IV

Remediation

8

Groundwater Quality, Pollution Control, and Climate Change

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Abstract

Given that almost half of the world's drinking water is from groundwater, and groundwater extraction is increasing, groundwater protection should be promoted, and groundwater restoration to various levels of water quality should be pursued where appropriate. Where naturally-occurring or anthropogenic (man-made) pollution exists, cost-effective remediation technologies are available to restore portions of an aquifer to quality levels that may be suitable for agricultural or industrial use. Remediation to drinking water quality levels will be more costly than for other uses, and take longer to achieve, but can likewise be attained. Usable water can be extracted within the radius of influence of a pumping well even where aquifer contamination extends beyond the well.

The study details the principal types of anthropogenic and naturally-occurring groundwater pollutants, and effective methods of groundwater remediation technologies. These conditions and processes are examined in the context of climate change. Additionally, successful case studies are presented, which demonstrate reduction of contaminant concentrations to usable levels by promoting growth of indigenous bacteria (biostimulation) to lower contaminant concentrations as bacteria can metabolize fuels, solvents or explosives.

Whenever possible, water managers should consider existing groundwater quality from an aquifer, so lower quality water is matched with the appropriate agricultural or industrial application, and ideally save high quality groundwater for use as a drinking water source.

Keywords

Groundwater, pollution. per- and polyfluoroalkyl substances (PFAS), climate change, remediation, bioremediation

01

Types of Groundwater Pollution

Groundwater pollution can be grouped into two categories: naturally-occurring and anthropogenic pollution. An example of natural pollution is the high concentrations of arsenic (As) in Bangladesh groundwater, which is generally believed to originate from the unconsolidated sediments (sands, silts, clays and gravels) that host the groundwater.

Most anthropogenic groundwater pollution can be categorized into either agricultural, sewage, or industrial pollution (Figure 8-1). There is widespread nitrate and phosphate pollution from agricultural and sewage sources, including fertilizers, animal manure and human sewage, and detergents.

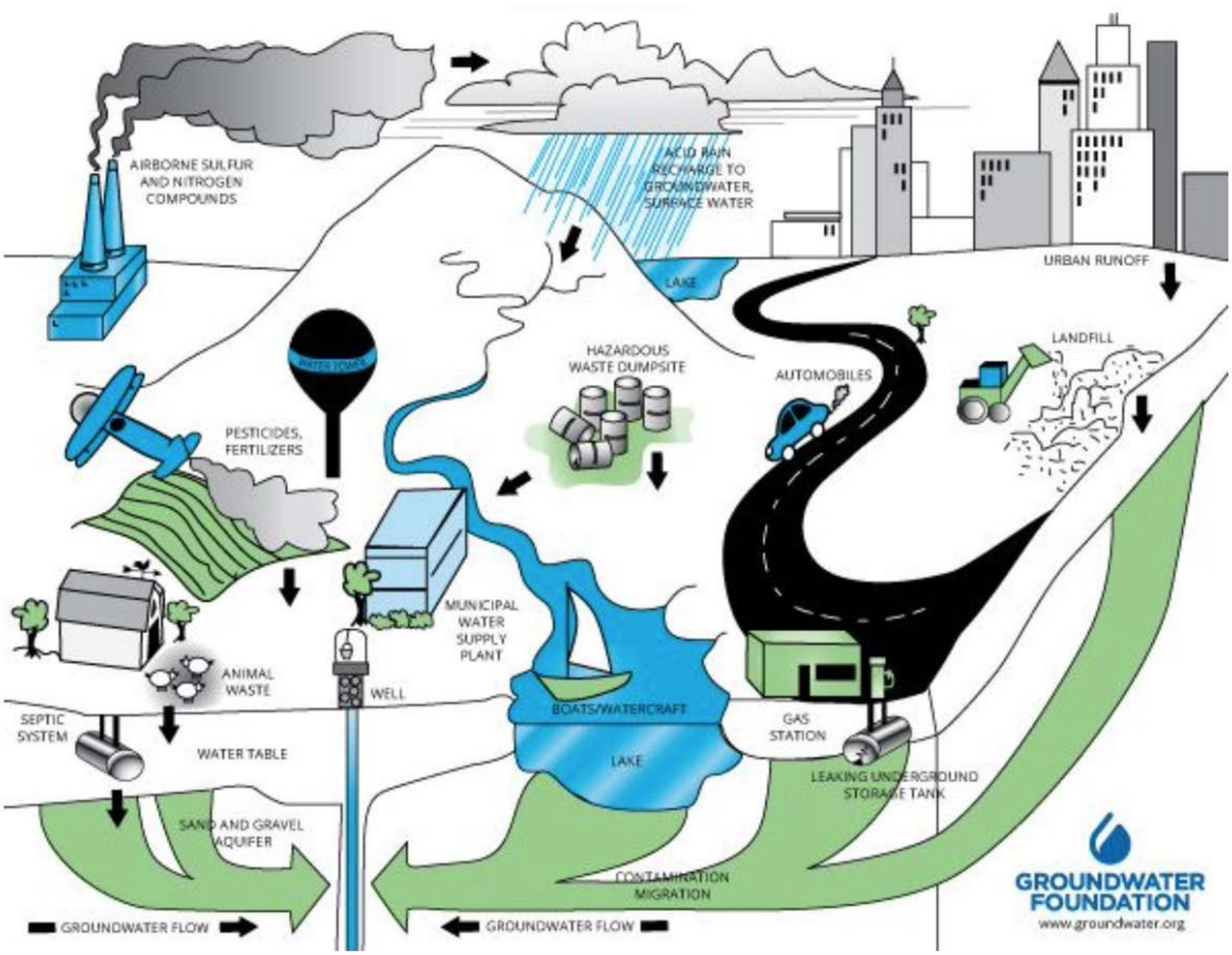
Industrial pollutants can be grouped as fuels (gasoline, diesel), solvents (degreasers including trichloroethylene),

metals (cars, batteries), semi-volatile organic compounds (pesticides, polychlorinated biphenyls [PCBs]), and wood treatment compounds (pentachlorophenol in creosote); explosives, and per- or polyfluoroalkyl substances (PFAS) in Teflon, Gore-Tex, aqueous fire fighting foam [AFFF], also known as aqueous film forming foam, and metal plating baths. PFAS are a widespread emerging class of compounds whose toxicity is still being defined.

The effects of climate change on the transport, fate and remediation of polluted groundwater are discussed in Section 5.

