

Hazard Assessment

GROUNDWATER UBIQUITY SCORE: A SIMPLE METHOD FOR ASSESSING PESTICIDE LEACHABILITY

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Abstract—Government agencies at both the state and federal levels now face increasing pressures to assess the likelihood of pesticide occurrence in well-water supplies. Screening methodologies are required in order to determine which pesticides now in use should receive the greatest attention with respect to groundwater, and in order to determine whether elaborate and expensive groundwater testing should be required in order to register a new pesticide. Several screening techniques have been proposed recently, some based on threshold values for critical physical properties of the pesticide, and others based on mathematical models of the leaching process. A different approach is taken in this paper, whereby an index is derived based entirely on the physical properties of those pesticides that have been found either leachable or essentially immobile. The index is based on graphical examination of a plot formed by two widely available pesticide properties: half-life in soil ($t_{1/2}^{soil}$) and partition coefficient between soil organic carbon and water (K_{oc}). Other physical properties, such as water solubility, octanol/water partition coefficient, and volatility from soil, have often been invoked as indicators of leachability, but they are found in this paper to have no useful power in discriminating between "leachers" and "nonleachers." Scores assigned with the new screening index agree with the results of several recent well-water monitoring programs, even though point-source events are thought to be responsible for some of the observed contamination. A nomogram is given that reduces the task of calculating the index to simply placing a straight edge on a diagram.

Keywords—Groundwater Pesticides Modeling Leaching Contamination
Well water

INTRODUCTION

There are immense differences in the degree to which pesticides exhibit the propensity to leach. Most importantly, pesticides have varying degrees of mobility in soil, by virtue of their different tendencies to sorb onto soil as percolating water encounters soil surfaces. Some pesticides, particularly those which are anionic at environmental pH's, move almost as freely as water through soil [1]. On the other hand, large and highly lipophilic chemicals such as DDT move very slowly through soil, because they are nearly always sorbed within immobile soil particles [1]. In addition, pesticides undergo chemical transformations and other dissipative processes at rates which also vary greatly from one chemical to the next. The persistence of pesticides ranges from highly recalcitrant materials such as DDT (half-life of many years) [1-4], to the almost ephemeral phosphate insecticides, some of which have hydrolysis half-lives of only hours [1-4].

Several authors have proposed screening methods for determining whether a pesticide is likely to

leach to groundwater in detectable quantities [2-8]. Some have attempted to set threshold values for a physical property or set of properties which, when exceeded, should indicate that the chemical will leach [3,8]. Others have proposed very simple analytical or numerical models which are run using the measured or estimated properties of the chemical in order to predict the likelihood of its leaching [2,4-7].

A different approach is taken in this paper. Groups of compounds are examined that have been categorized with respect to their leachability, and for which consistent sets of physical properties have been collected. To this extent, the method is similar to that recently used by the California Department of Food and Agriculture (CDFA) to assess leachability [3]. Unlike the CDFA, however, no numerical cutoffs for any single property will be sought. Instead, properties of the chemicals representing soil mobility and soil persistence are plotted together and examined graphically in order to define a region that appears to contain the leaching compounds.

As used in this paper, the term leachability

refers to the following pesticide property: that when used in a normal agricultural manner under conditions conducive to movement, it moves down through the soil in quantities sufficient to be detected in nearby wells of proper construction. Areas with direct connection between the surface and saturated zones, e.g., agriculture drainage wells or sink holes, are excluded in this definition. Traditional measures of soil mobility and soil persistence are combined to derive a classification system that appears to determine which chemicals are likely "leachers," "nonleachers," or "borderline compounds." This methodology would be suitable as the first part of a tiered approach for specifying which chemicals deserve the most attention during more intensive and expensive studies of leachability, such as the small-scale prospective groundwater studies now being proposed by the U.S. Environmental Protection Agency (EPA) [9]. If this screening method suggests that leaching may occur with the pesticide, then more sophisticated methodologies could subsequently be used to better determine the likely fate of the chemical. Such models would include, at a minimum, the effects of: planned use rate, vulnerability of the soils and aquifers in the planned use region, method and timing of pesticide application, and type of crop to be treated with the chemical [4,6]. If significant movement is still suspected, then the more expensive experimental work might be initiated in order to measure field behavior.

QUANTIFYING MOBILITY IN SOIL

Pesticides travel at varying rates through soil, mainly due to differences in their affinity for soil surfaces. Just as in a chromatographic column, there is an immobile phase (solid soil particles) and a mobile phase (water and, to a lesser extent, air). The theory of chromatography states that the rate of passage through the column is determined by the relative partitioning behavior of the solute between the stationary and mobile phases. The partition coefficient between soil and water is typically measured in batch equilibrium experiments at a number of concentrations. It is commonly assumed that the equilibrium concentrations measured in soil and water during such an experiment should form a constant ratio. Assuming such behavior, the ratio of concentrations in the soil (C_s) and aqueous (C_w) phases is denoted as K_D [1]:

$$K_D = C_s/C_w.$$

With C_w measured in [$\mu\text{g}/\text{mL}$] and C_s measured in [$\mu\text{g}/\text{g}$], the units of K_D are given in [mL/g]. Obviously, those chemicals with higher K_D values move more slowly through soil, because a higher fraction of the chemical is in the immobile soil phase at any time.

As pointed out by many researchers [1-8,10,11], the K_D values measured for a particular chemical on a range of different soils often vary proportionately with the organic carbon content (f_{oc} [g OC/g soil]) of the soil. This relationship has been used to derive a measure of mobility in which the effects of soil type are factored out:

$$K_{oc} = K_D/f_{oc}.$$

The advantage of K_{oc} is that it represents a soil-independent measure of compound mobility. For a single pesticide, the variability of K_{oc} is typically much less than that of K_D . Because of this, K_{oc} is generally used to estimate K_D for a soil in which the organic carbon content is known, but the partitioning behavior of the chemical has never been determined.

K_{oc} thus represents an almost universally accepted way to compare various pesticides in terms of soil mobility. The primary exception to this rule is those few pesticides for which the partitioning behavior is not well correlated with the organic carbon content of the soil. These chemicals, which are often ionic in character, sorb mainly to clay. In order to compare the average relative mobilities of such exceptional pesticides with chemicals on the K_{oc} scale, it is necessary to return to the definitions of the two partition coefficients.

K_{oc} is a good measure of the average mobility of a chemical that sorbs mainly to organic carbon. The average mobility of a chemical that does not sorb primarily to organic carbon may be estimated by its average K_D (arithmetic mean of measurements in a set of selected soils). Assuming this average K_D is truly representative of all U.S. soils, it may be converted to the K_{oc} scale simply by dividing through by the average organic carbon content of agricultural soils in the U.S. ($f_{oc} = 0.0174$ g OC/g soil) [12]. This mean f_{oc} represents an average of over 20,000 different soils.

As an example consider two pesticides. One is a nonionic organic material with a K_{oc} of 500 (mL/g OC). The other is a zwitter-ionic material whose measured K_D varies strongly with the type of clay present in the soil and the soil pH. Under natural conditions in a number of soils represent-

tative of U.S. soils, it has an average K_D (arithmetic) of 10 (mL/g soil). In order to compare its soil mobility with the first pesticide, we divide through by the average f_{oc} (0.0174) and obtain 575 (cc/g OC). On average, this second pesticide should be a bit less mobile than the nonionic pesticide having a K_{oc} of 500.

In closing this section on mobility, it should be noted that a number of correlations between K_{oc} and other chemical properties have been developed, particularly with water solubility and the octanol/water partition coefficient [1,10,11]. None of these correlations are sufficiently strong to be used as an adequate predictor of K_{oc} . As the leachability assessment methodology is developed below, the discriminating power of these ancillary properties will be checked. Water solubility would not be expected to play a predominant role in leaching, because the typical environmental concentrations of pesticides are many orders of magnitude less than their solubilities (ppb vs ppm). Similarly, the octanol/water partition coefficient, while an excellent model for sorption in biological membranes, is not chemically representative of the soil-water system, and no particularly strong correlation with leachability would be expected.

