Se through soils. This can be of aid in the design of land disposal systems for As and Se waste streams in general.

EXPERIMENTAL

Appropriate stock solutions of As(V) and As(III) were prepared by dissolving reagent grade Na_2HAsO_4 or $NaAsO_2$ in deionized water. Se(IV) stock solutions were prepared by dissolving pure selenium metal in a minimum amount of 1:1 HNO_3. Some heating of the solution was necessary to speed up the dissolution. All stock solutions were adjusted to about pH 5 before use.

Fifty ml aliquots of leachate were pipeted into 125-ml Erlenmeyer flasks containing from 1.00 to 5.00 g of either kaolinite or montmorillonite. The weight of clay used was chosen so that the amount of arsenate, arsenite, or selenite removed from the leachate solutions could be determined with some precision from the difference between the initial and final solution concentrations. Several replicates of each clay suspension were prepared. The pH values of the replicate clay suspensions were adjusted with HNO_3 or NaOH to different values over the pH range 1 to 9. The clay suspensions were shaken overnight and then 2.0 ml of an appropriate pH 5 stock solution of either As or Se was pipeted into the flasks. Of the several experimental procedures possible, the procedure used gave the most satisfactory results. The As or Se clay suspensions were then shaken in a constant temperature bath at 25 ± 0.5° C for at least 24 hours to insure complete equilibration. The equilibrium pH values of the clay suspensions were measured, the clay suspensions centrifuged, and the supernatant solutions analyzed for their As or Se concentration by atomic adsorption spectroscopy. A $NO-C_2H_2$ flame was used for As analyses, and air-C_2H_2 flame was used for Se analyses. Blanks (i.e., no clay) were prepared along with the clay suspensions and were also analyzed to determine the initial As or Se concentration. The amount of As or Se removed from solution by a given clay at a particular pH was determined as:

$$\text{(initial - equilibrium conc.)} \times \frac{\text{total sol'n vol. after pH adjustments}}{\text{sample weight.}} \qquad \{17\}$$

The amount of As or Se removed from solution was then plotted as a function of pH. From the initial concentration of As or Se in solution, the weight of clay used, the final solution volume after pH adjustments, and the removal versus pH curves themselves, "adsorption" or "removal" isotherms can be constructed at different pH values by use of the following equation:

$$\text{Equilibrium C (ppm)} = \text{Initial C (ppm)} - \frac{\text{Am't. removed } (\mu g/g) \times \text{Wt. Clay (g).}}{\text{Final solution volume (ml)}} \qquad \{18\}$$

RESULTS AND DISCUSSION

Arsenate (As(V)) and Arsenite (As(III)) Adsorption

Exhibit E

Curves for the removal of As(V) from leachate by kaolinite and montmorillonite versus pH are shown in Figure 35. It is interesting to note that the amount of As(V) removed from solution goes through a maximum at about pH 5. The distribution of arsenate species in solution as a function of pH is shown in Figure 36a. Comparison of Figure 35 with Figure 36a shows that the As(V) removal curves follow the monovalent $H_2AsO_4^-$ species curve reasonably well. Thus, it was concluded that the $H_2AsO_4^-$ ion is the principal As(V) ion being adsorbed by the clay minerals. The non-adsorption or depressed adsorption of the $HAsO_4^=$ ion is apparently due to the occurrence of negative charges on adjacent oxygen atoms in the tetrahedral $HAsO_4^=$ ion which results in repulsion of the ion from the clay surface. Some As(V) precipitation was observed to occur above approximately pH 9 and can be seen on the removal curves in Figure 35 as the curves turn upward around pH 9.

Curves for the removal of As(III) from leachate by kaolinite and montmorillonite versus pH are shown in Figure 37. In general, an increase in adsorption of As(III) is observed as pH increases in the range 3 to 9. The montmorillonite removal curves in Figure 37 show an interesting peak about pH 7. There is some question as to what As(III) species are present in the leachate solutions and which As(III) species is actually being adsorbed. From a study of As(III) adsorption by an anion exchange resin (Everest and Popiel, 1957), the $As_3O_5^-$ on $As_3(OH)_{10}^-$ species was proposed as the species being adsorbed in the pH range 5 to 6, but the fraction of the total As(III) in solution existing as the $As_3O_5^-$ ($As_3(OH)_{10}^-$) species is small and the amount of exchange adsorption was low. Other As(III) species apparently existing in solution are $As_2O_4^=$ ($As_2(OH)_8^=$), $As(OH)_3$, $As(OH)_4^-$, and $AsO_2OH^=$ -- with the latter two species becoming important above pH 9. Whatever As(III) species are present in solution, the fraction of the total As(III) in solution present as monovalent As(III) species will increase as pH increases. Thus, the amount of As(III) adsorption should increase as pH increases as observed in Figure 37. There is no apparent explanation for the observed peaks about pH 7 on the montmorillonite removal curves in Figure 37. Although no peaks are observed on the kaolinite removal curves in Figure 37, they might have appeared if more data points were obtained in the pH range 6.5 to 7.

Comparison of removal curves (not shown) for As(V) and As(III) from deionized water solutions obtained at a single concentration for each clay mineral with the corresponding leachate removal curves showed that the anion competition present in the leachate surpresses the adsorption by the clay minerals of As(V) slightly and of As(III) by some 30 to 50 percent.

Isotherms calculated from the removal curves in Figures 35 and 37 at pH 5.0 are shown in Figure 38. The higher adsorption of As(V) and As(III) by montmorillonite compared to kaolinite simply reflect the structural and surface area differences between the two clay minerals. Anion exchange sites are thought to exist primarily at the broken edges of clay minerals (Grim, 1968).

Montmorillonite clay was found to adsorb approximately twice as much As as kaolinite. Examination of the surface area data, as measured by N_2 gas adsorption given in Table 1, suggests that the montmorillonite has roughly twice as much edge surface area as the kaolinite. The tetrahedral $H_2AsO_4^-$ ion can align itself with the silica tetrahedral of the clay lattice and can form

Exhibit E

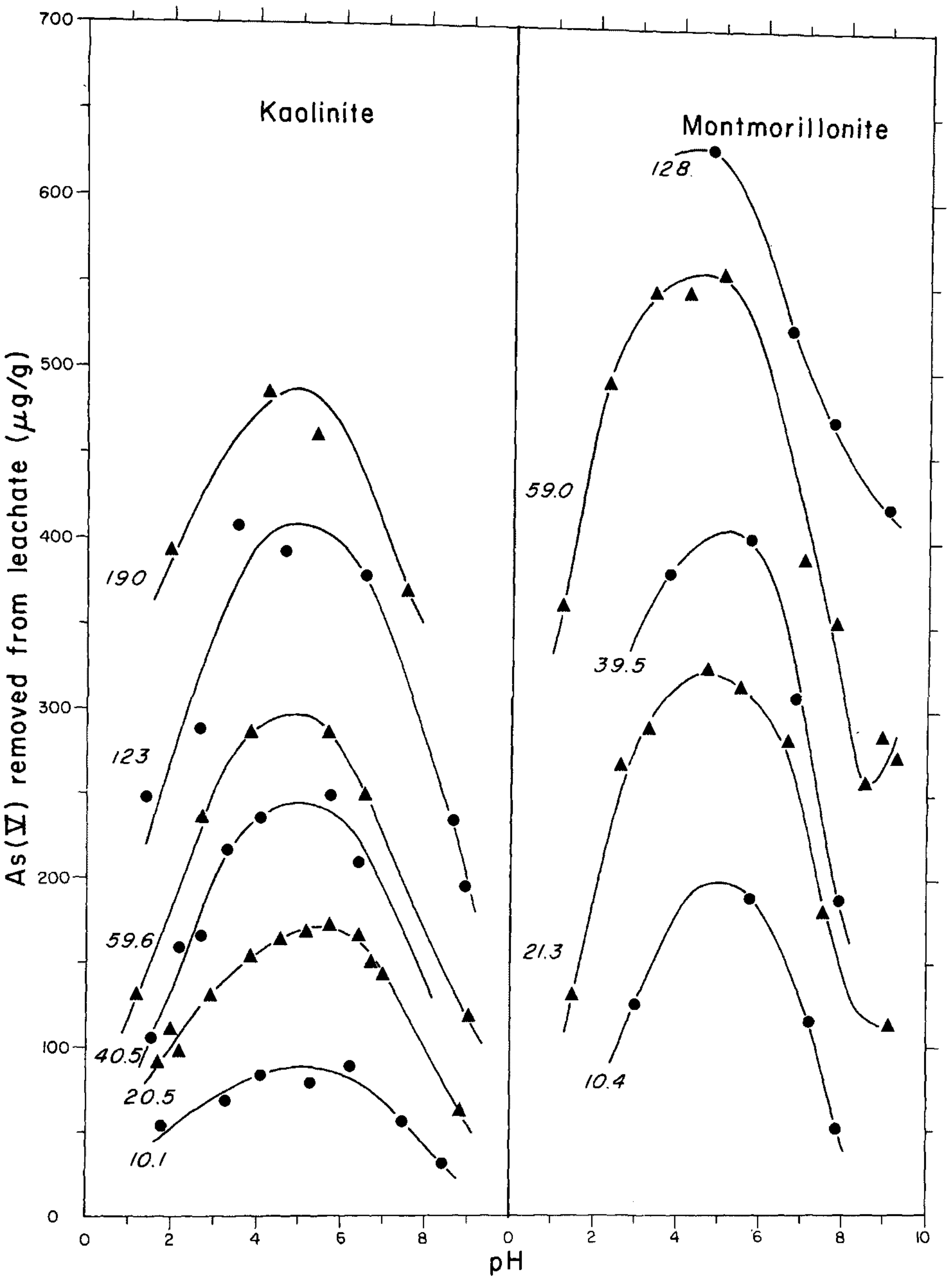

Figure 35. The amount of As(V) removed from DuPage leachate solutions by kaolinite and montmorillonite at 25° C plotted as a function of pH. Labels are the initial solution concentration of As(V) in ppm. Each datum point was obtained by using either 4 g of kaolinite of 1 g of montmorillonite in a total solution volume of 52.2 ml.

Exhibit E

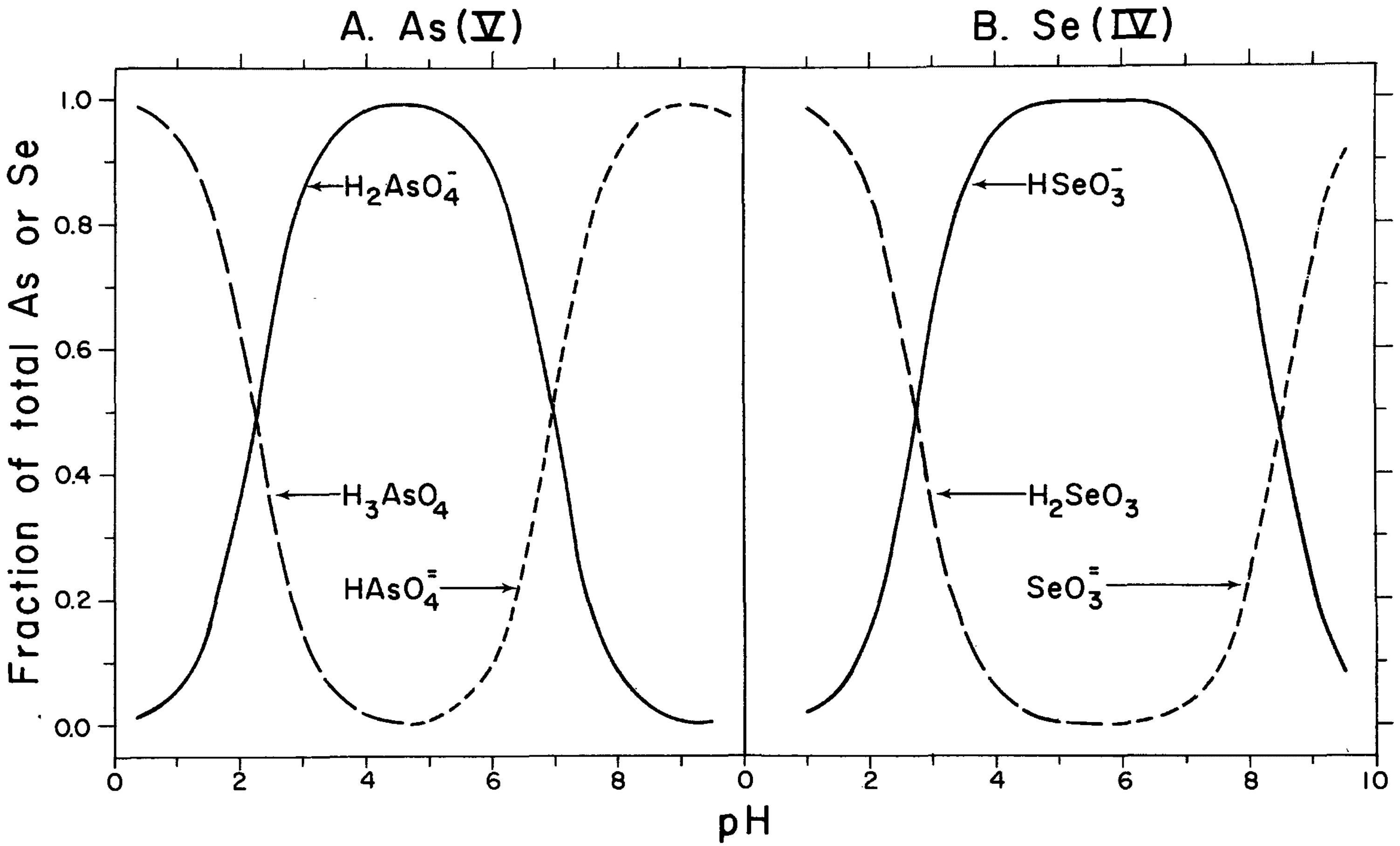

Figure 36. Species distribution diagram for As(V) and Se(IV).

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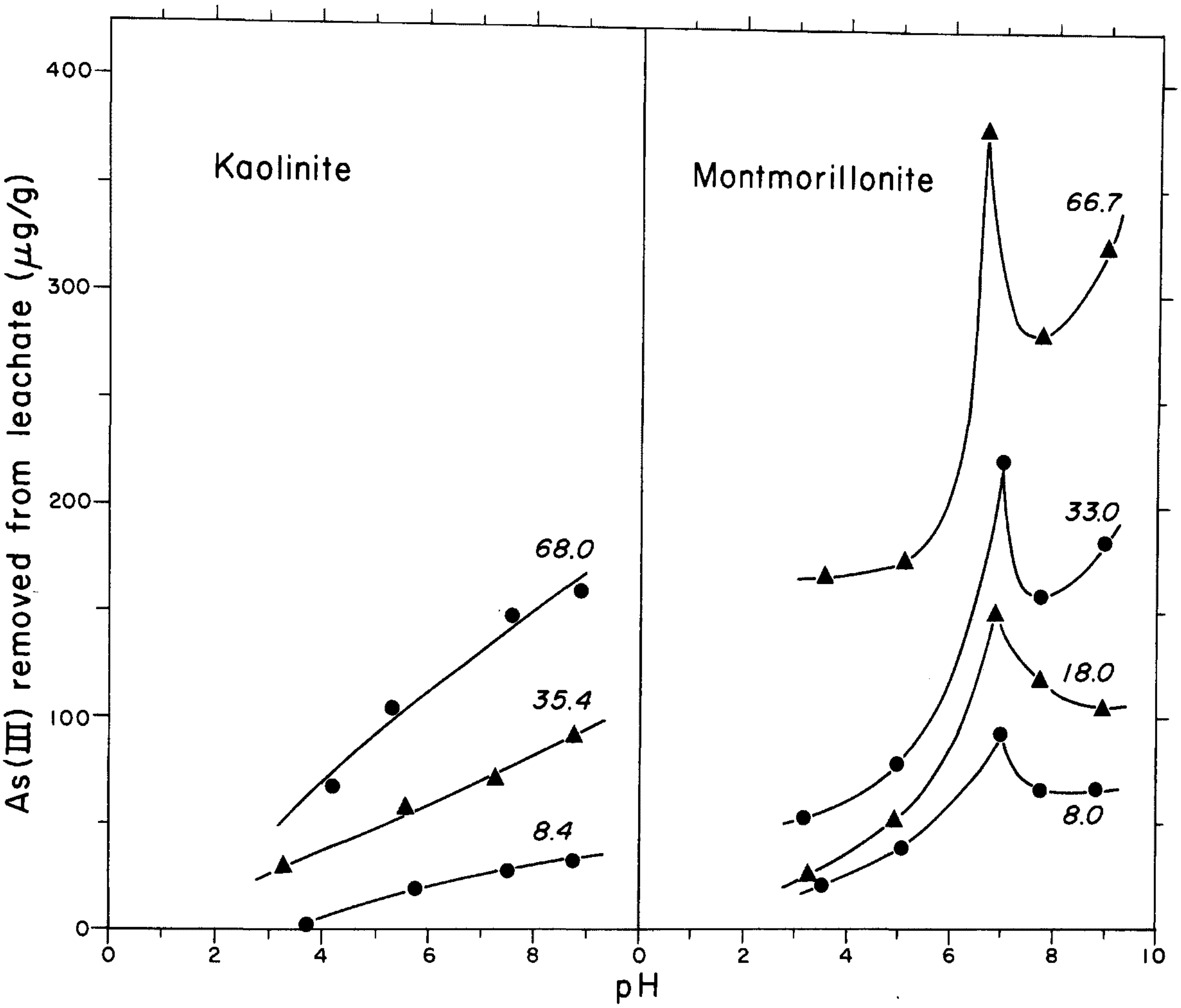

Figure 37. The amount of As(III) removed from DuPage leachate solutions by kaolinite and montmorillonite at 25° C plotted as a function of pH. Labels are the initial solution concentration of As(III) in ppm. Each datum point was obtained by using 4 g of clay in a total solution volume of 52.5 ml.

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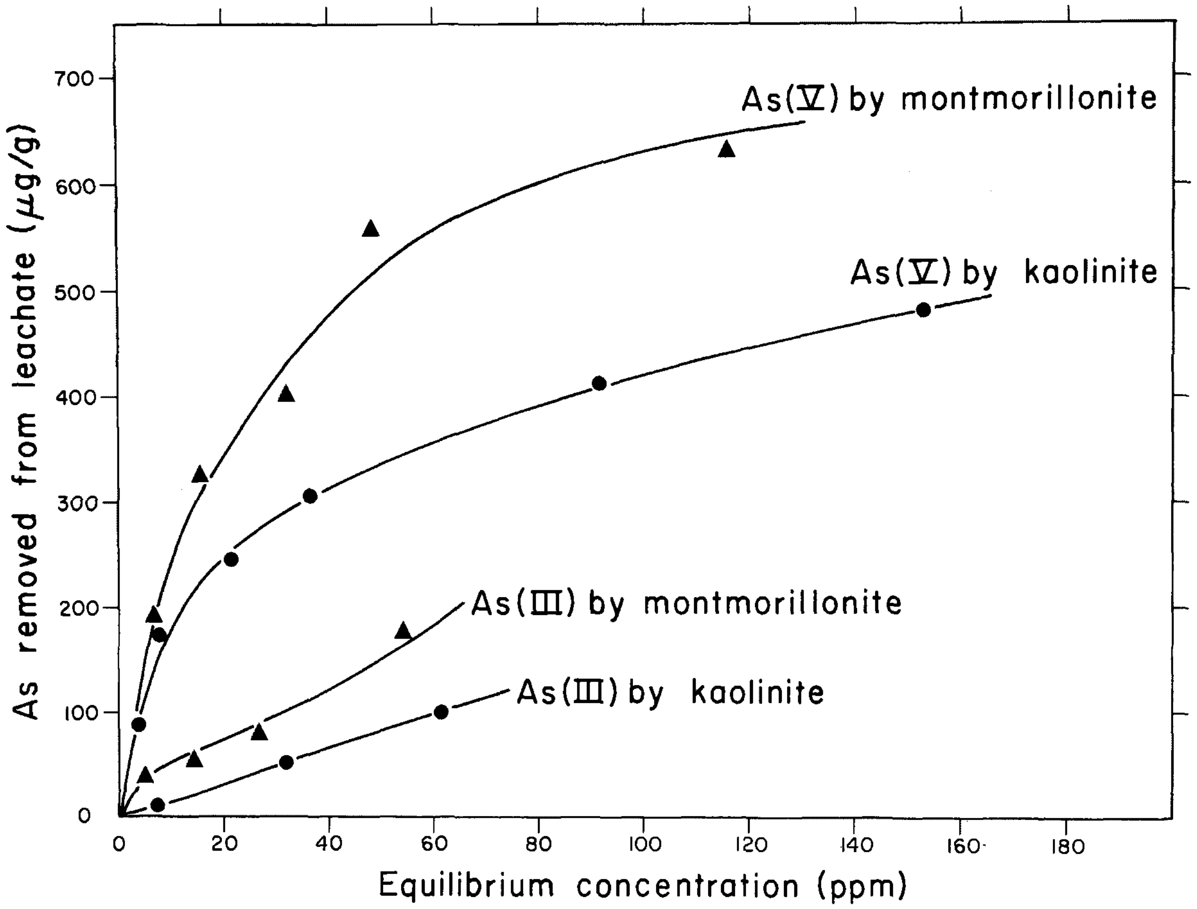

Figure 38. The amount of As(V) or As(III) removed from DuPage leachate solutions at pH 5.0 and 25° C per gram of clay plotted as a function of the equilibrium arsenic concentration.

Exhibit E

an extension of the crystal lattice which has a relatively high bond strength. The arsenate ion can be compared to the large $As_3(OH)_{10}^-$ ion which is not tetrahedral and thus is unable to align itself as effectively on the clay edges. It was therefore concluded that the principal adsorption mechanism was anion exchange of the monovalent species of each elemental form.

Selenite (Se(IV)) Adsorption

Curves for the removal of Se(IV) from leachate by kaolinite and montmorillonite versus pH are shown in Figure 39. The removal of Se(IV) goes through a maximum in the pH range 2 to 3 and then decreases as the pH increases. The distribution of Se(IV) species in solution as a function of pH is shown in the Figure 36b. Although it is not as apparent as for As(V), the monovalent $HSeO_3^-$ ion appears to be the species predominantly adsorbed by the clay minerals. It is evident from the data in Figure 39 that the adsorption of Se from solution is rapidly converging on zero removal at approximately pH 10, which is the value at which the $HSeO_3^-$ species disappears from solution.

This is evidenced by examining the species distribution diagram presented in Figure 36b. The $HSeO_3^-$ ion has a trigonal-pyramidal configuration which may account for its reduced adsorption; by contrast, the $H_2AsO_4^-$ ion has a tetrahedral configuration. Thus, the configuration of the $HSeO_3^-$ ion must be an inhibiting factor in its adsorption by the clay minerals. On the other hand, pH must play a significant role in modifying the clay mineral surface structure so that increasing adsorption occurs with decreasing pH until the point where a significant fraction of the total Se(IV) in solution is present as the H_2SeO_3 specie. At this point, adsorption starts to decline sharply as the pH is lowered below a value of 2.

Comparison of removal curves (not shown) for Se(IV) from deionized water solutions obtained at a single concentration for each clay mineral with the corresponding leachate removal curves showed that the leachate supresses the adsorption of Se(IV) by the clay minerals slightly. This is presumed to be due to competition for anion exchange sites by the high concentrations of anions present in leachate (Table 2) with the $HSeO_3^-$.

Isotherms calculated from the removal curves in Figure 39 at pH values 3.0, 5.0, and 7.0 are shown in Figure 40. The higher adsorption of Se(IV) by montmorillonite compared to kaolinite simply reflects the structural and surface area differences between the two clay minerals as previously discussed.

CONCLUSIONS

The results of this study indicate that pH has a pronounced effect on the amounts of As(V), As(III), and Se(IV) adsorbed from leachate by clay minerals. It was concluded that the principal adsorption mechanism was anion exchange and, from species distribution diagrams, that the adsorption was due principally to the monovalent species of each element studied, thus leading to the strong pH dependency of the adsorption process.

The results of the study suggest that optimum As removal by soil materials from waste streams would be achieved by conversion of any As(III) to

Exhibit E

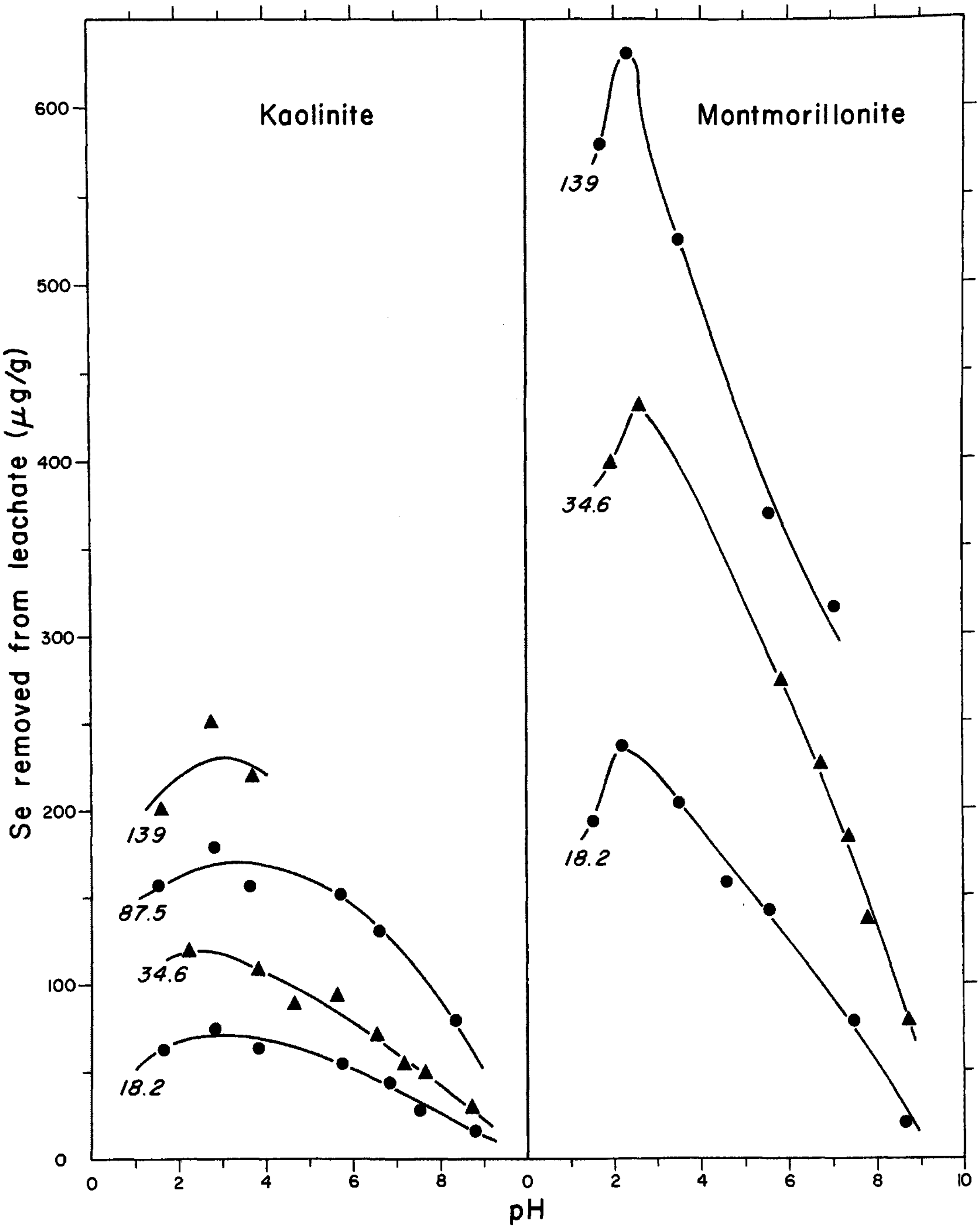

Figure 39. The amount of Se(IV) removed from DuPage leachate solutions by kaolinite and montmorillonite at 25° C plotted as a function of pH. Labels are the initial solution concentration of Se(IV) in ppm. Each datum point was obtained by using either 5 g of kaolinite or 1 g of montmorillonite in a total solution volume of 52.5 ml.

Exhibit E

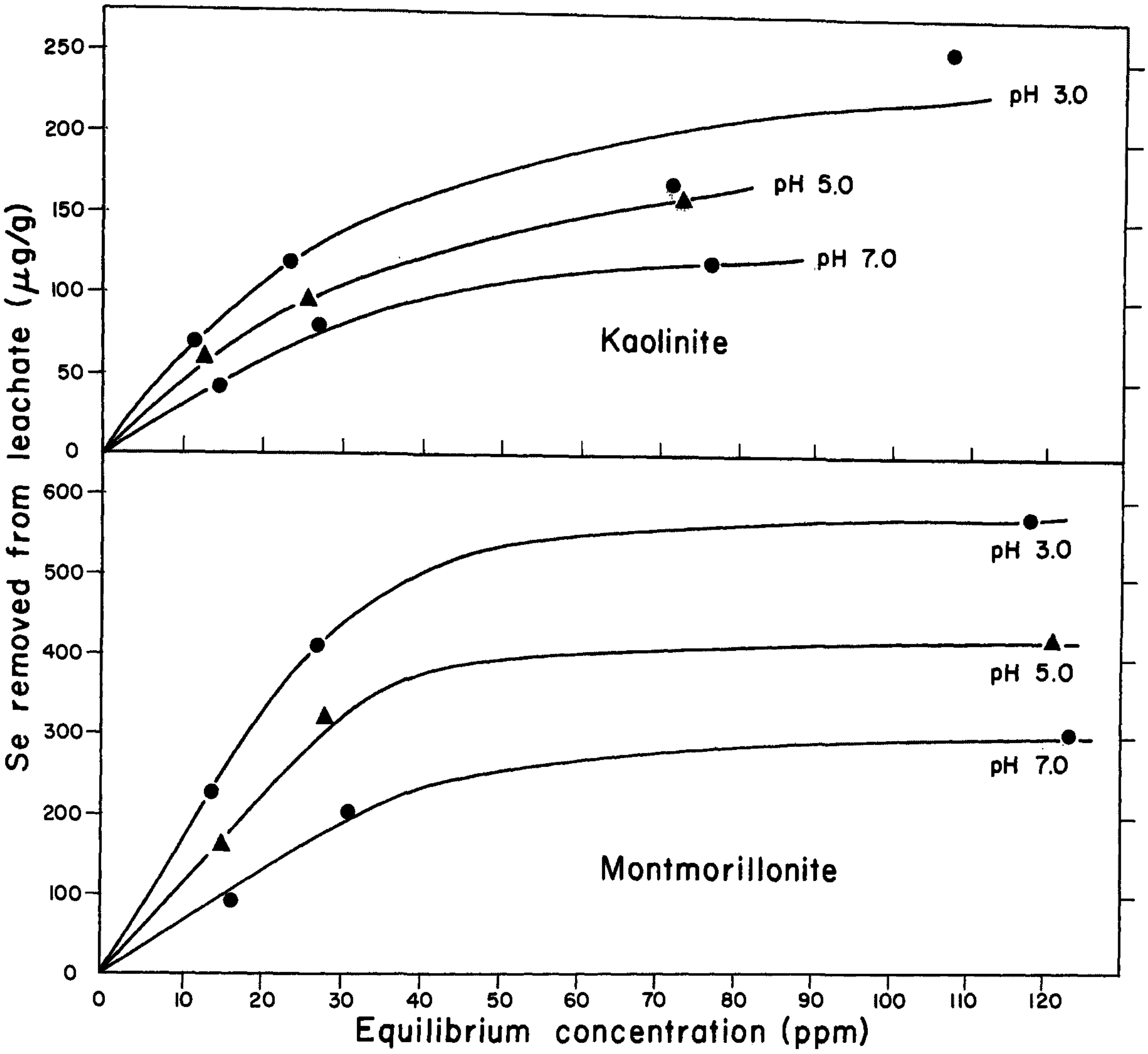

Figure 40. The amount of Se(IV) removed from DuPage leachate solutions at 25° C and several pH values per gram of clay plotted as a function of the equilibrium Se concentration.

As(V), and disposal of the waste in montmorillonitic soils at pH 5. Optimum Se(IV) removal would result from disposal in a montmorillonitic soil at a pH of 2 to 3. A high mobility and hence potential pollution hazard would be expected from land disposal of As(V) or Se(IV) wastes under alkaline conditions.

Exhibit E

SECTION 11

MERCURY REMOVAL FROM LEACHATE BY CLAY MINERALS[1]

ABSTRACT

Preliminary investigations regarding the effect of pH on the amounts of Hg removed from DuPage leachate solutions by the two clay minerals, kaolinite and montmorillonite, are reported.

Large amounts of Hg were removed from leachate, both in the presence and absence of clay. This removal of Hg increased as the pH was raised. It was estimated that 70 to 80% of the Hg was removed from leachate by precipitation and/or volatilization, thus indicating that these were the predominant attenuation mechanisms. Removal by clay accounted for 20 to 30% of the observed Hg removal. About two thirds of the Hg removed by the clay was found to be organic-Hg, and about one third was inorganic-Hg.

The results indicated that maximum Hg removal from leachate would be achieved by disposal in montmorillonite clays or soils under alkaline pH conditions.

INTRODUCTION

Because Hg has been the subject of many publications, its occurrence and toxicity will be discussed only briefly here. There are two basic sources of Hg in the environment: as it occurs in nature, and as it is redistributed in nature by man's actions. Hg is widely distributed in the air, soil, and water in low concentrations (Klein, 1972). Man in his utilization of Hg-related technology has at times redistributed this Hg in nature. It is this source of Hg in the environment that we must concern ourselves with since it often results in the release of dangerously high Hg concentrations (Goldwater, 1971).