The relationship between surface water and groundwater is of fundamental importance when considering the movement of pollutants.

In many environments, surface water seeps through soil and becomes groundwater. It is also common for groundwater to feed surface water sources. Common naturally-occurring and anthropogenic groundwater pollution sources are summarized in Table 8-1.

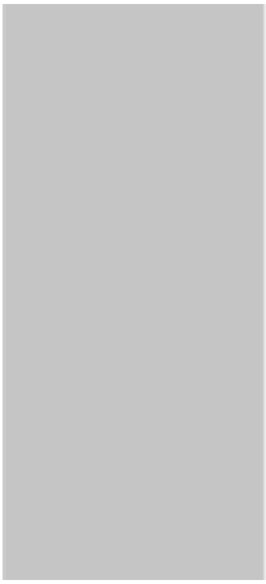


Agricultural, sewage, industrial, and other miscellaneous man-made pollution sources in air, surface water, soil and groundwater (Groundwater Foundation, 2020)

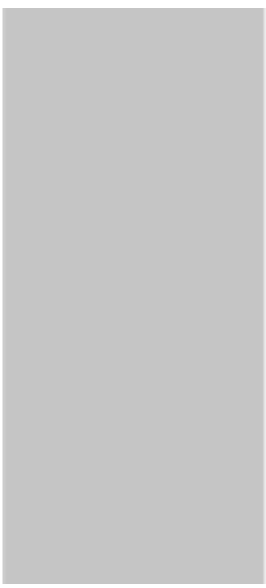
176 **Remediation**

Common naturally-occurring and anthropogenic groundwater pollution sources

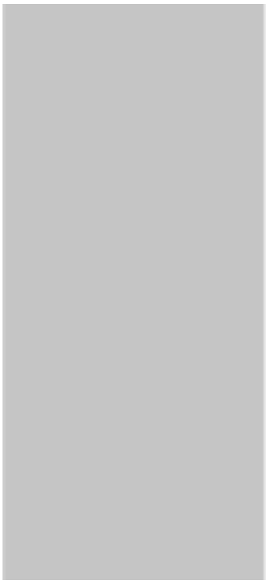
Arsenic



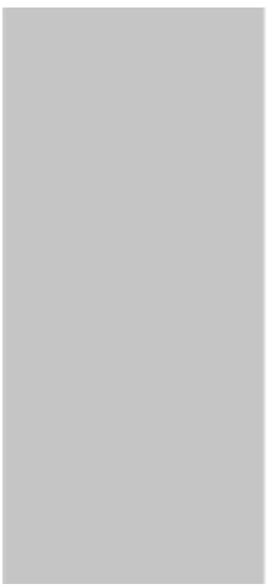
Copper, Lead, Zinc, Cadmium



Uranium and other radionuclides



Iron and Manganese



Selenium

Soils or bedrock

Higher concentrations in bedrock versus soil

Soil or bedrock, both igneous and sedimentary rock

Soil or bedrock

Associated with coal-bearing or volcanic rocks and soils

Gasoline and diesel fueling stations, large spill locations

Degreasers, cleaning solutions, pesticides, glues, resins

Mining and industrial air and water effluent; diesel exhaust

Mining operations, industrial effluent, road runoff, open burning

Metal and coal mining, effluent from power plants

Nuclear weapons production, nuclear power plants, coal and phosphate mining, uranium mining

Fertilizer runoff from agriculture, commercial or residential sources; septic systems.

Formerly used as a di-electric oily fluid in transformers, and a lubricant.

Flame-retardant in carpet, furniture; formerly in Teflon; still used in aqueous fire fighting foam (AFFF)

Creosote, a wood preservative

Septic systems and wastewater treatment plants (WWTP)

Plastic bags and containers Surficial soils in agricultural areas

Elevated arsenic may occur in many geologic environments.

Bedrock source areas may leach to groundwater

Elevated uranium is widespread in many aquifers in India.

Often found together in groundwater in elevated concentrations

Selenium is a significant pollutant that is released via metal and coal mining, power plant effluent

Gasoline: carcinogenic with benzene, toluene ethylbenzene

Perchloroethylene dry cleaning fluid formerly caused enormous groundwater pollution.

Occurs as arsenites and arsenates; carcinogenic

These heavy metals commonly occur together.

Increasingly recognized as a significant pollutant that occurs naturally but is mobilized during mining.

Uranium, radon and radium occur together in groundwater

Nitrates in urea or ammonium nitrate are most widely used in fertilizers

Very stable and present throughout food chain; Banned in USA and EU

Over 4,000 known PFAS compounds; exceedingly stable; incompletely studied

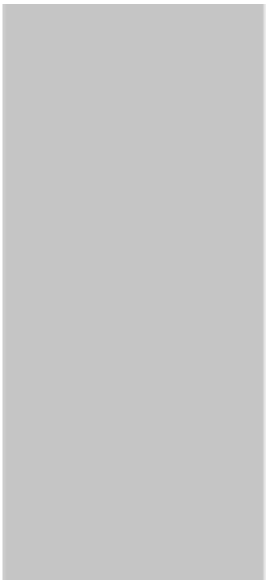
Very stable compound

Drugs such as antibiotics and blood-pressure medicines are being increasingly detected in groundwater

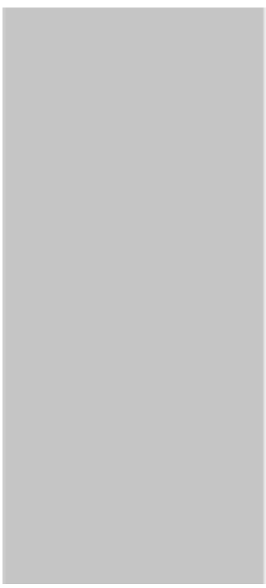
Presence and extent in groundwater is poorly known due to lack of sampling

Chemicals reach groundwater via runoff and leaching.