MEASURING PERSISTENCE IN SOIL

Although pesticide degradation is rarely a strictly first-order process, such kinetics are nearly always assumed [1,8,10,11]. The primary motivation for this is simplicity—both mathematically and conceptually—because the first-order degradation model is easy to explain and to implement. First-order processes may be represented by a half-life, the single parameter that most people think of when asked to characterize the persistence of a chemical. The half-life concept is particularly useful for making comparisons, because all of the more elaborate kinetic descriptions (second-order, hyperbolic, etc.) require information on concentration dependence—complicating the relative measures of persistence. The concept of an average half-life also masks several important physical effects on dissipation, including the effects of pretreatment, biotic capacity, and soil moisture content, but this does not reduce the parameter's utility as a relative measure of persistence.

In the case of leachability, the half-life of interest is the average time it takes, in the field, for soil residues of the parent molecule to decline by 50%, denoted in this document as $t_{1/2}$. The most appropriate type of experiment to collect this

information is a field study carried out under actual use conditions, although lab experiments can give quantitatively similar results [1]. Lab studies have the advantage that many of the important environmental conditions may be controlled (temperature, moisture, oxygen tension). Whenever possible, however, adequate field data should be used rather than lab data in order to assess leachability, primarily because many dissipative processes operate at different rates in the field (volatilization, photolysis, etc.) [1].

Volatility often plays a role in field persistence [1,2,13], and because of this, certain researchers have felt that some measure of volatility should be included in the derivation of an index of leachability [2]. This possibility will be investigated in the section that follows, but it should be remembered that when a field study is done to measure persistence, the effect of volatility is already taken into account. If we were to take this measured dissipation half-life and add an additional measure of volatility, then we would be "double-counting" the effect of volatilization. By basing the screening methodology on measured field half-lives, we should essentially bypass the need to include volatility in the index.

A METHOD OF COMBINING PERSISTENCE AND MOBILITY MEASURES

Clearly, any method of assessing leachability must account for both the persistence and the mobility of the chemical. A number of models of varying complexity have been derived to do just this [2,4-7,14-16], but a different approach will be taken here. Rather than depending on mathematical and computer models to define the physical property characteristics that determine leachability, the physical property data themselves will be used. The set of data which has been selected is the list compiled by the California Department of Food and Agriculture (CDFA) in producing its recent document on Specific Numerical Values [3]. These data were used because the methodology hinges on two factors: a consistent set of physical properties for a group of pesticides, and a consistent classification of the same pesticides as "leachers" or "nonleachers" following normal agricultural use (exclusive of point-source contamination events). Such were the criteria used by the CDFA in developing its list [3].

The CDFA compiled a list (see Table 1) of 44 pesticides which they classified as known contaminants of groundwater, known noncontaminants,

Table 1. Classifications and physical properties assigned by the CDFA in its specific numerical values document (number serves as key for the figures in this paper)

Key	Pesticide	K_{oc} (cc/g)	$t_{1/2}^{hyd}$ (days)	$t_{1/2}^{deg}$ (days)	S_{H_2O} (ppm)	GUS
Leachers						
1	Aldicarb	17	1,800	7	6,000	2.34
2	Atrazine	107	72	74	52	3.68
3	Chlorthal dimethyl	ND*	ND	100	3	ND
4	Cyanazine	ND	ND	14	171	ND
5	DBCP	40	7,050	ND	1,000	ND
6	Duron	389	113	188	41	3.21
7	EDB	78	2,100	ND	4,300	3.29
8	Merlchlor	99	210	44	530	3.29
9	Meribuzin	ND	90	37	1,200	ND
10	Naled	133	14	ND	0.3	ND
11	Oxamyl	26	6	8	269,000	2.33
12	Picloram	26	ND	206	430	5.98
13	Prometon	577	113	ND	750	ND
14	Prometryn	614	75	94	46	2.39
15	Propylene dichloride	955	ND	ND	2,700	ND
16	Simazine	138	ND	56	4	3.25
Nonleachers						
17	Aldrin	ND	ND	10	0.03	ND
18	Chloramben	ND	ND	ND	700	ND
19	Chlordane	19,269	ND	37	2	-0.45
20	Chlorothalonil	1,380	ND	68	0.6	1.58
21	Chlorpyrifos	6,085	44	54	1	0.37
22	2,4-D	53	ND	7	703	1.92
23	1,3-D	68	ND	ND	1,425	ND
24	DDD	45,800	ND	ND	ND	ND
25	DDT	213,600	ND	38,200	0.002	-6.09
26	Dicamba	511	30	25	6,150	1.81
27	Endosulfan	2,040	14	120	ND	1.44
28	Endosulfan sulfate	ND	ND	ND	0.1	ND
29	Endrin	11,188	180	2,240	0.3	-0.16
30	Heptachlor	13,330	180	109	0.06	-0.25
31	Lindane	1,727	113	569	11	2.10
32	Pendimethalin	ND	ND	ND	0.3	ND
33	Phorate	1,660	30	38	45	1.23
34	Propachlor	794	ND	4	660	0.66
35	Silvex	ND	ND	22	158	ND
36	Toxaphene	95,816	ND	9	3	1.23
37	Trifluralin	7,950	ND	83	0.5	0.66
Transition						
38	Alachlor	161	ND	14	203	2.06
39	Carbaryl	423	5	19	120	1.76
40	Carbofuran	55	28	37	700	3.34
41	Dieldrin	12,100	ND	934	0.2	-0.25
42	Dinoseb	5,900	30	30	63	0.34
43	Ethoprop	26	ND	63	750	4.65
44	Fonolox	5,105	ND	25	14	0.41

*ND = no data, or data did not meet restrictions established by CDFA.

and so-called transition pesticides for which conflicting evidence exists (as to whether leaching can occur). The CDFA also attempted to collect four physical properties for these pesticides, including both of the properties mentioned above as being the primary determinants of leachability: K_{oc} and

the soil half-life, $t_{1/2}^{deg}$ (the other two properties obtained were water solubility and hydrolysis half-life). For each property the CDFA computed simple arithmetic averages of all values meeting their selection criteria (mainly temperature and pH considerations). These average property values are

used throughout the analysis that follows. The issue of physical property variability is an important one, but it has been addressed here only peripherally, in a manner to be described below.

Shown in Figure 1 are the 22 leachers and nonleachers for which the CDFA was able to determine average values for both K_{oc} and $t_{1/2}^{deg}$. Table 1 serves as a key for this figure and the others that follow—it lists all 44 compounds classified by the CDFA and the physical properties that were assigned to each [3]. Closed circles are used for leachers and open circles are used for nonleachers. The logarithmic scales are in base 10 for this figure and for all subsequent figures. As expected, the leachers occupy the left and upper portions of the figure, corresponding to pesticides which are more mobile and more persistent in soil. The graph itself is a perfectly reasonable way to distinguish the leachers from the nonleachers, but, given the desirability of a numerical index, the curved nature

of the region containing the leachers suggests that a hyperbolic function should discriminate between the two classes of compounds. The two dashed curves in this figure are hyperbolas generated by two values of the following function:

$$GUS = \log_{10}(t_{1/2}^{deg}) \times (4 - \log_{10}(K_{oc})).$$

The two values of GUS (groundwater ubiquity score) in this figure are 2.8 and 1.8. These appear to bracket the region in which transition occurs from leachers to nonleachers. The derivation and sensitivity analysis of this equation are presented in Appendix A. If we replot the same data in Figure 1 on the GUS scale, we find that the leachers and nonleachers separate quite well (see Fig. 2). The dashed lines in Figure 2 appear at GUS values of 1.8 and 2.8, the same as were shown in Figure 1. These dashed lines are centered on 2.3, the actual separation point between the two groups. A