The main source of environmental Hg contamination has been in the industrial sector (D'Itri, 1972a), and much of this can be attributed to wastewater discharge into rivers and streams (Turney, 1972; Derryberry, 1972). A great deal of the mercurial waste, both organic and inorganic, disposed of in this manner can be directly or indirectly converted by anaerobic microbes into mono- or di-methyl-mercury (D'Itri, 1972a; Greeson, 1970), both of which have been found to be extremely toxic.

As a result of studies on Hg contamination and poisoning, the disposal

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[1] Authors: R. A. Griffin and G. D. Robinson

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of industrial mercurial wastes is carefully controlled. However, the potential for contamination still exists where gaps in knowledge preclude enlightened disposal practices. This potential also exists at municipal landfill sites accepting mercurial wastes. The leachates generated from these sites are anaerobic and therefore have the ability to convert mercurial wastes into their toxic forms. Since Hg is incorporated into many industrial or consumer products such as paints, pharmaceuticals, paper products, fluorescent lamps, mercury batteries, etc., the indiscriminate disposal of these products in landfills by an uninformed population represents an important potential environmental Hg contamination route (D'Itri, 1972b).

There has been very little research done on the chemical behavior of Hg in municipal leachates. The information that is available to date on Hg in municipal leachates is insufficient to evaluate the migration of Hg in landfills. It is therefore our purpose here to report the results of studies on the adsorption of Hg from leachate by clay minerals. These studies were initiated to determine whether or not clay minerals have potential for use as landfill liners for attenuation of Hg which may be present in leachates.

EXPERIMENTAL

In order to determine the amount of Hg removed from solution, a series of samples were prepared using $HgCl_2$ in DuPage landfill-leachate, and $HgCl_2$ in DuPage landfill-leachate with clay (kaolinite or montmorillonite) added. The latter two treatments were also used to determine the amounts of organic and inorganic Hg removed from solution.

The amounts of organically-bound Hg and inorganic Hg in solution were determined by the flameless Atomic Absorption Spectroscopy (AA) technique described in the appendix.

Eight samples were prepared for each solution in each experiment. Before addition of Hg, 50 ml aliquots of either deionized-H_2O, DuPage leachate, or DuPage leachate and 1.000 g kaolinite were added to 125 ml Erlenmeyer flasks. The pHs of the solutions were then adjusted using 0.1N, 1N, 3N, and/or conc. HNO_3 to obtain pH values between 1 and 9 (each set of samples spanned this range). The samples were placed in a shaking waterbath at 25 ± 0.5° C, and allowed to equilibrate overnight. The pH values were checked after 20-24 hours and 2 ml aliquots of 25 ppm Hg stock solution were added to each flask giving a total volume of 52 ml and a Hg concentration of approximately 0.962 ppm. The samples were again placed in the shaking waterbaths and allowed to equilibrate overnight. After 20 to 24 hours the final pH values of the samples were recorded, and each sample was transferred to a 50 ml centrifuge tube and centrifuged at 20,000 rpm for 5 minutes. The supernatant solutions were decanted, acidified, and analyzed for their Hg content using flameless AA.

The amount of Hg removed from solution by a given clay at a particular pH was determined as follows:

$$C_R = \frac{(C_I - C_{Eq}) \times V_F}{W} \qquad \{19\}$$

where C_R = amount of Hg removed in µg/g clay.

C_I = initial Hg concentration in ppm,

C_{Eq} = equilibrium Hg concentration in ppm,

V_F = total solution volume after pH adjustments in ml, and

W = weight of clay in grams.

The amount of Hg removed from solution was then plotted as a function of pH.

RESULTS AND DISCUSSION

Some examples of results obtained for Hg removal from various solutions plotted as a function of pH are presented in Figure 41. It can be seen from this figure that Hg is removed from solution, even from a presumably sterile and pure $HgCl_2$ solution (curve A). In the short time available for this study we were not able to satisfactorily isolate all the reasons for this removal of Hg. Three possible removal mechanisms are adsorption onto the walls of the glassware and plastic bottles, precipitation, or volatilization. At the lower pH values the Hg removal is thought to have been by adsorption onto the glassware, although standard solutions may be satisfactorily stored at pH 2. It is presumed that the adsorption in the sample solutions occurred at the higher initial pH values and that the Hg did not have sufficient time to totally desorb after the pH was adjusted to lower values. The increase in removal in the higher pH range (5-8) is apparently the result of both precipitation and adsorption. Volatilization was not considered as an important mechanism for the Hg losses observed from the $HgCl_2$ solutions since they were presumably sterile and stoppered.

An increasing amount of Hg removal is displayed in curve B (leachate blank) which illustrates the loss of Hg from a leachate solution. The removal of Hg from solution here is again probably due to the same mechanisms; that is, the increase in Hg removal (greater amount of Hg removed by leachate than by deionized-H_2O) is probably the result of either increased adsorption or increased precipitation. However, volatilization losses of organic Hg compounds due to microbial transformations in the leachate are also possible.

Curve C in Figure 41 shows the total amount of Hg removed from leachate with 1 g of kaolinite present. The amount of Hg removed by 1 g of kaolinite is taken as the difference between curve C and curve B in Figure 41. This is plotted as curve B in Figure 42.

Figure 42 shows a breakdown of various forms of Hg removal from leachate solutions. The amount of organic- and inorganic-Hg removed by clay was determined by placing an aliquot from each sample into each of two BOD bottles. One set was digested following the general procedure while the second set was analyzed undigested. A set of leachate blanks was treated in the same manner. There were then four separate sets in all, which included a digested blank ($HgCl_2$ in leachate), an undigested blank, a digested sample ($HgCl_2$ in leachate with 1 g kaolinite), and an undigested sample.

The total organic-Hg in solution was determined by taking the difference

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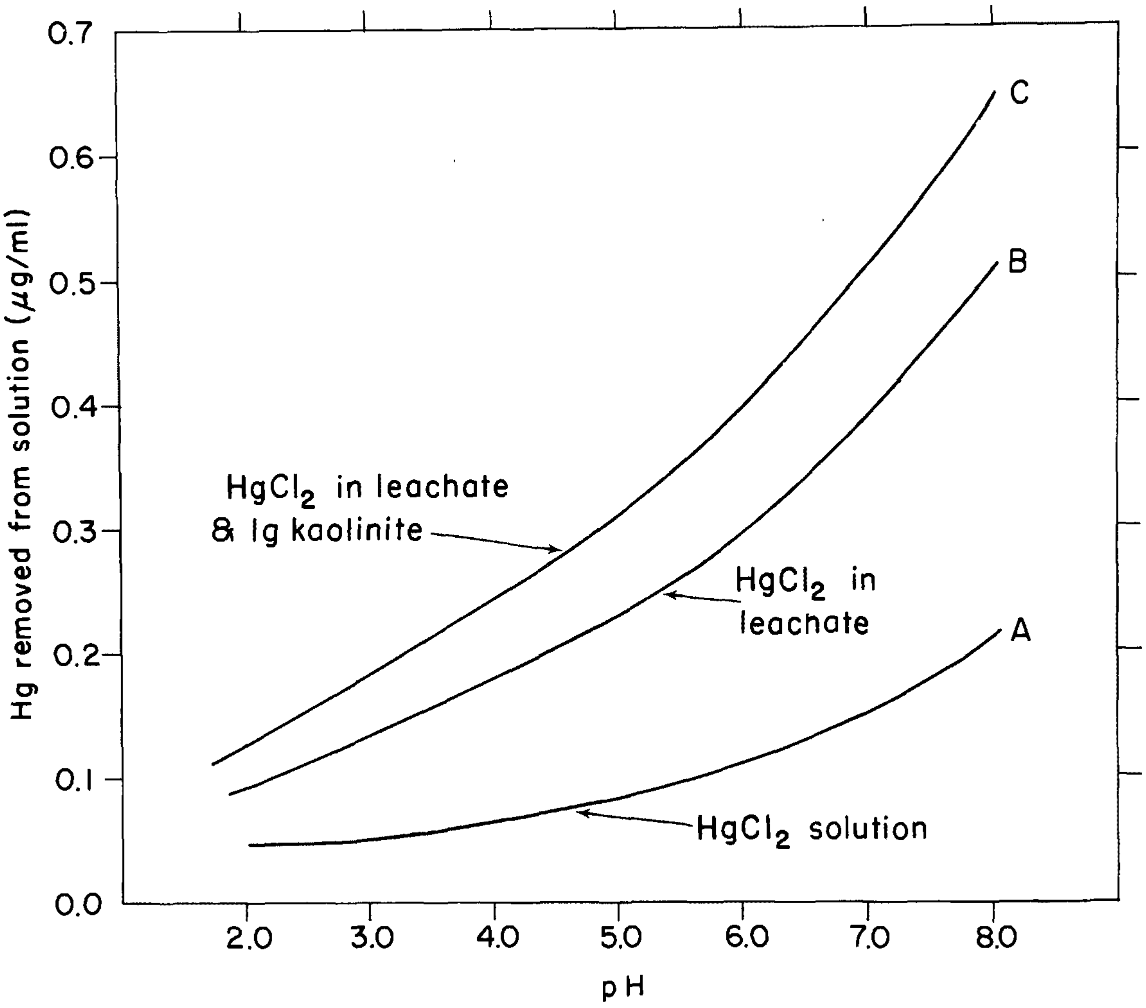

Figure 41. Removal of Hg from DuPage landfill-leachate and pure $HgCl_2$ solutions plotted as a function of pH at 25° C. The initial Hg concentration is 0.96 ppm and the final volume is 52 ml.

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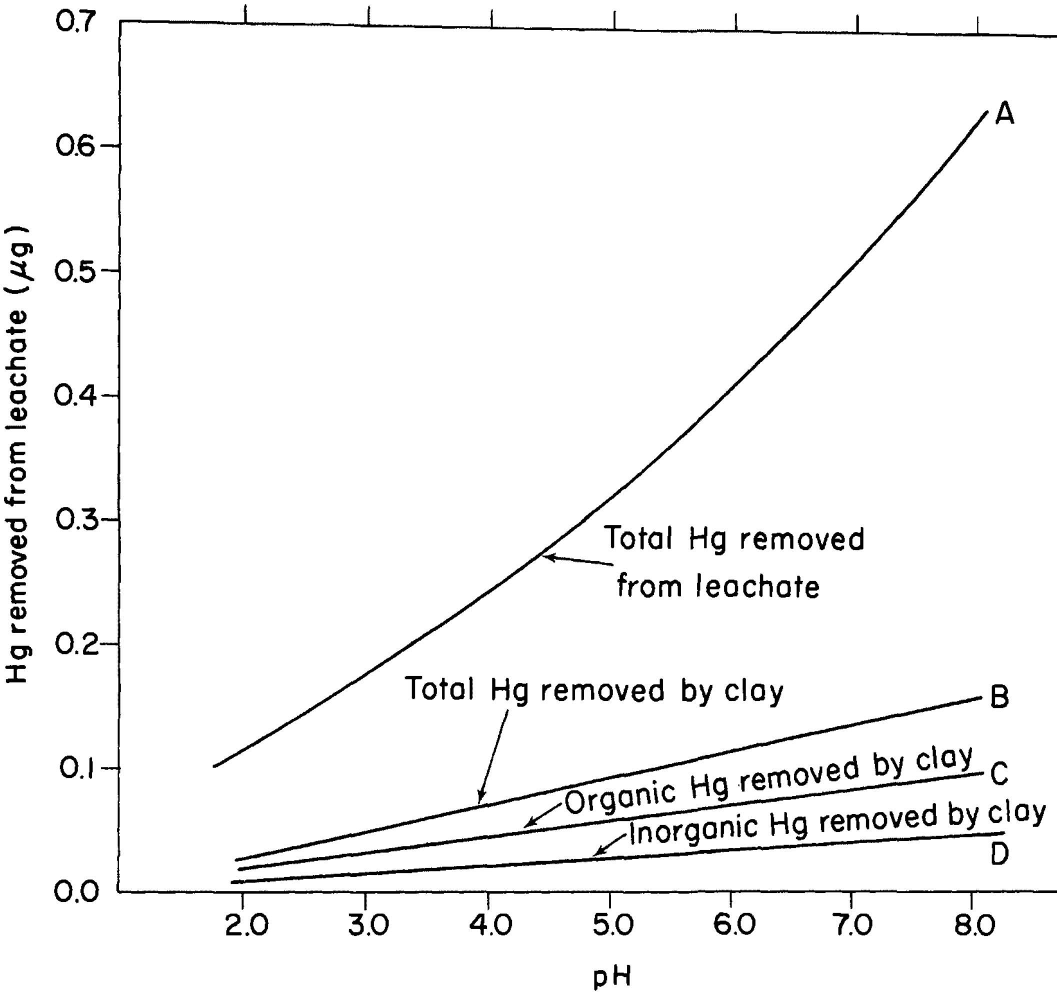

Figure 42. Removal of various forms of Hg from DuPage landfill-leachate solutions by kaolinite plotted as a function of pH at 25° C.

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between the digested and undigested blanks. The amount of organic-Hg in solution with 1 g kaolinite present was always less than the organic-Hg determined from the blanks. This difference was then taken as the amount of organic-Hg removed due to the presence of the clay. Figure 42 illustrates the relative amounts of organic-Hg (curve C) and inorganic-Hg (curve D) removed by 1 g kaolinite plotted as a function of pH. These results can be compared to the total Hg removed by 1 g kaolinite in curve B and with the total Hg removed from solution by all mechanisms in curve A.

The results given in Figure 42 illustrate that the Hg removal is pH dependent, with increasing amounts of removal as the pH is raised within the range 2 to 8.

From the data, it can be stated that approximately two thirds of the total Hg removed by 1 g kaolinite was organic Hg (curve C), while about one third of the Hg removed by the clay was inorganic Hg (curve D). The total Hg removed from solution (curve A) is apparently the result of several mechanisms operating simultaneously, i.e. adsorption by clay, volatilization, and precipitation. The amount of Hg removed as a result of the presence of clay was evaluated, as previously described, and accounted for approximately 20 to 30% of the total Hg removed from solution. It therefore appears that precipitation and volatilization account for the largest amounts of Hg removed in this study.

At this time, no data is available as to the relative amounts of Hg lost by volatilization from the leachate as opposed to precipitation. In any event, large amounts of Hg are lost from leachate solutions both in the presence and absence of clay.

In an unreplicated experiment, the removal of Hg from solution by montmorillonite was found to be approximately 5 times greater than the removal of Hg from solution by kaolinite. Since this experiment has not been repeated, the results are tentative. However, this ratio is similar to the ratio of the Cation Exchange Capacities (CEC) of these two clay minerals. Since this result is consistent with those for the previous heavy metal cations studied, it was concluded that the difference in adsorption between montmorillonite and kaolinite was due to the cation exchange of the various ionic forms of Hg which may be present in leachate solutions of variable pH.

CONCLUSIONS

The results of this study indicate that removal of Hg from leachate solutions is enhanced by clay minerals and is pH dependent. Substantial amounts of Hg were removed from leachate by the clays, and these amounts were concluded to be in proportion to the respective CEC values of the clays. Of the amount of Hg removed by the clays, it was concluded that about two thirds was organic Hg and one third inorganic Hg.

Large amounts of Hg were removed from solution, both in the presence and absence of clay. These results lead to the conclusion that adsorption by clays was not the major mechanism responsible for removal of Hg. Rather, precipitation and/or volatilization accounted for between 70 and 80% of the Hg

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removed from the leachate solutions and were concluded to be the predominant attenuation mechanisms in these experiments.

The results of this study suggest that maximum removal of Hg from leachate would be achieved by disposal under alkaline conditions. It is also suggested that montmorillonitic clays or soils will remove substantially more Hg than kaolinitic clays or soils.

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SECTION 12

SUMMARY OF ADSORPTION STUDIES

The results of these studies with heavy metals indicate that pH has a pronounced effect on the amounts adsorbed from landfill leachates by clay minerals. It was concluded that the principal adsorption mechanism is cation and anion exchange, a mechanism that led to the strong pH dependency of the adsorption process. In addition, species distribution diagrams led to the conclusion that it is the monovalent species of each element that is principally adsorbed by anion exchange.

A comparison of the relative amounts of heavy metals removed at pH 5.0 from 100 ppm equilibrium concentration solutions of the metals studied, both cationic and anionic, is presented in Table 14. The table indicates that the cationic heavy metals are generally adsorbed to a greater degree than the anionic forms. However, this ranking is somewhat pH-dependent, because the greatest anion adsorption occurs in acid solutions and the greatest cation adsorption in alkaline solutions. The ranking therefore changes somewhat at different pH values.

A significant point shown in Table 14 is the importance of the valence state of an element to the amount of that element removed from solution by clay minerals. Cr(III) species are removed to a much greater extent than Cr(VI) species. The clay minerals removed 30 to 300 times more Cr(III) from solution than Cr(VI). The table also shows more extensive removal of As(V) than of As(III). These results indicate that safer disposal of certain elements may be achieved if, prior to deposition at the landfill or disposal site, the element is converted to the form that would be most strongly attenuated.

The information derived from the studies of the various elements indicatesthat the amounts of heavy metals removed from leachate by clay minerals depends to a large degree on the element and the form of the element involved, the pH of the leachate, the adsorption capacity of the particular clay mineral in the liner, and the ionic strength of the leachate.

The adsorption capacity of the clay minerals and the reversible nature of exchange-adsorption reactions have important environmental consequences. For example, if industrial wastes containing heavy metals are placed in a landfill, changes in the ionic composition or pH of the leachate can occur. A change in pH may release large amounts of potentially toxic heavy metals into the aqueous phase, especially in places where precipitates may have accumulated. Other ions in the waste compete with the heavy metals and may

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TABLE 14. REMOVAL OF HEAVY METALS FROM SOLUTIONS BY KAOLINITE AT pH 5.0

Element	Amount removed at equilibrium concentration of 100 ppm (μmoles/g)	
	Pure solutions	Du Page leachate
Cr(III)	769*	576*
Cu	55.1	15.7
Pb	42.3	12.1
As(V)	†	5.3
Zn	33.6	3.8
As(III)	‡	2.0
Cd	26.7	1.9
Se	†	1.9
Cr(VI)	0.62	1.9

*Precipitation contributes to removal at pH 5.0.

†Removals from 40 ppm solutions were approximately the same as removals from leachate.

‡Removals from 40 ppm solutions were 30 percent greater than removals from leachate.

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exchange with them, thus allowing metal ions to come into solution. These multiple interactions must be considered when a disposal site is designed and when the environmental impact of adding heavy-metal wastes to municipal landfills is assessed.

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SECTION 13

APPLICATION OF THE RESULTS TO THE PROBLEM OF LANDFILL DESIGN

LANDFILL DESIGN

Regarding pollutant control, the design of a landfill should take into account three factors: the hydrologic system governing direction of pollutant travel, the geochemistry of the water-sediment system, and the release rate of unattenuated pollutants to surface or ground waters. The first item has been the subject of a number of papers and will not be addressed here.

Current landfill design and engineering practice are to construct clay liners, either natural or artificial, very thick and containing high clay percentages. The motive is to create relatively impermeable liners that will contain the leachate and therefore protect the groundwater resources. This approach can create difficulties in humid climates where infiltration exceeds the capacity of the liner to dissipate the leachate. This causes what is referred to as the "bathtub" effect wherein the relatively impermeable clay liner acts as a bathtub which fills up with leachate and then overflows. If the leachate is not collected and treated, the overflow manifests itself in the form of leachate springs on the surface and results in surface water pollution and surface environmental degradation instead of ground water pollution. Neither form of pollution is desirable; both might be prevented by using proper design features in the construction of the sanitary landfill. If one does not choose to collect and treat the leachate and wishes to avoid the "bathtub," the results of this research suggest an alternative landfill design.

The chemical attenuation study reported in Section 5 has indicated that most of the toxic constituents found in municipal leachates are moderately-to-highly attenuated by passage through laboratory columns containing relatively low percentages of clay minerals. If the assumption is granted that the "bathtub" effect is an undesirable feature of clay liners, then it follows that it is desirable to determine the point of "optimal" attenuation, i.e., the percentage of clay in a liner material which gives the maximum attenuation balanced with a maximized hydraulic conductivity. Figure 43 represents a dual scaled graph with the initial hydraulic conductivity of the montmorillonite columns as given in Table 3 plotted as a function of percentage of montmorillonite. The opposite scale is the attenuation number for the chemical constituent of interest also plotted as a function of the percentage of montmorillonite. The attenuation numbers (Table 5), as reported in Section 5, are the percentage of removal of the element from the leachate upon passage through 10 pore volumes of the clay-sand mixture. The attenuation

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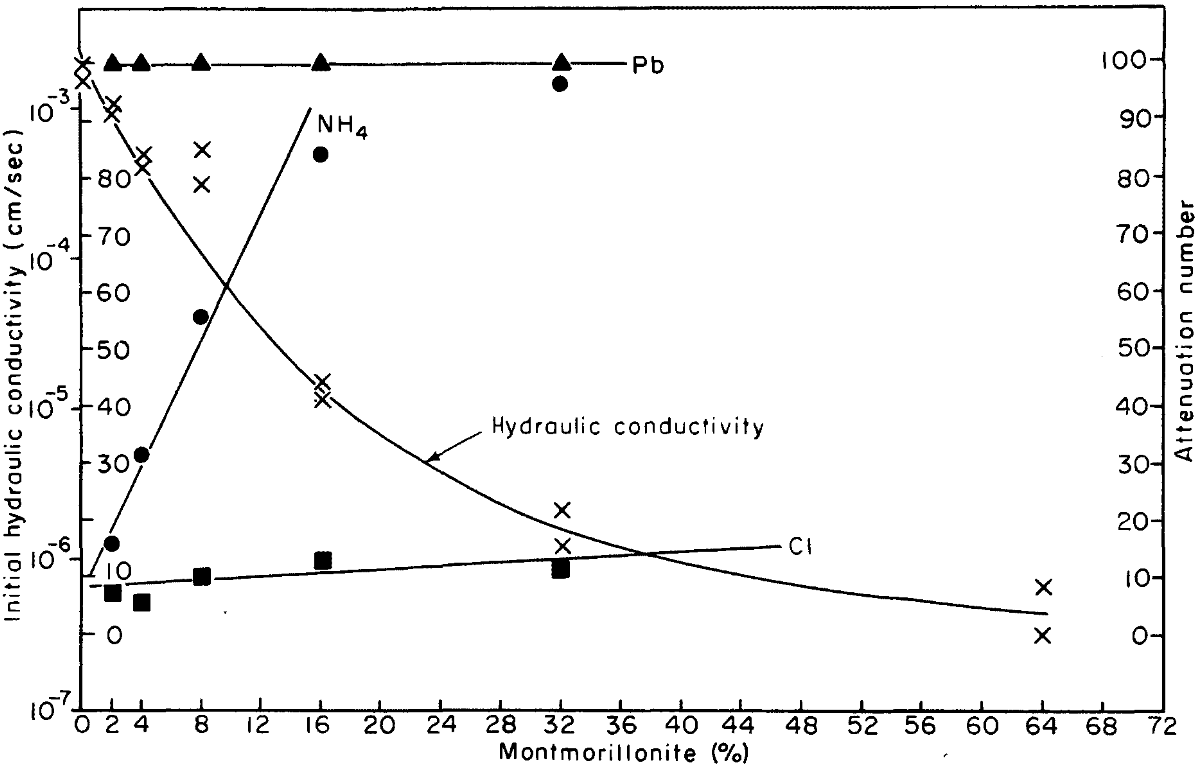

Figure 43. Effect of clay content on hydraulic conductivity and attenuation of Pb, NH$_4$, and Cl for a 40-cm thick liner. The bulk densities vary; densities for each clay content are shown in Table 3.

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number scale is given as 0 at the point of minimum hydraulic conductivity and 100 at the point of maximum hydraulic conductivity.

For the heavy metals (Pb is used here as an example), even small amounts of clay gave almost total removal. The heavy metals, even though toxic, represent a minimal pollution hazard in municipal leachates because they are attenuated very strongly and are usually present at low levels in leachates. Therefore they can usually be ignored as far as determining the optimal clay liner for a given leachate. At the other extreme are the relatively non-interacting constituents represented by Cl. Chloride as shown here is relatively unattenuated by even large amounts of clay. Figure 43 suggests that in order to prevent chloride migration, relatively impermeable clay liners would be necessary. Due to the non-toxic nature of the chloride ion, it also ranks low along with the heavy metals in the pollution hazard index (Table 6). In view of the problems associated with the "bathtub" effect, it seems unwise to design clay liners to optimize chloride attenuation. Rather, it seems prudent to design clay liners for optimum attenuation of the most hazardous constituents found in a particular leachate. In the case of the DuPage leachate used in this study, the pollution hazard index ranks NH_4^+ as 30 times more of a pollution hazard than any other constituent found in this leachate. It therefore seems reasonable to design a clay liner for DuPage leachate that gives optimal attenuation of NH_4^+ and all the other constituents should also be attenuated to relatively safe levels for minimal pollution of the groundwaters adjacent to the landfill site.

For the case of NH_4^+ (shown in Figure 43) if one extrapolates the curve, it is apparent that 18-20% montmorillonite would give nearly total removal from the leachate. If the 10% liner is doubled in thickness from the 40 cm used in this study to 80 cm, it will contain enough montmorillonite to give nearly total removal of the NH_4^+ in 10 pore volumes of leachate and still retain the relatively high hydraulic conductivity of 6×10^{-5} cm/sec. This illustrates that, for a given desired hydraulic conductivity, the removal capacity of the liner may be adjusted by changing its thickness (at the same clay content) without greatly affecting transmission of water through it.

LINER THICKNESS

The thickness of various mixtures of sand and clay, as represented by the total cation exchange capacity (CEC), to achieve total attenuation of selected relatively mobile ions was calculated (Table 15). The removal efficiency will differ in leachates, depending upon relative ion strength. The efficiencies used in Table 15 are based on the DuPage leachate used in this study. The concentrations are given in parentheses under the average concentration value. Increasing cation exchange capacity generally reflects increasing clay contents. Thus a thicker liner with greater hydraulic conductivity and lower CEC may be the optimal liner for attenuation.

Determining the release rate of nonattenuated or poorly attenuated contaminants from the clay liner (natural or man-made) to surface waters or ground-water aquifers is necessary for good landfill design. In designing a landfill, a decision must be made as to which ions should be totally attenuated

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TABLE 15. ESTIMATED LANDFILL LINER THICKNESS NECESSARY FOR ATTENUATION OF SOME LEACHATE CONSTITUENTS PER CUBIC METER OF REFUSE DURING A 20 YEAR FILL LIFE*

Constituent	Initial** Concentration		CEC					
			10		20		30	
	Ave. (ppm)	Max. (ppm)	Ave. (cm)	Max. (cm)	Ave. (cm)	Max. (cm)	Ave. (cm)	Max. (cm)
NH_4	379 (830)	1,106	32	92	16	46	11	31
Na	755 (740)	7,700	118	1,208	59	604	39	403
K	763 (530)	3,770	51	252	26	126	17	84
Mg	1,609 (240)	15,600	226	2,191	113	1,096	75	730

*Assumption: Bulk density = 1.8 g/cc; 100 liters of leachate generated per m^3 of refuse/yr.; initial concentration decreases linearly to zero at 20 yr.; removal efficiencies for each constituent were estimated using the average values given by Griffin, et al. (1975), NH_4 = 37.1%, Na = 15.4%, K = 38.2%, Mg = 29.3%.

**Concentrations taken from the twenty leachate analyses reported by EPA (1974); those in parenthesis, (830), are the values of Old DuPage landfill leachate used in this study.

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and which should be eventually released to the environment. The chloride ion, which moves essentially unattenuated, is the most obvious example of the latter type.

CONCLUSIONS

The results of this study suggest an alternative to landfill design. The use of hydraulic conductivity information and the pollution hazard rating for a given leachate or waste stream can allow a different approach than the prevalent "containment" type liner systems. These data suggest that overall pollution would be lessened by designing landfill liners for higher permeability and by selectively attenuating the most toxic pollutants from leachate and allowing the groundwaters to dilute the nontoxic components which can be tolerated at much higher concentrations than the toxic without deleterious effects. Thus landfill stabilization and use for other productive purposes could be achieved at much faster rates than can presently be achieved by containment type liners.

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SECTION 14

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APPENDIX A

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APPENDIX B

PROCEDURES USED IN CHEMICAL AND PHYSICAL CHARACTERIZATION OF CLAY MINERALS AND LIQUID SAMPLES

Clay Mineral Characterization

(W. A. White)

The kaolinite used in this study was collected from materials of Pennsylvanian age in Pike County, Illinois. The site description and location are given by White (1959), sample 996N. The montmorillonite used in the study was southern bentonite from the American Colloid Company. The illite was from the Minerva Company Mine of the Allied Chemical Company.

The clays were brought to the laboratory, where they were crushed, ground, and purified by sedimentation techniques to obtain the <2 μm particle fraction that contained essentially pure clay minerals. The purified clay was then floculated with 1 M $CaCl_2$, centrifuged, and spray dried. The clay minerals present in the <2 μm fraction were identified by X-ray diffraction techniques (Parham, 1962), and the results are given in Figure 44. The positions of the diffraction peaks identify which clay minerals are present in the sample. In addition, the areas under the peaks of the diffraction patterns give a crude estimate of the relative amounts of each clay mineral in the sample and were used to prepare the following summary:

(a) The montmorillonite sample was found to be almost completely monomineralic, containing approximately 95% montmorillonite and 5% mixed-layer materials close to montmorillonite in composition.

(b) The illite sample was found to be monomineralic, with mica minerals predominant. The sample contained approximately 70% illite and 30% mixed-layer materials close to illite composition.

(c) The kaolinite sample could be characterized as a moderately pure kaolinite, comparable to the Georgia hard kaolins. The sample contained approximately 87% kaolinite, 8% illite, 5% mixed-structure material, and a trace of quartz.

Atomic Absorption Methods for Cd, Fe, Mn, Pb, Si, Zn, Na, K, Ca, and Mg

(John Steele and David Heck)

Exhibit E

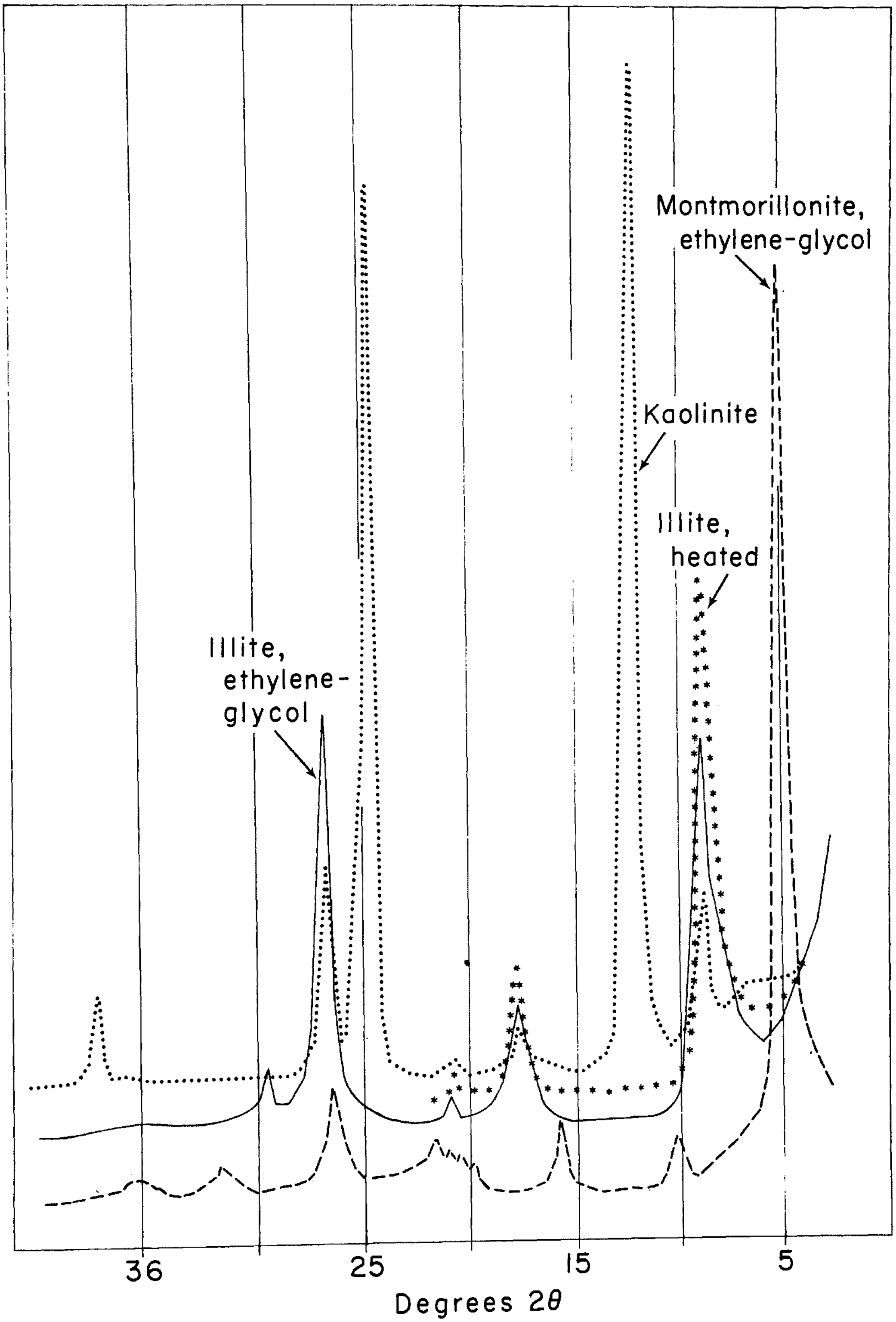

Figure 44. X-ray diffraction patterns of the clay minerals used in leachate pollutant attenuation studies.