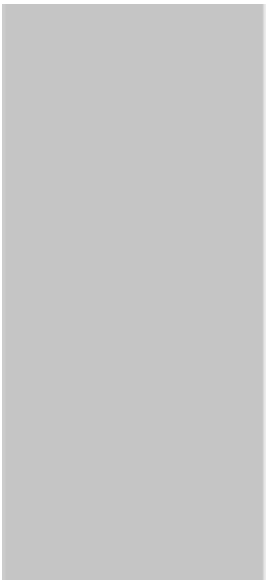
Fuels



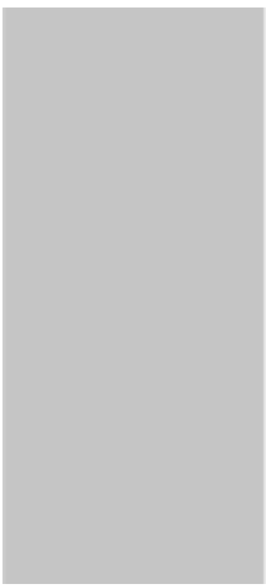
Solvents



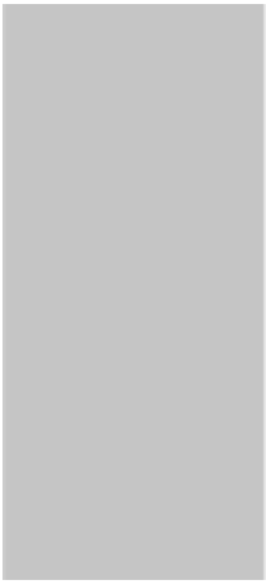
Arsenic



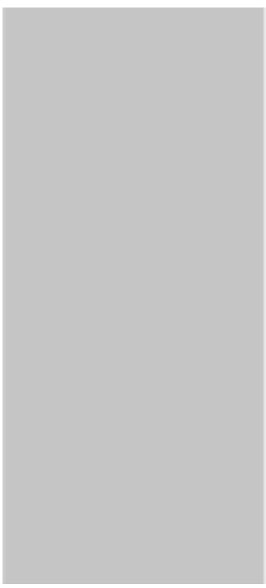
Heavy Metals:Copper, Lead, Zinc, Cadmium



Selenium



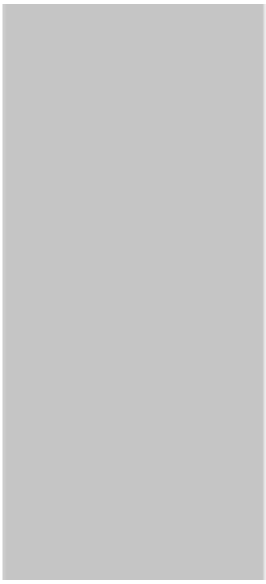
Uranium and other radionuclides



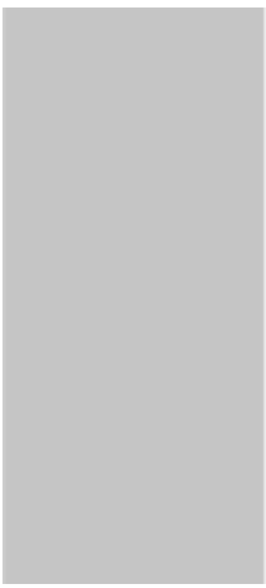
Nitrates, phosphates and potassium

Polychlorinated Biphenyls (PCBs)

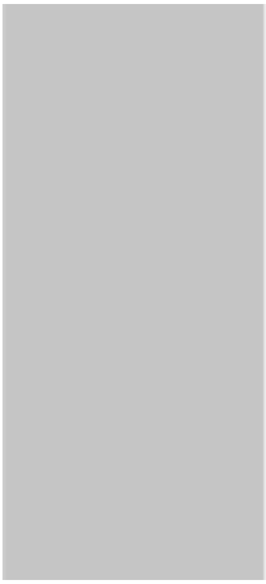
Per- and Polyfluoroalkyl substances (PFAS)



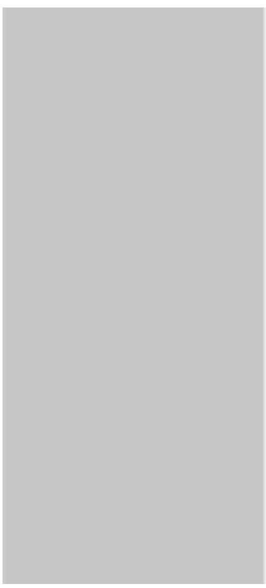
Pentachlorophenol



Prescription Drugs



Microplastics



Pesticides and Herbicides

02

Groundwater Remediation: Existing and Emerging Technologies

Groundwater remediation methods can generally be grouped into three categories: containment, removal, or treatment (Water Encyclopedia, 2020).

Containment. This involves containing the contaminants to prevent them from migrating from their source.

Removal. The principal method of groundwater remediation of industrial pollutants is extraction via pumping from groundwater wells and treatment by activated carbon;
or a combination of ion exchange, reverse osmosis, and/or distillation. However, it often must be operated for twenty years or more with decreasing effectiveness as the recovered contaminant mass steadily decreases. Annual operating costs remain constant and can typically range from $300,000- $500,000 USD, depending on the size of the contaminant plume (EPA, 2001, Gander, 2020) (Figure 8-2).

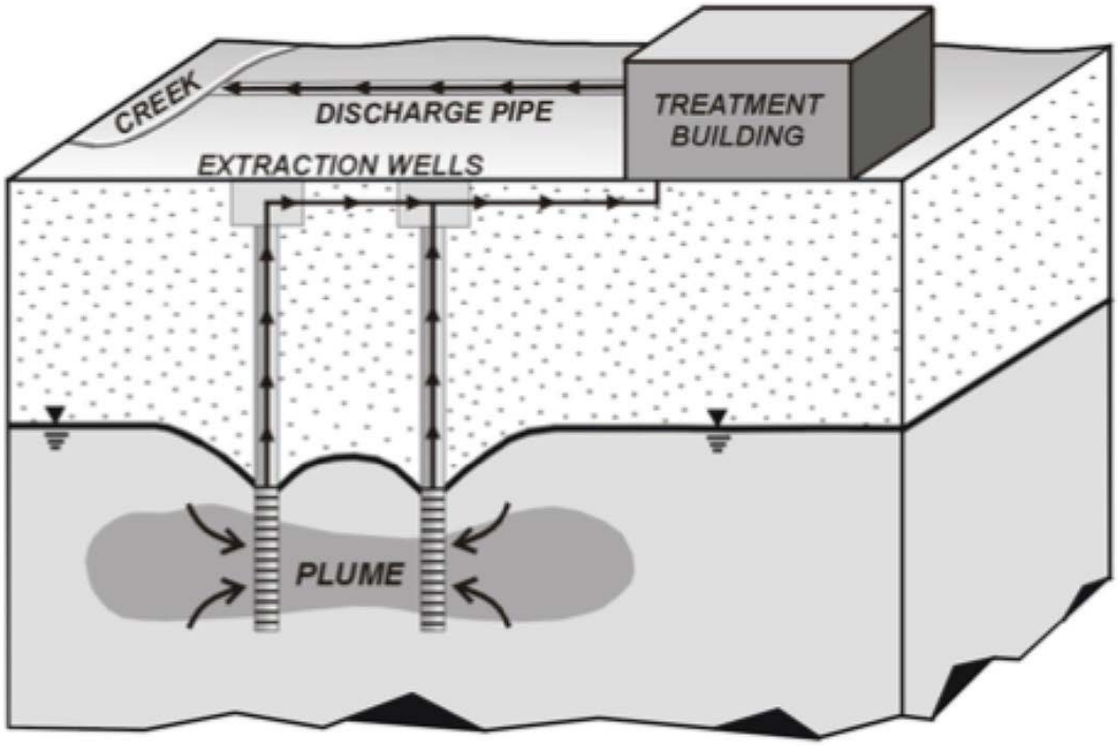
Treatment. This technology is applied in cases where the aquifer characteristics are complex and/or multiple contaminants exist, and it involves treating the water at