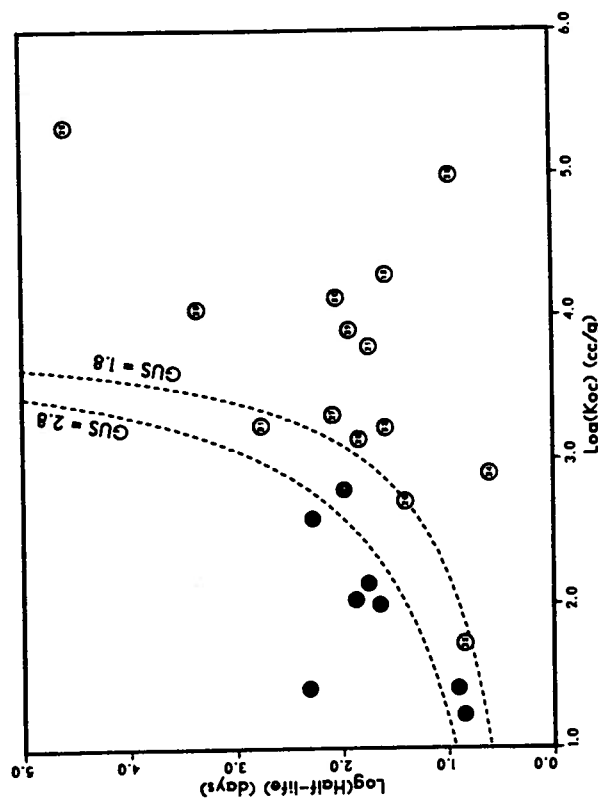


Fig. 1. Persistence and mobility properties of several agricultural chemicals as collected by the California Department of Food and Agriculture. Logarithms (base 10) are used in this figure and all logarithmic scales in subsequent figures. Closed circles are used for compounds which were said to contaminate groundwater via leaching, and open circles are used for noncontaminants. Points are numbered according to the key in Table 1. The dashed lines represent two values of the GUS function as described in the text.

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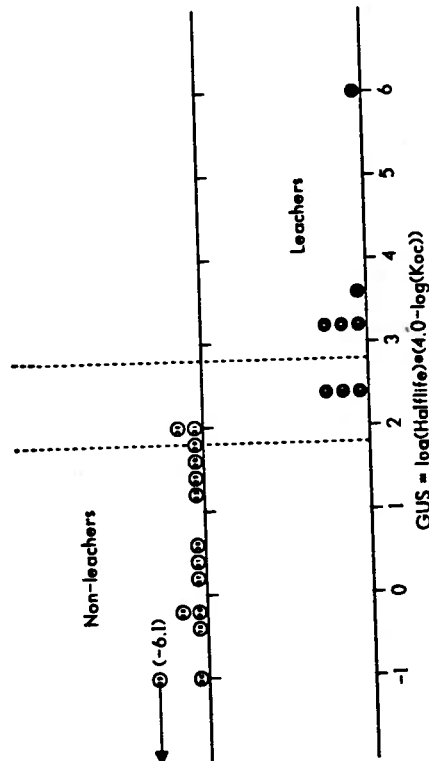


Fig. 2. Same data in Figure 1 now plotted on the GUS scale. Dotted lines are in the same positions as the curves in the previous figure. Points are numbered according to the key in Table 1.

width of one unit (on the GUS scale) for the transition zone was chosen based on the sensitivity analysis (see Appendix A), and examination of the data in Figures 1 and 2 indicates that it is reasonable. Certainly a transition zone of finite width is desirable, given the intrinsic uncertainties (as noted above) in the two average physical properties making up the GUS function, the uncertainties in the CDFA classification of these 22 chemicals, and the arbitrariness in the particular functional form chosen for GUS.

In practice, the three zones of Figures 1 and 2 could be used in the following way. Compounds which fall in the leacher or transition zone would require further investigation by the more sophisticated modeling technologies alluded to previously. The level of modeling effort required to show that a pesticide in the leacher zone ($GUS > 2.8$) is really not a "problem compound" would be somewhat greater than that for a chemical in the transition zone ($1.8 > GUS > 2.8$). Compounds which fall

in the nonleacher zone could safely be exempted from further consideration as possible leachers. However, it should be remembered that point-source contamination of wells is always a possibility when chemicals are used carelessly or wells are improperly installed in areas of pesticide use and/or storage.

The zones defined by this methodology are somewhat different from the zones established by previous authors. The CDFA, as mentioned above, attempted to establish strict cutoffs for the various physical properties, in the hope that single numerical values could be used as triggers for further investigation [3]. Unfortunately the curved nature of the region containing the leachers prevents this technique from working properly. As shown in Figure 3, "you can't fit a square peg in a round hole." The rectangular region defined by the CDFA misses three of the leachers, and misclassifies a nonleacher into the leacher region.

The triggers for K_{oc} and $t_{1/2}^{app}$ proposed by Cohen

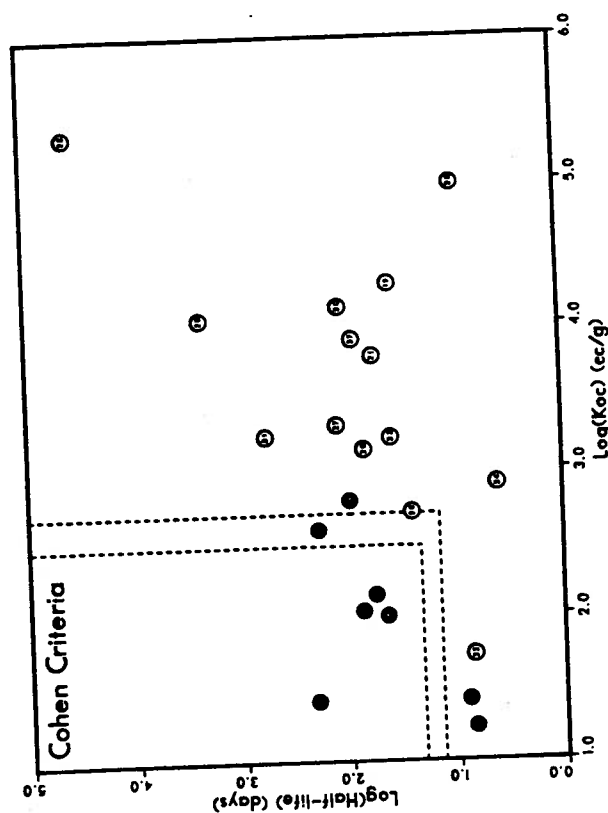


Fig. 4. Data of Figure 1 plotted showing the Cohen et al. (1984) [8] criteria for K_{oc} (300-500 cc/g) and $t_{1/2}^{app}$ (2-3 weeks). Points are numbered according to the key in Table 1.

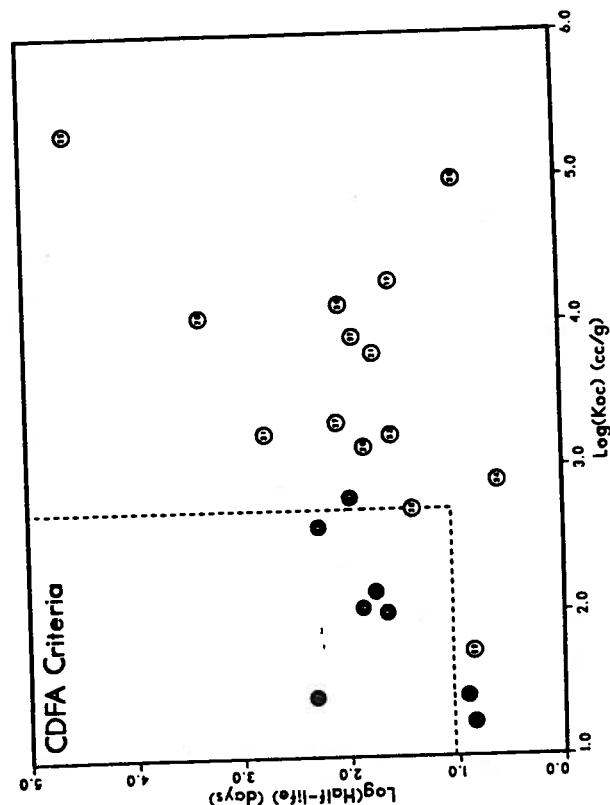


Fig. 3. Data of Figure 1 plotted showing the California Department of Food and Agriculture's proposed specific numerical values for K_{oc} (512 cc/g) and $t_{1/2}^{app}$ (11 days). Points are numbered according to the key in Table 1.

et al. [8] are very similar to the CDFA numbers, except that a range was quoted for each (see Fig. 4). The authors' text is somewhat unclear whether the chemical needs to exceed both triggers to be considered a leacher, but that has been assumed in the figure for consistency. The authors also list triggers for other physical properties, including one for water solubility (30 ppm). The utility of this water solubility criterion is examined below.