Atomic absorption methods were used for the following determinations: filtered and acidified leachate (dissolved metals) -- Cd, Fe, Mn, Pb, Si, and Zn; membrane filters (suspended metals) -- Cd, Fe, Mn, Pb, and Zn; ammonium acetate extracts (exchangeable cations) -- Cd, Fe, Mn, Pb, Zn, Na, K, Ca, and Mg; and column sections and original clays (total cations) -- Cd, Mn, Na, Pb, and Zn.

Atomic absorption measurements were made using a Perkin-Elmer Model 306 Atomic Absorption Spectrophotometer. In the case of the dissolved, suspended, and exchangeable metal determinations, measurements were recorded directly from the electronic digital readout in the auto-concentration mode. For the total cation determinations, absorbance measurements were recorded on a Perkin-Elmer Model 056 Recorder. The following Perkin-Elmer burner heads were used: a 4-inch-long slot, flat-head burner using an air-acetylene flame for all of the dissolved and suspended cation determinations except Si; a 2-inch-long slot nitrous oxide burner head using a nitrous oxide-acetylene flame for Si determinations; and a three slot high solids burner head with an air-acetylene flame for all of the exchangeable and total cation determinations. Standard single element hollow cathode lamps were used. Corrections for background absorption were made simultaneously for total cation determinations using a Perkin-Elmer Deuterium Arc Background Corrector.

All reagents used are ACS certified reagent grade chemicals, and standard stock solutions were prepared from high purity metals or compounds. Calibration standards prepared from diluted stock solutions contained the following matrices: dissolved metal standards -- 1% v/v distilled HNO_3; suspended metal standards -- 4% v/v distilled HCl; exchangeable cation standards -- 1 N ammonium acetate and 7.5% v/v distilled HNO_3; and total cation standards -- 1.2% v/v 48% HF, 1.5% v/v aqua regia (1:3:1 HNO_3-HCl-H_2O), and 0.54% w/v H_3BO_3. For total Na determinations, the standards contained, in addition to the above mentioned matrix for total cations, 1000 ppm Cs as CsCl. For determination of Ca and Mg in the leachate fraction, the standards were prepared to contain 1% w/v La_2O_3 and 2.5% v/v HCl. For determination of Na and K, the standards were prepared to contain 1000 ppm Cs as CsCl.

Sample preparation

The filtered-and-acidified leachate and the ammonium acetate extract samples required no sample preparation and were analyzed directly except that for the analysis of Ca and Mg, 1% La_2O_3 w/v and 1% v/v HCl were added. Also for the determination of K and Na, the final sample contained 1000 ppm Cs as CsCl.

Column section dissolution

The methods described below are modifications of those of Bernas (1968) and French and Adams (1973). Approximately 0.5 g of the clay-sand mixture, previously dried at 110° C for several hours, is transferred to a 125 ml linear polyethylene screw cap bottle. The sample is wetted with 1.5 ml aqua regia, and 1.2 ml of 48% HF is added. The cap is screwed tight, and the bottle is placed in a steam bath for 2 hours. The sample and acids are mixed by an occasional swirling of the bottle during this period. The bottle is removed from the steam bath, and 9 ml of a H_3BO_3 solution (0.06 g/ml) is added to the sample to complex the fluoride. The bottle is again sealed and placed on the steam bath for 0.5 hours, removed, and allowed to cool. The dissolved sample is transferred to a 100 ml polyethylene volumetric flask, the bottle is washed repeatedly with deionized H_2O, and the washings are added to the flask. The sample is diluted to volume with deionized H_2O and returned to the polyethylene bottle for storage.

Membrane filter dissolution

The membrane filters were treated according to methods modified from Parker (1972). The membrane is placed in a 250 ml Pyrex beaker, and 3 ml of distilled HNO_3 is added. The beaker is covered with a watch glass and heated on a hot plate where the acid is evaporated to dryness. The additions of acid and the heating steps are continued until a light residue is left. The residue is taken up with 2 ml of distilled 1:1 HCl and warmed gently. The sample is then transferred to a 50 ml Pyrex volumetric flask, and the beaker is washed repeatedly with small portions of deionized H_2O and the washings added to the flask. The sample is diluted to volume and transferred to a polyethylene bottle for storage.

Atomic Absorption Spectrophotometric Procedures

The following analytical wavelengths were used: 228.8 nm (Cd), 248.3 nm (Fe), 279.5 nm (Mn), 589.0 nm (Na), 283.3 nm (Pb), 251.6 nm (Si), 213.9 nm (Zn), 422 nm (Ca), 285 nm (Mg), and 766.5 nm (K). Where necessary, samples are diluted to bring the metal concentration within the linear portion of the calibration curve. For total Na determinations, samples are diluted 1 to 2 with the addition of 1000 ppm Cs as CsCl. In the case of the suspended, dissolved, and exchangeable metal determinations, the metal ion concentrations are determined directly from the electronic digital readout in the auto-concentration mode, after appropriate calibration. For the total cation determinations, the metal ion concentrations are calculated by solving for concentration in a least squares constructed calibration equation of absorbance vs. concentration. A new calibration curve equation is calculated for each set of analyses.

An estimate of the average relative standard deviation for the elements determined by atomic absorption spectrophotometry is 10 percent or better.

Determination of Hg by Flameless Atomic Absorption

(R. A. Griffin and G. D. Robinson)

The Hg samples obtained in the investigation of the removal characteristics of Hg from leachate solutions by clay minerals as a function of pH were analyzed by flameless Atomic Absorption Spectroscopy (A.A.) using a slight modification of the procedure described by the U. S. Environmental Protection Agency (EPA) (U.S.-EPA, 1971).

Variations of the standard procedure described by U.S.-EPA (1971) were implemented in order to gain maximum sensitivity from the procedure and the available instrumentation. The apparatus used was a Perkin-Elmer Model 360

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A. A. equipped with a Perkin-Elmer Flameless Mercury Analysis System. The absorption cell supplied by Perkin-Elmer was modified by replacing the plastic end windows with quartz windows which were glued in place with epoxy cement. This allowed greater light transmission and higher sensitivity and stability to be achieved for the Hg analyses.

Reagents used:

Sulfuric Acid reagent grade conc.
Nitric Acid reagent grade conc.
Potassium Permanganate 5% w/v 5g $KMnO_4$ in 100 ml DI H_2O
Potassium Persulfate 5% w/v 5g $K_2S_2O_8$ in 100 ml DI H_2O
Hydroxylanine Hydrochloride 5% w/v 5g $NH_2OH \cdot HCl$ in 100 ml DI H_2O
Stannous Chloride - Dissolve 50g $SnCl_2$ in 100 ml conc. HCl and 400 ml DI H_2O
Stock Mercury Solution 1000 ppm - Dissolve 1.080g HgO in min. vol. 1:1 HCl - dilute to 1 liter with DI H_2O
Working Mercury Solutions - Make successive dilutions of the stock Hg solution to obtain a standard containing 0.1 ppm. This should be made fresh daily and acidified to .15% HNO_3. Note: It was found that 10 and 25 ppm working Hg standards could be stored in plastic bottles several weeks if acidified to .15% HNO_3 with no apparent loss or adsorption of Hg. This greatly reduced the steps involved in making fresh working standards of .1 ppm.
Waste Hg Absorbing Media - .1 M $KMnO_4$ and 10% H_2SO_4.

A calibration curve was obtained following the procedure outlined in U. S.-EPA (1971) substituting a hydroxylamine-HCl solution for the hydroxylamine sulfate solution, and a stannous chloride solution for the stannous sulfate solution. It was found that this calibration curve had to be repeated with each set of samples.

The samples for Hg analysis were placed in 60 ml plastic bottles and acidified with conc. HNO_3 to pH ~2. A 1 ml aliquot was then taken from each sample and placed in a 300 ml BOD bottle (these were run in triplicates); the volume in the bottle was then brought up to 100 ml with DI H_2O. The samples were then digested to oxidize the organo-mercury compounds which would not otherwise respond to the flameless A. A. technique (U. S.-EPA, 1971).

The samples were digested by addition of conc. H_2SO_4 and 2.5 ml of conc. HNO_3 to each bottle with mixing after each addition. One ml of 5% w/v $KMnO_4$ solution was then added to each bottle, swirled, and allowed to stand for at least 15 minutes. Two ml of $K_2S_2O_8$ were then added and allowed to stand for at least 30 minutes. Two ml of $NH_2OH \cdot HCl$ were then added to each bottle to reduce the excess permanganate. Immediately prior to aerating through the absorption cell, 2 to 3 ml of $SnCl_2$ solution were added to each bottle. The samples were read on the absorbance mode and then converted to concentration mathematically using linear regression analysis (calibration standards were prepared fresh daily). The final Hg concentrations were then subtracted from the initial concentration (0.962 ppm) to obtain the amount of Hg removed from solution.

Exhibit E

Neutron Activation Analysis Methods for Hg and As

(Joyce Frost and Larry Camp)

Irradiations are carried out in the University of Illinois' Advanced TRIGA reactor, with a thermal neutron flux of 1.4 x 10^{12} neutrons cm^{-2} sec^{-1} (500 KW). The samples are contained in a rotary specimen assembly. Rotation at 1 rpm during irradiation ensures an equivalent integrated flux for each sample.

Samples and standards are irradiated in heat-sealed polyethylene snap-cap vials which were previously cleaned with deionized water and acetone.

The gamma-ray spectrometer system consists of a 3" x 3" NaI(Tl) crystal connected to a 400-channel analyzer. The analyses are comparative -- e.g. the activity of an element in the sample is compared to that of the element in a known standard to determine concentration of the element in the sample.

Determination of Hg by Instrumental Neutron Activation Analysis in "Spiked" Liquid Samples

This procedure was used for the column effluent samples (filtered and acidified leachate samples), solubilized membrane filter samples, and ammonium extract solutions of the clay column samples that originated after the original sterile leachate was spiked with mercury to a resulting concentration of 4.0 ppm.

A two-hour irradiation was carried out on 5 ml portions of the samples and two acidified mercuric nitrate standards, one containing 5.02µgHg/ml and the other 0.502µgHg/ml. The samples were left to decay one week to decrease interference from short-lived radioisotopes, especially 15 hour ^{24}Na and 36 hour ^{82}Br which gives a high background in the low energy region of the gamma ray spectrum. The activity in the samples and standards due to the 0.077 MeV gamma ray of 65 hours ^{197}Hg was then counted. At the same time uranium was determined in those column effluent samples that unexpectedly had a high concentration of uranium, up to 0.20 ppm; these were the first several sets of effluents collected from the columns that contained montmorillonite. The uranium activity counted was the 106.1 keV gamma ray of 56.4 hour ^{239}Np; the standard was 5 ml of a solution of $UO_2(NO_3)_2$ containing 1.02 µg U/ml.

Determination of Hg in Liquid Samples by Neutron Activation Analysis with Radiochemical Separation

This procedure was used for the original leachate and for the precise determination of mercury in some of the samples having a low mercury content.

The method follows closely that of Weiss, Koide and Goldberg (1971). The samples (1 to 3 irradiation vials, each containing 10 ml per sample) and standard (10 ml of 5.02µgHg/ml) were irradiated for 2 hours. After a day's decay, each sample was transferred to a beaker, and 10 mg of Hg^{++} carrier was added. The pH of the solution was adjusted to 1 and elemental mercury precipitated by the addition of stannous chloride solution. The mercury was separated on a Millipore filter and dissolved in aqua regia. This solution was neutralized with ammonium hydroxide, and thioacetamide solution was added. The precipitate of mercuric sulphide was separated on a Millipore filter; dissolved in aqua regia; transferred to a tared, glass, stoppered vial; and made up with deionized water to 25 ml. The activity of the solution due to the 0.077 MeV gamma ray of ^{197}Hg was counted. The radiochemical separation for the standard (250 µl) plus carrier was begun with the mercuric sulphide precipitation step. Radiochemical yields (85-98%) were determined by re-irradiation of a 1 ml aliquot of each sample and the standard.

Determination of Hg in Column Sections and Clay

One gram of sample was accurately weighed and irradiated for two hours as previously described. The irradiated sample was then mixed with ~1 gram of Alundum and transferred to a combustion boat which has had Hg carrier added as $Hg(NO_3)_2$. The boat was then placed in a Vicor tube which in turn is placed in a Lindberg "Heavy Duty" furnace, such that O_2 can flow through and the combustion gasses trapped in a dry ice cold trap. The furnace is operated for 15 minutes at 1000° C and allowed to cool.

The boat was removed from the cooled tube (at most, 400° C) and the cold trap section (dry ice removed) placed end down into a polyethene 100 ml centrifuge tube.

The foresection of the tube was washed with 10 ml of HNO_3, and this solution via transfer pipplets was used to wash down the cold trap section of the tube. This was repeated twice more, but H_2O substituted for the HNO_3, giving 30 ml of total solution. The centrifuge tube was placed in H_2O bath and heated. When hot (90° C or +), the solution was stirred and solid NH_4Br (AR) added, red Br_2 was evolved, and the solution was stirred. Solid $Ag(NO_3)_2$ was added to remove the excess Br (much of the radioactive Br had isotopically exchanged) and the solution was centrifuged. The liquid was transferred to a 4 oz. wide mouth jar and labeled.

Ten ml of warm (90+° C) HNO_3-H_2O (1-3) was added to the ppt in tube and again centrifuged. This solution was added to the original 30 ml, and the solution counted for 77.6 KEV γ ray of Hg^{197} (65.5 hour $t_{½}$) on a NaI detector. One ml of this solution was removed and put in 1 dram vial, sealed, and labeled and irradiated at 15 minutes at 500 KW. This was compared with a "carrier vial" and a "yield" factor found for correction.

Determination of Arsenic in Liquid Samples by Neutron Activation Analysis with Radiochemical Separation

Ten ml of sample and 10 ml of an arsenic trioxide standard were irradiated for 1 hour, then left to decay for a day. The sample with 30 mg of As^{+++} carrier added, in a distillation flask, was oxidized by boiling it for 5 min. with 3 ml of 30% H_2O_2, to decompose organic arsenic compounds present (EPA, 1971). Then, after the addition of hydrochloric and hydrobromic acids, arsenic was distilled from the solution (NAS-NS #3002, 1965). Elemental arsenic was precipitated from the distillate by the addition of sodium hypophosphite. The precipitate was separated on a weighed filter paper, reweighed, and the activity due to the 0.56 MeV gamma ray of 26.5 hour ^{76}As was counted. The standard was carried through the same radiochemical separation.

Determination of Arsenic in Clay Samples by Neutron Activation Analysis with a Radiochemical Separation

The procedure followed was that used by Ruch, Kennedy and Shimp (1970) for the determination of arsenic in sediments. The irradiated clay samples, with added As^{+++} carrier, are dissolved with hydrofluoric and perchloric acids and hydrogen peroxide, and the silicon tetrafluoride evaporated off. The residue was taken up in hydrochloric acid and arsenic was separated by a hydrogen bromide distillation; the procedure henceforth was the same as that used for liquid samples.

X-Ray Fluorescence Method for Mg, Al, Si, Ca, K, Ti, Fe, and P

(John Kuhn and Ray Henderson)

The column section samples and clays were air dried then ground to ~200 mesh and oven dried at 105° C for 6 hours. From the dried sample, 125 mg was weighed into a graphite crucible containing 1.000 g of lithium tetraborate. A depression made in the tetraborate prior to addition of the sample prevented its contact with the crucible wall. Next, 125 mg of lanthanum oxide was added as a heavy-element absorber, and the contents of the crucible were mixed, with a glass rod, as thoroughly as possible without scraping the crucible wall or bottom. The mixture was fused in a furnace for 15 minutes at 1000° C, removed, covered with a second crucible and allowed to cool to room temperature. The resulting fused pellet was weighed alone to determine fusion loss and placed in the grinding vial of a No. 6 Wig-L-Bug with 2 percent by weight of Somar Mix (a commercial mixture used as a grinding and plasticizing agent). The sample was ground for 3 minutes, transferred to a die, and pressed at 40,000 psi. Samples were then exposed to X-rays and the data compared to values acquired from standard rock pellets prepared in the same manner. The resulting concentrations determined on the samples are quantitative for those major and minor elements listed (Mg, Al, Si, Ca, K, Ti, Fe, and P).

Optical Emission Spectrometry Method for Be, V, Cr, Co, Ni, Cu, and Mo

(Gary Dreher)

Direct reading optical emission spectrometry was used to determine trace element concentrations in the original clay materials. The procedure used was to prepare a mixture of 1 part $Ba(NO_3)_2$ (5 mg), 8 parts sample (40 mg) and 31 parts SPEX graphite powder (Spex Industries, Inc.) (155 mg) in a 1/2 inch diameter, 1 inch long polystyrene vial containing two 1/8 inch diameter polystyrene beads. The sample mixture was shaken in a Wig-L-Bug for 60 seconds. Fifteen milligrams of this mixture was loaded into each of 4 electrodes, 1/8 inch in diameter, having thin wall craters. The sample electrodes were arced at 15 A. short-circuit current for 65 seconds with an arc gap of 4 mm, and surrounded by a 10 SCFH flow of a gas mixture 80% in argon and 20% in oxygen.

Determination of Total Carbon (TC), Inorganic Carbon (IC), and Organic

Exhibit E

Carbon (OC)

(David Heck and Larry Kohlenberger)

Total Carbon (TC) and Inorganic Carbon (IC) were determined in the column sections and clay samples. Organic Carbon (OC) was determined by difference of TC and IC. The procedures are as follows:

Total Carbon

A zirconium silicate combustion boat containing a layer of dry alumina powder (to prevent sample fusion to boat) is accurately weighed. A layer of sample (1.5 to .30 g) is added, and the boat is reweighed in order to obtain the sample weight. A Nesbitt absorption bulb containing a bottom layer of magnesium perchlorate and topped with CO_2 absorbent (lithasorb or ascarite) is also weighed. The weighed absorption bulb is placed on the exit end of a zirconium silicate combustion tube which is heated to 1350° C in a high temperature furnace. With dry oxygen flowing through the tube continuously, the sample boat is slowly pushed into the hot zone at a rate which will neither crack the boat nor blow out the sample. After the sample has been in the hot zone for 4 minutes, the sample boat is removed, the absorption bulb closed off, and the sample allowed to cool. It is reweighed, the CO_2 absorbed determined by difference, and % total carbon calculated.

Inorganic Carbon

A modified ASTM (1968) procedure, D 1756, is used whereby CO_2 is formed by decomposing ~0.5 g sample with acid and absorbing the gas on Lithosorb.

Methods for NH_4^+, TDS, COD, and Chloride

(Don Dickerson)

Ammonium ion (NH_4^+) was determined in the filtered (but not acidified) leachate samples as follows. A suitable volume of leachate (1 ml 0.01 N HCl is equivalent to 180 mg NH_4^+/liter) is placed in a Kjeldahl flask and diluted to ~20 ml with NH_4^+ free water. The flask is connected to the Kjeldahl distillation apparatus. The receiver contains 30 ml of 4% boric acid solution. Fifty percent KOH solution is slowly added into the flask port followed by 5 ml of $NaOH\text{-}Na_2S_2O_3$ solution (25 g NaOH, 5 g $Na_2S_2O_3$, and 75 ml H_2O). The solution is steam distilled for 4 minutes after NH_4^+ starts coming over. Three drops of methyl red-bromocresol green indicator is added and the solution is immediately titrated to the orange-pink end point with 0.01 N HCl solution.

Determination of Exchangeable NH_4^+

Exchangeable NH_4^+ was determined on the column sections according to a modified procedure by Jackson (1958). One sample (containing approximately .8 - 1.0 mg NH_4^+) is analyzed by the normal Kjeldahl procedure. A second sample is combined with 20 ml of 1.0 N, acidified NaCl and distilled similarily following the Kjeldohl procedure.

Exhibit E

Determination of Chloride

Chloride was determined in the filtered (but not acidified) leachate samples as follows. A sample containing not more than 4 mg of Cl^- is diluted to 25 ml with Cl-free water and then combined with 25 ml of isopropyl alcohol. While stirring, 2 drops of bromophenol blue is added and the pH adjusted to slightly acid by the addition of 1.0 N NaOH solutions or 1.0 N HNO_3 solutions as needed. One half ml of a saturated solution of diphenyl carbazone in isopropyl alcohol is added and the solution titrated to the endpoint with 0.1 N Hg^{++} (as $Hg(NO_3)_2$ in dilute HNO_3).

Determination of Chemical Oxygen Demand (COD)

The following procedure, adopted from Leithe, (1947) was used to analyze filtered (but not acidified) leachate samples. A 1-10 ml leachate sample diluted to 50 ml with distilled water and 25 ml 0.10 N $K_2Cr_2O_7$ solution was added to 0.5 g $HgSO_4$ in a 300-ml ground-joint flask with a Friedrich condenser. Concentrated sulfuric acid (75 ml) containing 1 g Ag_2SO_4 was added in small portions with thorough swirling as well as two boiling stones as anti-bumping aids, and refluxing was carried out for 2 hours. The mixture was cooled, washed into a 500-ml Conical flask, diluted to 350 ml with distilled water, treated with 3 drops ferroin indicator and titrated with 0.1 N Fe $(NH_4)_2(SO_4)_2$ solution to a stable color change from blue-green to reddish-brown. A blank value was determined using 50 ml of distilled water under the same conditions.

Determination of Total Dissolved Solids (TDS)

TDS was determined in the filtered (but not acidified) leachate samples as follows. Ten ml was placed in a weighed beaker, covered with a watch-glass, and placed in an oven preheated to 250° F until evaporation was completed. The temperature was then raised to 350-375° C for an hour. The residue was finally cooled in a vacuum desicator and weighed.

Methods for Sulfate, Phosphate, and Boron

(David Heck)

Sulfate was determined in the original leachate solutions as follows. Fifty ml of sample was neutralized with concentrated HCl and then 0.5 ml added in excess and the sulfate precipitated in almost boiling solution with 10 ml of 10% $BaCl_2$ added drop by drop with constant stirring. After digesting one hour until the $BaSO_4$ settled, another drop of barium chloride was added to make sure the precipitation was complete, and the $BaSO_4$ filtered off, washed with hot water, ignited in the muffle furnace one hour at 1000° C and weighed as $BaSO_4$.

Determination of Phosphate

Phosphate ion was determined in the original leachate solutions as follows. Fifty ml of sample was brought to boil with 15 cc HNO_3 and 40 cc H_2O, digested for an hour, cooled, filtered. The filtered material was washed with a dilute HNO_3-NH_4NO_3 solution. The residue was discarded, the filtrates were

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combined and 11 ml ammonium citrimolybdate reagent added, brought cautiously to a boil, and then let to stand overnight. The resulting precipitate was filtered through a fritted crucible, washed with the above solution and water, dried at 100-105° C, cooled, and weighed.

Determination of Boron

Boron was determined on the column sections and clay samples according to the following procedure.

A 25-50 mg solid sample was weighted into a clean 4 oz. plastic bottle, and 10 ml of 2.5 NH_2SO_4 and 4 ml 5% HF added. The bottle was fitted with a tight cap, swirled, and allowed to stand overnight. The sample was diluted to a total volume of 20 ml, and 10 ml of .001 M methylene Blue (.374 g/l) and 25 ml of purified ethylene dichloride added. The bottle was shaken for at least 30 minutes, removed from shaker, and layers allowed to separate. A 5 ml portion of the lower layer was pipetted into a 25 ml volumetric flask and diluted to volume with ethylene dichloride. Unknown sample was then compared to known standards (1-6 ppm range) on a Beckman DBG Spectrophotometer at 660 μm. A reagent blank was required for standards and samples. Boron was determined in the leachate fractions according to the same procedure, however, two ml were used as the sample.

Determination of Base Exchange Capacity

(Bill Armon)

Base Exchange Capacity was determined on the column sections according to a procedure by Peech (1947), with slight modification. The 10 g sample was leached with ammonium acetate to remove exchangeable cations and to saturate the exchange complex with ammonia. The excess ammonia was removed by leaching with ethyl alcohol and the remaining, exchangeable ammonia removed and determined by distillation in a Kjeldahl apparatus.

Determination of Surface Area

(Joe Thomas)

The surface areas of the clays were determined by the B.E.T. method (Brunauer, Emmett, and Teller, 1938) using nitrogen as the adsorbate in a continuous flow system (Nelsen and Eggertsen, 1958).

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TECHNICAL REPORT DATA

(Please read Instructions on the reverse before completing)

1. REPORT NO. EPA-600/2-78-157	2.	3. RECIPIENT'S ACCESSION NO.

4. TITLE AND SUBTITLE ATTENUATION OF POLLUTANTS IN MUNICIPAL LANDFILL LEACHATE BY CLAY MINERALS	5. REPORT DATE August 1978 (Issuing Date) 6. PERFORMING ORGANIZATION CODE
7. AUTHOR(S) R. A. Griffin and N. F. Shimp	8. PERFORMING ORGANIZATION REPORT NO.
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12. SPONSORING AGENCY NAME AND ADDRESS Municipal Environmental Research Laboratory--Cin., OH Office of Research and Development U.S. Environmental Protection Agency Cincinnati, Ohio 45268	13. TYPE OF REPORT AND PERIOD COVERED Final Report 12/72 to 8/75 14. SPONSORING AGENCY CODE EPA/600/14

15. SUPPLEMENTARY NOTES

Project Officer: Mike H. Roulier (513) 684-7871

16. ABSTRACT

The first part of this project was a laboratory column study of attenuation of pollutants in municipal solid waste landfill leachate by mixtures of sand and calcium-saturated clays. Chloride, Na, and COD were relatively unattenuated by passage through the clay columns; K, NH_4, Mg, Si, and Fe were moderately attenuated; and the heavy metals Pb, Cd, Hg, and Zn were strongly attenuated even in columns with small amounts of clay. Calcium, B, and Mn were higher in column effluents than in the applied leachate. Precipitation was the principal attenuation mechanism for the heavy metals; cation exchange was responsible for any attenuation of the other elements. The clays, in order of increasing attenuation capacity, were Kaolinite, Illite, Montmorillonite.

The second part of the project involved batch studies of adsorption of Cr, Cu, Pb, Cd, Hg, and Zn by Montmorillonite and Kaolinite from water solutions and from landfill leachate. Adsorption of the cations Cr(III), Cu, Pb, Cd, Hg, and Zn increased with increasing pH; adsorption of the anions Cr(VI), As, and Se decreased with increasing pH. Above pH $\approx$ 5.3 precipitation of the cations was an important mechanism while adsorption was the principal mechanism for the anions over the pH range studied. Because adsorption/mobility of any element was affected by other solutes in leachate, adsorption information on one leachate may not be directly applied to predicting adsorption of the same element at the same concentration in another leachate.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS		b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group
Attenuation	Industrial Wastes	Pollution Hazard Rating	13B
*Transport Properties	Chromium	Chemical Oxygen Demand	
*Soil Chemistry	Iron	Groundwater Pollution	
Contaminants	Lead (Metal)	Clay Liners	
Arsenic	Mercury (Metal)	Municipal Solid Waste	
Cadmium	Selenium	Leachate	
Copper	Zinc	Ammonium (ion)	

18. DISTRIBUTION STATEMENT RELEASE TO PUBLIC	19. SECURITY CLASS *(This Report)* UNCLASSIFIED	21. NO. OF PAGES 157
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Physical properties governing groundwater flow in a glacial till catchment

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ABSTRACT

Hinton, M.J., Schiff, S.L. and English, M.C., 1993. Physical properties governing groundwater flow in a glacial till catchment. J. Hydrol., 142: 229–249.

Hydraulic conductivity, surface topography and sediment thickness influence the spatial and temporal pattern of groundwater flow and stream discharge in an unconfined aquifer in a 3.7 ha headwater catchment in central Ontario, Canada. Groundwater levels in the soils adjacent to the stream also significantly influence the magnitude and spatial distribution of stream discharge. Topographic convergence in plan and decreasing sediment thickness along flowpaths result in surface saturation and groundwater discharge. Hillslope gradients adjacent to discharge areas determine how fluctuating groundwater levels influence the extent of spatial variations in surface saturation and saturation within the soils. As a result of spatial differences in hillslope gradients, the spatial patterns of both groundwater and stream discharge change with fluctuating groundwater levels. Unsaturated sediments in upslope locations store water infiltrating during wet periods such that groundwater flow from upslope sediments maintains high groundwater levels near the stream and supplies baseflow during dry periods. The direction of horizontal groundwater flow in Harp 4-21 is not perpendicular to topographic contours so that subcatchment boundaries based on topographic divides differ by as much as 57% from their true subcatchment boundaries based on groundwater divides. Therefore, groundwater flow models based on surface topography may incorrectly predict the spatial pattern of stream discharge.

INTRODUCTION

Stream chemistry and the neutralization of acidic deposition is greatly influenced by the geological, hydrological and biological factors that control the movement of water through catchments. Groundwater discharge to streams and lakes is particularly important in acid sensitive areas such as the Canadian Shield where the alkalinity of groundwater is the main buffer of acidic deposition (Bottomley et al., 1986). Groundwater flow and discharge

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are also significant components of nutrient cycling in catchments (Likens et al., 1977).

From isotopic hydrograph separations, groundwater ('old' water) is found to be a significant component of streamflow in many glacial till catchments underlain by crystalline bedrock (Fritz et al., 1976; Sklash and Farvolden, 1979; Rodhe, 1981, 1984, 1987; Hooper and Shoemaker, 1986; Moore, 1989). Flowpaths to the stream can be inferred from hydrograph separations using 'in-stream' parameters such as isotopic ratios or chemical concentrations (e.g. Maulé and Stein, 1990; Wels et al., 1991a,b). However, these reconstructed flowpaths provide little information on the physical properties that govern hydrological processes and therefore hydrograph separations alone have little predictive power. To study and predict the interactions between groundwater and surface water, it is necessary to shift our investigations beyond the boundaries of the stream and also examine how the physical properties of a catchment influence the dominant hydrological processes in a catchment.

A considerable amount of research has focused on the physical properties that influence the location and size of surface saturated areas since these areas can generate much of the streamflow in humid regions by saturation overland flow. Following the definitions of Dunne et al. (1975), saturation overland flow includes both return flow, which is groundwater that has discharged to the ground surface, and direct precipitation onto saturated areas. In a theoretical study, Kirkby and Chorley (1967) suggested that surface saturation is most probable in locations of (1) slope convergence in plan view, (2) slope concavities in section and (3) thinning sediments. Extensive field studies by Dunne et al. (1975), Anderson and Burt (1978a, b) and Beven (1978) demonstrated that areas of topographic convergence (in plan) are preferential locations of surface saturation, are areas of convergent groundwater flow, and are areas that generally produce greater stream discharge per unit catchment area than divergent or straight hillslopes. Dunne et al. (1975) showed that the extent of surface saturated areas varies both seasonally and during storms, with the largest changes occurring along gentle topographic slopes adjacent to discharge areas. They also attempted to relate the extent of surface saturation to soil properties, vegetation and hydrologic parameters. Ward (1984) remarked that there is a lack of field evidence demonstrating that the thinning of sediments results in saturated overland flow. In a recent review of catchment hydrology, Goodrich and Woolhiser (1991) concluded that there is a need to improve the linkages between surface water and groundwater in catchment models. To improve such models it is first necessary to understand the properties and processes that govern interactions between surface water and groundwater.

The purpose of this paper is twofold. First, field data from a glacial till

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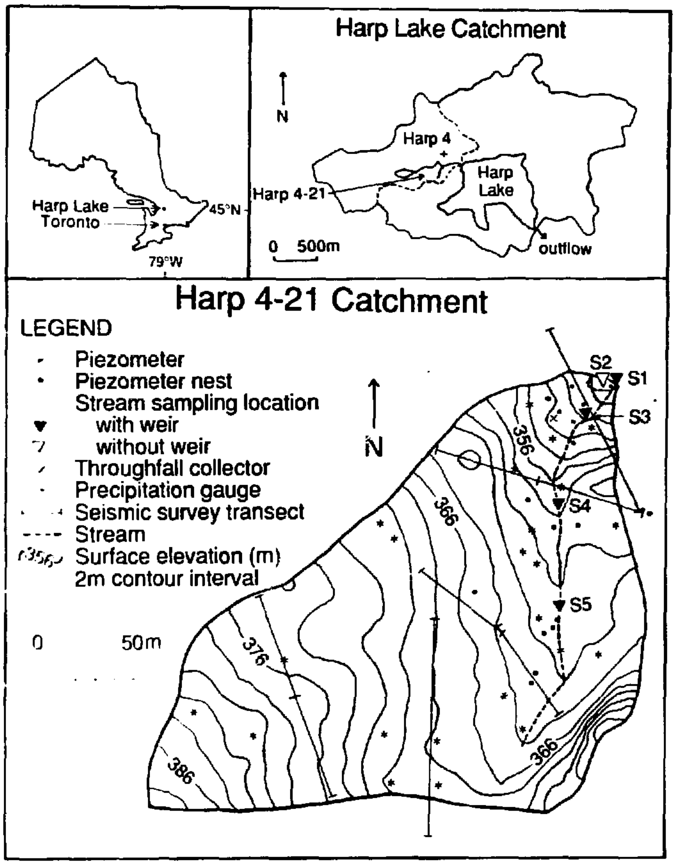

Fig. 1. Location and instrumentation of the Harp 4-21 catchment.

catchment are examined to determine the influence of hydraulic conductivity, surface topography and sediment thickness on groundwater flow and groundwater discharge. The second goal is to explain the observed spatial and temporal pattern of stream discharge based on our knowledge of the physical properties of the catchment.