its point of use. The most common forms of treatment
are reverse osmosis, ion exchange, or distillation. Reverse osmosis is a water purification process that uses a partially permeable membrane to remove unwanted molecules from drinking water, and is often a pre-treatment phase followed by ion exchange. Ion exchange is a purification process using a polymeric resin such as spherical beads to capture ionic species. Distillation removes dissolved solids, some bacteria, and inorganics such as nitrates by boiling water and the vapor is collected into a container.

Bioremediation is a form of treatment where naturally-occurring microorganisms metabolize (break down) many contaminants and are being increasingly used as a remediation method.
In some cases, bacteria are introduced (bioaugmentation) into groundwater after small-scale pilot testing establishes their ability to thrive and break down contaminants in a specific environment. Bacteria are provided a carbon substrate (e.g., fructose), and this biostimulation can enable achievement

of clean up levels (CULs) within the radius of influence of the biostimulation within several years. Groundwater remediation technologies are summarized in Table 8-2.

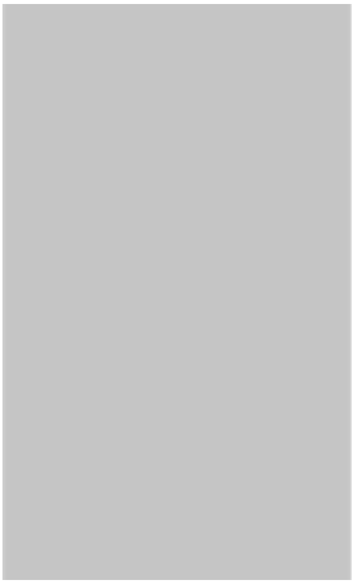
PFAS compounds are unusual in that they are generally
not amenable to microbial degradation. Some PFAS can be treated with activated carbon, whereas others are amenable to ion exchange. Enormous monetary resources are currently being devoted internationally to developing PFAS treatment technologies,



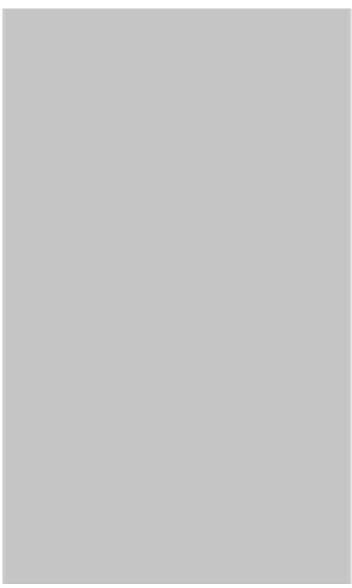
Typical pump and treat system where contaminated groundwater is extracted; pumped through carbon; and clean water is discharged (EPA, 2001)

Overview of groundwater remediation technologies, including technologies under development

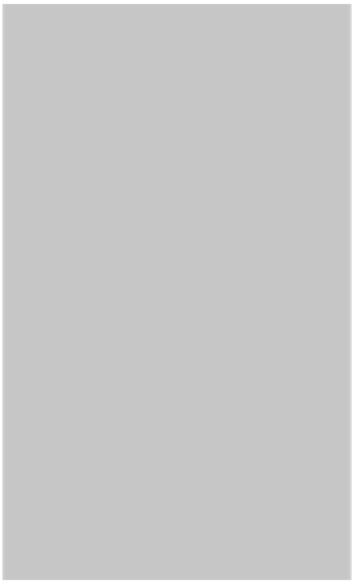
Pump & treat (P&T), primarily with activated carbon



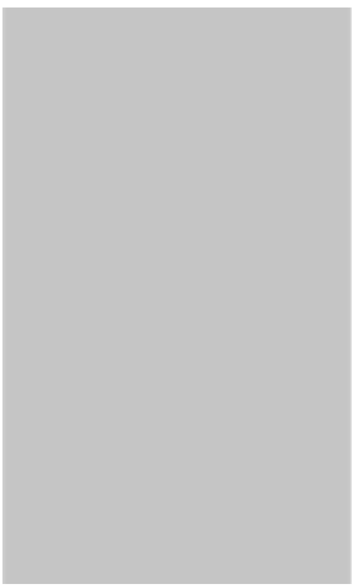
Bioremediation



pH adjustment, chemical treatment



Ion exchange, reverse osmosis, and/or distillation



Supercritical water oxidation

Fuels, solvents, creosote (pentachlorophenol), PFAS, explosives (e.g., TNT), PCBs

Fuels, solvents, creosote (pentachlorophenol), explosives (e.g., TNT), nitrates and radionuclides (e.g., uranium), metals

Arsenic (a metalloid)

Metals: Copper, Lead, Zinc, Cadmium; PFAS; Selenium

PFAS

2.1. Emerging remediation technologies

Supercritical Water Oxidation. This technology has been highly effective in small-scale laboratory pilot tests (Rosansky, 2020) in the destruction of PFAS compounds. Testing to
date has achieved PFAS concentrations to five ppt (initial concentrations ~100-500 ppt) while processing 100 ml/minute, or 144 l/day (38 gallons/day). An expanded pilot test of 379 l/ day (100 gallons/day) is planned for a PFAS contaminated site in Fall 2020.