Finally, there is the paper of Jury et al. [4] in which the authors have conducted a particular model simulation in order to derive a screening method. This model reduces to the following inequality, in which a and b are constants determined by the environmental situation:

$$K_{oc} < a(t_{1/2}^{app}) - b.$$

This inequality appears linear on a log-log scale after b becomes relatively small, as shown in Figure 5. While the curvature at low K_{oc} appears to

follow quite well with the classified leachers and nonleachers, Jury's model departs from the data at partition coefficients (K_{oc} 's) of 1000 and greater. The model predicts that chemicals such as DDT will eventually reach detectable levels in groundwater as a result of leaching, even though such immobile materials have not been seen. In fairness, the authors predict that such chemicals would not reach typical water table depths for many decades or even millennia, but one would think that a few instances of contamination would have been observed in highly vulnerable areas if there had indeed been a process of significant leaching underway with these materials.

The discrepancy may be due to Jury's choice of a model in which dispersion and diffusion, both known and demonstrated phenomena, are neglected. A model similar to Jury's, but with dispersion included [16], is derived in Appendix B. It predicts a curved shape for the contaminant region that is much more similar to the observed area (see

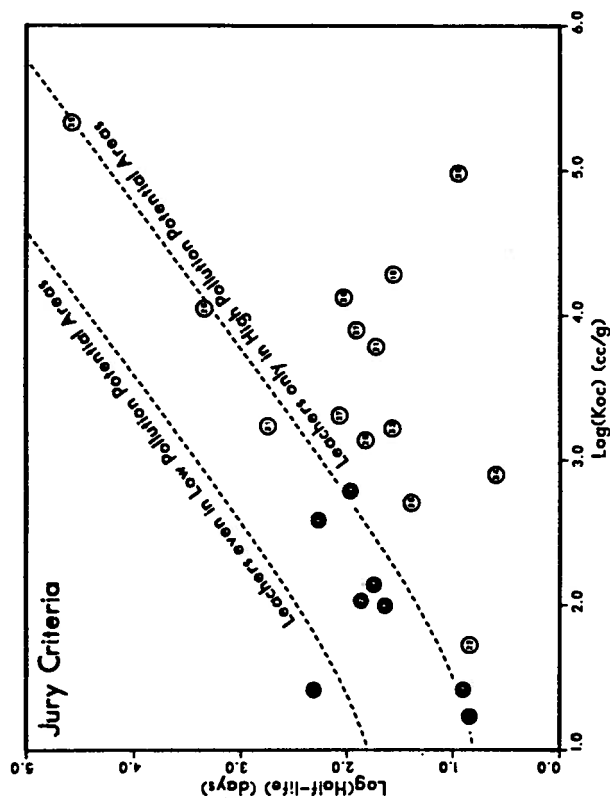


Fig. 5. Data of Figure 1 plotted showing the Jury et al. (1987) [4] criteria corresponding to the linear inequality reported in the text. Points are numbered according to the key in Table 1.

Fig. 6). This suggests that dispersion and diffusion, both relatively slow processes that lower concentrations, would act to ameliorate long-term leaching with highly persistent but almost immobile materials.

UTILITY OF OTHER PHYSICAL PROPERTIES AS LEACHING INDICATORS

An attempt was made to see whether any other physical properties might enhance the classification power of the GUS function. Shown in Figure 7 is a plot of water solubility (as given by CDFA) against the GUS values of the CDFA-classified materials. Again, solid circles are used for leachers and open circles are used for nonleachers. The CDFA was unable to identify K_{oc} and/or $t_{1/2}^{app}$ values for sev-

eral of these compounds, preventing calculation of GUS, but they were able to find water solubilities meeting their selection criteria [3]. These twelve have been included in the plot by placing them in a floating box (their water solubilities are plotted using the same left-hand scale). Obviously, there is a fairly strong correlation between water solubility and the GUS function, but there does not appear to be any useful additional separation of the leachers and nonleachers. Also shown in Figure 7 are the two water solubility criteria that have been proposed by the CDFA [3] and Cohen et al. [8] as indicators of leachability. While it is true that most of the leachers have solubilities above these two thresholds, it is also true that many of the nonleachers are above the line, rendering such a criterion of little use in discriminating leachers

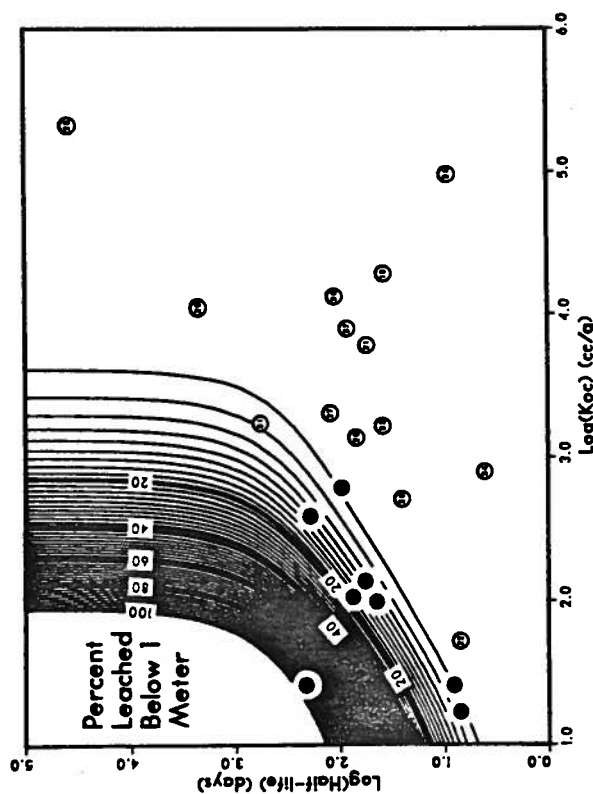


Fig. 6. Superposition of Figure 1 data with the predictions of Equation A2, an analytical solution to the convective-dispersion equation. Contour lines represent equal percentages of the applied amount which leaches below 100 cm for the following parameter values: growth rate of the dispersion coefficient is 0.5; mean velocity of water is 1 cm/day; density of soil is 1.4 g/cc; and field capacity is 0.2 cc/cc. Each line represents a 2% increase in the amount leached. The 100% contour line was drawn even though it is physically unrealistic; its position was dictated by the round-off necessary to convert the numerical integration results into contours. Points are numbered according to the key in Table 1.

from nonleachers. The water solubility criteria are particularly ambiguous for the twelve chemicals whose GUS values could not be calculated, which is unfortunately exactly when such a secondary trigger could have been useful.

Two other versions of Figure 7 have been generated by replacing water solubility with octanol/water partition coefficient (Fig. 8) and volatility (Fig. 9). In both instances, the physical properties making up the y-axes were not tabulated by CDFA, but they are widely available from other sources [1,7,11,17]. For volatility, a regression equation developed by Ralph Nash was used based on Henry's Law constant, K_{oc} and molecular weight [13]. As with water solubility, these two other properties do not appear to provide any additional separation power in discriminating leachers from

nonleachers. This was not unexpected, as explained previously.