Other physical properties of the catchment can also influence groundwater flowpaths and groundwater discharge, in particular macroporosity (Beven and Germann, 1982), vegetation and the unsaturated characteristics of the sediments. These additional properties are not specifically addressed in this paper. The influence of the unsaturated zone on streamflow generation is the subject of an ensuing study in Harp 4-21 (MacLean, 1992).

STUDY SITE

The study site is Harp 4-21, a small 3.7 ha headwater catchment located within the Harp Lake catchment in the Muskoka–Haliburton region of Ontario near the southern margin of the Canadian Shield (Fig. 1). The site is

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monitored by the Ontario Ministry of the Environment (MOE) as part of the Acid Precipitation In Ontario Study (APIOS) to determine the effects of acidic deposition on several lakes and streams in the region. Results of hydrological and hydrogeochemical studies of the Harp 4 and Harp 5 catchments are reported by LaZerte and Dillon (1984), Bottomley et al. (1984), Seip et al. (1985), Sklash (1986), Rustad et al. (1986), Devito et al. (1990), Schiff et al. (1990) and Wels et al. (1990, 1991a).

The mean annual precipitation for the region is 1033 mm (1976–1989) (MOE, unpublished data) of which approximately 26% falls as snow (Shibatanni, 1988). Stream discharge from Harp 4-21 is perennial and accounts for approximately 48% of the incoming precipitation (1989–1990). Approximately two-thirds of the annual streamflow occurs between 1 March and 30 June when groundwater levels are highest owing to spring melt and rainstorms (1989–1990). Although the precipitation for the region has an average pH of 4.3 (1982–1986) (Dillon et al., 1988), the mean pH and alkalinity of the Harp 4-21 stream are 6.8 and $184\,\mu\mathrm{Eq.l}^{-1}$, respectively (B. LaZerte, unpublished data, 1984–1990) indicating that this catchment effectively neutralizes the incoming acidic deposition despite the lack of carbonate minerals in the sediments and bedrock of the catchment (Aravena et al., 1992).

The catchment is underlain by metamorphic Canadian Shield bedrock composed predominantly of granitized biotite and hornblende gneiss (Jeffries and Snyder, 1983). Groundwater from a bedrock well has tritium (^{3}H) levels above cosmogenic background values indicating that the fractured bedrock surface does not form an impermeable boundary. However, low yields from nearby domestic wells drilled through up to 150 m of bedrock suggest that the permeability of the bedrock is low and the majority of groundwater flow occurs within the overburden (Wills, 1992).

The overburden in Harp 4-21 forms an unconfined aquifer consisting of glacial tills overlain by soils. The tills range in texture from loamy sands to sandy clay loams with less than 25% clay-sized particles (Dankevy, 1989). Coarser sediments from pebbles to boulders are frequently observed during drilling and excavating, and are visible at the ground surface. A horizontally discontinuous layer of compact till (densipan) approximately 0.2–0.5 m thick is often observed at the base of the soil profile at depths ranging from 0.5 to 1.2 m. This layer is most prominent in the upper half of the catchment. Densipan layers are common in many other catchments such as Hubbard Brook (Likens et al., 1977) and Sleepers River (Dunne and Black, 1970a, b). Compact tills are also found at greater depths (greater than 2.5 m) in portions of the upper catchment but there are insufficient data to determine the spatial extent and thickness of these layers. Water levels in piezometers screened above and below compacted layers do not indicate the presence of perched

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water tables so that the aquifer is assumed to be unconfined throughout the catchment. Therefore, in this paper groundwater flow specifically relates to saturated subsurface flow in the unconfined aquifer including both the tills and the soils.

Soils in Harp 4-21 belong to the podzolic order (Agriculture Canada Expert Committee on Soil Survey, 1987); the physical and chemical characteristics of soils in the Harp 4 catchment are summarized by Lozano et al. (1987). The soils are generally characterized by surface organic horizons (L, F and H), a dark-coloured humic-rich mineral horizon with many roots (Ah), a dark brownish and reddish iron-rich mineral horizon with many roots (Bhf or Bf) and occasionally a light grey mineral horizon with few roots (BC) above the parent material (C). Soils near the stream are frequently saturated and have thicker organic horizons and humic-rich A horizons.

Harp 4-21 is covered by a mixed hardwood forest dominated by *Acer saccharum* (sugar maple), *Betula alleghaniensis* (yellow birch), *populus spp.* (poplar species), *Abies balsamea* (balsam fir) and *Tsuga canadensis* (hemlock).

METHODS

A comprehensive topographic survey of the Harp 4-21 catchment was conducted using a Wild Leitz total station (Fig. 1). Slopes along the upper half of the stream are slightly concave, decreasing from as much as 17% in the uppermost catchment to 8% adjacent to the stream. Slopes draining to the lower half of the stream are slightly convex and steepen to as much as 30%. However, the base of these slopes are concave in the lowermost portion of the catchment where hillslope gradients decrease to approximately 15%.

The depth of sediments to bedrock was measured by seismic refraction along five 110 m transects using a OYO McSEIS 1500 Digital Seismograph and a geophone spacing of 5 m (Fig. 2) (Redpath, 1973). The sediments are thickest along the northwestern margin of the catchment where overburden thickness ranges from 11 to 15 m. The overburden gradually thins to less than 3 m in the northeastern portion of the catchment and to a bedrock outcrop in the southeastern portion of the catchment (Fig. 2).

A network of 47 stainless steel drive-point, 35 PVC and 7 ABS piezometers was established to measure hydraulic conductivities, horizontal and vertical gradients and to collect groundwater samples (Fig. 1). Piezometers were installed both in the soils and the tills and were screened over intervals ranging from 0.15 to 0.6 m. Some of the deeper 3.8 cm (1.5″) to 6.4 cm (2.5″) diameter PVC and ABS piezometers were installed using augering drill rigs. The 1.3 cm (0.5″) diameter drive-point piezometers were installed in vertical nests of two

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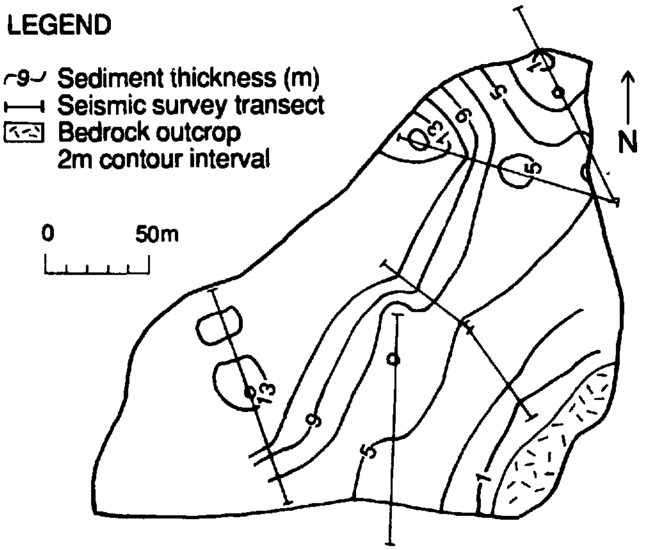

Fig. 2. Sediment thickness in Harp 4-21 as determined from seismic survey. Contours between geophysical transects are approximate.

to eight piezometers using a Cobra portable vibrating rock drill. This installation method was the most effective at penetrating compacted tills, although it did not allow for the collection of sediment samples. The hydraulic conductivity of the sediments was determined by slug and/or bail testing of the piezometers (Hvorslev, 1951). These results compare reasonably well (generally within one order of magnitude) to the hydraulic conductivities obtained using permeameter tests and grain size analyses (Dankevy, 1989).

Piezometric levels and stream discharge were monitored during 15 runoff events between March, 1989, and May, 1990. Baseflow conditions between storms were monitored regularly. Stream discharge was gauged at S1 using a 90° V-notch weir enclosed in a heated structure to maintain ice-free conditions (Fig. 1). A continuous record of stream discharge was obtained using a Leopold and Stevens (model A71) float-operated water level recorder and a stage–discharge relationship established from manual discharge measurements. Beginning in October 1989, stream discharge was measured manually from V-notch weirs installed at S3, S4 and S5 (Fig. 1). Discharge at S2 is assumed to equal the difference between discharge at S1 and S3, since the area contributing directly to S1 is small and little discharge from this area was observed. Piezometric levels were recorded manually using either an electronic water level tape or ping-pong ball floats in selected PVC piezometers (Gillham, 1984).

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RESULTS AND DISCUSSION

Hydraulic conductivity of the sediments

The glacial tills in Harp 4-21 have a large range of horizontal hydraulic conductivities from $2.6 \times 10^{-5}\,\mathrm{m\,s^{-1}}$ to $1.8 \times 10^{-9}\,\mathrm{m\,s^{-1}}$ ($n = 56$) with a geometric mean of $2.3 \times 10^{-7}\,\mathrm{m\,s^{-1}}$. Four drive point piezometers have conductivities of less than $1 \times 10^{-9}\,\mathrm{m\,s^{-1}}$. This range is typical for glacial tills and silty sands (Freeze and Cherry, 1979) and emphasizes the heterogeneous nature of the Harp 4-21 tills.

Thin layers of significantly different permeability are evident within the tills of Harp 4-21. For example, hydraulic conductivities in one piezometer nest vary by four orders of magnitude over a 0.3 m depth. The influence of layering on groundwater flow is dictated by the spatial extent of these layers. No distinct pattern of large-scale layering emerges from the slug and bail test results of the tills. Regressions between log-hydraulic conductivity and both piezometer screen elevation and screen depth below ground surface indicate that there are no catchment-scale patterns in hydraulic conductivity either horizontally or parallel to the ground surface ($r^2 = 0.06$ and 0.03, respectively). If there is any continuous layering, it is either at a scale smaller than the distance between piezometers or it is neither horizontal nor parallel to the ground surface. Variable stratigraphy between nearby excavations and boreholes suggests that layering is only continuous over distances of the order of 5 m. The resulting groundwater flowpaths in the till are probably tortuous and difficult to define precisely. Owing to the numerous heterogeneities and the difficulity of drilling into the tills, the measurement of hydraulic conductivity is not a practical way of obtaining detailed information concerning the continuity of layering within the tills.

The hydraulic conductivities of the soils vary over a much smaller range from $3.0 \times 10^{-5}\,\mathrm{m\,s^{-1}}$ to $3.7 \times 10^{-7}\,\mathrm{m\,s^{-1}}$ ($n = 13$) with a geometric mean of $2.7 \times 10^{-6}\,\mathrm{m\,s^{-1}}$. The absence of horizons of low hydraulic conductivity should result in higher effective hydraulic conductivities in the soils. Therefore, the flux of groundwater discharge from the catchment should increase substantially as groundwater levels rise within the soil. Furthermore, the groundwater levels within the soils should determine the relative importance of groundwater flow from the soils and tills. There are insufficient data in Harp 4-21 to examine the differences in hydraulic conductivities between the soil horizons. However, increases in bulk density and decreases in root density with depth (Lozano et al., 1987) suggest that hydraulic conductivities decrease with depth within the soil profile.

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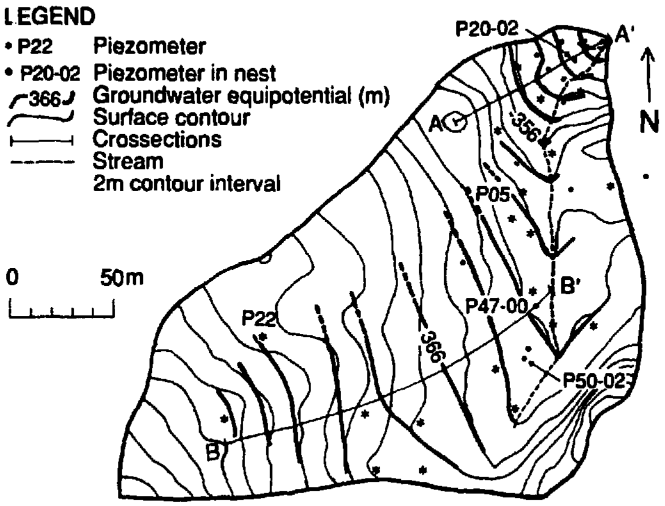

Fig. 3. Groundwater equipotentials in Harp 4-21 following spring melt on 1 May 1989. Dashed lines indicate approximate locations of equipotentials where the piezometer network is sparse. Surface elevations are also shown. Cross-sections A–A′ and B–B′ are shown in Fig. 5.

Surface topography

Surface topography is generally assumed to indicate the horizontal direction of groundwater flow in local groundwater flow systems. Where groundwater levels are very near or at the ground surface, the maximum horizontal hydraulic gradient is directed parallel to the maximum surface slope. Assuming horizontally homogeneous and isotropic hydraulic conductivities, groundwater flow is perpendicular to topographic contours. In Harp 4-21, topography indicates the direction of groundwater flow adjacent to the stream and in the lowermost portion of the catchment where the water table is at the ground surface and the equipotentials are parallel to the topographic contours (Fig. 3). Topographic convergence in the lowermost portion of the catchment results in horizontal convergence of groundwater flow and discharge to the ground surface such that surface flow is maintained at S2 throughout the year.

In the middle and upper portions of the Harp 4-21 catchment, groundwater equipotentials are not parallel to topographic contours indicating that groundwater flow is not parallel to the steepest topographic slope (Fig. 3). For groundwater levels to fluctuate without changing the direction of flow, groundwater levels for all locations at a given elevation must fluctuate simultaneously and by the same amount. Many factors influence the spatial pattern of groundwater recharge and discharge such that groundwater levels at a given elevation in Harp 4-21 fluctuate neither simultaneously nor equally. Therefore, the direction of groundwater flow varies with groundwater level

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fluctuations. In general, the direction of groundwater flow is not perpendicular to surface topography wherever the depth to the groundwater table changes along any given topographic contour. This phenomenon is not unique to Harp 4-21. It can be shown from patterns of surface saturation (e.g. Dunne et al., 1975) that in portions of many other catchments, the direction of groundwater flow differs from the steepest topographic slope (Hinton, unpublished notes, 1992).

The discrepancy between the directions of groundwater flow and steepest topographic slope has significant implications for interpreting hydrological data from catchments and for modelling catchment hydrology. Catchment boundaries are generally defined using surface topography based on the assumption that groundwater flow is perpendicular to the topographic contours. However to identify the contributing area of a catchment correctly, it is necessary to determine catchment boundaries from a map of groundwater equipotentials (Fig. 3). Slight deviations in the direction of groundwater flow from the direction of steepest slope can result in substantial errors when determining the contributing area of a catchment (Fig. 4, Table 1). Based on topographic divides, the S2 and S3 subcatchment areas are underestimated by 57 and 13%, respectively, whereas subcatchments for S4 and S5 are overestimated by 41 and 23%, respectively. These results emphasize the need to identify locations where groundwater flow does not conform to topographic contours. Furthermore, if the direction of groundwater flow changes with fluctuating groundwater levels, then the locations of catchment boundaries will vary such that the contributing area of catchment may also change with groundwater level fluctuations. Digital elevation models (DEM) are being used to automate the subdivision of catchments to provide spatially distributed hydrologic models (Moore and Grayson, 1991). In catchments where subsurface flow is significant, incorrect subcatchment areas and groundwater flow directions may result in errors in the predicted spatial distribution of stream discharge.

The magnitude of the topographic slope influences the extent of surface saturated areas and their expansion and contraction with fluctuating groundwater levels. As groundwater levels increase, a much larger area saturates to the surface along gentle slopes (Fig. 5(B)) than along steeper slopes (Fig. 5(A)). Since hillslopes are more gentle adjacent to the upper portion of the Harp 4-21 stream than in the steeper lower catchment, surface saturated areas expand much more adjacent to the upper stream than in the lower catchment (Figs. 5 and 6). Similarly, groundwater levels rising from the tills into the more permeable soils result in a greater spatial extent of saturation within the soils along the gentle hillslopes adjacent to the upper stream than along the steeper slopes in the lower catchment. As a result of these spatial changes in surface

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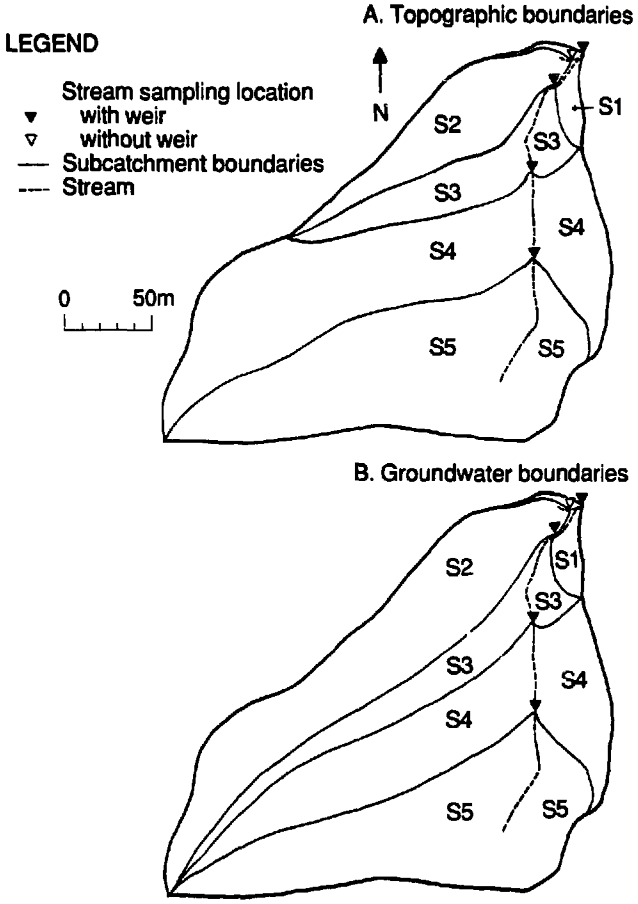

Fig. 4. Approximate subcatchment boundaries determined from (A) surface topography (Fig. 1) and (B) groundwater equipotentials on 1 May, 1989 (Fig. 3). Subcatchment areas are shown in Table 1.

TABLE 1

Areas contributing directly to each subcatchment as determined from surface topography (A) and groundwater equipotentials (B) shown in Fig. 4

Subcatchment	A Topographic area (m^2)	B Groundwater area (m^2)	Error (A-B)/B (%)
S1	790	860	−8
S2	4570	10720	−57
S3	3860	4420	−13
S4	14170	10050	41
S5	14090	11430	23

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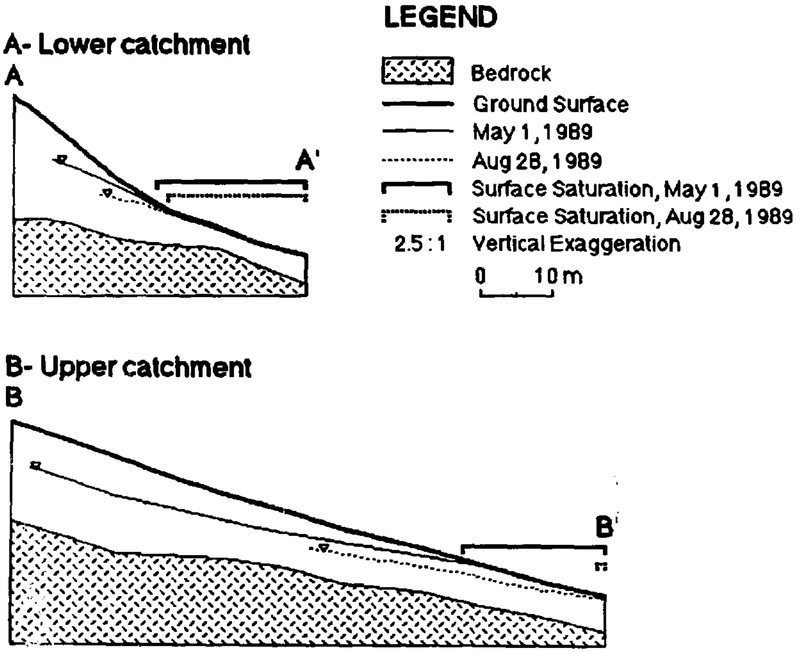

Fig. 5. Cross-sections indicating the change in saturated areas resulting from groundwater level fluctuations. More gentle topographic slopes adjacent to the stream in the upper catchment (B) result in larger seasonal changes in the area of surface saturation than in the lower catchment (A). Cross-section locations are shown in Fig. 3.

and soil saturation, the spatial pattern of stream discharge and water flowpaths is expected to change significantly with fluctuating groundwater levels.

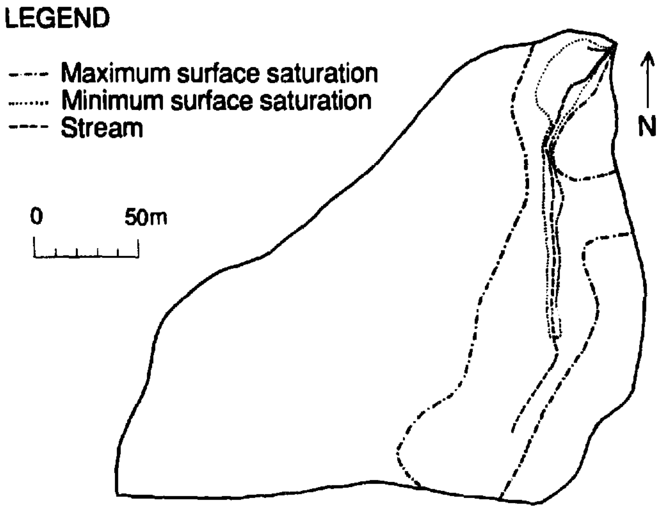

Fig. 6. Approximate maximum and minimum extent of surface saturation in Harp 4-21 in 1989. Surface saturation was determined from visual observations and groundwater level measurements. Small unsaturated hummocks within the areas are ignored.

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Sediment thickness

Assuming that there is no horizontal convergence or divergence of groundwater flow, decreasing sediment thickness along a flowpath requires a proportional increase in the horizontal hydraulic gradient or conductivity at the point of thinning to transmit the flux of groundwater from upslope. Where groundwater levels are at the surface, thinning sediments can result in groundwater discharge since the horizontal hydraulic gradients are limited by the ground surface and cannot increase to transmit the flux of groundwater from upslope. Decreasing sediment thickness along flowpaths (Fig. 5) can therefore influence the locations and extent of groundwater discharge to the surface. In the lowermost portion of the catchment, decreasing sediment thickness and horizontal convergence of groundwater both contribute to groundwater discharge. Between elevations 356 and 348 m in the S2 subcatchment (Fig. 3), the dimensions of the saturated zone perpendicular to the horizontal direction of flow decrease from 42 m wide and 6.2 m deep to 14 m wide and 2.3 m deep indicating that the relative importance of decreasing sediment thickness and horizontal convergence is approximately equal.

Along the upper portion of the stream where horizontal groundwater convergence is minimal, locations of decreasing sediment thickness (Fig. 2) correspond to the locations of surface saturation (Fig. 6) suggesting that changes in sediment thickness are responsible for groundwater discharge. However, it is incorrect to attribute all groundwater discharge to decreasing sediment thickness along a flowpath since other factors can contribute to groundwater discharge. For example, a symmetrical flow boundary at the base of a hillslope can result in groundwater discharge regardless of changes in sediment thickness.

The presence of thick unsaturated sediments in the upslope portions of Harp 4-21 significantly influences the catchment's hydrological regime. Individual storms have little influence on groundwater levels in these areas since there is generally considerable storage available within the unsaturated zone. However, during spring melt there is sufficient infiltration to replenish much of this storage and cause a large increase in groundwater levels (Fig. 7). Since groundwater levels decline slowly, most of the infiltration into these thick unsaturated tills has little direct influence on stormflow but has a significant effect on baseflow. Therefore, the thick unsaturated sediments have the effect of reducing the effective runoff (the proportion of runoff to precipitation) from storms and increasing the quantity of baseflow during the remainder of the year. Groundwater recharging to these upslope sediments gradually flows down-gradient such that the range of seasonal groundwater level fluctuations decreases towards the stream (Fig. 7). Consequently, soils

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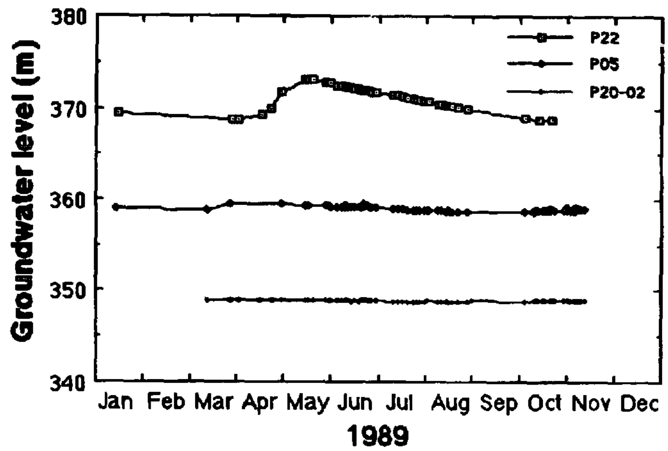

Fig. 7. Seasonal groundwater fluctuations in three slope positions. The magnitude of groundwater level fluctuations is greatest in the upper catchment (P22) where the thickness of unsaturated sediments is greatest and decreases towards the stream (P05 and P20-02). Piezometer locations are shown in Fig. 3.

adjacent to the stream remain nearly saturated most of the year and baseflow is sustained during dry periods. The amount of available storage in the unsaturated sediments is not strictly dependent on sediment thickness but is also determined by the porosity and the moisture content of the sediments. The moisture content and the thickness of unsaturated sediments are, in turn, influenced by many other factors such as surface topography, the hydraulic properties of the unsaturated sediments, evapotranspiration and the configuration of the groundwater table.

Although hydraulic conductivity, surface topography and sediment thickness are discussed separately, the fluxes, flowpaths and discharge areas of groundwater flow are determined by the interactions among various physical properties. Even within a catchment as small as Harp 4-21, knowledge of only the physical properties is insufficient to predict their effect on stream discharge since the relative importance of these properties varies both spatially and temporally with fluctuating groundwater levels. Therefore, it is necessary to specify the range of hydrologic conditions for which the possible effects of given physical properties influence stream discharge.

Spatial and temporal pattern of stream discharge

Fluctuations in groundwater levels significantly influence stream discharge in Harp 4-21. Stream discharge remains low over a large range of groundwater levels and then increases significantly for small increases in groundwater levels (Fig. 8). These large changes in stream discharge suggest that the relative importance of different physical properties, hydrological processes and pathways change as groundwater levels fluctuate. The rapid increase in stream

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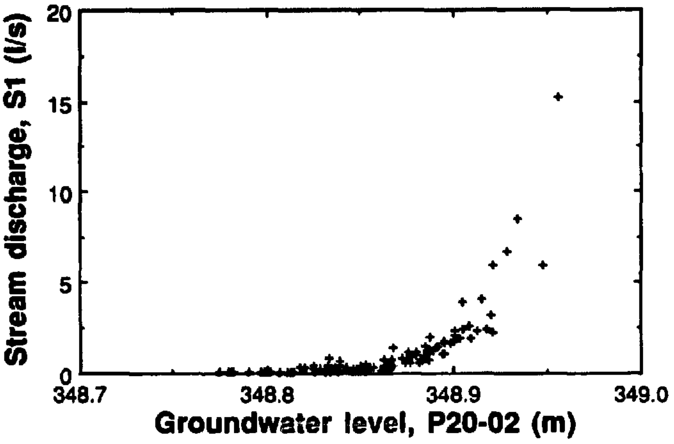

Fig. 8. Stream discharge at S1 as a function of piezometric levels adjacent to the lower portion of the stream (P20-02, 0.69 m depth). Similar results are found for other piezometers in proximity of the stream (for example P05). Piezometer locations are shown in Fig. 3.

discharge for high groundwater levels can be attributed to the higher effective hydraulic conductivities of the soils relative to the underlying tills and to the gentle topographic slopes adjacent to discharge areas. As groundwater levels increase, there is an increase in the saturated thickness within the soils and a consequent increase in flow within the soils. Furthermore, preferential pathways such as macropores in the upper soil horizons may only become significant flowpaths when these horizons become saturated by high groundwater levels. As previously discussed, increasing groundwater levels also result in a large expansion of discharge areas along gentle slopes and an increase in saturated overland flow.

Fluctuations in groundwater levels also significantly influence the spatial distribution of stream discharge. The average proportion of discharge originating upstream of S4 increases from 43% when groundwater levels are low to moderate in the autumn to 69% when groundwater levels are highest in the spring (Table 2). These changes are related to the differences in topographic slope adjacent in the upper and lower portions of the stream. As groundwater levels rise, upstream areas of soil and surface saturation expand substantially owing to the gentle topographic slope (Figs. 5(B) and 6) and the relative importance of upstream sources of stream discharge increases as a result of increasing groundwater discharge and saturation overland flow (Fig. 9). Since the expansion of saturated areas in the lower catchment is limited by steeper slopes (Fig. 5(A)), the resulting increase in discharge is smaller so that the relative proportion of discharge from the lower catchment decreases as groundwater levels increase.

Changes in the spatial distribution of stream discharge during storms are similar to the seasonal changes since increasing groundwater levels adjacent

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TABLE 2

Seasonal change in the spatial pattern of stream discharge

Location	Percentage of the stream discharge at S1	
	October–November 1989	April 1990
S5	7 ± 2[a]	22 ± 2[a]
S4	43 ± 7	69 ± 5
S3	61 ± 6	77 ± 3
S2	39 ± 6	23 ± 3
S1	100	100

[a] The proportion of discharge at S5 is underestimated since some stream discharge flows along the surface around the S5 weir.

Groundwater levels were low to moderate in October and November 1989, and high in April 1990. Stream discharge at S2 is determined as the difference between discharge at S1 and S3. Stream gauging locations are shown in Fig. 1.

to the upper stream result in a relative increase in upstream discharge during storms. Although there are differences in the stream response between storms, there is a basic pattern common to several storms. During the initial portion of the storm, a greater proportion of stream discharge originates in the lowermost portion of the catchment where groundwater levels are close to or at the ground surface and saturation overland flow occurs readily (Fig. 10). Along the upper portion of the stream, groundwater levels respond more slowly with increasing distance from the stream, resulting in a more gradual increase and a later peak in stream discharge at S4. Consequently, the

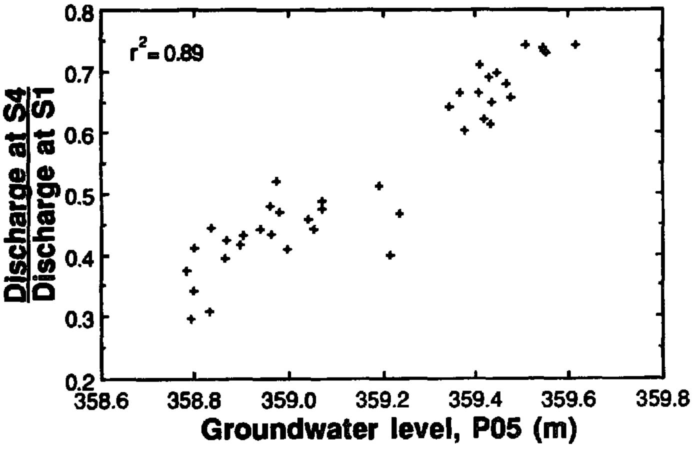

Fig. 9. The proportion of stream discharge at S4 relative to S1 as a function of piezometric levels in P05 near the upper portion of the stream. Data collected during storms and at baseflow are included. The locations of stream gauging site S4 and piezometer P05 are shown in Figs. 1 and 3, respectively.

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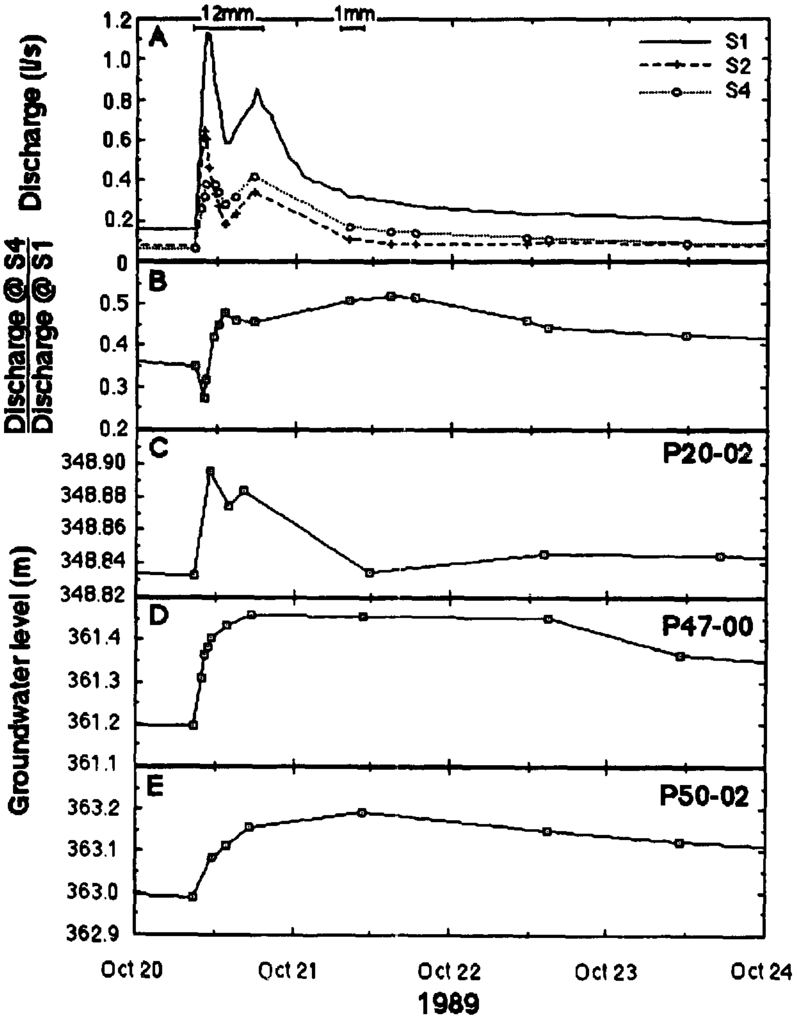

Fig. 10. Changes in stream discharge (A), the proportion of stream discharge at S4 relative to S1 (B) and piezometric levels along the lower (C) and upper (D–E) portions of the stream during the rainstorm on 20 October, 1989. Piezometer and stream gauging locations are shown in Figs. 1 and 3.

proportion of discharge at S4 increases throughout the remainder of the storm, and peaks following the storm when groundwater levels in the upper catchment are peaking and groundwater levels in the lowermost catchment have declined. The proportion of discharge at S4 then gradually decreases as water levels along the upper portion of the stream decrease. Similar spatial changes in the proportion of stream discharge are observed during spring melt episodes. However, the magnitude of these changes are much smaller than in the autumn since the relative increase in discharge from baseflow to peak flow is smaller and since further expansion of discharge areas adjacent to the upper portion of the stream produces a smaller relative increase in the upstream discharge area.