Supercritical water involves subjecting water to very high temperatures and pressures where the gas and liquid phases become indistinguishable. Under these conditions, oxidation is greatly enhanced to the point where the recalcitrant chlorine-fluorine bond in PFAS compounds is broken, enabling dissociation of the compound.

Phosphate-Mediated Remediation of Metals and Radionuclides. The metals lead, zinc and cadmium, and radionuclides such as uranium, are common groundwater pollutants from miscellaneous industrial activities, and nuclear weapons production plus coal and phosphate mining, respectively. Through laboratory and field experiments,
the introduction of various phosphate compounds can readily precipitate in situ insoluble metal- and radionuclide-phosphate minerals that immobilize these contaminants over a wide pH range (Martinez *et al*., 2014). Additionally, certain microorganisms' life-sustaining requirement for phosphorus serves as a mechanism to consume metals and radionuclides within polyphosphate compounds and store them within the cell structure.

P&T systems are reliable methods of groundwater treatment but routinely become less efficient as concentrations decrease over time.

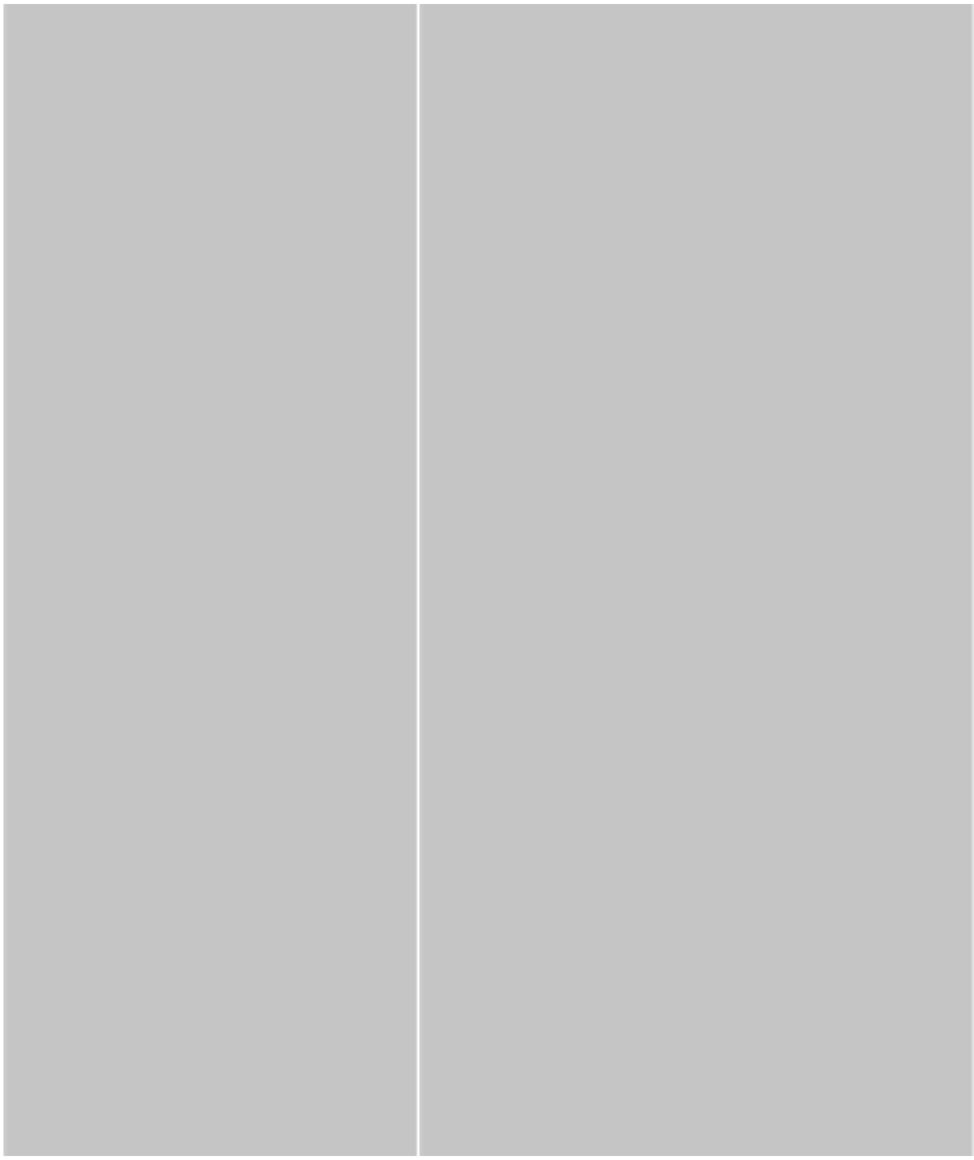
Microbes metabolize fuels, solvents, explosives, nitrates. In pilot tests, microbes liberate phosphate that can immobilize (sequester) uranium and metals.

Immobilization by: a) pH adjustment via hydrated lime addition to inhibit oxidation of arsenical pyrite; or b) maintenance of oxidizing conditions where pyrite is absent but high As is present and immobile under oxidizing conditions.

These techniques can achieve drinking water quality conditions.

Pilot testing successful to <10 parts per trillion (below health advisory)

This holds promise for large-scale bioremediation as the biological sequestration of contaminants is possible as long as the groundwater pH and oxidation-reduction potential is controlled. Separately, small-scale, laboratory-based studies have verified microbial mineralization (destruction) of heavy metals including cadmium and copper, and radionuclides including uranium and strontium (Martinez *et al*., 2014, Gadd, 2007). Mineralization of metals and radionuclides is ideal because the contaminant mass is destroyed and control of pH and oxidation-reduction potential is unnecessary.



03

Case Studies

Two case studies are presented that detail the use of microorganisms (bioremediation) to reduce explosives and chlorinated solvent contaminant concentrations to levels suitable for either agricultural or industrial use, or for drinking water. A third case study of two large agricultural basins is summarized, where nitrate concentrations in groundwater are being reduced through pumping the contaminated groundwater, efficient addition of fertilizer and manure to the recovered groundwater, and land application of the amended groundwater.

3.1. Explosives in Groundwater

Explosives compounds contamination in groundwater is very poorly known and assumed present in many areas in Cambodia, Laos, Vietnam, North Korea, South Korea, Afghanistan, Yemen, Iraq, Angola and Chechnya. Activities regarding explosives has almost exclusively directed funding toward the removal of unexploded ordnance, which remains a severe health hazard. Approximately twenty percent of the land area of Cambodia, Laos and Vietnam have unexploded ordnance (Martin *et al*., 2019).