COMPARISON WITH MONITORING DATA

The GUS index has been derived as a classification system for determining when non-point-source leaching of pesticides may occur. A stringent test of the method, therefore, is to compare its gross classifications with the results of well-water monitoring programs in which both non-point- and point-source pollution may be occurring. Such is the nature of most monitoring programs that have been conducted in agricultural areas [18-21]. In spite of the fact that many of the positive findings in such surveys have been shown to be unrelated to simple non-point-source leaching, there is still a high level of agreement between the moni-

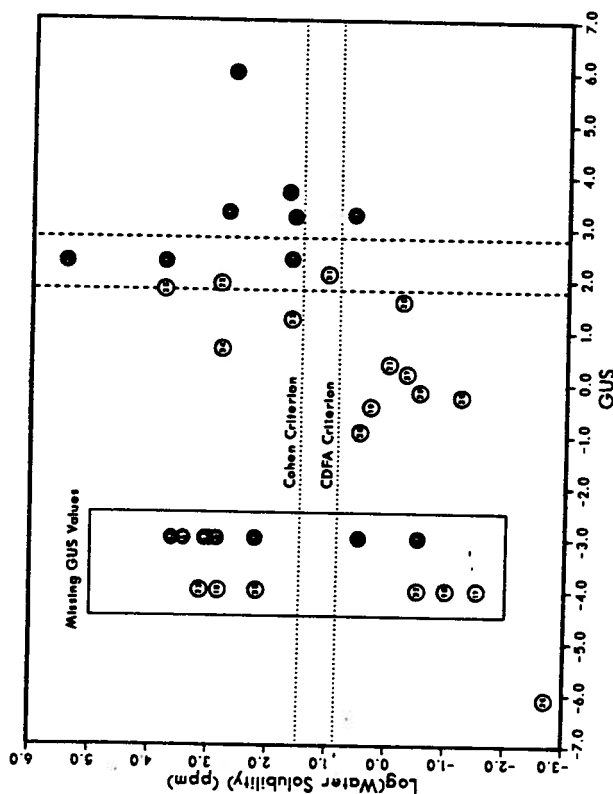


Fig. 7. Water solubilities (according to CDFA) for leachers (closed circles) and nonleachers (open circles). Compounds for which GUS cannot be calculated due to a missing K_{oc} or a missing 10^3 are plotted in the floating box for which the known water solubilities are read off the same scale. The dashed lines are placed at GUS values of 2.8 and 1.8, the boundaries of the transition region from leachers to nonleachers. The two dotted lines show water solubility criteria specified by the CDFA (7 ppm) and Cohen et al. [8] (30 ppm) as being indicators of leachability. Points are numbered according to the key in Table 1.

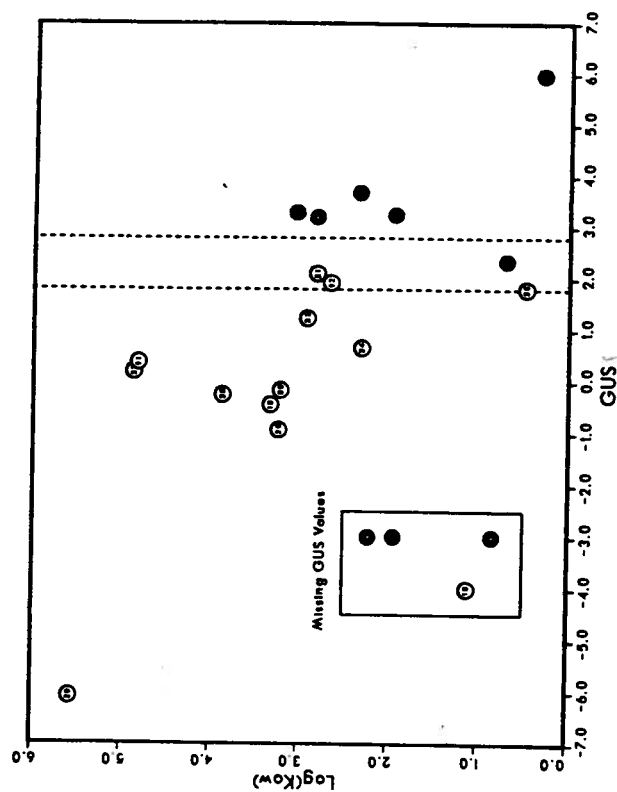


Fig. 8. Octanol/water partition coefficients taken from the literature for all chemicals classified as leachers or nonleachers by the CDFA. Compounds for which GUS cannot be calculated due to a missing K_{oc} or a missing 10^3 are plotted in the floating box for which the known octanol/water partition coefficients are read off the same scale. The dashed lines are placed at GUS values of 2.8 and 1.8, the boundaries of the transition region from leachers to nonleachers. Points are numbered according to the key in Table 1.

toring results and the leacher zone defined as part of the GUS methodology. This is probably due to the fact that when spills or other mishandling incidents occur near wells, the immobile materials are still prevented from showing up in the water due to strong binding and subsequent dissipation within the upper layers of the contaminated soil. An exception to this observation would be point-source incidents in which the pesticide is placed directly into the well (such as with back siphoning).

As one example, the results of Iowa's recent one-time monitoring program [21] are summarized in Figure 10. Iowa sampled all its public water supply systems (853) once during 1986, including several surface water systems. After removing these surface water systems from the data set, the positive and negative findings of the one-time sampling were compared for those chemicals whose GUS

values could be calculated from the CDFA list of pesticides (i.e. from the data in Table 1).

The compounds not detected in well water have lower GUS values, whereas those that were found tend to have higher scores, generally above the 1.8 threshold set for the transition region. The one exception is fonofos (GUS = 0.4), an insecticide which the CDFA classified as a transition compound—one for which the evidence of leaching was either incomplete or contradictory. Indeed, the K_{oc} given by the CDFA for fonofos (5105 cc/g) is contradictory with the value given by Jury et al. [4] and Rao et al. [2] (68 cc/g). Use of the lower K_{oc} value with the CDFA half-life yields a GUS value of 3.0, above the two thresholds previously described. These data suggest that the K_{oc} given by the CDFA for fonofos may be high by a factor of 100, an error that commonly occurs during the

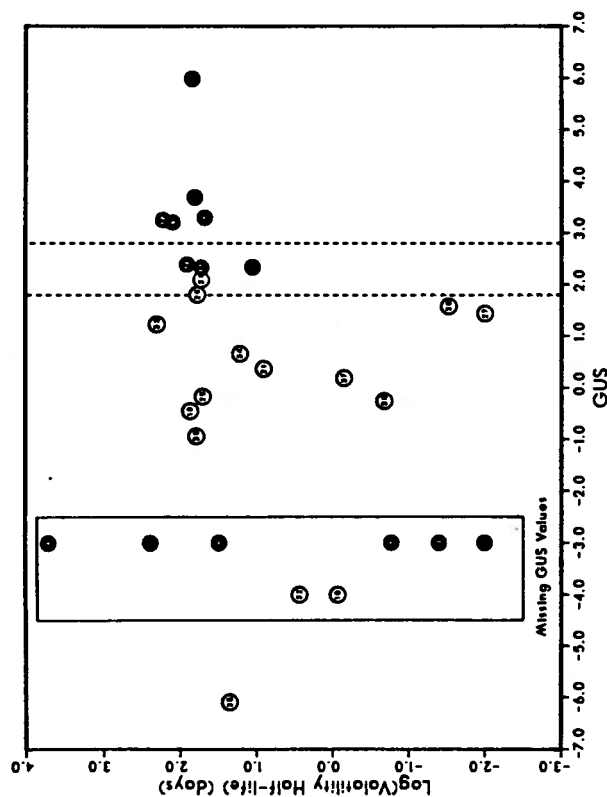


Fig. 9. Volatilities taken from the literature for all chemicals classified as leachers or nonleachers by the CDFA. Compounds for which GUS cannot be calculated due to a missing K_{oc} or a missing f_{ow} are plotted in the floating box for which the known volatilities are read off the same scale. The dashed lines are placed at GUS values of 2.8 and 1.8, the boundaries of the transition region from leachers to nonleachers. Points are numbered according to the key in Table 1.

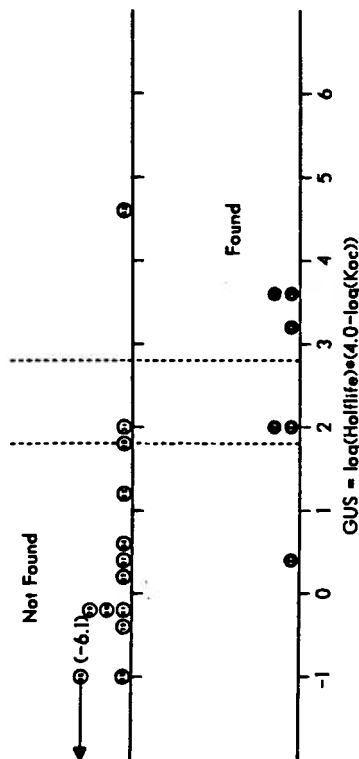


Fig. 10. GUS values for pesticides found (closed circles) and not found (open circles) in the Iowa Department of Natural Resources' one-time sampling program of public water supply systems (surface water systems excluded). No effort was made to eliminate positive findings due to point-source contamination. The dashed lines are placed at GUS values of 2.8 and 1.8, the boundaries of the transition region from leachers to nonleachers. Points are numbered according to the key in Table 1.

calculation of K_{oc} when the fraction soil organic carbon is mistaken for the percent soil organic carbon.