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The similarities between the seasonal and storm patterns of stream discharge suggest that examination of the seasonal changes in hydrologic pathways could be helpful for understanding some of the changes in flow pathways that occur as a result of groundwater level fluctuations during storms. However, caution must be used when making such comparisons since the pattern and degree of saturation in the catchment change prior to each storm and may significantly influence the flow pathways and stream response for each storm.

CONCLUSIONS

Groundwater flow plays a significant role in controlling streamflow in Harp 4-21. Groundwater flow contributes directly to stream discharge and governs the formation of discharge areas that influence both groundwater and event water contributions by saturation overland flow. To understand how groundwater flow influences streamflow generation and water flowpaths in glacial till catchments it is useful to study the physical properties that control groundwater flow.

The combined effects of surface topography, sediment thickness and hydraulic conductivity within the catchment largely control the direction of groundwater flow and the locations and extent of groundwater discharge areas in Harp 4-21. No single physical property of the catchment is sufficient to explain the pattern of groundwater flow and flow pathways completely. It is also important to recognize that the relative importance of these physical properties changes both spatially and temporally as a result of fluctuating groundwater levels.

Although the role of sediment thickness on streamflow generation is frequently ignored, results from Harp 4-21 show that decreasing sediment thickness may be as important as convergent topography in producing surface saturation and groundwater discharge. Furthermore, the pattern of sediment thickness within the catchment also influences its hydrological regime. Much of the infiltration during wet periods is stored within the thick unsaturated sediments in the upslope portions of Harp 4-21. Infiltration during spring melt causes large increases in groundwater levels which sustains baseflow during dry periods. Very different hydrological regimes are found in nearby catchments where the streams are ephemeral and the lack of available storage in the thin sediments results in higher effective runoff during spring melt (e.g. Wels et al., 1991b). The influence of sediment thickness on groundwater flow and stream discharge also depends on other factors such as the hydraulic conductivity, surface topography and the configuration of the water table. Consequently, it is useful to consider the importance of these factors to predict

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how sediment thickness will affect groundwater flow and streamflow in a particular catchment. If the role of sediment thickness is to be examined in larger catchments, then there is a need to develop more practical geophysical methods that can be used to determine sediment thickness at many locations over larger areas.

The hydraulic conductivities of the tills do not show any large-scale pattern of layering despite the presence of compact layers in boreholes and excavations. The lack of low hydraulic conductivities within the soil suggests that the effective permeability of the soils is greater than that of the tills so that groundwater flow from the catchment is greatly dependent on water levels in the soils. The extremely heterogeneous nature of the tills and the difficulties of instrumenting the tills does not allow a detailed description of its hydraulic properties from piezometer tests. For applications in which detailed knowledge of the hydraulic properties is not required, instrumentation and methods that provide larger-scale measurements of the effective hydraulic properties of the tills may be preferable.

Surface topography indicates the direction of groundwater flow where groundwater levels are very close to the ground surface. However, it is incorrect to assume 'a priori' that the direction of groundwater flow is perpendicular to surface contours everywhere in a catchment. In Harp 4-21, subcatchment divides based on topographic contours and groundwater equipotentials are substantially different. Furthermore, spatial differences in groundwater level fluctuations indicate that the locations of subcatchment boundaries change with fluctuating groundwater levels. Hydrological models based on DEMs would be best applied if the DEM was based on groundwater equipotentials rather than surface topography. However, data for groundwater equipotentials are rarely available in most catchments such that it is necessary to use topography to select catchment boundaries, even though this can result in significant errors in the predicted spatial pattern of stream discharge.

Groundwater levels significantly influence the spatial pattern of stream discharge and the relative importance of different flowpaths in Harp 4-21. Consequently, fluctuating groundwater levels may have a significant impact on stream chemistry. Knowledge of the groundwater levels in a catchment prior to a storm may be useful for determining the stream response to a storm and for identifying differences in the dominant flowpaths during storms. To model the effect of such spatial differences in hydrologic processes using hydrological and hydrochemical models would require distributed models such as TOPMODEL (Beven and Kirkby, 1979) and DEM based models (Moore and Grayson, 1991) since lumped models such as Birkenes (Christopherson et al., 1982) do not account for spatial differences in flow processes.

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The heterogeneous tills, variable sediment thickness and variable hillslope gradients found in Harp 4-21 are typical of many glacial till catchments in the Canadian Shield. Despite similarities between many of these catchments, their hydrological responses often differ. From a simplistic understanding of hydraulic conductivity, surface topography and depth of sediments in Harp 4-21, it has been possible to explain some of the observed patterns of groundwater flow and stream discharge in a complex groundwater flow system. Therefore, these properties may also be useful for predicting the differences in hydrological processes between catchments.

ACKNOWLEDGEMENTS

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Fractured Bedrock Aquifer Hydrogeologic Characterization for a Bioaugmentation Pilot Study

Paul Jeffers and Veryl Wittig, GeoSyntec Consultants

Abstract

A hydrogeologic characterization was performed to evaluate the nature of groundwater flow in an alluvial and underlying fractured bedrock aquifer in the area between an unlined, inactive landfill and a river in southern California. The hydrogeologic characterization was used to enhance the site conceptual model for the site, and to design a bioaugmentation pilot test to evaluate the use of enhanced in-situ bioremediation (EISB) to treat chlorinated VOCs, primarily PCE, TCE, 1,1-DCA, cis-1,2-DCE, and VC in the fractured rock aquifer beneath the site.

The pilot test area (PTA) is characterized by a thin veneer of alluvium overlying fractured tonalite (bedrock). Groundwater beneath the site is unconfined within the alluvium and fractured bedrock and flows from the landfill and through the PTA toward the river. Chlorinated VOCs have been detected in shallow, intermediate and deep monitor wells installed in the PTA at depths of up to 300 feet below ground surface (bgs). To date, VOCs have not been detected in surface water or shallow groundwater samples along the northern river margin.

Using lineament analyses and geophysical surveys, subsurface bedrock fracture zones and potential zones of higher groundwater flow rates were identified. Three multi-level monitoring well clusters were installed in the PTA in areas believed to be within significant fracture zones. The upgradient and intermediate monitoring clusters consist of a shallow well screened in the alluvium, an intermediate well screened in the upper highly fractured bedrock aquifer, and a deep well screened in the lower fresh, slightly fractured bedrock aquifer. The downgradient monitoring cluster includes an additional deep bedrock well. Downhole geophysical logging conducted in select boreholes prior to well construction included caliper, electrical logging, acoustic televiewer (ATV), and borehole image processing system (BIPS) logging. Additional testing performed on selected borings included thermal flow meter testing and hydrophysics.

A 48-hour continuous rate pumping test and a 72-hour recovery test were performed to evaluate the hydraulic connection between well clusters and different screened intervals within the PTA. Aquifer test analyses indicated that hydraulic conductivities (K) ranged from 25 to 40 feet per day (ft/day) in the fractured rock aquifer, and 13 to 17 ft/day in the alluvium. However, due to the low effective porosity of the fractured rock aquifer, groundwater velocities as high as 40 ft/day per day were estimated, compared to velocities of less than 2 ft/day for the alluvium.

A qualitative dye tracer study using three distinct dyes was performed in the PTA to evaluate hydraulic communication between the three clusters and intervals under passive, non-pumping conditions. Results of the tracer study confirmed that groundwater within the fractured rock aquifer was moving rapidly under passive conditions, and confirmed communication between the upgradient and downgradient wells within the pilot test area. The hydrogeologic characterization demonstrated that sufficient hydraulic communication is present within the PTA and that plans for a passive EISB pilot test should proceed.

Background

The site consists of a Class III landfill that was operated between 1960 and 1978. The landfill was constructed without a liner, leachate collection and removal system, or leak detection system. A landfill gas extraction system was installed in 1996. Groundwater monitoring initiated at the site in 1990 identified volatile organic compounds (VOCs) and elevated concentrations of chloride and total dissolved solids. The landfill is located in a southerly trending canyon that drains to an ephemeral river. The river drains into a drinking water reservoir approximately 2 ½ miles southwest of the landfill. The potential for discharge of landfill-related constituents to the river is of paramount importance and therefore the focus of the hydrogeologic characterization. The

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hydrogeologic characterization will be used to design a bioaugmentation pilot test to evaluate the use of enhanced in-situ bioremediation (EISB) to treat chlorinated VOCs in the fractured rock aquifer beneath the site.

Geologic and Hydrogeologic Setting

The landfill is located within the Peninsular Range geomorphic province of southern California near the western margin of the southern California batholith. The southern California batholith is comprised primarily of Jurassic- to Cretaceous-age igneous rocks, ranging in composition from gabbro to granite, which were intruded into Jurassic-age metavolcanic and metasedimentary rocks (IT, 1999). Compositionally, bedrock beneath the site consists of tonalite with isolated exposures of Jurassic-age metamorphic rocks. The upper 30 to 60 feet of the site consist of grus, *in situ*, highly weathered bedrock. Recent alluvial deposits consisting of silty sands and gravels form a thin veneer over the underlying bedrock in the southern portion of the site along the northern margin of the river.

Surface features and lineaments mapped in the vicinity of the site generally trend N45°E and N50°W and are typically composed of high angle fractures (IT, 1999). Fractures observed at the surface appear to be randomly oriented and horizontally discontinuous.

Groundwater at the site is unconfined and occurs within the porous media of the alluvium/grus and in the fractures of the competent granitic bedrock. Groundwater flow within the alluvium/grus is controlled by the river system and mimics the direction of flow of the river (southwest). Groundwater within the fractured bedrock flows through fractures at depth and follows the preferential orientation of these fractures towards the river (Figure 1). Once the groundwater reaches the fracture set that defines the river valley, the groundwater at depth follows the direction of the river. Groundwater in the PTA between the landfill and the river is impacted with tetrachloroethene (PCE), trichloroethene (TCE), 1,1-dichloroethane (1,1-DCA), cis-1,2,-dichloroethene (cis-1,2-DCE), and vinyl chloride in shallow, intermediate and deep monitor wells at depths of up to 300 feet bgs. The main pathway for landfill-related constituent migration from the site is through the fractured bedrock. To date, VOCs have not been detected in surface water or shallow groundwater samples along the northern river margin.

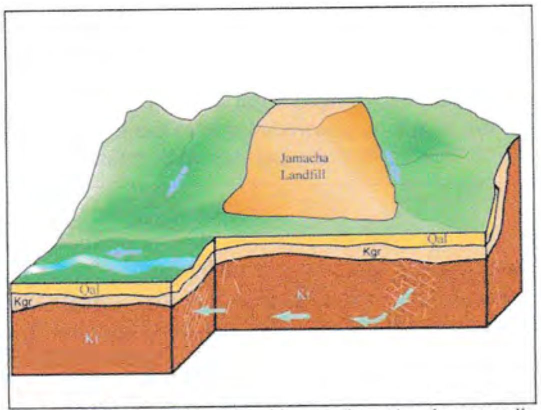

Figure 1 - The landfill is situated in a northwest/southeast trending fracture canyon. The primary pathway for offsite migration of landfill constituents is through the fractured bedrock.

Surface Geophysical Surveys

Lineament analyses and geophysical surveys were performed to identify subsurface bedrock fracture zones and potential zones of higher groundwater flow rates. Geophysical surveys conducted include very low frequency (VLF), electromagnetic induction (EMI), and STING Resistivity Surveys (Figure 2).

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Two VLF and EMI geophysical profiles were performed to identify the primary fracture trends and to assist in the siting of downgradient monitor wells for the pilot test area (PTA). Optimum coupling with a VLF transmitting station was achieved by orienting the survey perpendicular to a subsurface structure and using a transmitter station located perpendicular to the survey line. Attempts were made to align the survey lines at right angles to the northwest- and northeast-striking structures identified during geologic field mapping. The actual survey line orientations were adjusted in the field based on accessibility and to avoid interference from cultural features such as overhead power lines, fences, and underground utilities. The EMI anomalies correlated well with each other, indicating fractures striking approximately N85°W. The VLF survey was influenced by one cultural feature, a power line that produced significant noise. The results indicated the presence of two geophysical anomalies, distinguished by total field peaks and in-phase signal crossovers. At the time the survey was conducted, one of these anomalies appeared to coincide with one of the site paleodrainages; however, following corrections to the survey line locations on the site base map, neither anomaly coincided with the paleodrainages underlying the landfill.

Figure 2 - EMI surveys identified anomalies oriented N85°W which correlate to high-angle joints in outcrops west of the site. VLF surveys identified several anomalies with apparent orientations of N55°E.

A STING resistivity survey was conducted to further characterize the fracture network along the toe of the landfill (Figure 3). The STING resistivity survey uses regularly spaced electrodes to measure the resistance of subsurface materials to identify areas of high and low resistivity which can be used to interpret the locations of fracture zones. For instance, a water-filled fracture or fracture zone surrounded by unfractured rock shows up as a low-resistivity or conductive anomaly. The resistivity survey was performed over a length of 900 feet and penetrated to a depth of 200 feet. The results of the resistivity survey are somewhat masked by local cultural interference effects, however, the survey indicated a significant conductive anomaly that correlates to the main fracture canyon.

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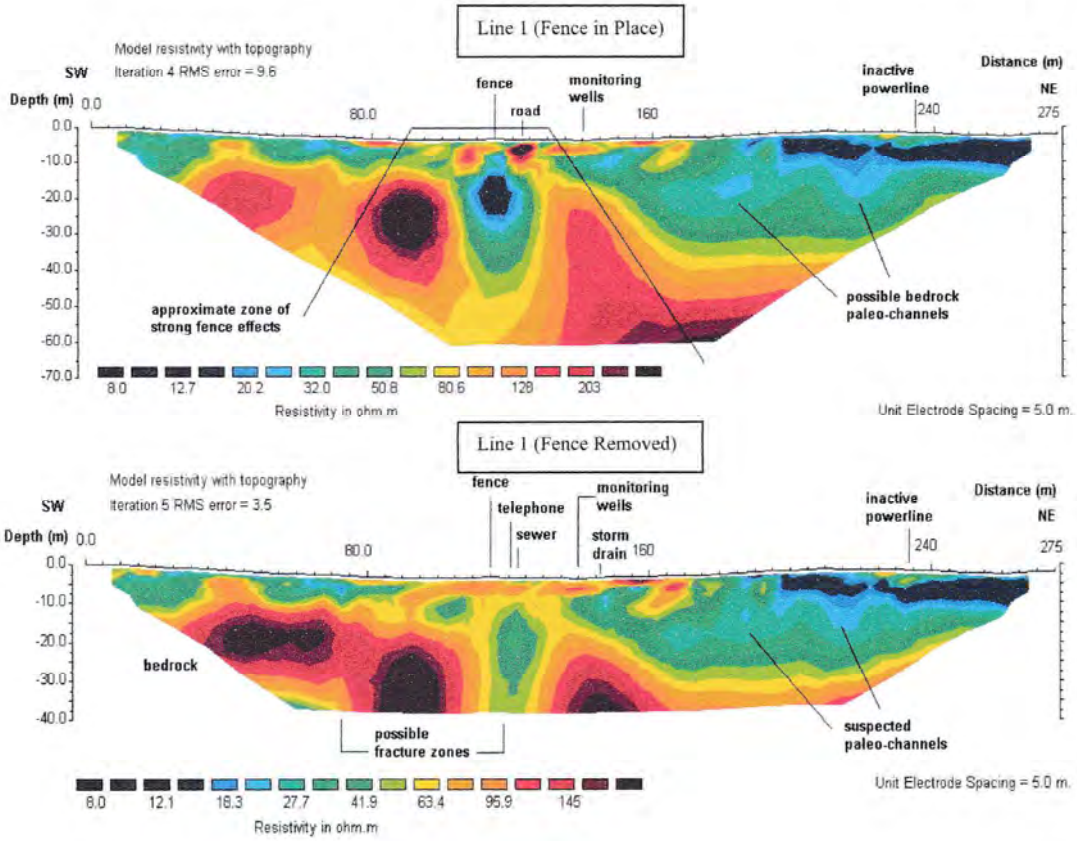

Figure 3 - The STING Resistivity survey identified a significant anomaly which appears to correlate with the main fracture set which forms the canyon containing the landfill.

Borehole Geophysics

Downhole geophysical logging conducted in select boreholes prior to well construction included caliper, electrical logging, acoustic televiewer (ATV), and borehole image processing system (BIPS) logging (Figure 4). Additional testing performed on selected borings included thermal flow meter testing and hydrophysics. Based on data collected from the geophysical logs, the contact between the grus and competent granite appeared to be gradational, occurring from 76 to 78 feet bgs in JAGW-10A, from approximately 82 to 84 feet in JAGW-10D, and at approximately 69 feet in JAGW-10E. The boreholes appeared moderately fractured from 80 to 100 feet bgs and from 115 to 125 feet bgs. JAGW-10D is also moderately fractured from 133 to 143 feet bgs. JAGW-10E is highly fractured from 130 to 260 feet bgs and again from 270 to the bottom of the borehole. Fracture data from the geophysical logs suggested shallow, intermediate, and deep fracture zones that appeared to be hydraulically connected. When plotted on a rose diagram, the fracture orientation data collected from the three borings listed indicate three distinct fracture orientations including N75°E, N30°W, and N45°E with dips ranging from 35 to 75 degrees. The dominant strike and dip of fractures identified using BIPS logging is N30°W, with a dip of 55 degrees to the southwest.

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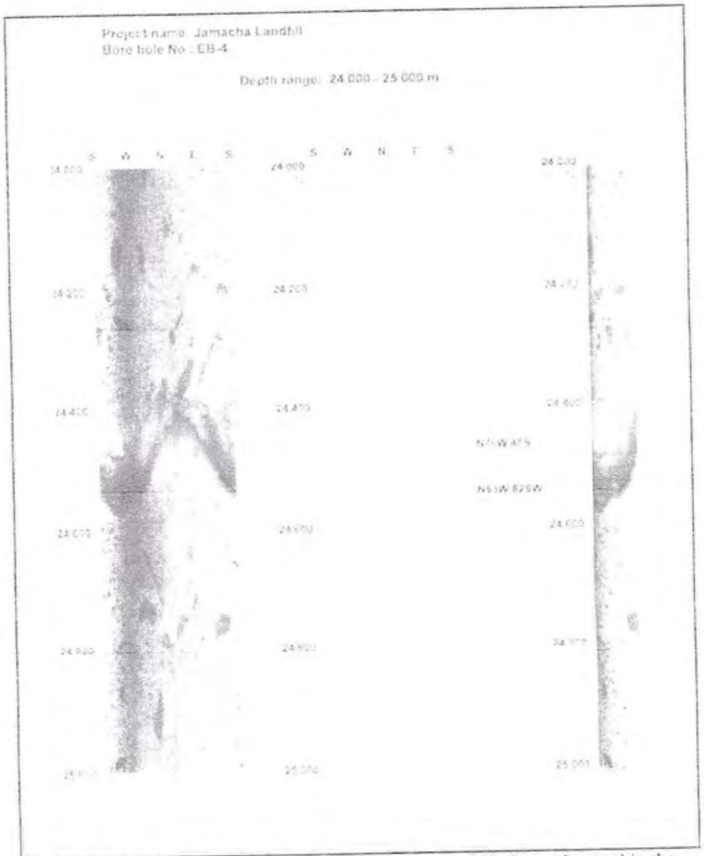

Figure 4 - BIPS logs were performed for several bedrock borings advanced in the study area to identify orientation and continuity between boreholes.

Pilot Test Area (PTA)

The PTA is located in the downgradient direction of the landfill in an area between the landfill and the river. The PTA consists of shallow, intermediate and deep groundwater monitor wells arranged in three separate clusters located 100 feet apart (Figure 5). The upgradient (JAEB-4, JAEB-5, and JAEB-6) and intermediate (JAPW-1, JAPW-1A, and JAPW-1B) monitoring clusters consist of a shallow well screened in the alluvium, an intermediate well screened in the upper highly fractured bedrock aquifer, and a deep well screened in the lower, slightly fractured bedrock aquifer. The downgradient (JAGW-10, JAGW-10A, JAGW-10D, and JAGW-10E) monitoring cluster includes an additional deep bedrock monitor well. The JAGW-10 well cluster is located within the main fracture canyon. The well cluster was designed to be utilized as the downgradient monitoring point within the PTA. Monitor wells JAGW-10, JAGW-10A, JAGW-10D, and JAGW-10E were installed to depths of 85, 94, 150, and 300 feet bgs, respectively. Three upgradient injection wells (JAEB-4, JAEB-5, and JAEB-6) were installed in the primary fracture canyon 100 feet upgradient of the JAGW-10 well cluster. The major fracture set was identified through lineament analysis, surface geophysics, and the examination of downhole geophysics from monitor wells in the JAGW-10 cluster. The location of these borings was selected to assist in discerning the hydrogeologic properties of this potential pathway of fluid migration during aquifer tests. The depths of the wells (34, 100, and 150 feet bgs) were selected to approximate the depths of three of the wells in the JAGW-10 cluster (10, 10A, and 10D). The JAPW-1 well cluster is located 25 feet downgradient from the injection well cluster and is utilized as an intermediate monitoring point within the PTA. The depths of the wells (30, 100, and 150 feet bgs) were selected to approximate the depths of the three upgradient injection wells (JAEB well cluster).

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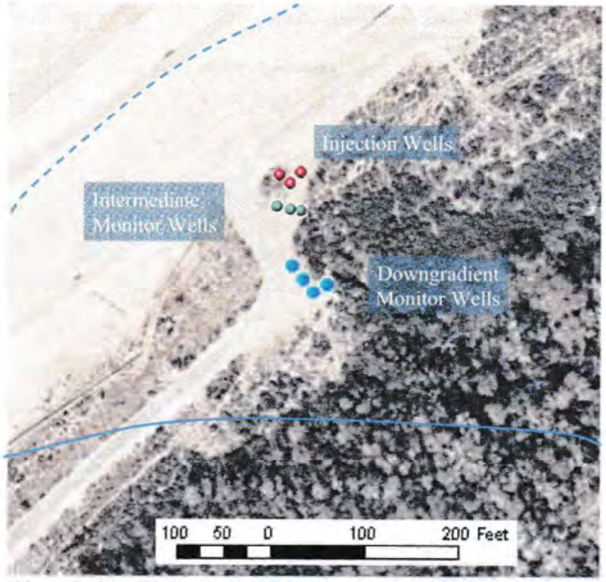

Figure 5 - The PTA is situated at the toe of the landfill, in what is believed to be the primary fracture pathway. JAEB-4, -5, -6 are upgradient injection wells, JAPW-1, -1A, -1B are intermediate monitor wells, JAGW-10, -10A, -10D, and -10E are downgradient montor wells.

Aquifer Tests

Aquifer tests were performed to evaluate the hydraulic connection between well clusters and different screened intervals within the PTA. A 48-hour aquifer pump test and a 72-hour recovery test were performed in the PTA to evaluate the hydraulic connection between the alluvium, grus and unweathered granitic bedrock. The data collected during these tests were analyzed using the AQTESOLV™ program. The results of these tests were used to determine the hydraulic properties of the water bearing units in the vicinity of the PTA.

Prior to beginning the aquifer test, an abbreviated step-drawdown test was performed to determine a pumping rate that could be maintained by the pumping well for the duration of the test. Monitor well JAGW-10A was pumped at a rate of 10, 20, and 30 gallons per minute (gpm) for one hour per step with one hour of recovery in between each step. Water levels were measured by hand in the pumping well and two observation wells (JAGW-10 and JAGW-10D). Evaluation of the results of the step-drawdown test suggested that a pumping rate of 30 gpm could be maintained for the duration of the 48-hour test without drawing water below the level of the pump.

A 48-hour pump test was performed to determine the hydraulic properties in the vicinity of the fractured zone within the PTA. This fracture zone corresponds to the drainage on the northern portion of the landfill. Monitor well JAGW-10A served as the pumping well for the aquifer test and was pumped at a constant rate of 30 gpm for 48 hours. Immediately following the pumping phase, recovery was monitored for 72 hours. The JAEB well cluster, located approximately 100 feet from the pumping well, JAGW-10A, were monitored during the aquifer test. The results of the pump test and recovery were recorded through the use of pressure transducers and a datalogger. Pressure transducers were placed in the pumping well and eight observation wells, six of which are located within the same fracture set within 150 feet of the pumping well.

Monitor wells JAGW-10, JAGW-10D, and JAGW-10E, located in the immediate vicinity of the pumping well (JAGW-10A) were monitored during the pump test and recovery. Each observation well is located less than 30 feet from the pumping well, and are screened at various depths. Three upgradient injection wells, located approximately 100 feet from the pumping well JAGW-10A, were also monitored during the aquifer test. The

Exhibit E

depths and screens of the wells were constructed to be similar to JAGW-10, JAGW-10A, and JAGW-10D. The pumping and recovery data were analyzed by the Theis solution and the Cooper-Jacob approximation for unconfined aquifers using the program AQTESOLV™. Table 1 summarizes the aquifer tests analysis and the following subsections detail the results from each of the observation wells and the pumping well.

Table 1

	JAGW-10A	JAGW-10	JAGW-10D	JAGW-10E	JAEB-4	JAEB-5	JAEB-6
Transmissivity[1] (ft^2/day)	202	212	273	430	-	247	360
Hydraulic conductivty[1] (ft/day)	20	14	27	22	-	17	36
Storativity[1] (dimensionless)	-	0.14	0.01	0.04	-	0.003	0.001
Transmissivity[2] (ft^2/day)	-	187	418	547	-	338	403
Hydraulic conductivty[2] (ft/day)	-	13	42	27	-	27	40
Storativity[2] (dimensionless)	-	0.15	0.04	0.02	-	0.001	0.001

1 - Theis solution for unconfined aquifers using the program AQTESOLV™.

2 - Cooper-Jacob approximation for unconfined aquifers using the program AQTESOLV™.

- Not analyzed

JAGW-10A

JAGW-10A, the pumping well, is screened between 80.5 and 90.5 feet bgs. Monitor well JAGW-10A was pumped at a constant rate of 30 gallons per minute (gpm) for 48 hours, at which time the pump was turned off. The recovery of the water levels within the pumping well in addition to the observation wells were monitored for 72 hours. At the end of 48-hours of pumping, JAGW-10A had approximately 59 feet of drawdown. The effect of pumping was evident in the observation wells located within 150 feet of the pumping well. The Theis method provided the best curve fit for the data. The semi-logarithmic plot of time versus drawdown from the pumping well showed no significant changes in slope, which indicates that no hydraulic boundaries were encountered within the radius of influence of the test. Analysis of the drawdown data from the pumping well was performed to obtain an estimated transmissivity. In order to analyze the data using the Theis method, the distance to the observation well was assumed to be the radius of the well casing. The length of the well screen was taken as the saturated thickness of the aquifer, 10 feet. The calculated transmissivity from the Theis solution for unconfined aquifers was 202 $feet^2$/day, with a hydraulic conductivity of 20 ft/day. The recovery data were also analyzed using the Theis recovery solution. This solution yielded a transmissivity value of 317 $feet^2$/day.

JAGW-10

Monitor well JAGW-10 is completed within the alluvium/grus and is located approximately ten feet from the pumping well, JAGW-10A. The well is constructed with a total depth of 26.5 feet with a screened interval from 11.5 to 26.5 feet bgs. The saturated thickness of the aquifer is assumed to be the length of the well screen, 15 feet. Ten feet of drawdown was recorded in this monitor well during the test. The Theis solution produced a transmissivity of approximately 212 $feet^2$/day and a storativity of 0.14. These data indicate that for a saturated thickness of 15 feet, the hydraulic conductivity of the alluvium/grus is approximately 14 feet/day. The Cooper-Jacob approximation solution yielded values for transmissivity of 187 $feet^2$/day and a storativity of 0.15. Similarly, for a saturated thickness of 15 feet, the hydraulic conductivity of the alluvium/grus is approximately 13 feet/day. Based on the data from the aquifer test, JAGW-10 and JAGW-10A are hydraulically connected.

JAGW-10D

Monitor well JAGW-10D is screened exclusively in the fractured bedrock and is approximately 14 feet from the pumping well. This well is 148 feet deep and screened between 137 to 147 feet bgs. Eight feet of drawdown was recorded during the test. The transmissivity from the Theis solution is 273 $feet^2$/day and the storativity is 0.01. Based on these data for a saturated thickness of 10 feet, the hydraulic conductivity of the fractured bedrock at this depth and location is approximately 27 feet/day. The Cooper-Jacob approximation solution yielded values for transmissivity of 418 $feet^2$/day and a storativity of 0.04. Similarly, for a saturated thickness of 10 feet, the hydraulic conductivity of fractured bedrock at this depth and location is approximately 42 feet/day. The results from the aquifer tests indicate that monitor wells JAGW-10A and JAGW-10D are hydraulically connected.

JAGW-10E

Monitor well JAGW-10E is screened from 275 to 295 feet bgs in fractured bedrock. During the development of this well, a pumping rate of 30 gpm was easily sustained. Four feet of drawdown was recorded in this monitor well during the pump test. The Theis solution produced a transmissivity of approximately 430 feet^2/day and a storativity of 0.04. Based on these data and for a saturated thickness of 20 feet the hydraulic conductivity of the fractured bedrock at this depth and location is approximately 22 feet/day. The Cooper-Jacob approximation solution yielded values for transmissivity of approximately 547 feet^2/day and a storativity of 0.02, and a hydraulic conductivity of 27 feet/day. The results from the test indicate that monitor wells JAGW-10A and JAGW-10E are hydraulically connected.

JAEB-4

Well JAEB-4 is screened from 140 to 150 feet bgs. The construction of this well is analogous to JAGW-10D. The well is approximately 100 feet from the pumping well. At the time of the aquifer test, JAEB-4 had not fully recovered from development. The decision was made to proceed with the test and monitor the well response during the aquifer test. The water level in the well continued to recover throughout the constant rate test at a steady rate. Based on the aquifer test results and the fact that JAEB-4 was still recovering from well development and continued to recover throughout the constant rate test suggest this well is not hydraulically connected to the main fracture set or the pumping well.

JAEB-5

JAEB-5 is a shallow well that is screened in the alluvium/grus similar to JAGW-10. This well is located approximately 100 feet from the pumping well and is screened from 13 to 28 feet bgs. Almost 7 feet of drawdown was recorded during the test. The saturated thickness of the aquifer was taken as the length of the well screen, 15 feet. The results from JAEB-5 were plotted and matched to the Theis curve. The transmissivity from the Theis solution is 247 feet^2/day, the storativity is 0.003, and the hydraulic conductivity of the alluvium/grus at this depth and location is 17 feet/day. Using the Copper-Jacob approximation, the transmissivity calculated for this solution is approximately 338 feet^2/day, the storativity is 0.001, and the hydraulic conductivity of the alluvium/grus at this depth and location is 22 feet/day. The results from the aquifer test indicate that there is a hydraulic connection between the pumping well and well JAEB-5.

JAEB-6

Well JAEB-6 was constructed similarly to the pumping well, JAGW-10A. The well is located approximately 105 feet from the pumping well and is screened from 90 to 100 feet bgs. The maximum drawdown observed in JAEB-6 was 6.5 feet. The saturated thickness of the aquifer for calculation of the hydraulic conductivity was taken as the length of the well screen, 10 feet. The results from JAEB-6 were plotted and matched to the Theis curve. The transmissivity from the Theis solution is approximately 360 feet^2/day, the storativity is 0.001, and the hydraulic conductivity of the fractured bedrock at this depth and location is approximately 36 feet/day. The transmissivity from the Cooper-Jacob approximation yielded values of approximately 403 feet^2/day, a storativity of 0.001, and a hydraulic conductivity of the fractured bedrock at this depth and location is approximately 40 feet/day. The results from the aquifer test indicate that there is a connection between the pumping well and this well.

The aquifer test yielded estimated horizontal hydraulic conductivity values of 25 to 40 feet/day for the fractured bedrock and from 13 to 17 feet/day for the alluvium/grus. The groundwater velocity within the alluvium/grus is approximately 180 feet/year. The groundwater velocity of the fractured bedrock within the main fracture canyon is approximately 6,600 to 16,000 feet/year. These data demonstrate that zones of the fractured bedrock within the fracture canyon can be more permeable than the overlying alluvium/grus. These data and analyses suggest that the fractured bedrock in the major fracture canyons is the predominant pathway for the migration of landfill related constituents in groundwater.