The United States, Canada and Germany have by far conducted the most applied research and development concerning groundwater remediation of explosives, as the United States and Canada have over 50 million acres of contaminated lands from training and testing (Pichtel, 2012), and Germany has legacy contamination for World War II activities.

The most common explosives compounds are 1,3,5-hexahydro-1,3,5-trinitro toluene (RDX) and trinitrotoluene (TNT).

3.1.1. Pump & Treat with Bioremediation, Umatilla Chemical Depot, Umatilla, Oregon, USA

Summary Statement: At the Umatilla Chemical Depot (UMCD), bioremediation of explosives in groundwater by indigenous anaerobic bacteria achieved concentrations of 0.5 - 10 ug/L in 3-5 years in a portion of a larger 800 meter groundwater plume, using a drinking water clean-up level of 2.1 ug/L as

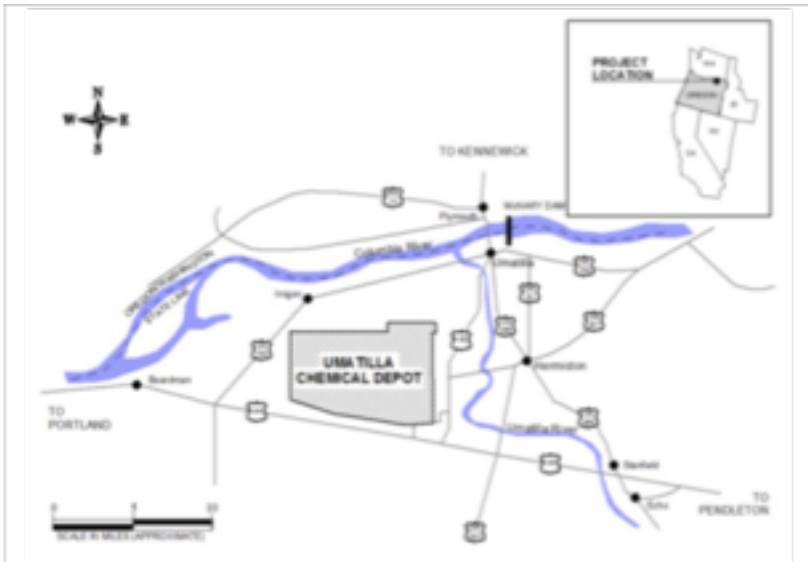
a benchmark. This remediated water could be extracted at a rate of ~ 76 liters per minute (lpm) (20 gallons per minute) in multiple wells and used for industrial applications such as a closed-loop cooling system or open evaporative cooling system that polishes effluent with carbon to capture residual explosives.

3.1.2. Background

The UMCD (Figure 8-3) operated from 1941 until 2011, and activities included ordnance storage and destruction of chemical agents and munitions. Chemical agents were typically incinerated and conventional munitions were subjected to a steam melt-out and rinsing process. The wastewater from rinsing formed the washout lagoon

and explosives compounds leached to groundwater, about 60-70 feet below ground surface. RDX and TNT are the most prevalent contaminants, with subordinate amounts of trinitrobenzene (TNB), dinitrobenzene (DNB), 2,4-dinitrotoluene (2,4-DNT), 2,6-dinitrotoluene (2,6-DNT), and octahydro-1,3,4,7-tetranitro-1,3,5,7-tetrazocine (HMX).

A pump and treat (P&T) groundwater treatment system was installed in 1997 and continues to operate. Due to the extremely long (>50 years) remediation timeframe anticipated to achieve the cleanup level, a bioremediation program was initiated in 2010 in order to more aggressively remove contaminant mass and reduce the remediation timeframe. The centerpiece of the bioremediation effort is the periodic injection of fructose corn syrup mixed with UMCD formation water, termed biostimulation.



Location of Umatilla Chemical Depot, Umatilla, Oregon, USA (USACE, 2015)

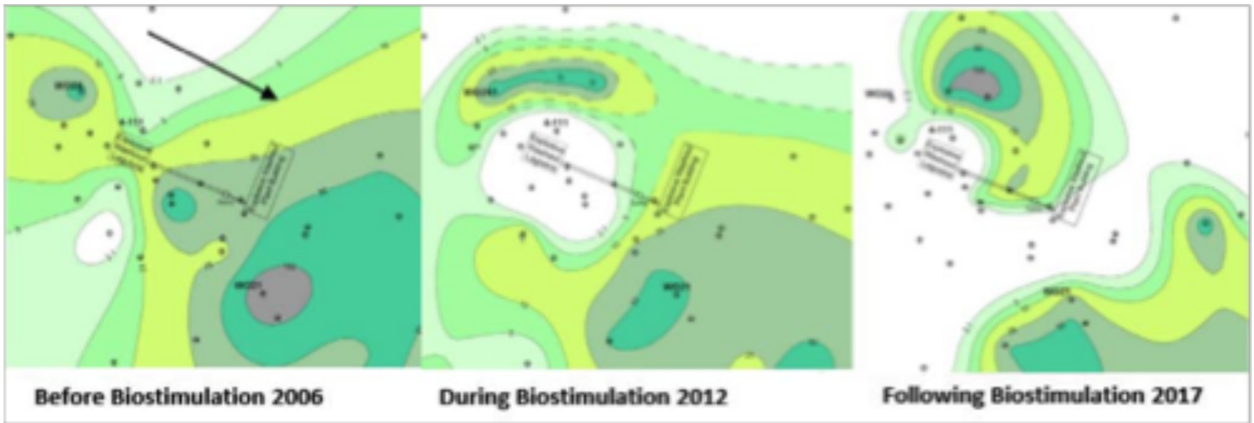
3.1.3. Bioremediation Implementation

Figure 8-4 is a plan view of the RDX groundwater contaminant plume, which presents the progressive decrease of RDX concentrations by depicting relative concentrations before, during and after biostimulation. The highest concentrations are centered at the former washout lagoon area coincident with well 4-111.