Other examples of monitoring programs are shown in Figure 11-13 (Minnesota [18], Wisconsin [19], and West Germany [20]). Fewer of the compounds analyzed in these monitoring programs were from the CDFA list of pesticides, but the results corroborate the conclusions reached through the comparisons with the Iowa data.

Richard Fawcett (Iowa State University) has determined that many of the positive results of the Iowa monitoring program arise from wells near agricultural dealers [R. C. Fawcett, personal communication]. In addition, both the Iowa and Minnesota studies include numerous well-water samples in regions with Karst topography, where direct hydraulic conduits from the surface to the "ground"-water are known to exist. These results suggest that the GUS methodology may be generalizable to point-source problems, albeit possibly with slightly different GUS threshold zones.

A NOMOGRAM FOR CALCULATING GUS VALUES

The GUS value is easy to calculate from the soil persistence and soil mobility of the pesticide, assuming one has ready access to a calculator or

computer with a logarithm function. If such computing "power" is not available, then the nomogram in Figure 14 may be used. A straightedge is lined up along the half-life and soil/water partition coefficient values for the chemical, and the GUS value is then simply read off the bottom scale. Two examples are shown to demonstrate the use of the nomogram. The first example (see Fig. 15) is for DBCP, a nematocide whose use was discontinued after it was found in thousands of wells in California [3,4]. The other example (Fig. 16) is for glyphosate, unique among herbicides because of its combination of high water solubility and extremely low soil mobility (due to ionic interactions). Average physical properties for both chemicals were calculated from all available literature data [17]. Each of the compounds is properly categorized by the nomogram. A dynamic version of this nomogram has been developed on a Macintosh (II and SE) personal computer, upon which the straightedge in Figure 15 and 16 may be dragged with a "mouse" by one of its handles along either the $t_{1/2}^{(w)}$ or the K_{oc} scale. This dynamic tool is particularly useful for investigating the effects of uncertainty in one or both of the physical properties making up the index. Readers interested in obtaining the program or the Pascal source code may contact the author.

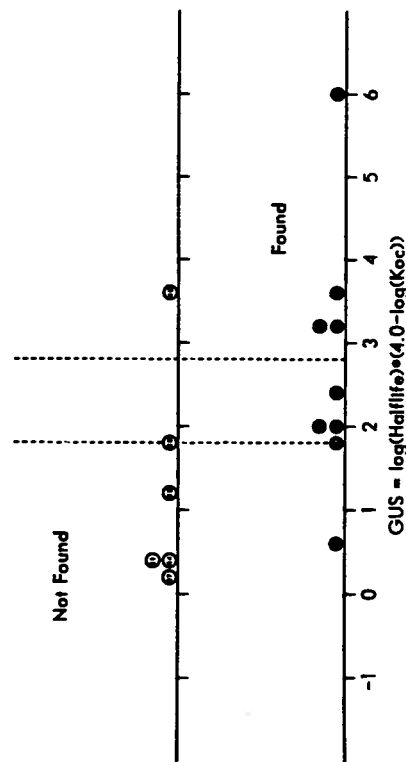


Fig. 11. GUS values for pesticides found (closed circles) and not found (open circles) in the Minnesota Department of Natural Resources' monitoring program of wells in areas with vulnerable groundwater. No effort was made to eliminate positive findings due to point-source contamination. The dashed lines are placed at GUS values of 2.8 and 1.8, the boundaries of the transition region from leachers to nonleachers. Points are numbered according to the key in Table 1.

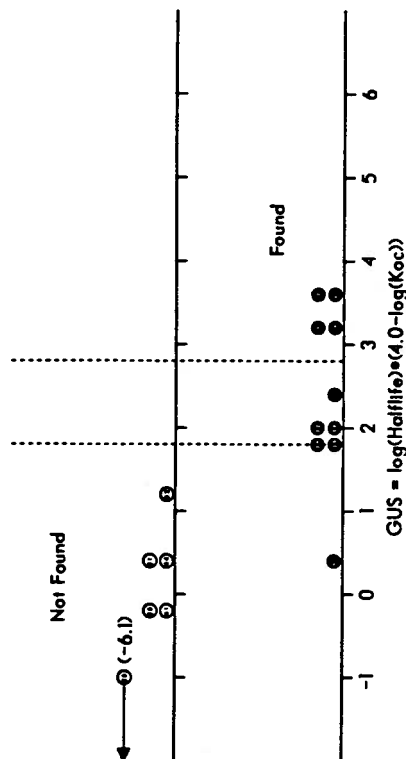


Fig. 12. GUS values for pesticides found (closed circles) and not found (open circles) in the Wisconsin Department of Natural Resources' monitoring program of wells in areas with known contamination problems. No effort was made to eliminate positive findings due to point-source contamination. The dashed lines are placed at GUS values of 2.8 and 1.8, the boundaries of the transition region from leachers to nonleachers. Points are numbered according to the key in Table 1.

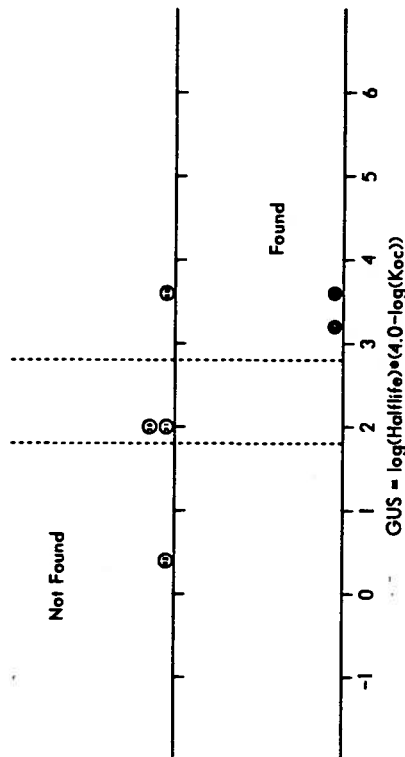


Fig. 13. GUS values for pesticides found (closed circles) and not found (open circles) in the West Germany Industrial Board's monitoring program of wells in areas with extensive agricultural activity, but where point-source contamination is not thought to have occurred. The dashed lines are placed at GUS values of 2.8 and 1.8, the boundaries of the transition region from leachers to nonleachers. Points are numbered according to the key in Table 1.

CONCLUSIONS

Summarizing, this analysis has shown that, for a group of 22 pesticides classified by the CDFA, soil mobility (as measured by K_{oc}) and soil persistence (as measured by $t_{1/2}^{soil}$) serve to indicate

which compounds should leach and which should not. A particular functional combination of these two properties yields an index that reliably separates leaching from nonleaching chemicals. None of the other physical properties commonly associated with leachability (water solubility, octanol/

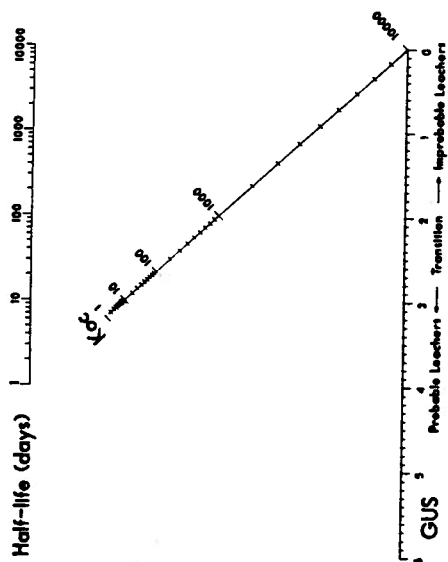


Fig. 14. A nomogram for calculating the GUS value of a pesticide.