Tracer Study

Exhibit E

A fluorescent dye-tracer study was conducted under ambient conditions within the PTA to further analyze hydraulic connectivity in the PTA. A unique dye was placed into JAEB-4, JAEB-5, and JAEB-6, respectively (Figure 6). The downgradient wells were monitored with carbon dye receptors, which were exchanged every two weeks and analyzed with a spectrofluorophotometer for the presence of dyes potentially adsorbed onto the carbon packs.

Positive detections of the dye placed into the intermediate upgradient well (JAEB-6) were observed in JAPW-1A and JAPW-1B after two weeks and JAGW-10 after four weeks. Tentative detections (less than ten times background results) were recorded in JAGW-10A and JAGW-10D after two weeks, however, these concentrations were too low to be considered true positives. The dyes injected into the shallow and deep upgradient wells have not been detected in any downgradient wells. The dye placed into the alluvium may be migrating slowly, or dispersing too much to be detected in downgradient wells, and based on the results of the aquifer test, the deep upgradient well does not appear to be in fracture communication with the downgradient monitor wells, and the dye placed in JAEB-4 was not detected.

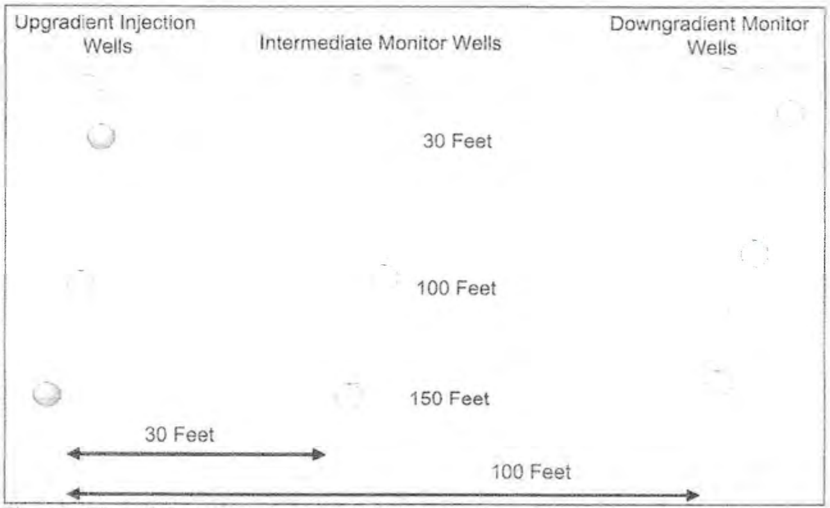

Figure 6 - Three distinct dyes were injected into the upgradient wells, one into each interval. Carbon receptors were placed into downgradient wells and were analyzed for dye every two weeks.

Summary

The results of the hydrogeologic characterization suggest the PTA is located near the primary fracture set that forms the canyon containing the landfill. Aquifer testing results suggested hydraulic communication exists between all wells and intervals in the PTA. Tracer study confirmed that groundwater within the fractured rock aquifer was moving rapidly under passive conditions, and confirmed communication between the upgradient and downgradient wells within the PTA. The hydrogeologic characterization demonstrated that sufficient hydraulic communication is present within the PTA and that plans for a passive EISB pilot test should proceed.

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Biographical Sketches

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Impact Statement for the
Proposed Campo Regional LF
Project, Feb. 2010

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Linnaeus ECO-TECH 2012
Kalmar, Sweden, November 26-28, 2012

ENVIRONMENTAL AND SOCIO-ECONOMIC IMPACTS OF LANDFILLS

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ABSTRACT

A modern landfill is an engineered method for depositing waste in specially constructed and protected cells on the land surface or in excavations into the land surface. Despite the fact that an increasing amount of waste is reused, recycled or energetically valorized, landfills still play an important role in waste management strategies. The degradation of wastes in the landfill results in the production of leachate and gases. These emissions are potential threats to human health and to the quality of the environment. Landfill gas consists mainly of methane and carbon dioxide, both important greenhouse gases. Landfill sites contribute 20% of the global anthropogenic methane emissions. Furthermore, it usually contains a large number of other gases at low concentrations, some of which are toxic. Leachate can migrate to groundwater or even to surface water through the flaws in the liners and this poses a serious problem as aquifers require extensive time for rehabilitation. Construction and management of landfills have ecological effects that may lead to landscape changes, loss of habitats and displacement of fauna. Socio-economic impacts of landfills include risks for public health derived from surface or groundwater contamination by leachate, the diffusion of litter into the wider environment and inadequate on-site recycling activities. Nuisances such as flies, odors, smoke and noise are frequently cited among the reasons why people do not want to reside close to landfills. Various researches conclude that landfills likely have an adverse negative impact upon housing values depending upon the actual distance from the landfill. The present paper reviews the environmental and socio-economic impacts related to landfills and presents existing modeling approaches to assess these impacts. Furthermore, this review is complemented with suggestions to minimize the environmental burden of landfills and to re-introduce the buried resources to the material cycle.

KEYWORDS

Landfill, Landfill gas, Leachate, Environmental impacts, Socio-economic impacts, Bio reactor, ELFM.

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1 INTRODUCTION

Despite the fact that the EU waste hierarchy, as set by the Waste Framework Directive (2008/98/EC) establishes the preference of reuse, recycling and recovery of waste above landfilling, a significant amount of waste is still landfilled. It is a well-known fact that landfilling has environmental effects, mainly due to the long term methane emission and leachate production. Landfill gas consists mainly of methane and carbon dioxide and it can also contain a large number of other gases at low concentrations some of which are toxic[1]. The substances that are present in landfill gas are known to contribute to several environmental problems such as global warming, acidification, depletion of the quality of ecosystem as well as social issues like human health [2-7]. Leachate production is also a major concern as leachate can migrate to surface and groundwater. This is more serious than river pollution because aquifers require extensive time for rehabilitation [1]. Landfill leachate may present significant concentrations of trace metals, nutrients such as nitrate and phosphate, ammonia and chlorides. Apart from the environmental burdens, occupation and requirement of the enormous space for landfills generates the issue of land scarcity for the development of human society and eco systems. Moreover, landfills decrease the market value of the surrounding area [4, 5]. Different modeling approaches to quantify landfill emissions have been developed. Most of the models concentrate on landfill gas and leachate and a few of them address nuisances like odor, dust, noise and etc. In addition to the generation models, a few studies have been performed to model the impacts of landfills. Landfill modeling in life cycle analysis (LCA) is the most common approach.
The purpose of our research is to review the existing literature on environmental and socio-economic impacts of landfills. An attention has been given to the available modeling approaches to assess the landfill emissions and their impacts. Furthermore, this paper highlights evolving landfill concepts such as landfill bio reactors and enhanced landfill mining as to minimize the risk and environmental burdens of landfills and to re-introduce the disposed resources to the material cycle.

2 LANDFILLS AND LANDFILL EMISSIONS

A modern landfill is an engineered method for depositing waste in specially constructed and protected cells on the land surface or in excavations into the land surface. Within the landfill, biological, chemical and physical processes occur and they promote the degradation of wastes and result in the production of leachate and gases. The landfill ecosystem is quite diverse due to the heterogeneous nature of waste and the variety of landfill operating characteristics. The diversity of the ecosystem promotes stability; however the system is strongly influenced by environmental conditions such as temperature, pH, the presence of toxins, moisture content and the oxidation reduction potential. The stabilization of wastes proceeds in five sequential and distinct phases [8]:

1) Initial adjustment phase: This phase is associated with initial deposition of solid waste and accumulation of moisture within landfills. An acclimatization period is observed until sufficient moisture develops to support an active microbial community.
2) Transition phase: In the transition phase transformation from aerobic to anaerobic environment occurs.
3) Acid formation phase: The continuous hydrolysis of solid waste followed by the microbial conversion of biodegradable organic content results in the production of intermediate volatile organic acids at high concentrations throughout this phase.
4) Methane fermentation phase: Intermediate acids are consumed by methanogenic bacteria and converted into methane and carbon dioxide.

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5) Maturation phase: During the final state of landfill stabilization, nutrients and available substrate become limiting, gas production dramatically drops and leachate strength stays steady at much lower concentrations.

Apart from landfill gas and leachate emission, wind-blown litter, vermin and insects are also identified as the minor emissions of the landfills. But the following discussion is limited to the landfill gas and leachate as they are the most important causes for number of environmental and socio economic impacts.

2.1 Landfill Gas

In theory the biological decomposition of one ton of municipal solid waste produces 442 m^3 of landfill gas containing 55% methane and a calorific value of 15 - 21 MJ/m^3 [9], which is approximately half that of natural gas. The major components of landfill gas are methane (CH_4) and carbon dioxide (CO_2), with a large number of other constituents at low concentrations such as ammonia, sulfide and non-methane volatile organic compounds (VOCs) [1]. Chemical and biochemical transformations within the landfill create new organic or inorganic substances; e.g. tri- and per-chlorethylene to vinylchloride; amino acids to methyl- and ethyl-mercaptans; or sulphur compounds to hydrogen sulphide (H_2S). For these reasons, inclusion of large amounts of particular types of industrial waste in a landfill can generate high quantities of other gaseous compounds. For example, a very large proportion of plasterboard (i.e. gypsum, $CaSO_4$) may cause the emission of H_2S [10]. The US EPA [11] listed 94 non-methane organic compounds found in air emissions from municipal solid waste landfills, which included benzene, toluene, chloroform, vinyl chloride, carbon tetrachloride, and 1,1,1trichloroethane. Forty-one are halogenated compounds. Toluene, xylenes, propylbenzenes, vinyl chloride, tetrachloroethylene, methanethiol and methanol have been reported from landfills that received both municipal and industrial wastes [12]. CH_4 and CO_2 are greenhouse gases which were the main focus of the 1997 Kyoto Agreement and of subsequent efforts at world-wide emission reduction. Landfill sites contribute 20% of the total global anthropogenic methane emission [13].

Landfill gas is generally controlled by installing vertical or horizontal wells within the landfill. These wells are either vented to the atmosphere or connected to a central blower system that pulls gas to a flare or treatment process. Intergovernmental Panel on Climate Change (IPCC) report that the landfill gas collection efficiencies ranging from 9-90% and estimates an average of 20% [14]. The uncaptured gas can pose an environmental threat because methane is a greenhouse gas and many of the VOCs are odorous and toxic. This issue is discussed in the other sections of this paper.

2.2 Leachate

Leachate is defined as any liquid percolating through the deposited waste and emitted from or contained within a landfill. As it percolates through the waste it picks up suspended and soluble materials that originate from, or are products of the degradation of the waste. The principal organic contents of leachate are formed during the breakdown process described above and its organic strength is normally measured in terms of biochemical oxygen demand (BOD), chemical oxygen demand (COD), or total organic carbon (TOC) [1]. The municipal solid waste leachate contains a wide variety of hazardous, toxic or carcinogenic chemical contaminants [6]. Moreover, mining wastes, sewage sludge and residual solids from air pollution control equipment contain high concentrations of trace metals, a range of acids and even radioactive material. Under the acidic conditions hazardous trace metals such as copper, cadmium, zinc and lead dissolve and travel with leachate [1].The characteristics of leachate produced are highly variable depending on the composition of the waste, precipitation rates,

Exhibit E

site hydrology, compaction, cover design, waste age, sampling procedures and interaction of leachate with the environment and landfill design and operation.

It is important to control and manage the leachate production and discharge due to the potential threat of it to both the environment, particularly groundwater, and human health. An effective leachate collection and removal system is a prerequisite for all non-hazardous and hazardous landfill sites and it must function over the landfill's design lifetime.

3 MODELING APPROACHES TO ASSESS THE LANDFILL EMISSION AND THEIR IMPACTS

Modeling landfill emissions and their impacts already exists for several decades. Many researchers have conducted studies to evaluate the landfill emission management. Most of the studies are mainly about landfill gas and leachate and a few of them address nuisances like odor, dust and noise. This section summarizes the different modeling approaches available to evaluate and quantify the landfill emission and their environmental and socio-economic impacts.

Attempts to model landfill gas formation stem from the early '80's. The first landfill gas formation models were made to help determine the size of landfill gas recovery projects. They estimate the amount of formation and including future expectation and gas recovery. More recent models quantify methane emission. As described in the review of Oonk H. [15], modeling of methane emission generally requires modeling of methane generation, measuring landfill gas recovery and assuming some methane oxidation. The emission equals the gas generation minus the gas recovery minus the gas oxidation.

According to Oonk, the major issue when modeling methane emissions is the modeling of the methane or landfill gas formation. Most of the models are based on a first order decay model (a first order decay models have one half-time of biodegradation) or a multi-phase model (multi-phase models consider 3 fractions: fast, moderate and slow degradation of waste, each with their own half-time of biodegradation). Modeling oxidation has received less attention: in most cases 10% of the methane flux through the top layer simply is assumed to be oxidized. Nevertheless, more recent models are being developed for the evaluation of methane oxidation as well. The most widely applied generation models are the IPCC model, the TNO model, GasSim Lite, Landgem, the Afvalzorg-model, the French E-PRTR-model and the Finnish E-PRTR-model [15]. The IPCC model is intended to give guidance to national authorities in the quantification of methane emissions from all landfills in a country. But the model itself can also be used for individual landfills. The choices exist between a first order decay model and a multi-phase model. The IPCC model accommodates for 4 different climate regions [16]. TNO is the first model in which model parameters were based on real data of landfill gas generation in a larger group of landfills. Both a first order and a multi-phase model were made, that describe landfill gas generation as a function of amount of waste deposited from different origin ([17, 18]. GasSim Lite quantifies all landfill gas problems of a landfill, ranging from methane emissions, effects of utilization of landfill gas on local air quality to landfill gas migration via the subsoil to adjacent buildings [15]. Landgem is a first order decay model, with separate default values for the rate constant of biodegradation for conventional and arid regions [19]. The Afvalzorg model itself is a multi-phase model and is intended to give a more realistic prognosis of methane generation at landfills with little or no household waste deposited. The French E-PRTR-model is a simplified first order decay model and the Finnish E-PRTR-model is a multi-phase model with model parameters for different climatic regions [15]. In addition to these models, three dimensional models have been developed for transport and reaction of gaseous mixtures in a landfill [20-24].

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Successful prediction of the amount of landfill leachate generated and its composition is a highly complex and difficult task. As discussed in previous sections, the amount of leachate generated is primarily a function of water availability, waste characteristics and landfill surface conditions. Similar to landfill gas, numerous leachate generation and transport models have been developed. These models can be classified into two types: (1) models that emphasized only the quantity of leachate generated; and (2) models that combined both quantity and composition [25]. Among these models that can estimate the volume of leachate generated from a landfill, the Water Balance Method (WBM) is the most commonly used [25-27]. The WBM simply states that water infiltrating through the landfill cover and past the depth influenced by evapotranspiration will eventually emanate from the landfill as leachate. This is valid after the solid waste reaches absorptive capacity for holding water, which may take several years. Although this method is theoretically correct and simple, a great degree of uncertainty is associated with estimating its variables [28]. Demetracopoulos, Sehayek et al. [29] built up a mathematical model for the generation and transport of solute contaminants through a solid waste landfill. A three dimensional mathematical model has been developed by Demirekler, Rowe et al. [30] to estimate the quality and quantity of the leachate produced. The model takes the effects of changing hydraulic conductivity with overburden pressure and time dependent landfill development into consideration. Laner, Fellner et al.[31] suggested a methodology to estimate future emission levels, mainly leachate, for a closed municipal solid waste landfill. The approach is based on an assessment of the state of the landfill including detailed analysis of landfill monitoring data, investigations of the landfill waste and an evaluation of engineered landfill facilities.

Apart from these gas and leachate generation models, many modeling approaches have been developed for assessing the environmental and socio economic impact of the landfills. Landfill modeling in life cycle analysis (LCA) is the most common approach. Obersteiner, Binner et al. [32] introduce and discuss the different approaches concerning time horizon and life cycle inventory data for landfills in Central Europe. Damgaard, Manfredi et al. [3] performed an economic and environmental evaluation of landfill leachate and gas technologies by using waste LCA model EASEWASTE. A methodology to estimate future emission rates and evaluate the response of the affected environment based on the current state of the landfill and its surroundings has been introduced by Laner, Fellner et al. [31]. They present a modeling approach to evaluate residual environmental impacts in view of different post closure management strategies. In addition to that numerous LCA studies have been conducted to compare the environmental impact of landfills with that of other waste treatment technologies [33-35]. Furthermore, Úbeda, Ferrer et al.[36] developed a Gaussian dispersion model to evaluate the odor impact from a landfill area. Apart from environmental modeling a few studies report for economic models of landfills. Similar to the environmental modeling, landfilling has been compared with the other waste management systems from an economic point of view [7, 37]. Some studies have been performed to assess the social impacts of landfills. Assessing the impact of landfills on residential property values is an example [4, 5, 38].

4 ENVIRONMENTAL IMPACT OF LANDFILLS

As with any waste management activity, landfilling is also a potential threat to the quality of the environment due to its gaseous and leachate emissions as well as wind-blown litter and dust. There are also substantial environmental effects associated with waste transport and collection. In this section the environmental effects of landfilling are discussed, making use of the results of above mentioned modeling approaches towards landfill emission and their

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impacts. Three major categories of environmental impacts are considered: (1) Landfill construction (2) Landfill gas (3) Leachate.

4.1 Impact of landfill construction

Site selection of waste management facilities can be a major issue as all infrastructural projects have the capacity to damage the ecology of the site on which they are developed, causing landscape changes, loss of habitats and displacement of fauna. Such impacts are generally site specific and need to be assessed on a case by case basis [1, 39-41].

The soils on selected sites tend to suffer from high levels of disturbances and their chemical and physical properties differ from those of the surrounding areas due to the general removal of topsoil as well as specific process related changes. Soil is an important resource which supports a variety of ecological, economic and cultural functions. The factors like porosity, density, water holding capacity and aggregate strength that operates the soil quality are best developed in the top soil fraction, subsoil being more poorly developed and having a lower ability to support plant growth. This quality can be disturbed during the construction activities. The movements of heavy machinery can lead to excessive compaction of topsoil and subsoil, and in deeper soil this may only be reversible over relatively longer time periods. There is a considerable impact on flora and fauna during the construction phase of landfills due to the removal of existing vegetation. But this damage could be recovered after the closing phase of the landfills. The studies have shown that landfills are capable of supporting a rich and varied fauna including exotic species during the operational and closing phase of landfills [42].

4.2 Impact of landfill gas

The environmental impact of gaseous emission from landfills, which are of global or regional significance, can be mainly grouped as contribution to the greenhouse effect and damage to the eco system. Apart from that, risk of explosion and odor problem due to some trace gases can also be identified as significant impacts.

As described in earlier sections of this paper, CO_2 and CH_4 are the primary constituents of environmental importance in landfill gas. They act as greenhouse gases of global significance, with CH_4 being the most active but CO_2 being produced in the greatest quantities [2]. The LCA modeling performed by Damgaard, Manfredi et al. [3] shows that landfills are main contributors for global warming and photochemical and stratospheric ozone formation. According to Clarke [43], O'Neill [44] and Wellburn [45], CH_4 reacts with hydroxyl radicals and oxygen in the atmosphere to generate CO_2 within a period of days to a few years, thereby losing some of their greenhouse gas potential. Small amounts of methane are also consumed after absorption by soil [46]. Nevertheless, control of these emissions at the source is necessary from an environmental protection viewpoint and to address the obligations under the Kyoto protocol.

Gaseous pollutants have significant effects on plants, animals and entire eco systems. The lateral migration of gas through soil beyond landfill boundaries causes the displacement of oxygen from soil. This results in a decline in soil faunal populations and burrowing animals and causes vegetation dieback. Mainly the vegetation around the landfill and the newly planted vegetation on a closed landfill can be damaged due to the suppression of air around the roots by migrated landfill gas [1]. The acidic gaseous constituents contribute to the phenomenon of acid rains and its secondary effects on the acidification of soils and ecosystems. Ammonia is a major acidic constituent which can be found in the landfill gas. It is a secondary acidifying agent following its atmospheric oxidation to nitric acid. It has effects on plants, causing a loss of stomatal control, a reduction in photosynthesis, enzyme

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inhibition, changes in synthetic pathways and depressed growth and yield. Hydrogen sulfide is also having a considerable impact on ecosystem. It is an extremely biotoxic gas, effective at a few parts per billion in mammals. Plants are far less sensitive to direct toxicity effects but have a threshold of 1µg/g [45, 47]. The most severe impact on plants is inhibition and destruction of root growth and vegetation cover due to the anaerobic soil conditions created by high concentration of sulfides which laterally seepage from landfill sites. VOCs play a significant role in formation of ground level ozone. High concentrations of ground level ozone tend to inhibit the photosynthesis, reduce growth and depress the agricultural yields [48, 49].

Gendebien, Pauwels et al.[50] say that the lateral migration of gas through soil has been the cause of a number of hazardous explosions as methane is inflammable and explosive when it mix with sufficient amount of air. Moreover, an unpleasant odor can be caused by the series of trace elements present in the landfill gas especially organic fatty acids from the acid phase and H_2S and other sulfur containing compounds. These impacts are discussed further in this paper under the section of socio- economic impacts of landfills.

4.3 Impact of leachate

The leachate production decreases very slowly and some parameters might be of environmental relevance for many decades to centuries. The main constituents of landfill leachate are dissolved methane, fatty acids, sulfate, nitrate, nitrite, phosphates, calcium, sodium, chloride, magnesium, potassium and trace metals like chromium, manganese, iron, nickel, copper, zinc, cadmium, mercury and lead. Leachate can migrate through the soil to groundwater or even to surface water due to the absence of proper liner system or damages of the liners and this results a serious problem as aquifers require extensive time periods for rehabilitation. Moreover, soil can retain the constituents of the leachate like metals and nutrients and can cause adverse impacts on the eco system.

The metals retained by the soil uptake by plants and thereby provide a key route for entry of metals into the food chain. Deposition of trace metals in the plants can affect crop growth and productivity and also pose a greater threat to animal health. Those metals such as lead, zinc and cadmium show differential mobility through the vegetation and invertebrate trophic levels and must be assessed by case by case basis [1]. Uptake by plants is affected by soil pH and salinity and also cadmium and lead uptake is enhanced by the chloride complexation of the metals present in the leachate [51]. Eutrophication is the most extensive threat when the leachate is mixed with the surface water with higher concentrations of nitrate and phosphates [52]. Eutrophic conditions invariably cause excessive production of planktonic algae and cyanobacteria in the open sectors of the lakes. This excessive production of algae results adverse impacts on fish species in the lake by limiting the light penetration into the lake. Ammonia generated from leachate within landfills will migrate through the soil horizons where it is progressively nitrified to nitrite and nitrate and cause eutrophication problem. A number of chemicals can disrupt the reproductive behavior in a range of species by acting as oestrogen mimics. Dempsey and Costello [53] found the landfill leachate as a potential source for these substances.

Above mentioned metals can be present in the leachate either in large or small concentrations depending on the waste categories deposed in the landfills. Mercury is one of the best studied contaminant. It is one of the most toxic metals within the food chain, being readily absorbed by animals, fish and shellfish. Landfills are potential mercury emitters to the eco system due to the disposal of batteries and paint residues in the landfills. Alloway [51] revealed that the chromide to chromate conversion in the landfills is environmentally significant as chromate is more toxic to plants than chromide.

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5 THE HEALTH AND SOCIAL IMPACTS OF LANDFILLS

Apart from the environmental impacts, landfills are sources for several socio-economic impacts like public health issues due to the exposure to landfill gas and to the ground and surface water contaminated by landfill leachate. Although modern landfill sites are well designed to reduce emissions, the emissions from landfills continue to give rise to concerns about the health effects of living and working near these sites, both new and old. The exposure to contaminants and emissions can be via direct contact, inhalation or ingestion of contaminated food and water. Drinking water contamination has been identified as the source of exposure to harmful substances in many studies [54-56]. Those studies revealed that congenital malformations, birth weight, prematurity and child growth and cancers have a significant impact on landfill emissions. In a multi- site study of residents of New York State, a 12% increased risk of congenital malformations in children born to families within one mile of hazardous waste sites were reported [57]. Fielder, Poon-King et al.[58] and Vrijheid, Dolk et al. [59] also found an increased risk of congenital malformations in populations live near landfill sites. A multi-site European study called EUROHAZCON discovered a 33% increase in non- chromosomal birth defects among the residents living within 3 km of the 21 hazardous waste landfill sites studied [60]. This conclusion was confirmed by the study conducted by Elliott, Briggs et al.[61]. A number of studies revealed that there is a higher risk of developing cancer among the people near landfill sites and the elevated risks were observed for cancers of the stomach, liver and intrahepatic bile ducts and trachea, bronchus, lung, cervix and prostate [62, 63]

In addition to the health issues, landfills create considerable impacts on land value, land degradation and land availability. Various researches conclude that landfills likely have an adverse negative impact upon housing values depending upon the actual distance from the landfill [4, 5, 38]. Potential hazards such as flies, odor, smoke, noise and threat to water supplies are cited as reasons why the public do not want to reside close to the landfills. Reichert, Small et al. [38] revealed that 40% of participants to their survey reported odor and unattractiveness as the most severe nuisance while 35 % reported about the toxic water runoff and methane gas emission. Their study concluded that landfills have a negative impact of 5.5-7.3% of market value depending on the distance to landfills. Akinjare, Ayedun et al.[5] found that all residential property values increased with the distance away from landfill sites at an average of 6%. Ready [4] performed a meta-analysis that included all available hedonic price studies of the impact of landfills on nearby property values. It showed that landfills that accept high volumes of waste (500 tons per day or more) depresses the value of an adjacent property by 12.9% while a low volume landfill depresses this value only by 2.5%. Furthermore, occupation and requirement of the enormous space for landfills contribute to land scarcity for the development of human society and eco systems.

6 EVOLVING LANDFILL CONCEPTS

Despite the landfilling has become the final option of the waste hierarchy defined by the EU waste directive (2008/98/EC), it is still expected to be applied in several cases because of the growing amount of solid wastes and a lack of suitable techniques to treat all kinds of wastes. But it is very clear that the landfill concept should evolve to minimize the potential risks and environmental burden of landfills and on the other hand to re-introduce the buried resources to the material cycle. One approach is engineered bioreactor landfills in which a controlled degradation is allowed in order to guarantee the long term stability of the landfill [64]. Another approach is the concept of enhanced landfill mining (ELFM) that reduces the emission and potential hazard of landfills and valorize the resources contained in it. Several

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studies have been conducted on ELFM both in environmental and economic point of view [65-68].

6.1 Landfill as a reactor

Waste decomposing period of a MSW landfill is estimated as over fifty years. There is considerable interest in techniques for shortening this time because it has the potential of reducing overall costs and risks. One method is considering a landfill as a bio-reactor in which the degradation processes is provocatively accelerated [1]. A bioreactor landfill is a sanitary landfill site that uses enhanced microbiological processes to transform and stabilize the readily and moderately decomposable organic waste constituents within 5 to 8 years of bioreactor process implementation [64] . According to Warith's study, the bioreactor landfill significantly increases the extent of organic waste decomposition, conversion rates and process effectiveness over those occur within the traditional landfill sites. The environmental performance measurement parameters (landfill gas composition and generation rate, and leachate constituent concentrations) remain at steady levels. A bioreactor landfill site requires effective operation of liquid addition and management. Other than that waste shredding, pH adjustment, nutrient addition and balance, waste pre-disposal and post-disposal conditioning, and temperature management may also serve to optimize the bioreactor process. The advantages of bio reactor landfills are: enhancement the landfill gas generation rates, reduction of environmental impact, production of end product that does not need land filling, overall reduction of land filling cost, reduction of leachate treatment operational cost, reduction in post-closure care, maintenance and overall reduction of contaminating life span of the landfill due to a decrease in contaminant concentrations during the operating period of the bioreactor landfills.

6.2 Enhanced landfill mining (ELFM)

The previous sections of this paper highlighted that landfills have related implications such as long term methane emissions, local pollution concerns, settling issues and limitation on urban development. Landfill mining consisting of excavation, processing, treatment and/or recycling of deposited materials has been suggested as a strategy to address such problems [67]. ELFM includes the combined valorization of the historic waste streams as both materials and energy. As mentioned in the review of Krook, Svensson et al. [67] massive amounts of important materials such as metals have accumulated in landfills. On a global level, the amount of copper situated in such deposits (393 million metric tons) has been estimated as comparable in size to the present stock in use within the technosphere (330 milion metric tons). The same study revealed that apart from metals, the amount of potential waste fuel situated in municipal waste landfills is enough to cover the district heating demand in the country for 10 years. Apart from old landfills, ELFM is also applicable to new landfills by considering them as temporary storages. In that approach landfills become future mines for materials which could not be recycled with existing technologies or show a clear potential to be recycled in a more effective way in near future [69, 70]. Recently, Van Passel, Dubois et al.[66] address the economics of ELFM both from private point of view as well as from a societal perspective. Their analysis shows that there is a substantial economic potential for ELFM projects on the wider regional level. Furthermore, the feasibility of ELFM is studied by synthesizing the research on the Closing the Circle project, the first ELFM project targeting the 18 million metric ton landfill in Houthalen-Helchteren in the East of Belgium [71]. They highlighted the worldwide potential of ELFM in terms of climate gains, materials and energy utilization, job creation and land reclamation. Nevertheless, for ELFM to reach its full potential, developing standardized frameworks for evaluating critical factors for environmental and economic

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performance is necessary. Moreover, strategic policy decisions and tailored support systems, including combined incentives for material recycling, energy utilization and nature restoration, are also required [67, 71].

7 CONCLUSIONS

Landfills mainly emit gas and contaminated water as well as wind-blown litter and dust. Landfills are potential threat to the quality of the environment, although the full extent of this threat has not always been scientifically validated. The main potential impacts are due to landfill gas and leachate. Both are highly complex mixtures and vary from site to site and with waste composition and age of the landfill. It is clear that enough attention has been given to modeling of landfill emission in order to quantify the landfill gas and leachate production. But on the other hand, studies that model the impacts of landfill emission are scarce. A few LCA studies have been performed to compare landfilling with other waste management technologies but by our knowledge an integrated assessment of the impacts of landfills has not been addressed yet. Nevertheless, available literature highlights that the landfills create significant impacts on global warming, eco system, ground and surface water, human health, land value and land availability. In order to minimize the potential risk and environmental burden of landfills and on the other hand to re-introduce the buried resources to the material cycle the landfill concepts should be made operational in the future. Further development of the concepts of landfill bioreactors and enhanced landfill mining can be seen as a promising approach to reduce the environmental impact and the negative socio-economic impacts.

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Exhibit E

April 2021 Newsletter

Newsletter Team: Peggy Hawman, Eric Hawman, Doris Theriault

1. Our Logo – we have this
2. A Tale of Two Cities and About – we have this from earlier newsletters
3. **President's Message – Noel (due by March 19th)**
4. New Officers for 2021 – we have this
5. Benefits of Membership – we will write this and include link to membership brochure
    a. Cultural learning
    b. In person visits: Prescott members to Caborca and Caborca members to Prescott
    c. Language practice partnerships
    d. Links to State and International Organizations
    e. **If anyone has anything else that we should include please send to Peggy before March 19th**
6. **International Insights – Ed Williams and Fred Czarnowski (due by March 19th)**
7. Linkable Headlines in Caborca – Sukey Jones, The Masks of Mexico (done)
8. Language Practice Partnerships – Eric will write this
9. Profile of Members from Prescott and Caborca, including pictures – Doris Theriault (done) and **Mario will provide by March 19th**
10. Member News – Bob Greniger recovering from bypass surgery (we will get up to date information from Donna Baldwin) and Cecil LaVance honored for more than 50 years of work with the Arizona Desert Bighorn Sheep Society (we have the details on this) – **other submissions to Peggy by March 19th**

We will create an English and Spanish version of the newsletter. Mario has agreed to edit the Spanish version for us prior to distribution.

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EXHIBIT C

The State of New Hampshire
DEPARTMENT OF ENVIRONMENTAL SERVICES

Robert R. Scott, Commissioner

FP 2024-74, Env-Sw 800, Landfill Requirements
Summary of Comments on Initial Proposal with NHDES Responses
October 16, 2024

Introduction

The existing rules, Chapter Env-Sw 800, Landfill Requirements, specify minimum standards for where a landfill is located, and how it is designed, constructed, operated, and closed, including how post-closure care is managed. The existing rules also specify provisions for reclaiming a landfill, and for permit-exempt landfills.

The New Hampshire Department of Environmental Services (NHDES) conducted a hybrid public hearing at the New Hampshire Department of Motor Vehicles (DMV) Auditorium at 23 Hazen Drive in Concord, and via Microsoft Teams on May 20, 2024. Thirty-nine members of the public attended the public hearing remotely and 18 members of the public attended the hearing in-person. The public comment period remained open through June 5, 2024, to allow the submittal of written comments. By the close of the comment period, 60 members of the public submitted written comments. The comments and the Department's responses are summarized below. The written comments received from the Office of Legislative Services, Administrative Rules (OLS) were mostly editorial, with the exception of those addressed beginning on page 20.

Env-Sw 802.02 re: Application requirements

Comment:

The rules do not specify any detailed requirements for the environmental impact assessment. Improvement: Include a comprehensive environmental impact assessment requirement detailing the potential impacts on local ecosystems, groundwater, and community health.

Response: Application content is identified in Chapter Env-Sw 300 and the attendant application forms. NHDES has noted this comment for consideration during review of Chapter Env-Sw 300. NHDES is not proposing changes to Chapter Env-Sw 800 based on this comment.