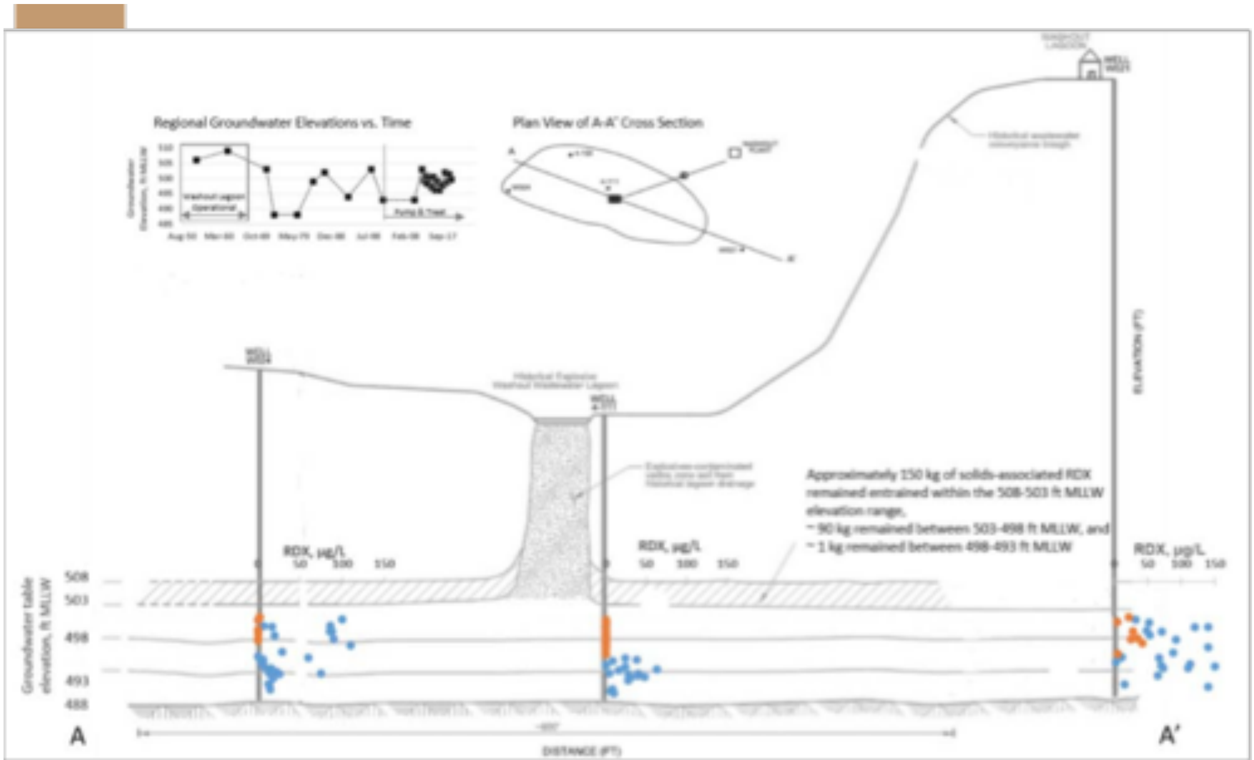
Figure 8-5 is a cross-sectional view showing the explosives disposal lagoon in the center. Favorable bioremediation

results were achieved in the vicinity of well 4-111 (near the source area), and peripheral wells WO-21 and WO-24; these three wells were used for injection of nutrients for bacteria. For these wells, the explosives (RDX) concentration was reduced to a range of <2.1 - 10 ug/L in three to five years following biostimulation using fructose.

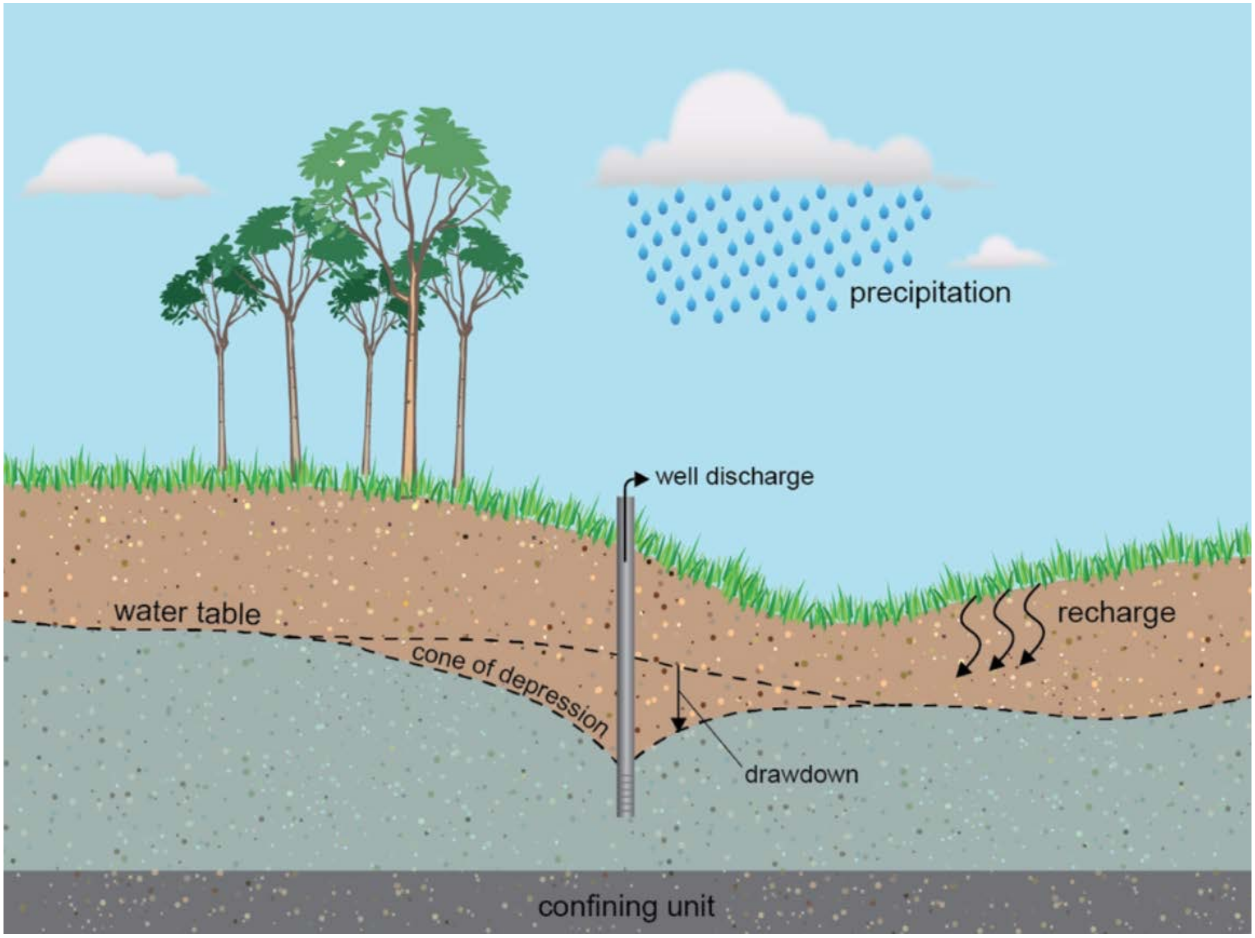
The injection wells could be converted to pumping wells and bioremediated water could be pumped at a rate of 80 liters per minute in each well. The radius of influence of 15 meters surrounding a pumping well is a conservative