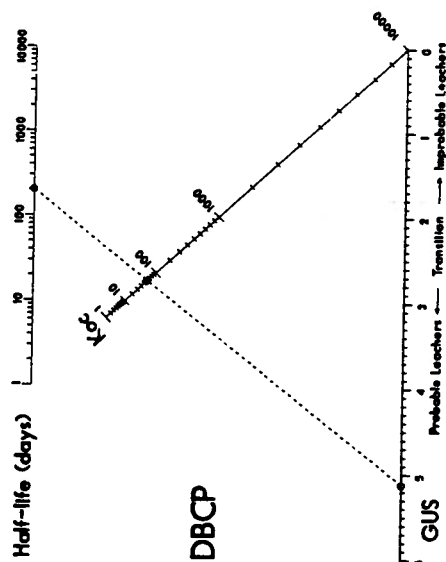


Fig. 15. Example use of the nomogram for DBCP. DBCP's use as a nematocide was discontinued after it was found to have contaminated thousands of wells in California as a result of non-point-source leaching.

water partition coefficient, volatility) appear to provide any additional discriminating power in separating leachers from nonleachers. Three decision zones have been proposed based on the index, and they could be used to trigger or prevent additional modeling and/or experimental work specific-

ically intended to measure the leachability of a pesticide in the field.

Acknowledgement—Larry R. Holden, a Fellow with Monsanto Agricultural Company, provided numerous suggestions on the statistical methodologies employed in this paper, and his assistance was greatly appreciated.

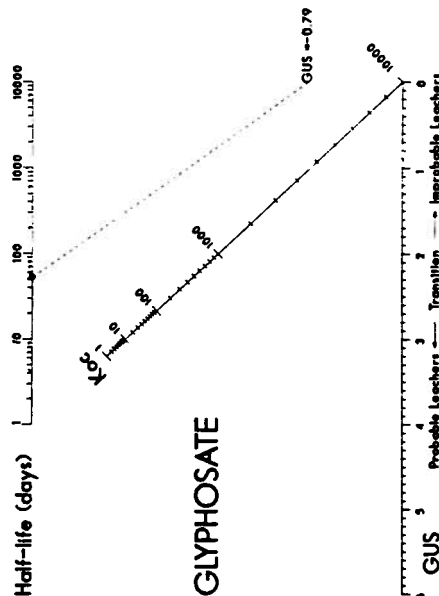


Fig. 16. Example use of the nomogram for glyphosate. Glyphosate is water soluble, but bound very tightly to soil due to its positively charged amino group. This results in a very high K_{oc} value (~30,000, or off the scale of this nomogram).

REFERENCES

1. Lyman, W.J., W.F. Reith and D.H. Roseblatt. 1982. *Handbook of Chemical Property Estimation Methods: Environmental Behavior of Organic Compounds*. McGraw Hill Book Company, New York, NY.
2. Rao, P.S.C., A.G. Horsley and R.E. Jessup. 1985. Indices for ranking the potential for pesticide contamination of groundwater. *Proc. Soil Crop Sci. Soc. Fla.* 44:1-8.
3. Wilkerson, M.R. and K.D. Kim. 1986. *The Pesticide Contamination Prevention Act: Setting Specific Numerical Values*. California Department of Food and Agriculture, Environmental Monitoring and Pest Management, Sacramento, CA.
4. Jury, W.A., D.D. Focht and W.J. Farmer. 1987. Evaluation of pesticide groundwater pollution potential from standard indices of soil-chemical adsorption and biodegradation. *J. Environ. Qual.* 16:422-428.
5. Enfield, C.G., R.F. Carrel, S.Z. Cohen, T. Phan and D.M. Walters. 1982. Approximating pollutant transport to ground water with PESTAN. *Ground Water* 20:711-722.
6. Carrel, R.F., C.N. Smith, L.A. Mulvey, D.J. Dean and P.P. Jowise. 1984. *Users Manual for the Pesticide Root Zone Model (PRZM)*. Release 1. EPA-600/3-84-109. U.S. Environmental Protection Agency, Athens, GA.
7. Dean, J.D., P.P. Jowise and A.S. Dongjian, Jr. 1984. *Leaching Evaluation of Agricultural Chemicals (LEACH) Handbook*. EPA-600/3-84-068. U.S. Environmental Protection Agency, Athens, GA.
8. Cohen, S.Z., S.M. Creeger, R.F. Carrel and C.G. Enfield. 1984. Potential for pesticide contamination of groundwater resulting from agricultural uses. In R.F. Kruger and J.N. Seiber, eds., *Treatment and Disposal of Pesticide Wastes*. ACS Symposium Series No. 259. American Chemical Society, Washington, DC, pp. 297-325.
9. U.S. Environmental Protection Agency. 1987. *Small Scale Prospective Study Design*. Draft document. Washington, D.C.
10. Karickhoff, S.W. 1984. Organic pollutant sorption in aquatic systems. *J. Hydraul. Eng.* 110:707-735.
11. Nicholls, P.H. 1988. Factors influencing entry of pesticides into soil water. *Pest. Sci.* 22:123-137.
12. Soils 5 Database. 1988. University of Illinois and U.S. Army Corps of Engineers, Champaign, IL.
13. Nash, R.G. 1988. Dissipation from soil. In R. Grover, ed., *Environmental Chemistry of Herbicides: Volume 1*. CRC Press, Boca Raton, FL, pp. 131-170.
14. Voss, C.I. 1984. *A Finite-Element Simulation Model for Saturated-Unsaturated, Fluid-Density-Dependent Groundwater Flow with Energy Transport or Chemically Reactive Single-Species Solute Transport (SUTRA)*. USGS Water-Resources Investigations Report 84-369. United States Geological Survey, U.S. Government Printing Office, Washington, DC.
15. Jury, W.A. and G. Spottis. 1985. Field calibration and validation of solute transport models for the unsaturated zone. *Soil Sci. Soc. Am. J.* 49:1331-1341.
16. Gustafson, D.I. 1988. Modeling root zone dispersion: A comedy of error functions. *Chem. Eng. Comm.* 73:77-94.
17. PHYS: Physical Property Database. 1988. Monsanto Agricultural Company, St. Louis, MO.
18. Klees, T.G., G.C. Buskirk and E.C. Schaefer.

1988. *Pesticides and Groundwater: Surveys of Selected Minnesota Wells*. Minnesota Departments of Health and Agriculture. Minneapolis (Department of Health) and St. Paul (Department of Agriculture), MN.

19. Wisconsin Department of Natural Resources. 1987. *Summary of the Problem Assessment Monitoring Program*. Madison, WI.

20. Industrieverband Pflanzenschutz, *Federal Republic of Germany*. 1988. *IPS raw water monitoring: An in-depth analysis of the occurrence of the active ingredients of pesticides in drinking water resources*. Bonn, West Germany.

21. Iowa Department of Natural Resources. 1988. *Pesticide and Synthetic Organic Compound Survey: Report to the Iowa General Assembly on the Results of the Water Systems Monitoring Required by House Bill 2303*. Des Moines, IA.

22. Bear, J. 1972. *Dynamics of Fluids in Porous Media*. Elsevier, New York, NY.

23. Dullien, F.A.L. 1979. *Porous Media: Fluid Transport and Pore Structure*. Academic Press, New York, NY.

24. Wang, H.F. and M.P. Anderson. 1982. *Introduction to Groundwater Modeling: Finite Difference and Finite Element Techniques*. W.H. Freeman and Company, San Francisco, CA.

25. Bettess, S. and T.J. Day. 1978. A field study of longitudinal dispersion. *Can. J. Civil Eng.* 5:572-585.

26. Doolin, A., G. Matheron and G. de Marsily. 1981. Growth of the dispersion coefficient with the mean traveled distance in porous media. *Sci. Total Environ.* 21:319-328.

27. de Gennes, P.G. 1983. Hydrodynamic dispersion in unsaturated porous media. *J. Fluid Mech.* 136:189-200.

28. Anderson, M.P. 1984. Movement of contaminants in groundwater: Groundwater transport—Advection and dispersion. In *Groundwater Contamination: Studies in Geophysics*. National Academy Press, Washington, DC, pp. 37-45.