Env-Sw 804 re: Groundwater and Surface Water Protection - Setbacks

Comment:

Multiple commenters asserted that setbacks to protect groundwater and surface water should be site-specific and based on groundwater travel-time. A few commenters asserted that the setbacks should be similar to the State of Maine's standards. Commenters proposed a setback equating to a groundwater travel time of 5 years to various water resources.

Response: The proposed setbacks are site-specific. Rule Env-Sw 804.02(b) and (c) require that a landfill and all associated stormwater, leachate, and decomposition gas infrastructure be located only in areas where groundwater monitoring for release detection, characterization and remediation can be conducted prior to a release having an adverse impact on groundwater quality at the property line or a water supply. This provision effectively sets the site-specific groundwater travel time based on site-specific conditions and site-specific groundwater monitoring. Typically, groundwater monitoring wells are sampled at least four (4) times per year. The distance between the landfill and associated infrastructure, and the property line or a water supply, paired with the frequency of site-specific groundwater sampling and site-specific hydrogeological conditions, dictates the minimum site-specific setback distance required between the landfill and associated infrastructure, and a property line or water supply well. This requirement compels consideration of groundwater and contaminant travel time, and makes the minimum required travel time consistent with site-specific conditions and groundwater monitoring requirements. NHDES is not proposing a change based on these comments.

Env-Sw 804.02 re: Groundwater Protection Standards

Comment:

Add requirement stating, "Subsurface investigations are required in sufficient numbers and locations to properly describe the surficial stratigraphy and bedrock beneath and adjacent to the proposed solid waste boundary… Pump tests must be conducted at selected locations as needed to evaluate aquifer yield and connectivity of bedrock fractures."

Response: NHDES has proposed changes to the hydrogeologic investigation requirements for clarity. See Env-Sw 804.02(f).

Comment:

Add the following requirement: The minimum in-situ groundwater travel time between a release and the closest surface water receptor for any landfill site is 5 years, measured between the edge of waste or leachate handling area and closest surface water receptor, whichever is closest. Travel time is determined from groundwater flow based on the geometric mean of representative in-situ hydraulic conductivity field tests with, conservatively, no attenuation.

Response: The rules compel consideration of groundwater and contaminant travel time, and makes the minimum required travel time consistent with site-specific conditions and groundwater monitoring requirements as discussed above in a response to the comment regarding Env-Sw 804 on page one. NHDES is not proposing a change based on this comment. See also responses to comments on Env-Sw 804.03 below.

Env-Sw 804.02(b) re: Groundwater Protection Standards – Infrastructure areas

Comment:

Consider language that allows for the applicant to request specific variances from this rule (such as for landfill gas pipelines to adjoining properties or stormwater conveyance channels and outfalls), or limit the infrastructure to the major categories of stormwater ponds, leachate storage tanks, and decomposition gas destruction devices or similar.

Response: NHDES has revised the requirement to exclude "pipelines carrying leachate and decomposition gas offsite for processing or treatment" from the requirement only as it relates to groundwater quality at the property line because it is not possible to implement such requirement when the subject infrastructure is intended to cross property lines.

Env-Sw 804.02(c), renumbered in the FP as Env-Sw 804.02(d), re: Groundwater Protection Standards – Hydraulic conductivity

Comment:

Do as other states do and set a smaller hydraulic conductivity. Use "representative" instead of "average" hydraulic conductivity. Clarify how the measure would be determined to be "representative."

Response: NHDES has revised the provision to require that the undisturbed in-situ soils for 5 feet immediately beneath the landfill footprint have a representative saturated hydraulic conductivity of $1x10^{-3}$ centimeters per second (cm/sec) or less, or to require that at least 24 inches of $1x10^{-4}$ cm/sec soil be placed beneath the footprint.

Comment:

The condition as worded is not clear in how it would be applied if there is not undisturbed in-situ soil immediately beneath the footprint. We suggest the following language: "The uppermost 5 feet of existing undisturbed in-situ soil beneath the footprint shall have an average saturated hydraulic conductivity of 5x10^{-3} centimeters per second (cm/sec) or less."

Response: NHDES has revised the requirement and believes it is now more clear.

Comment:

A commenter requested more specific information regarding the development of the proposed hydraulic conductivity standard in Env-Sw 804.02(c), renumbered in the FP as Env-Sw 804.02(d), including whether the agency relied on a(n unspecified) soil map, whether any comparisons with other states' hydrogeologic conditions and regulatory requirements were made, and whether it precludes expansion of existing landfills.

Response: The commenter did not identify the "soil map" to which they were referring; therefore, NHDES is unable to respond to the map-specific comment; however, NHDES notes that soil conditions in New Hampshire vary significantly across short distances, and site-specific subsurface explorations are necessary to understand geologic and hydrogeologic conditions at a proposed landfill site. NHDES reviewed the hydrogeologic conditions for existing landfill sites, and found that hydraulic conductivity ranged between 1x10^{-2} cm/sec and 1x10^{-8} cm/sec in overburden soils, with most hydraulic conductivities in the 1x10^{-3} to 1x10^{-5} cm/sec range. Further, NHDES reviewed the in-situ soil hydraulic conductivity standards required by other Northeastern states and found that the requirements varied. Of the eight states reviewed, only two states specified an in-situ hydraulic conductivity. Maine requires an in-situ hydraulic conductivity less than or equal to 1x10^{-4} cm/sec and Vermont requires an in-situ hydraulic conductivity less than or equal to 1x10^{-5} cm/sec; however, for both states, variances to these requirements may be considered on a case-by-case basis. The other six states set hydraulic conductivity standards for placed materials, that is, base course materials placed and compacted beneath the landfill footprint, or as part of the landfill's liner system(s).

NHDES has revised the hydraulic conductivity standard to encourage interested persons to seek sites with a hydraulic conductivity of 1x10^{-3} cm/sec or less, but to allow sites that do not meet this standard and that are otherwise suitable for a landfill to be developed if the applicant/permittee includes in the landfill's design a 2-foot-thick layer of 1x10^{-4} cm/sec soil placed beneath the landfill footprint.

Comment:

The rule states that undisturbed in-situ soils for 5 feet beneath the footprint should have a hydraulic conductivity of 5 x 10^-3 cm/sec or less, which may not prevent contamination. Improvement: Lower the allowable hydraulic conductivity to 1x10^-5 cm/sec or less to enhance protection against groundwater contamination.

Response: NHDES has lowered the in-situ hydraulic conductivity as noted in the preceding response.

Comment:

The siting of a landfill should require measuring the hydraulic conductivity at the bedrock level. Measuring the hydraulic conductivity at the bedrock level is critical to landfill siting and design. It helps to protect groundwater resources, enhance site characterization, design effective containment systems, and ensure public safety. Implementing such measures can significantly reduce the risk of environmental contamination and improve the long-term performance of landfill facilities. To measure hydraulic conductivity at the bedrock level, conduct hydraulic testing using packer tests, slug tests, or pumping *tests; and conduct an integrated site investigation that combines bedrock hydraulic conductivity measurements with other site investigation techniques, such as geophysical surveys and groundwater modeling to provide a comprehensive understanding of the site's hydrogeology.*

Response: NHDES has revised the hydrogeologic investigation requirements to specifically identify that site soils and bedrock must be characterized; however, NHDES has not identified specific measures to be taken or methods to be used to characterize bedrock, instead relying on the purpose of the hydrogeologic investigation to inform the level of investigation required and the methods by which such investigation must be conducted. The investigation must be performed by a qualified professional in accordance with RSA 310-A. This approach provides sufficient instruction to the applicant, allows flexibility depending on site-specific conditions, and ensures a qualified professional oversees the subsurface investigation(s).

Comment:

Why should leachate be allowed to move at all?

Response: Leachate is required to be collected and managed within engineered waste containment systems at the site. If leachate is released from these systems, it will travel through soil and/or bedrock – neither of which are impermeable. Pre-existing site soils will have some ability to allow leachate to travel. Design and operating requirements are focused on preventing releases and alerting facility personnel when a release occurs so that they can take corrective action. Prompt notification to NHDES of such releases is also required. Siting requirements are focused on minimizing the potential for a release to reach potential receptors, such as water supplies, before the permittee can intervene, intercept, and correct the issue.

Comment:

Revise the hydraulic conductivity standard to read as follows: Undisturbed in-situ soils for 5 feet immediately beneath the footprint and infrastructure area shall have an average saturated hydraulic conductivity of 1 x 10^{-4} centimeters per second (cm/sec) or less.

Should allow for the option of constructing the equivalent of a 5-foot thick layer of 5 x 10^{-3} centimeters per second soil. Construction of such a layer would be subject to oversight and testing and hence would effectively be more protective than a natural soil layer.

The proposed rule is confusing when related to statements in Env-Sw 805 relative to landfill subgrade and subbase. A definition of the landfill liner system would be helpful (i.e., soil/geosynthetic layers as appropriate). We propose that the NHDES consider revising the above proposed rule as follows to provide clarity. "Where present, undisturbed in-situ soil within 5 feet below the landfill liner system shall have an average saturated hydraulic conductivity of 5 x 10-3 centimeters per second (cm/sec) or less."

Response: NHDES has revised the saturated hydraulic conductivity requirement, in part, to allow the option of constructing a base with a hydraulic conductivity of $1x10^{-4}$ cm/sec where the in-situ soils do not meet the $1x10^{-3}$ cm/sec siting requirement. The components of a landfill liner system are identified in Env-Sw 805.05(a).

Env-Sw 804.02(d), renumbered in the FP as Env-Sw 804.02(e), re: Groundwater Protection Standards – Bedrock separation

Comment:

Given the escalating impact of climate change, the base of the bottom most liner system should be increased to be greater than 6 feet above the seasonal high groundwater table.

Revise the bedrock separation requirement to read as follows: The base of the bottom most liner system, or the base of the facility if unlined, shall be a minimum of 8 feet above the seasonal high groundwater table and the confirmed bedrock surface.

Response: NHDES has reviewed other New England and Northeastern states' regulations relative to separation distances between the bottommost liner of a landfill and seasonal high groundwater as well as a bedrock surface. For bedrock, separation distances range from 4 to 10 feet. For groundwater, separation distances, if specified, range from 3 to 8 feet. Further, NHDES has not observed groundwater contamination issues in bedrock where the 6-foot separation requirement is met. NHDES is not proposing a change based on these comments.

Env-Sw 804.02(e), renumbered in the FP as Env-Sw 804.02(f), re: Groundwater Protection Standards – Hydrogeologic investigation

Comment:

Revise the hydrogeologic investigation requirements to read as follows: Identification of the areas cited in (b) through (e) above shall be based upon a comprehensive hydrogeologic investigation which provides all site-specific information required to model the pre-construction and post-construction groundwater and surface water regimen, including nearby bedrock water supplies, and other sensitive receptors as applicable to demonstrate compliance with the siting criteria.

Response: NHDES has proposed revisions to the hydrogeologic investigation requirements.

Env-Sw 804.03 re: Surface Water Protection Standards

Comment:

The rule allows for potential contamination of surface waters by only requiring a demonstration that adverse impacts can be prevented or minimized. Improvement: Mandate a buffer zone at least 1000 feet from any surface water body and require engineered barriers to prevent contamination.

Response: NHDES has proposed a setback (also known as a buffer zone) between the footprint of a landfill and leachate storage units of 200 feet from any first or second order perennial stream and 500 feet from a stream, pond or lake. Waste is required to be contained in the landfill and leachate contained in the landfill and various piping and tank systems, which are engineered barriers. In addition, the subject rule requires that potential adverse impacts must be prevented or minimized and mitigated by facility design. If engineered barriers are needed to meet the standards in rule, the rules require such barriers be constructed and maintained. In consideration of this comment, NHDES has added a requirement that liner systems extend at least 3 feet beyond the limit of waste to reduce, by design, the potential for leachate to discharge outside the waste containment system. See Env-Sw 805.05(m). In addition, NHDES proposed to strength the leachate management requirements by specifying that the purpose of the leachate collection and removal system is, in part, to prevent leachate discharges.

Comment:

To protect the surrounding environment, including streams, wetlands, rivers, lakes, estuaries, and other bodies of water, the requirements must be expanded to ensure that no discharge, spill, leachate release, etc. can reach any of these ground/surface waters in less than five (5) years. This requirement is supported by sound science and allows adequate time for mitigation in the case of a discharge event. It is critical to protect all our water resources, including drinking water (downstream and wells).

Response: The rules compel consideration of groundwater and contaminant travel time, and make the minimum required travel time consistent with site-specific conditions and groundwater monitoring requirements as discussed above in a response to the comment regarding Env-Sw 804 on page one. NHDES is not proposing a change based on this comment.

Env-Sw 804.03(b) re: Surface Water Protection Standards – Landfill and infrastructure areas

Comment:

Add to the requirement the following language: including the requirement that leachate storage and handling areas be constructed in areas underlain by the same liner system required for waste disposal described in Env-Sw 805.

Response: NHDES has proposed adding leachate storage units to the setback requirements in Env-Sw 804.03, and additional design requirements for leachate handling areas to Env-Sw 805.06.

Env-Sw 804.03(c) re: Surface Water Protection Standards – Landfill and infrastructure areas

Comment:

Add to the requirement the following language: as determined by a minimum 5-year travel time between the spillage and the closest perennial water body, as determined in Env-Sw 804.

Response: The rules compel consideration of groundwater and contaminant travel time, and make the minimum required travel time consistent with site-specific conditions and groundwater monitoring requirements as discussed above in a response to the comment regarding Env-Sw 804 on page one. NHDES is not proposing a change based on this comment.

Env-Sw 804.03(d) re: Surface Water Protection Standards – Perennial surface water setbacks

Comment:

Revise the language to read: The footprint of a landfill, including the location of its leachate storage and handling infrastructure, shall not be located within a 5-year travel time of any perennial surface water body, measured from the closest bank of a stream and closest shore of a pond or lake, as applicable. Travel time is determined as described in Env Sw 804.

Response: NHDES has added leachate storage units to the rule. The rules compel consideration of groundwater and contaminant travel time, and make the minimum required travel time consistent with site-specific conditions and groundwater monitoring requirements as discussed above in a response to the comment regarding Env-Sw 804 on page one.

Env-Sw 804.03(f) re: Surface Water Protection Standards – Water reservoirs and intakes

Comment:

Revise the language to read: The footprint of a landfill shall not be located within 5-year travel time of a surface water reservoir or intake used for a community drinking water supply. The travel time is determined as described in Env Sw 804.

Response: The rules compel consideration of groundwater and contaminant travel time, and make the minimum required travel time consistent with site-specific conditions and groundwater monitoring requirements as discussed above in a response to the comment regarding Env-Sw 804 on page one. NHDES is not proposing a change based on this comment.

Env-Sw 804.03(h) re: Surface Water Protection Standards – Hydrogeological investigation

Comment:

Revise (h)(3) to read: (3) Any potential release of contaminants to surface waters can be prevented or, in the case of a release, detected and remediated prior to reaching a surface water resource.

Response: NHDES has revised the language to clarify the requirement, including a reference to hydrologic investigation. In addition, hydrology was added to Env-Sw 805.08(a) for consistency.

Env-Sw 804.04 re: Set-back requirements

Comment:

The buffer zones of 100 feet from property lines and 300 feet from roads are not sufficient to protect nearby communities and ecosystems. Improvement: Increase the buffer zone to at least 500 feet from property lines and 1000 feet from public roads to provide better safety and minimize nuisances such as odor and noise.

Response: The setbacks for the property line and roads are not proposed for change. NHDES has proposed improvements to reduce the potential for migration of nuisance conditions by requiring vegetation in accordance with Env-Sw 805.11(l), requiring inspections of fences in accordance with Env-Sw 806.08(c)(11), and weekly litter inspections and removals in accordance with Env-Sw 806.08(d). Further, in accordance with Env-Sw 1005.01(d), a permittee is required to control to the greatest extent practical dust, litter, insects, odors, vectors, spills, the production of leachate, fire hazards, the generation of methane and other hazardous gases, noise, and other nuisances. NHDES is not proposing a change based on this comment.

Comment:

Restore language from the October 2023 draft regarding the Wendell Ford Act.

Response: NHDES has not included language relative to the Wendell Ford Act in the Final Proposal because the requirement already exists by reference in Env-Sw 802. NHDES has proposed a change to the notification requirements in Env-Sw 300 to request that the Federal Aviation Administration (FAA) evaluate the applicability of the Wendell Ford Act to any applicable application.

Env-Sw 805 re: Design Requirements

Comment:

25- and 50-year design storms aren't going to cut it (due to climate change).

Response: NHDES revised the design storm requirements from 25-years to 50-years and removed the 20% increase requirement for clarity and consistency. Landfills are designed in phases over time. Final design and construction plans are typically approved 1-2 years prior to construction. As such, final design and construction plans will be required to address changes to design storms over time.

Env-Sw 805.01(a)(1) re: Applicability of Design Requirements

Comment:

The proposed language should be revised to be consistent with the proposed language of Env-Sw 804.01(a)(1) to exempt landfills for which a permit or permit modification was issued prior to the 2024 readoption of the solid waste rules. The commenter proposes the following language: "Portions of existing facilities for which a permit or permit modification was issued prior to the 2024 readoption of the solid waste rules."

Response: NHDES has revised the language for clarity but has not revised the intent behind the rule. Standard permits and Type I-A permit modifications provide preliminary plan approval. It is important that final designs are updated as information and technologies evolve. For example, a preliminary plan may be approved 10 years before a final design plan. In the 10-year timeframe, design storms may change. The final plans must be adjusted to reflect the changed design storm. This is one example of why the exemption applies to existing (already built) facilities and facilities with final construction plan approval. Also, NHDES revised the language in 804.01(a)(1) for clarity and to be consistent with the change made to 805.01(a)(1).

Env-Sw 805.03 re: Landfill Subgrade and Base Grade Standards

Comment:

Remove the word "undisturbed" from section (e) to eliminate any potential lack of clarity about the ability to compact, apply moisture, or otherwise improve (without removing) the twelve inches of base soils in order to meet the requirements of (d) 1 through 4.

Response: NHDES has revised the requirements for clarity.

Comment:

The statements in the proposed rule are confusing when related to statements in Env-Sw 804 relative to landfill subgrade and subbase. We propose that the NHDES consider revising the above proposed rule as follows to provide clarity.

> *Env-Sw 805.03 Landfill Subgrade Standards.*
>
> *(a) The landfill subgrade shall:*
>
> > *(1) Be the layer of soil directly below the bottom liner;*
> >
> > *(2) Be graded and prepared for landfill construction; and*
> >
> > *(3) Have sufficient structural integrity to support the facility under all anticipated loading conditions during all phases of construction, operation, and closure.*
>
> *...*
>
> *(d) For geomembrane lined facilities, the soil layer directly below the bottom liner shall:*
>
> *...*
>
> *(f) Landfill liner grades shall be sloped to facilitate compliance with Env-Sw 805.06 and Env-Sw 806.05.*

Response: NHDES has revised the requirements for clarity.

Env-Sw 805.05 re: Liner System Design Standards

Comment:

The rule allows for single-liner systems in certain conditions, which increases the risk of leachate leakage. Improvement: All landfills, regardless of waste type, must have double-liner systems, with one liner being a composite liner that meets stringent hydraulic conductivity standards.

Response: NHDES is proposing that at least one liner in a landfill be a composite liner, regardless of whether the landfill is single-lined or double-lined. NHDES believes that single-lined landfills are appropriate for management of a limited subset of waste types, namely, construction and demolition debris only or coal ash only, provided the characteristics of the waste are consistent and do not pose a threat to groundwater quality. NHDES notes that a double liner is required for these waste types if the characteristics of the wastes cannot be consistently determined or assured, or the characteristics pose a threat to groundwater quality. NHDES has adjusted the language to ensure that, when a double-liner is required, that one liner is composite.

Env-Sw 805.05(j) re: Liner System Design Standard – Penetrations of the Liner

Comment:

The proposed restriction should be limited to the landfill base liner at the bottom of the landfill where leachate may collect. The commenter proposed the following language "The base of the bottom most liner system shall not be penetrated by any appurtenances."

As proposed, the restriction of not penetrating the liner system will eliminate the potential of landfill over liner designs. Penetrations can be engineered and installed in a manner that is protective of the liner *system with engineered and fabricated systems of high-density polyethylene (HDPE) material (the same material as the geomembrane) that would allow for a safe alternative other than an unconditional prohibition on liner system penetrations. These systems can be designed and manufactured in a manner to allow integrity testing after installation.*

Response: The subject rule has been clarified by removing "including at the low point" to prohibit penetrations of liner systems, regardless of whether the penetration is at a low point or not because leachate does not travel only in low areas. If a unique situation arises that warrants a site- or circumstance-specific allowance, applicants/permittees may apply for a waiver. NHDES believes these circumstances are exceptionally rare, and is not proposing a change based on this comment.

Env-Sw 805.06 re: Leachate Collection and Removal System Design Standards

Comment:

Leachate management area/load out area is the weak spot. The rules should require that any area where there is leachate management taking place should be as protective as the double-lined landfill. Leachate handling areas should be double-lined in the event of a spill.

Response: NHDES proposed adding minimum design requirements for leachate transfer areas. See Env-Sw 805.06(t). May cause increase in cost unless the facility has an existing concrete pad; however, the requirement wouldn't apply unless a facility design change is proposed.

Comment:

Trucking of leachate is antiquated. The next landfill should not have trucks responsible for transporting leachate.

Response: Leachate must be transported to a wastewater treatment facility for disposal. The rules allow transportation by pipeline or by hauling. Not all landfills are or can be located near a wastewater treatment facility that allows for efficient piping; therefore, hauling leachate by tanker truck or other transport method is an appropriate alternative. NHDES is not proposing a change based on this comment.

Comment:

The rule allows up to 7 days of leachate storage on the liner, posing a risk of overflow during heavy rainfall events. Improvement: Limit the storage time to 48 hours and require redundant systems to ensure immediate leachate removal, preventing hydraulic head build-up.

Response: NHDES has clarified the requirements regarding the prevention of leachate discharges; however, leachate systems must be able to store leachate generated from the 100-year storm event. In addition, a permittee is required pursuant to Env-Sw 1005.01(d) to minimize the production of leachate and prevent spills. Further, NHDES has added a requirement to Env-Sw 805.05 that requires separation between the limit of the waste containment system and the limit of waste. These requirements, combined, minimize the potential for leachate overflow. NHDES has not proposed a change to the storage timeframe due to practical considerations for leachate removal and leachate receipt at an authorized wastewater treatment facility.

Comment:

Reconsider the 25-year storm standard for leachate management design. Given the potential environmental risks, upgrading this to a 50-year or 100-year storm standard could provide greater protection.

Response: NHDES revised the design storm requirements from 25-years to 50-years and removed the 20% increase for clarity and consistency. See Env-Sw 805.09(b), (f), and (g).

Comment:

In proposed Env-Sw 805.06(f) through (g), certain statements are confusing specifically as to how/where the 20 percent requirement is to be accounted for and the reference to time of concentration, which would yield a lower than intended rainfall amount. We propose that the NHDES consider revising the above proposed rule statements as follows to provide clarity and to be consistent with other related calculations.

> *(f) Leachate collection and removal systems shall be designed to maintain one foot or less of hydraulic head on all portions of the liner, excluding the leachate collection sumps if any. This condition shall be met during routine operations and the precipitation from 25-year, 24-hour storm event that is increased by 20 percent.*
>
> *(g) Leachate collection and removal systems shall be designed to manage the quantity of leachate to be generated by the 100-year, 24-hour storm event in a manner which shall:*
>
> *[...]*
>
> *(h) Leachate collection and removal systems which are not directly connected to a permitted wastewater treatment facility shall provide capacity for storing leachate as follows:*
>
> > *(1) At least 15% of the 100-year, 24 hour storm event storage volume, as specified by (g) above, shall be provided in primary storage units located outside the waste deposition area or in sumps located within the waste deposition area*
> >
> > *[…]*
> >
> > *(3) Containment for the volume of leachate produced by the 100-year, 24-hour storm event which exceeds the volume of the primary storage units shall be provided:*
> >
> > *[...]*

Response: NHDES has revised the 25-year storm event plus 20 percent to be the 50-year storm event. Using a storm event without adjustments is consistent with other requirements relative to stormwater management, and less confusing. NHDES notes that the 25-year storm event increased by 20% is about equal to a 50-year storm event. NHDES has also adjusted the requirements to base the design on a 24-hour storm event. Further, NHDES has replaced “operations” with “leachate flows” for clarity.

Env-Sw 805.06(c) re: Leachate Collection and Removal System Design Standards – Leak Tight

Comment:

The rule should acknowledge that existing piping need not be upgraded to the new standard.

Response: A grandfathering provision is provided in Env-Sw 805.01(a)(1). NHDES is not proposing a change based on this comment.

Env-Sw 805.06(k) re: Leachate Collection and Removal System Design Standards – Solvent welded pipes

Comment:

Revise the requirement to read: Pipes which require solvent welding may only be used in leachate vaults that provide secondary containment and are equipped with a highwater alarm, a backup high-water alarm, and automatic dialers in accordance with (q) below.

Response: NHDES made modifications to the rule which added the language regarding being equipped with a high-water alarm, a backup high-water alarm, and automatic dialers. NHDES is not proposing to add the language regarding secondary containment because the leachate vault provides secondary containment for leachate piping, therefore, the suggested language is unnecessary.

Env-Sw 805.06(q) re: Leachate Collection and Removal System Design Standards – Tanks, sumps and other storage units

Comment:

Revise the requirement to read: Tanks, sumps, and other storage units associated with leachate collection and removal systems shall be co-located with the same leak detection liner system as required for waste disposal as specified in Env Sw 805 and be equipped with high-water alarms, backup high-water alarms, and automatic dialers.

Response: The proposed change to add that such systems "be co-located with the same leak detection liner system as required for waste disposal" would add a third containment system. The proposed change would create financial and operational burdens, as well as complicate engineering design and construction. The proposed change exceeds existing requirements for the management of gasoline, petroleum, and hazardous wastes. NHDES is not proposing a change based on this comment.

Env-Sw 805.06(r) re: Leachate Collection and Removal System Design Standards – Secondary containment

Comment:

Additional language should be added to this section clarifying that existing underground pipes in-ground prior to the 2024 readoption of this chapter can be used to manage leachate from new piping (with double wall or with secondary containment), without having to upgrade the containment status of the existing piping. This will ensure new leachate piping constructed after readoption of the rule may be piped/discharged and combined into existing leachate mains at an upstream point in a facility to utilize the existing infrastructure.

Response: NHDES has revised the language for clarity.

Comment:

Revise the requirement to read: Pipes, tanks, sumps, and other conveyance or storage units associated with leachate collection and removal systems located outside the waste deposition area shall be co-located with the same leak detection liner system as required for waste disposal and have secondary containment or be double-walled except for underground pipes, manholes, and other buried leachate systems existing prior to the 2024 readoption of this chapter.

Response: NHDES proposes to add secondary containment systems, including double-walled piping, to the leachate management system design requirements. The proposed change to add that such systems "be co-located with the same leak detection liner system as required for waste disposal" would add a third containment system. The proposed change would add financial and managerial burdens, as well as complicate engineering design and construction. The proposed change exceeds existing requirements for the management of gasoline, petroleum, and hazardous wastes. NHDES is not proposing a change based on this comment.

Env-Sw 805.09 re: Stormwater Management System Design Standards

Comment:

Designing for the 25-year storm event is not deemed sufficient, given the increasing storm intensity due to climate change. Improvement: Design the stormwater management system to handle the 100-year storm event to ensure robustness against extreme weather conditions.

Stormwater management systems should be designed to handle 100-year storm events, or even 200-year storm events, due to climate change.

Response: The rule, as proposed, increases the design storm from a 25-year event to a 50-year event in consideration of extreme weather conditions. NHDES is not proposing a change in response to this comment.

Comment:

We propose that the NHDES consider revising the [...] proposed rule statements as follows to provide clarity and to be consistent with other related calculations.

> *(b) Stormwater management systems shall be designed to accommodate the 50-year, 24-hour storm event.*
>
> *[…]*
>
> *(g) Peak surface run-off from the landfill site during the 50-year, 24-hour storm event shall be controlled and maintained at the pre-development discharge rate, in accordance with RSA 485-A*

Response: NHDES has revised the rule as suggested.

Env-Sw 805.09(g) re: Stormwater Management System Design Standards – Design Storm

Comment:

A grandfathering/exemption statement for existing permitted facilities should be provided. Using historical design criteria for existing facilities and new facilities, when combined/co-located, and the update precipitation data requirement may make this requirement difficult to meet.

Response: A grandfathering provision is provided in Env-Sw 805.01(a) for "Portions of existing permitted facilities which were constructed or a facility for which final design plans and specifications are approved for construction in accordance with Env-Sw 315 as of the 2024 effective date of this chapter" in the proposed rules. Construction of new facilities and expansion of existing facilities, regardless of whether they are co-located with previously constructed facilities, must meet new design standards to protect public health, safety and the environment. NHDES is not proposing a change based on this comment.

Env-Sw 805.10 re: Landfill Capping System Design Standards

Comment:

The rule does not specify detailed requirements for erosion-resistant measures in capping systems. Improvement: To ensure long-term stability, mandate the use of advanced erosion control materials and methods, such as reinforced geomembranes and vegetative cover with deep-rooted plants.

Response: Env-Sw 805.10(e)(5) requires that the final layer on a landfill cap must "stabilize the capping system against the forces of wind and water erosion," among other requirements. There are many effective erosion control measures that may be deployed, and these measures continue to evolve. At this time, NHDES prefers to specify performance standards for this particular requirement rather than the method in which the performance standard must be met. NHDES is not proposing a change based on this comment.

Comment:

In section (q), revise the exception for the maximum slope of 2.5:1 to include access roads along with stormwater infrastructure. Establishing viable access roads to the top deck of the closed landfill is important, and the short slopes along the edges of the access road may require steep slopes to tie into the existing waste and cap slopes.

Response: NHDES has revised the language to allow access roads to have steeper side slopes when needed.

Env-Sw 805.12(a) re: MSW Landfill Design Standards

Comment:

In general, there is some confusion in the proposed revised language relative to liner systems and subgrades. Specifically, relative to Env-Sw 805.12(a) and the requirement for one of the liners to be a composite liner, the language should be revised to also reference Env-Sw 805.05(k) to clarify CGLs [sic] only need to extend across the base and 10 feet up the side slopes ("and one of the liners shall be a composite liner pursuant to Env-Sw 805.04(c) and Env-Sw 805.04(c) *[sic]").*

Response: NHDES has revised the language in Env-Sw 805.12 through 15 to also reference Env-Sw 805.05(k), as applicable.

Env-Sw 805.16 re: Quality Assurance/Quality Control Plan

Comment:

Recommend that references to specific ASTM standards in Env-Sw 805.16 (Quality Assurance/Quality Control (QA/QC) Standards for Liner and Capping Systems) be removed as these standards change over time. The NHDES should require that the QA/QC plans include the appropriate and applicable ASTM, GRI, and other relevant standards/guidance and hold applicants accountable to using the current and active standards/guidance.

Response: In accordance with NH rule writing requirements, NHDES is obligated to include specific detailed references for standards, including edition numbers and dates.

Env-Sw 805.16(c)(5) re: Quality Assurance/Quality Control – Reporting

Comment:

Suggest elimination of the term QA as it is not used in Env-Sw 1104.04 and not defined in Env-Sw 100.

Response: NHDES has revised Env-Sw 805.16(c)(5) for clarity.

Env-Sw 806.03(f) re: Landfill cover during operations – Alternate daily cover

Comment:

There appears to be a typo and the referenced section should be (e)(2)d. instead of (d)(2)d.

Response: NHDES has revised Env-Sw 806.03(f) as suggested.

Comment:

Suggest that the reference to (d)(2)d be changed to (e)(2)d.

The commenter proposes that Env-Sw 806.03(f) be amended to eliminate the requirement that permittees apply for two (2) separate permit modifications, once to obtain approval of a demonstration project and then again for approval for use of the alternate daily cover material. As the Department knows, each request for a permit modification under this proposed rule change would include a maximum 180-day review period (see proposed Env-Sw 305). In addition to this lengthy permitting timeframe, the rule requires a 60-day demonstration period. Thus, under the proposed rules, it could take a permittee well over a year to secure approval by DES for use of an alternate daily cover material. The commenter believes the goal of this section can be achieved in a single step permit modification process with a 30-to-60-day demonstration period.

Response: Current rules require a landfill permittee interested in using a new alternate daily cover to submit an application to certify a waste-derived product. If the application is approved, the landfill permittee must then submit a Type III permit modification application to use the approved alternate daily cover. The proposed rules, including proposed changes to Chapter Env-Sw 300, require: (1) the permittee to submit a proposed demonstration via a Type III permit modification application, and, (2) following the demonstration project, the permittee to submit a request to use the alternate daily cover material via a Type II permit modification application. Review times between the two approaches are anticipated to be relatively similar. Regardless of review times, this change will improve conformance with the performance standards for cover materials in Env-Sw 806.03 and allows the permittee greater flexibility in demonstrating a specific composition and thickness of alternate daily cover material will meet the performance standards. The demonstration period of 60-days was selected based on a review of other states' demonstration project requirements and comments from interested persons during the rulemaking process. NHDES is not proposing a change to Env-Sw 800 based on this comment.

Env-Sw 806.03(j) re: Landfill cover during operations – Relying on demonstration projects by others

Comment:

Suggest that (f) and (g) be changed to (g) and (h) to reference the correct section of the solid waste rules.

Response: NHDES has revised Env-Sw 806.03(j) as suggested.

Env-Sw 806.03(k) re: Landfill cover during operations – Intermediate cover

Comment:

As worded, the condition could be interpretated to require intermediate cover at a frequency of every 90 days. Intermediate cover is typically placed over the waste once and not at a recurring frequency. We suggest the following language: "At landfills receiving MSW, an intermediate cover shall be placed over all waste no more than 90 days following the last any waste was added to the area and shall consist of at least:"

Response: NHDES has adjusted the language for clarity.

Comment:

Please add language defining intermediate cover as a total of 12 inches of soil, which may include the bottom 6 inches which can be previously placed daily cover soil. Also, revise (1) and (2) above to allow use of soil with exceedances of the soil remediation standards ("contaminated soil") in the lower 6 inches of the 12-inch thick intermediate cover profile (or under temporary geomembrane). In practice, landfills that use 6 inches of contaminated soil as daily cover (per Env-Sw 806.03(e)(2)(e)) will have to place an additional 12 inches of soil to create an intermediate cover layer, effectively creating an 18 inch cover layer (daily + intermediate cover), when a total of 12 inches of soil should suffice. There should be no restriction on placing temporary geomembrane over 6 inches of contaminated soil to create an intermediate cover layer. The geomembrane eliminates leaching (re-directs precipitation from infiltrating) and human/ecological exposures to the contaminated soil. Moreover, use of soil that does not exceed the soil remediation standards should be allowed in the top 6 inches of the 12-inch thick intermediate cover profile. Soil remediation standards were established such that at concentrations below which human and ecological expose and leaching are insignificant.

Importing 12 inches of soil to establish intermediate cover over 6 inches of daily cover soil will result in a substantial cost increase to pay for the imported soil, will strain available clean borrow resources, and will potentially add an additional 6 inches of soil to the daily/intermediate cover profile (18 inches total) that will offset precious MSW air space. Not allowing use of contaminated soil (soil with soil remediation standard exceedances) in the lower 6 inches of the intermediate cover profile (or immediately below temporary geomembrane) will strain limited available regional outlets for contaminated soil disposal/management as landfills will be forced to reduce the volumes of contaminated soil accepted.

Landfills that rely on tipping fees from contaminated soil will also be forced to pass cost increases in other service areas to recoup lost revenue from reducing contaminated soil acceptance and incurring costs to import clean, natural soil.

Response: In NHDES' experience, during placement and initial stabilization, intermediate cover has a tendency to erode and travel into stormwater systems. Soils with concentrations of regulated contaminants below the soil remediation standard (SRS) in Env-Or 606.19 are anticipated to create no appreciable health risk. To ensure the risk to public health and the environment is minimized, contaminated soil that does not exceed the SRS may be used for intermediate cover; however, soil with regulated contaminants that exceed the SRS may not be used for intermediate cover. NHDES has revised the rule to allow the full 12-inch thick depth of intermediate cover to contain regulated contaminants below SRS.

The proposed rules do not preclude or restrict the permittee from requesting that alternate daily cover with regulated contaminants below the SRS be allowed as part of intermediate cover. If a permittee elects this path, the permittee must request approval of an updated facility operating plan.

Env-Sw 806.03(l) re: Landfill cover during operations – Final cap

Comment:

An exemption to the 5-year time frame for final capping should be specifically granted if a temporary seam-fused geomembrane is used to create an intermediate cover layer.

Response: The proposed rule includes the ability to seek an alternative schedule, therefore, an exemption for a specific type of temporary cap is not required. NHDES is not proposing a change based on this comment.

Env-Sw 806.05 re: Leachate Management Requirements

Comment:

In the proposed rule, certain statements are confusing specifically as to how/where the 20 percent requirement is to be accounted for. We propose that the NHDES consider revising the above proposed rule statements as follows to provide clarity and to be consistent with other related calculations.

> *(c) A leachate management plan shall be developed, included in the facility's operating plan, and implemented at all lined landfills, based on the following criteria:*
>
> > *(1) Routine facility operations, including operations during the 25-year, 24-hour storm event, increased by 20 percent, shall not result in more than one foot of hydraulic head on the liner system(s);*
>
> *[…]*
>
> *(f) If approved by the department, the practice of leachate recirculation shall:*
>
> > *[…]*
>
> *(2) Not cause the facility to operate in excess of 12 inches of hydraulic head on the liner. This condition shall be met during routine operations and the precipitation from 25-year, 24-hour storm event increased by 20 percent.*
>
> *(g) Storage capacity shall be required to contain the leachate generated by the precipitation from the 100-year, 24-hour storm event in accordance with Env-Sw 805.06.*

Response: NHDES has revised the 25-year storm event plus 20 percent to be the 50-year storm event. Using a storm event without adjustments is consistent with other requirements relative to stormwater management, and less confusing. NHDES notes that the 25-year storm event increased by 20% is about equal to a 50-year storm event.

Env-Sw 806.08(d)(3) re: Inspection, Maintenance, Monitoring, Recordkeeping, and Reporting Requirements – Secondary System Measurements

Comment:

It should be clearly acknowledged that leachate measurements may be obtained through electronic/telemetric means.

Response: The proposed rules do not prohibit or preclude measurement using electronic/telemetric means. For clarity, NHDES has added a provision specifically in consideration of the use of electronic measurement systems, including SCADA, and inspection requirements for such systems.

Env-Sw 806.08(k) re: Inspections, Maintenance, Monitoring and, Reporting, and Recordkeeping Requirements – Odor Control Evaluation

Comment:

Env-Sw 806.08(k) will create a third odor and landfill gas reporting requirement for landfills. For landfills regulated under a Title V air permit and required to file periodic Landfill Gas Collection and Control System Operation and Monitoring Reports pursuant to the air permit, there is substantial overlap with the proposed requirements under 806.08(k). A majority of the required information is already being reported to the NHDES in the Landfill Gas Collection/Operation Monitoring reports (submitted to the Air Resources Division-ARD) and with information being provided in Landfill Quarterly and Annual Operations Reports (Env-Sw 806.08(e) and (g)(7)), submitted to the SWMB.

If the odor control evaluation requirement stands, the commenter assumes the content and level of effort in preparing the annual odor control evaluation and responding to the requirements of Env-Sw 806.08(k)(1 through 8) will be commensurate with the number and type of odor complaints received by the facility over the past year's evaluation period.

Response: Air regulations require the monitoring of landfill gas emissions through indicator parameters such as flammable gases, but do not require odor control, monitoring, and evaluation. Further, prior to this rule readoption, there are no requirements for reporting and evaluating landfill odors in a solid waste annual facility report (ref. Env-Sw 806.08(g)) or a solid waste quarterly operations report (ref. Env-Sw 806.08(e)). While evaluation of a landfill gas control system is one element of the proposed annual odor control evaluation, the report requires a comprehensive review of odor control practices (beyond use of only a landfill gas collection and control system), industry best management practices, a holistic review of odor complaints received, and identification and implementation of specific actions the permittee can take to address odor issues. NHDES is not proposing a change based on this comment.

Comment:

The proposed rule requires landfill operators to prepare and submit an annual odor control evaluation that is overly burdensome and does not add value to the landfill operation nor the environment. The proposed rule is clearly intended for landfills that have odor issues, which should not be applied ad hoc to every site. Rather, a more effective and meaningful annual evaluation requirement for a landfill that is not experiencing odor issues would be as follows:

o Facility Description, including a description of the gas collection and control system (GCCS), and system changes since the previous reporting year;

o Odor Control / Complaint Evaluation, consisting of a summary of odor control practices and measures employed by the facility during the reporting period that includes the location(s) of the practices and their effectiveness as evidenced by odor complaints;

o Anticipated Landfill Gas Collection System Changes, summaries anticipated GCCS expansion for the next year;

o Action Items, including planned physical and operational changes deemed necessary based on the previous year's performance and anticipated landfill development; and

o Supporting Information, including current, next year, and final depictions of the GCCS, a figure showing odor complaints by location, figure depicting landfill cover types, summary of current year's surface emissions monitoring results, and logs of odor complaints and waste loads rejected due to odors.

The above does not prevent the NHDES from requiring additional information from landfills that have significant odor issues.

Response: Odor issues related to landfills are not predictable, therefore, maintaining a consistent rule for all landfills is the most effective and equitable way to address odor issues. NHDES is not proposing a change based on this comment.

Env-Sw 806.08(k) and (l)(3) re: Inspections, Maintenance, Monitoring and, Reporting, and Recordkeeping Requirements – Average Secondary System Flow Rates

Comment:

Decreasing the reporting threshold of the average secondary leachate flow rates from 100 to 50 gallons per tributary acre per day. While this change may appear to be environmentally protective, in reality, the associated increase in water thickness that over [sic] a liner system is negligible. Because of this, a change in the rule is unnecessary a[s] it would result in an increase in incident reports (and an increased burden on the operator and the NHDES) for a condition that has no environmental impact.

Response: The secondary leachate collection system is also known as the leak detection system for the primary liner. Monitoring of secondary flow rates serves the purpose of identifying potential leaks in the primary liner system, as well as identifying performance issues related to the primary and secondary liner systems, and leachate measurement, monitoring, pumping, and removal systems. NHDES has proposed to lower the investigation threshold for the rolling 30-day average secondary flow rate from 100 gallons per acre per day (gpad) to 50 gpad based on a review of historical secondary flow rate data.

Secondary flow rates in excess of 50 gpad, and not related to construction, have been consistently associated with damage to liner systems. NHDES has observed that well performing landfill systems have average secondary flow rates less than 25 gpad, with periodic increases due to operational changes. Further, NHDES has observed that flow rates between 25 and 100 gpad generally trigger an internal investigation by landfill permittees. The change may result in a limited increase in formal investigation reports required to be filed with NHDES; however, to protect public health, safety, and the environment, potential damage to liner systems must be promptly and thoroughly investigated and repaired. NHDES is not proposing a change based on this comment.

Comment:

DES has provided no justification for reducing the threshold for which a response action plan (investigation report) is required from 100 gallons per tributary acre per day to 50 gallons per tributary acre per day. The commenter proposes that the rule should remain unchanged. The initial reporting for rates which exceed 25 gallons per acre per day is sufficient to monitor facility performance and no justification has been provided for requiring a response action plan below the current rules' 100 gallons per tributary acre per day threshold.

The commenter offers the below calculations for DES's consideration, which provide the equivalent thickness in both inches and millimeters of film of leachate flowing over the secondary liner geomembrane corresponding to daily tributary flows of 25 and 100 gallons per acre per day (gpacd).

*At 25 gpacd, the equivalent film thickness is 25 gpacd * 1 cubic foot/7.481 gallons * 1 acre/43,560 square feet * 12 inches/foot = 0.00092 inch * 25.4 millimeters/inch = 0.023 millimeters (mm).*

*At 100 gpacd, the equivalent film thickness is 100 gpacd * 1 cubic foot/7.481 gallons * 1 acre/43,560 square feet * 12 inches/foot = 0.0037 inch * 25.4 millimeters/inch = 0.094 mm.*

The Department has not identified any additional environmental benefit by reducing the secondary leachate flow from 100 gpacd to 50 gpacd, or reducing the equivalent film thickness from 0.094 mm to 0.047 mm (quite literally the equivalent of a fraction of a millimeter), which will not result in any appreciable decrease in the hydraulic head driving leachate across the liner.

In addition, the proposed rule should allow up to 60 days from the initial reporting of the flow rate for the permittee to submit a response action plan. The establishment of this lower value with the proposed actions outlined in Env-Sw 806.08(m)(2) provides regulatory structure that will lead to the pre-mature closure of landfill airspace as a result of 0.047 mm less of film being identified in the secondary collection system. This difference in thickness does not result in a driving hydraulic head leading to harm to the environment or public health.

Response: The secondary leachate collection system is also known as the leak detection system for the primary liner. Monitoring of secondary flow rates serves the purpose of identifying potential leaks in the primary liner system, as well as identifying performance issues related to the primary and secondary liner systems, and leachate measurement, monitoring, pumping, and removal systems. NHDES has proposed to lower the investigation threshold for the rolling 30-day average secondary flow rate from 100 gallons per acre per day (gpad) to 50 gpad based on a review of historical secondary flow rate data from NH's double-lined municipal solid waste landfills. Secondary flow rates in excess of 50 gpad, and not related to construction, have been consistently associated with damage to liner systems. NHDES has observed that well performing landfill systems have average secondary flow rates less than 25 gpad, with periodic increases due to operational changes. In addition, NHDES has observed that flow rates between 25 and 100 gpad generally trigger an internal investigation by landfill permittees. These internal investigations have found holes in liner systems that, had a leachate head been present, would have produced secondary flow rates greater than 100 gpad. Because the defects were identified on sideslopes, where leachate was being rapidly removed from the liner system, the secondary flow rate investigation threshold was not triggered. Permittees have demonstrated that waiting for the 100 gpad threshold is not in the best interests of the permittee or the public.

For additional context, permeation through the types of liner systems specified by the NH Solid Waste Rules under 1 foot of leachate head is about 0.1 gpad based on the work of J. P. Giroud and R. Bonaparte (1989). Under the same 1 foot of head on the liner, a small hole (0.08 inch diameter) can produce about 100 gpad, and a large hole (0.445 inch diameter) can produce about 3,000 gpad. With the addition of composite liner systems to the rules, these numbers will be lowered significantly (up to about 0.7 gpad for large holes). While both proposed and existing systems will be subject to the lowered investigation threshold, exceeding the threshold does not compel closure of a landfill. A number of other options are available to address secondary flow rates that exceed 50 gpad, and closure of a landfill would be an extreme measure reserved for those situations in which no other solution can be found or implemented to address leachate flow rates in secondary systems that indicate a significant defect in the liner system(s).

NHDES is not proposing a change to the thresholds based on this comment, but has increased the time allotted for an investigation.

Env-Sw 808.02 re: Pre-requisites for Landfill Reclamation

Comment:

Landfill reclamation projects have demonstrated considerable environmental benefits and are anticipated to be a viable solution for many sites, and therefore should be encouraged, not discouraged. As such, if any revision to this section of the rules is made, the revision should help simplify and streamline the reclamation process. Please revise to describe the procedure for obtaining approval of a feasibility scope of work – is it a permit modification? Permit modifications should be limited to approval of the landfill remediation [sic] work plan. A permit modification shouldn't be needed for submitting a request for a feasibility study.

Response: Landfill reclamation requirements have been streamlined for clarity and consistency. A feasibility study that involves subsurface explorations must be approved by the department via a permit or permit modification process because the work involves exploration within the waste mass, which can damage landfill systems. Further, the department is instructed in RSA 149-M to administer a permit system and thus must issue approvals within the framework of the permitting system. In consideration of this comment, NHDES has made minor adjustments to Env-Sw 808.01 for clarity.

Other re: Regional Impact Assessments

Comment:

Recent legal changes regarding regional impact assessments. Could you please clarify whether these updates will be incorporated into the forthcoming requirements?

Response: HB 1221 proposed revisions to regional impact in RSA 36, *Regional Planning Commissions*. As RSA 36 relates to the actions required of regional planning commissions and local land use boards, NHDES has not proposed revisions based on this bill.

Other re: Staffing

Comment:

Consider requiring every landfill operator to have at least one person, such as a guard, on site every hour of every day of the year. The intent is that this individual will be present if a system fails.

Response: NHDES notes that areas where liquids may leak are required to have alarms and, as proposed, automatic dialers that notify facility staff when an alarm has been triggered. NHDES is not proposing a change to staffing based on this comment, but has further clarified the requirements related to alarms and automatic dialers. Specifically, NHDES has added a requirement that automatic dialers attempt to contact facility personnel every 10 minutes until personnel respond to the site to reset or turn off the dialer.

Other re: Changes, Assumptions and Objectives

Comment:

Provide a comparison of what is improved in the new regulations versus the old.

Response: See the initial and final rule proposals for changes.

Comment:

Please identify assumptions and objectives in the Department's rule making process. What purpose are the rules to serve?

Response: As stated in Env-Sw 101, the purpose of the rules in subtitle Env-Sw is to minimize risks to the environment and public health and safety by assuring proper management of solid waste.

From OLS:

Env-Sw 803.03(f)(3)

Comment: *Unclear/Edit - Technically, the definition in the CFR is for "Director of an Approved State".*

Response: NHDES has added this language for clarity and consistency with the CFR.

Env-Sw 803.04(a)(2)

Comment: *Unclear – Why is 40 CFR 258.22 [Disease vector control], 40 CFR 258.25[Access Requirements], 258.26 [Run-on/run-off Control systems], and 258.27 [Surface Water Requirements] not required? These also seem like important operation criteria.*

Response: NHDES has approved delegation for the entire section in 40 CFR 258 and this section does not include those that are less stringent than the administrative rules.

Env-Sw 803.04(a)(5)

Comment: *Unclear – Why is only one paragraph required, when the entire section has closure requirements?*

Response: The other requirements in 40 CFR 258.60 conflict with and are less stringent than the state requirements.

Env-Sw 804.03(d)(1) and (2)

Comment: *Edit - Reword so number is not at the beginning. "For any first or second order perennial stream, 200 feet; and "For any other perennial surface water body, measured from the closest bank of a stream and closest shore of a pond or lake, as applicable, 500 feet."*

Response: NHDES has revised the wording as suggested and added the language "as measured from the closest bank of a stream" to Env-Sw 804.03(d)(1) for consistency and clarity.

Env-Sw 805.03(d)(3)

Comment: *In Env-Sw 805.03(d)(3), OLS identified that "ASTM" is an abbreviation and must be spelled out.*

Response: NHDES reviewed the current naming convention of ASTM International and found that, in 2001, the "American Society of Testing and Materials" was renamed "ASTM International." As such, NHDES has not made a change based on this comment.

Second part of comment, Incorporation by Reference included with package. This publication is also referenced in 805.16(3)(1)(a).

Env-Sw 805.05(d) and (e)

Comment: *Env-Sw 805.05(a) does not reference a "one liner" or "2 liner" system, just a "liner system".*

Response: The rule text has been revised to remove, "as specified in Env-Sw 805.05(a)" from both provisions and language has been added to Env-Sw 805.05(a)(3) for clarification.

Env-Sw 805.11(p)

Comment: *Edit: Could delete this "shall" as there is already a "shall" in the intro sentence.*

Response: The rule text has been revised as suggested.

Env-Sw 805.11(r)

Comment: *Edit: Could delete this "shall" as there is already a "shall" in the intro sentence.*

Response: The rule text has been revised to address the comment.

Env-Sw 805.16(c)(1)

Comment: *Unclear: What criteria will the department use to determine whether to approve the plan? If the criteria is in another rule, say "Be approved by the department, pursuant to Env-Sw [rule number], as a..."*

Response: The rule has been revised to strike this provision.

Env-Sw 805.16(e)(2)

Comment: Is this meant to be g. or the end of f.?

Response: No change made – meant to be Env-Sw 805.16(e)(2).

Env-Sw 806.03(c), Env-Sw 806.03(d), and Env-Sw 806.03(l)

Comment: *OLS requested clarification on how an approval will be granted and the criteria related thereto.*

Response: NHDES clarified that approval is granted in accordance with Env-Sw 314 or Env-Sw 315, and added a demonstration requirement for Env-Sw 806.03(l).

Env-Sw 806.03(k)(1)

Comment: *Edit: "Twelve", as it is starting the sentence.*

Response: The rule text has been revised as suggested.

Env-Sw 806.03(l)

Comment: *Unclear: what is the process to obtain the approval and what criteria will the department use to make the decision to approve or deny the request?*

Response: The rule text has been revised to reference the rules governing the approval process and also includes two new provisions to address this comment.

Env-Sw 806.05(f)

Comment: *Unclear: What are the criteria the department will use to make this approval?*

Response: The rule was revised to remove, “if approved by the department.”

Env-Sw 806.08(d)(3)b.

Comment: *Edit: "(k)" was re-lettered to "(l)" below, so make sure this is still the correct citation.*

Response: Additions made by NHDES in response to public comment (i.e., Env-Sw 806.08(h)) necessitated changes to lettering in this section. As such, (l) was revised to read (o), and that citation is correct in the rule text filed as part of the Final Proposal package.

Env-Sw 806.08(d)(6)

Comment: *Edit: all highlighted letters need to be lowercase.*

Response: The rule was revised remove capitalization as suggested, with the exception of “Kjeldahl,” as this is an individual’s name. Also removed capitalization from per- and polyfluoroalkyl substances.

Env-Sw 806.08(k)(3)

Comment: *Edit: Do not use "i.e.". Consider: "for example, phased installation, system and well field coverage, or system design,"*

Response: The rule text has been revised to use “for example” rather than “i.e.”

Env-Sw 806.08(k)(4)

Comment: *Edit: Do not use "e.g.". Consider: "such as, time-of-day or seasonal,"*

Response: The rule text has been revised to use “such as” rather than “e.g.”

Env-Sw 806.08(k)(4)

Comment: *Unclear: summary of what?*

Response: The rule text has been revised for clarity by moving the requirement for a summary to the beginning of the rule.

Env-Sw 806.08(m)(2)

Comment: *Unclear: When will these actions be required?*

Response: The rules have been revised/restructured to address this comment. Note that the list of potential response actions was relocated from Env-Sw 806.09(g).

Env-Sw 806.08(o)

Comment: *What are the criteria the department will use to make this approval?*

Response: The rule was revised for clarity.

Env-Sw 806.08(o)(2)

Comment: *Unclear: when will these actions be required?*

Response: The rule text has been revised for clarity and to reflect that Env-Sw 806.08(o)(2)(a) through (f) provide a range of potential actions to be provided based on the likely cause of the elevated secondary flow rates.

Env-Sw 806.12(g)

Comment: *Unclear/Legis. Intent: RSA 149-M:27, V states, "Beginning February 1, 2025...". If these rules become effective before that date, this rule will be unclear and may be against legislative intent.*

Response: Language was added to this rule text to clarify the effective date and resolve any concern regarding legislative intent.

Env-Sw 807.03(d)

Comment: *Unclear: Retro-active requirement? What about landfills that existed prior to October 1997 that closed prior to this rule, will they need to get written legal rights if they did not initially?*

Response: The word “written” was removed from this rule.

Env-Sw 807.05(b) and (e)

Comment: *What are the criteria the department will use to approve a post closure care plan?*

Response: Modifications were made to section Env-Sw 807.03 to clarify the method by which a post closure plan is approved by the department, Env-Sw 807.05(b) was revised, and Env-Sw 807.05(e) was struck because the language is redundant.

Env-Sw 807.05(n)(8)

Comment: *What are the criteria the department will use to make the approval?*

Response: The rule was revised to clarify that a permit modification is required per Env-Sw 311 through 315.

Env-Sw 808.02(a)(4)

Comment: *Unclear/Edit: If the approval is from the department, say "receive approval from the department". If it is someone else, need to specify.*

Response: The rule was revised to clarify that approval is “from the department.”

Env-Sw 808.05(a)

Comment: *Edit: Do not have a stand alone paragraph. Move this sentence to after the section title and renumber (1)-(4) to (a)-(d).*

Response: The rule has been revised as suggested.

Env-Sw 808.06

Comment: *Unclear: What are the criteria the department will use to make this approval?*

Response: The rule has been revised for clarity and Env-Sw 1104 was revised to include approval for reclamation.

Env-Sw 810.03(a)

Comment: What criteria will the department use to make this approval?

Response: The approval is obtained through the applicable compliance and enforcement process procedures.

805.06(l)(1), 805.07(b), 805.11(b), 807.05(l)

Comment: *OLS identified incorrect rule citations in the rule text.*

Response: The rules have been revised to reflect the correct citations.

805.05(h), 805.10(q)

Comment: S*pell out numerals as words (i.e. 1 change to one).*

Response: The rules were not revised because the numbers are industry standard/known and not quantities per the OLS Drafting Manual.

Various citations

Comment: *OLS provided various editorial comments.*

Response: The Department has made editorial changes to the rule as shown in the final proposal-annotated text. The editorial changes include addition of commas, correction of capitalization, and formatting changes needed to conform to the OLS drafting manual.

The following changes were made for consistency, clarification, or correctness after further review and comment by NHDES staff:

Env-Sw 804.02(d) and Env-Sw 805.03(e)

Staff comment: NHDES staff noticed the reference in each rule to be incorrect based on renumbering of sections Env-Sw 804.02 and Env-Sw 805.03.

Response: The reference in Env-Sw 804.02(d) was revised to Env-Sw 805.03(e) and Env-Sw 805.03(e) was revised to reference Env-Sw 804.02(d).

Env-Sw 805.06(c)

Staff comment: NHDES staff noticed that the word “cleaning” should appear in this rule to be consistent with Env-Sw 805.06(j)(2).

Response: Added “cleaning” to rule text for clarity and consistency.

Env-Sw 805.06(e)

Staff comment: NHDES staff noted that leachate chemical composition and its effects can be temperature dependent and thus temperature must also be considered in the design of leachate collection and removal systems.

Response: Added “temperatures” to the rule text.

Env-Sw 805.06(h)(3)(b)2. and Env-Sw 805.06(i)(3)

Staff comment: NHDES staff noticed that the phrase “and dialers” should appear in these rules to be consistent with changes made in response to public comment to 805.06(k) and 805.06(p).

Response: Added “and dialers” to the rule text for clarity and consistency.

Env-Sw 805.08(a)

Staff comment: NHDES staff noticed errors in the wording of the rule regarding the number of wells and sampling points.

Response: Added “and number” and “there” to the rule text.

Env-Sw 805.09(c)

Staff comment: NHDES staff noticed that the word “care” should appear in this rule to be consistent with the definition at Env-Sw 104.12

Response: Added “care” to rule text in this location.

Env-Sw 806.08(a)

Staff comment: NHDES staff noticed that the words “and recordkeeping” should appear in this rule to be consistent with the revised title of this section.

Response: Added “and recordkeeping” to this rule text.

Env-Sw 806.08(e)

Staff comment: NHDES staff noticed that the rule could be clarified by adding “reviewed by the permittee” to the rule text.

Response: Added “reviewed by the permittee” to the rule text.

Env-Sw 806.08(e)(3)b.

Staff comment: NHDES staff noticed that the rule reference was incorrect based on renumbering. Also, while reviewing the referenced rule, NHDES staff made other changes to the rule text for clarification.

Response: Rule revised to reference (n) instead of (o). Also, the language in (n) was revised for clarification and (n)(3)b. was revised to include language that was removed from another section that was inadvertently eliminated from the rules.

Env-Sw 806.08(o)

Staff comment: NHDES staff noticed an incorrect reference.

Response: Rule revised to reference (n) instead of (l).

Env-Sw 806.08(i)

Staff comment: NHDES staff noticed that the rule could be clarified by revising “Facilities” to “Permittees.”

Response: Revised the rule text to read “permittees” for clarity.

Env-Sw 806.12(d)

Staff comment: NHDES staff noticed that "lithium-ion batteries” and “electronic devices” should appear in this rule to align with changes to RSA 149-M:27, II.

Response: Added “lithium-ion batteries” and “electronic devices” to the landfill prohibition list in this rule.

Env-Sw 807.05(l)

Staff comment: NHDES staff noticed that a reference was inadvertently struck.

Response: Rule revised to accurately reference a numbering change.

EXHIBIT D

Colby, Jaime

From:	Kimberly Crosby <Kimberly.Crosby@casella.com>
Sent:	Friday, September 6, 2024 3:51 PM
To:	Colby, Jaime; Daun, Mary
Cc:	McKenna, Leah
Subject:	NCES Incident Reported
Attachments:	9 6 2024 NCES Incident Report.pdf

Good Afternoon –

Attached is the Incident Report for NCES. Please feel free to reach out if you should need additional information or have any questions.

Have a great weekend,

Kim Crosby, CES
Director of Environmental Compliance

Permits, Compliance & Engineering
408 East Montpelier Road, Montpelier, VT 05602
c. 802-585-5442
e.kimberly.crosby@casella.com • w. casella.com

CASELLA
RECYCLING • SOLUTIONS • ORGANICS • COLLECTION • ENERGY • LANDFILLS

Incident Report Form for Solid Waste Management Facilities –

Permitted and Permit-Exempt Facilities

Waste Management Division, SWMB

RSA/Rule: Env-Sw 1005.09(c)

Instructions: Complete form in its entirety, utilizing additional pages, as necessary. Maps and diagrams are recommended for clarity. A written report is due within 5 working days of the incident / situation date. Form meets the requirements of Env-Sw 1005.09(c) for "written report" if completed in its entirety and submitted in accordance with submission timeframe requirements.

Section I – General Information		
1. Date & Time of Incident / Situation:	**2. Date of Report Submission to NHDES:**	**3. Name of Person Preparing Report:**
09/09/2014-06/27/2024	9/6/2024	Kim Crosby
4. Facility Name:	**5a. Affected Area Within Facility**	**5b. Physical Address, Town / City:**
North Country Environmental Services	North Country Environmental Services	581 Trudeau Road, Bethlehem, NH 03574
6. NHDES SW Permit Number:	**7. Permittee Name on Permit:**	**8. Mailing Address:**
DES-SW-SP-03-002	North Country Environmental Services	P.O. Box 9 Bethlehem, NH 03574

Section II – Parties Involved in Incident / Situation

9. Persons:

	Name:	Title:	Affiliation:
a.	Joe Gay	Engineer	NCES
b.	Kevin Roy	General Manager	NCES
c.	Bruce Grover	Operations Manager	NCES
d.	Kim Crosby	Director of Compliance	NCES
e.			
f.			

Section III – Details

10. The quantity and types of wastes and material(s) involved in the incident or situation and in the clean-up activities:

While conducting an investigation into the cause of increased flows in the landfill liner secondary system discussed in the June 24, 2024 Letter of Deficiency No. SWMB 24-006, Casella's investigators determined that the overliner for Stage IV, Phase I, which has both a primary and a secondary leachate collection system, had been penetrated via the drilling of landfill gas well GW-202 on February 7, 2024. The overliner was required as part of a Stage IV permit issued to NCES in 2003 because the underlying Stage I double liner did not include a geotextile overlay for enhanced leachate travel time because geotextile was not required when the Stage I liner was placed. In 2013, NCES applied for and received a waiver for an overliner for an adjacent lift of waste over the Stage I liner. Casella's investigators learned that NCES's on-site manager and its overseeing company engineer mistakenly concluded that in light of the 2013 waiver the existing overliner could be treated as decommissioned. The investigators also learned that beginning in 2014 and continuing until early this year NCES's landfill gas management consultant oversaw the installation of eleven LFG management wells (enumerated with installation and decommissioning dates below) that penetrated both liners of the overliner sytem to extract LFG from the waste mass beneath the overliner. Casella's investigation also revealed that GW-202 has been pulling leachate from the waste mass underlying the overliner and discharging a significant portion of the leachate into the secondary collection system of the overliner. Because the sump for the overliner's secondary is plumbed to the Stage IV, Phase I, secondary, it is apparent that the placement and operation of GW-202 has been a substantial contributing factor to the increased leachate flows in the base liner system and particularly the Stage IV, Phase I, secondary. NCES will supplement this report and its response to the June 24, 2024, LOD, with a detailed explanation of how these gas wells have contributed to the increased leachate flows in the Stage IV, Phase I, secondary system.

Well Number	Installation Date	Decommisioning Date
GW-88	9/9/2014	12/2017
GW-102	4/24/2015	3/2019
GW-103	4/23/2015	12/2020
GW-105	4/30/2015	7/2024
GW-113	5/12/2016	10/2022
GW-134	8/18/2018	5/2023
GW-146	9/17/2020	ACTIVE
GW-148	9/15/2020	2/2024 NOTE: GW-202 drilled as a replacement
GW-172	4/27/2023	ACTIVE
GW-202	2/7/2024	ACTIVE
GW-206	6/27/2024	ACTIVE

Of the eleven wells identified, 146, 172, 202 and 206, remain active for gas collection in the area of the overliner.

11. Measures employed to contain releases caused by the incident or situation:
No release to the environment was caused by these incidents. As mentioned above, there is a double-liner system beneath the overliner that is intact and functioning as designed. All secondary detection liquids are captured and managed in the leachate collection system and transported off site for treatment.
12. Assessment of actual or potential hazards to the environment, safety and human health related to the incident:
Casella's investigation has concluded that while liquid levels on the base liner secondary are exceeding an action level, the magnitude of the increase is within the hydraulic capacity of the systems. Additionally, the Stage I primary and secondary leachate systems are functioning properly, and leachate is being managed in a manner that has prevented a release to the environment. Leachate passing through the penetrations in the overliner have no pathway to the environment and are instead captured by the Stage I liner.
13. Measures the permittee has or intends to apply to reduce, eliminate, and prevent a recurrence of the incident or situation:
To reduce the secondary leachate flows in the areas of the gas wells discussed, NCES proposes to seal off wells 202, 146 and 148 via the use of a cement and bentonite grout mix to an elevation above the area of penetration. Sealing and grouting will put a thin grout down the center tube running down the entire column of each well. The grout mixture will push out of the perforated piping and into the stone pack around the edge of the overliner, sealing off the penetration area. NCES will ensure that all personnel and third party contractors are notified of the existence and status of the overliner, i.e., that it is not out of service and must not be further damaged.

14. If measures not completed by time of report submission, expected date of completion:	October 2024

Section IV – Signatures

15a. Person Preparing Report:

Name:	**Title / Affiliation:**	**Signature:**
Kim Crosby	Director of Compliance	Kim Crosby

Phone Number:	**Email Address:**

15b. Permittee:

Name:	**Title / Affiliation:**	**Signature:**
North Country Environmental Services, Inc.	Director of Compliance	Kim Crosby

Phone Number:	**Email Address:**

Form Submittal Instructions:

Submit the completed report in PDF via email to SolidWasteInfo@des.nh.gov.