APPENDIX A. SENSITIVITY ANALYSIS

It is intuitive that as either mobility or persistence increases, any index of pesticide leachability should also increase. In this sense the GUS function clearly satisfies this intuitive notion. The hyperbolic form employed for GUS is arbitrary, however, and it is important to demonstrate that it is robust to the uncertainty in the two reported physical property values used in its development.

In classical sensitivity analysis, the goal is to quantify the variability in the model output induced by variability (or uncertainty) in the model parameters. However, the GUS model does not fit nicely into this mold. Similar to a regression model, it is the data that determine the single parameter P in the GUS function:

$$GUS = \log_{10}(1/r^2) \times (P - \log_{10}(K_{oc})). \quad (A1)$$

where P was set to 4 in the proposed methodology.

As with regression models, different data sets would induce different values for P , which would in turn yield different GUS predictions. One important question is then how sensitive is the value of the single GUS parameter P to the variability in the reported values for pesti-

cide mobility in soil and pesticide persistence in soil? In addition, how sensitive is the ability of GUS to distinguish leachers from nonleachers in light of the known (or estimated) data uncertainty?

Method for estimating P

Given a particular value of P , GUS values for all leachers and nonleachers can be calculated directly. The value of GUS separating the two groups Q is defined as:

$$Q = \frac{1}{2} (\text{Min } GUS_{L,j} + \text{Max } GUS_{N,j}). \quad (A2)$$

where $GUS_{L,j}$ and $GUS_{N,j}$ are the GUS values for the j th leacher and j th nonleacher, respectively. Thus Q is completely determined by P .

A perfect classification results if all GUS values for leachers are above Q and all GUS values for nonleachers are below Q , since complete segregation of the two classes would be achieved. The equation quoted in the paper (with $P = 4$) achieves such separation (with $Q = 2.3$). A continuous measure of lack-of-segregation or penalty function f was defined as:

$$f_L = \text{Exp}(5(Q - GUS_{L,j})/h_{L,N}). \quad (A3)$$

for leachers, and for nonleachers:

$$f_N = \text{Exp}(5(GUS_{N,j} - Q)/h_{L,N}). \quad (A4)$$

The distances on the GUS scale between the boundary Q and the particular pesticide have been standardized by dividing by the estimate of the pooled within-class standard deviation, $h_{L,N}$. This minimizes scale effects for different values of Q . The exponential form of the penalty function was chosen in order to obtain a function whose value approaches zero for properly categorized pesticides far removed from Q , unity for GUS values at Q , and sharply increasing values greater than unity for miscategorized pesticides. The sharpness is influenced by the coefficient 5, which was chosen in order to place most emphasis on pesticides within one standardized unit of Q .

A combined penalty F , associated with a given estimate of P is then defined as:

$$F(P) = \frac{1}{n_L} \sum_{j=1}^n f_{L,j} + \frac{1}{n_N} \sum_{j=1}^n f_{N,j} \quad (A5)$$

The average penalties for each class are used in order to place equal weight on leachers and nonleachers.

A simple iterative direct search procedure was used to select the value of P that minimized $F(P)$. Possible values for P were examined in the range 2.0 to 6.0. Using the original set of physical properties as given by the CDFA, the total penalty was minimized at $P = 3.84$. Complete segregation of the two groups was achieved for P anywhere from 3.6 to 4.1. Use of $P = 4$ can be justified as the simplest numerically, although a slightly lower value may be somewhat more optimal.

Before proceeding, a note about the form of Equation A1 is in order. One could propose a more general form of (A1) in which the term, $\log_{10}(1/r^2)$, is replaced by $\log_{10}(1/r^2) - P_2$, where P_2 is another parameter to be estimated. This form of (A1) was examined, and it was found that the optimization surface (as described

Table A1. Monte Carlo simulation of the GUS methodology: Goodness of classification (number of misclassifications during 2,000 runs)

Type of misclassification	Number of pesticides misclassified with $\sigma = 0.1$				
	0	1	2	3	4
$GUS_1 < Q$	1,286	642	68	4	
$GUS_1 < Q - 0.5$	2,000	0	0	0	
$GUS_N > Q$	1,286	595	112	7	
$GUS_N > Q + 0.5$	2,000	0	0	0	
Number of pesticides misclassified with $\sigma = 0.2$					
	0	1	2	3	4
$GUS_1 < Q$	620	989	326	53	11
$GUS_1 < Q - 0.5$	1,868	128	3	1	0
$GUS_N > Q$	620	880	419	72	7
$GUS_N > Q + 0.5$	1,868	125	6	1	0

above) was relatively flat near the optimal P_2 of -1.0 , with $P_2 = 0$ giving essentially the same result. Thus P_2 was set equal to zero for a more parsimonious single parameter model.

Monte Carlo simulation

A Monte Carlo simulation technique was employed to investigate the effect of uncertainty in the physical properties of the pesticides on the estimate of P and on the misclassification rate. Examination of an in-house database [17] revealed that median standard deviations for $\log_{10}(K_{oc})$ and $\log_{10}(f_{1/2})$ were 0.2246 and 0.2487, respectively, for all pesticides in the database that had at least five different experimental values. For most currently registered pesticides these physical properties are calculated as means from four to five individual measurements; thus the standard deviation (or standard error) of a typical average physical property could be reasonably estimated by the median standard deviation divided by $\sqrt{4}$ or $\sqrt{5}$. A standard deviation of 0.1 to 0.2 for both average $\log_{10}(K_{oc})$ and average $\log_{10}(f_{1/2})$ might therefore be regarded as typical.

For each of the 2,000 Monte Carlo runs, the two physical properties for each pesticide were perturbed by a random normal deviate with mean zero and standard deviation 0.1 or 0.2. Using the new set of pesticide properties, a new P was estimated. Also recorded were the following statistics of the new classification:

- The number of leachers with GUS values less than Q ?
- The number of nonleachers with GUS values greater than Q ?
- The number of leachers with GUS values less than $Q - 0.5$?
- The number of nonleachers with GUS values greater than $Q + 0.5$?

These four summary statistics characterize the goodness of classification and are shown in Table A1. Shown in Figure A1 is a dot-plot of the frequency distribution of P . Complete segregation was achieved in 64.3% of the runs with $\sigma = 0.1$ and in 31.0% of the runs with $\sigma = 0.2$.

questioned, because the dispersion coefficient, assumed to be a constant in the conventional CDE derivation, actually tends to increase with the scale of the problem [15,16,25-28]. An analytical solution to the CDE can be obtained for certain simple boundary conditions. A solution for the case of constant water velocity and all of the chemical initially at the soil surface is:

$$C = \frac{e^{-k_1 t} (1 - e^{-k_2 t}) / 2}{\sqrt{\frac{\pi k_2 v_w}{2} \left(\text{erf} \left(\frac{1}{\sqrt{2k}} \right) + 1 \right)}} \quad z \geq 0, \quad (\text{B1})$$

in which the various terms are defined as: C = concentration of the leaching species (averaged areally, and normalized to an initial value of 1); z = distance from the soil surface; t = time; k_1 = first-order degradation rate constant; v_w = mean velocity of water; $v = v_w / (1 + (K_{oc}/f_{1/2}))$; K_{oc} = soil/water partition coefficient; ρ_s = dry bulk density of the soil; θ_{FC} = field (moisture-holding) capacity of the soil. The dispersion coefficient has been assumed to increase proportionately with the mean distance traveled, $D_L = k v_w t$, where k is the dispersion

growth rate constant; $\text{erf}(x)$ = the error function of x , $\int_0^x e^{-u^2} du$.

This analytical solution to the CDE would not be expected to accurately represent the concentration profiles at any single location, but the nature of the interactions between persistence and mobility should be properly expressed by the equation. The equation may be used to calculate the amount of applied material likely to leach below a given depth. Mathematically, this is simply a suitably weighted integral of the chemical flux at some depth z :

$$f_z = \frac{\int_0^\infty C(z) dz}{\int_0^\infty C(0) dz} \quad (\text{B2})$$

in which f_z = fraction of the applied material which leaches below indicated depth z .

Due to the relative complexity of Equation B1, the Integral in Equation B2 is most easily calculated by numerical means. An Euler integration method with a step size of 1 day was used to calculate the theoretical contours shown in Figure 6 of this paper.