RDX concentrations in the former washout lagoon source area before, during and after bioremediation. Purple is >100 ug/L; dark green is 50-100 ug/L; gray is 25-50 ug/L; yellow-green is 10-25 ug/L; green is 5-10 ug/L; and light green is 0-5 ug/L (Michalsen et al., 2021)

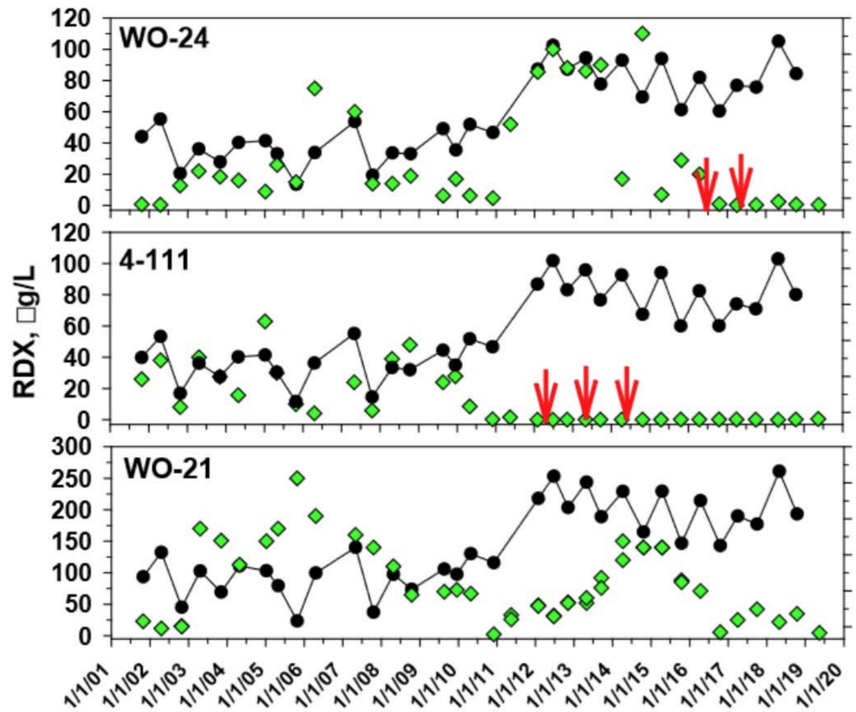


Cross-sectional view showing the explosives disposal lagoon in the center and RDX-bearing wastewater source area to right. RDX concentrations in site wells before and after biostimulation (blue and orange circles, respectively) vs. groundwater elevation illustrate that bioremediation is capable of: a) achieving cleanup levels; and b) sustaining treatment benefit for years. Each dot is representative of the sample depth within the well, and each dot also indicates RDX concentrations from discrete samples over time (Michalsen et al., 2021)



A cone of depression forms laterally away from a pumping well. The radius of influence is defined as that point where the cone of depression flattens to intersect the existing water table. At UMCD, the depth to water is about 20 meters, and the radius of influence envisioned for utilizing minimally- to non-contaminated water is about 15 meters (Gross, 2018)

Time-series plots present the progressive decrease in RDX concentrations (green diamonds) over time in the wells presented in Figure 8-5. The black dots represent changes in groundwater elevation over time, and the red arrows depict injection events (Michalsen et al., 2021)



estimate of capture of water with <2.1 – 10 ug/L RDX; water outside this radius of influence will have increasingly higher concentrations of explosives because it is farther from increased biological activity stimulated by the injectate. Figure 8-6 is a schematic diagram of the cone of depression that forms during pumping and defines the radius of influence of a pumping well.

Figure 8-7 presents time-series plots of the progressive decrease in RDX concentrations (green diamonds) over time in the wells presented in Figure 5. The black dots represent changes in groundwater elevation over time, and the red arrows depict biostimulation injection events (Michalsen
et al., 2021). Whereas biostimulation involved injection
of a mixture of fructose and water, the overall increase in groundwater elevations over time are a result of weather events.

The rough order-of-magnitude cost of three 100-foot wells, groundwater modeling, three episodes of nutrient injection, installation of pumps, laboratory testing and associated labor is $0.75 million dollars (United States dollars [USD]) (Gander, 2020). Periodic biostimulation into the three wells every five years would cost about $0.2 million dollars USD.

3.2. Solvents in Groundwater

Chlorinated solvents are a large family of organic solvents that contain chlorine in their molecular structure. Since World War II, they have been widely used in the United States and Europe for cleaning and degreasing, and

in adhesives, pharmaceuticals, pesticides, and textile processing. The most common forms include carbon tetrachloride, perchloroethylene, trichloroethylene and 1,1,1-trichloroethane.

3.2.1. Chlorinated Solvent Bioremediation at a Fuel Service Station, State of Washington, USA

Summary Statement: At a fuel service station, a suite of common chlorinated solvents has undergone successful bioremediation in groundwater by indigenous anaerobic bacteria. Concentrations below the drinking water clean-up level of 5 ug/L were achieved in 3-5 years in a portion of a larger 1,000 meter groundwater plume. This remediated water could be extracted at a rate of ~ 172 liters per minute (lpm)

(45 gallons per minute) in multiple wells and used for drinking water or industrial applications.

3.2.2. Background

The fuel service station, within the area known as Operable Unit 8 (OU 8), is located within the boundaries of Naval Base Kitsap - Bangor, in the town of Silverdale, Washington, United States (Figure 8-8).

In 1986, gasoline from a leaky underground storage tank and associated piping was discovered. An array of groundwater

Location of fuel service station within Operable Unit 8, Washington State, USA (SES, 2018)

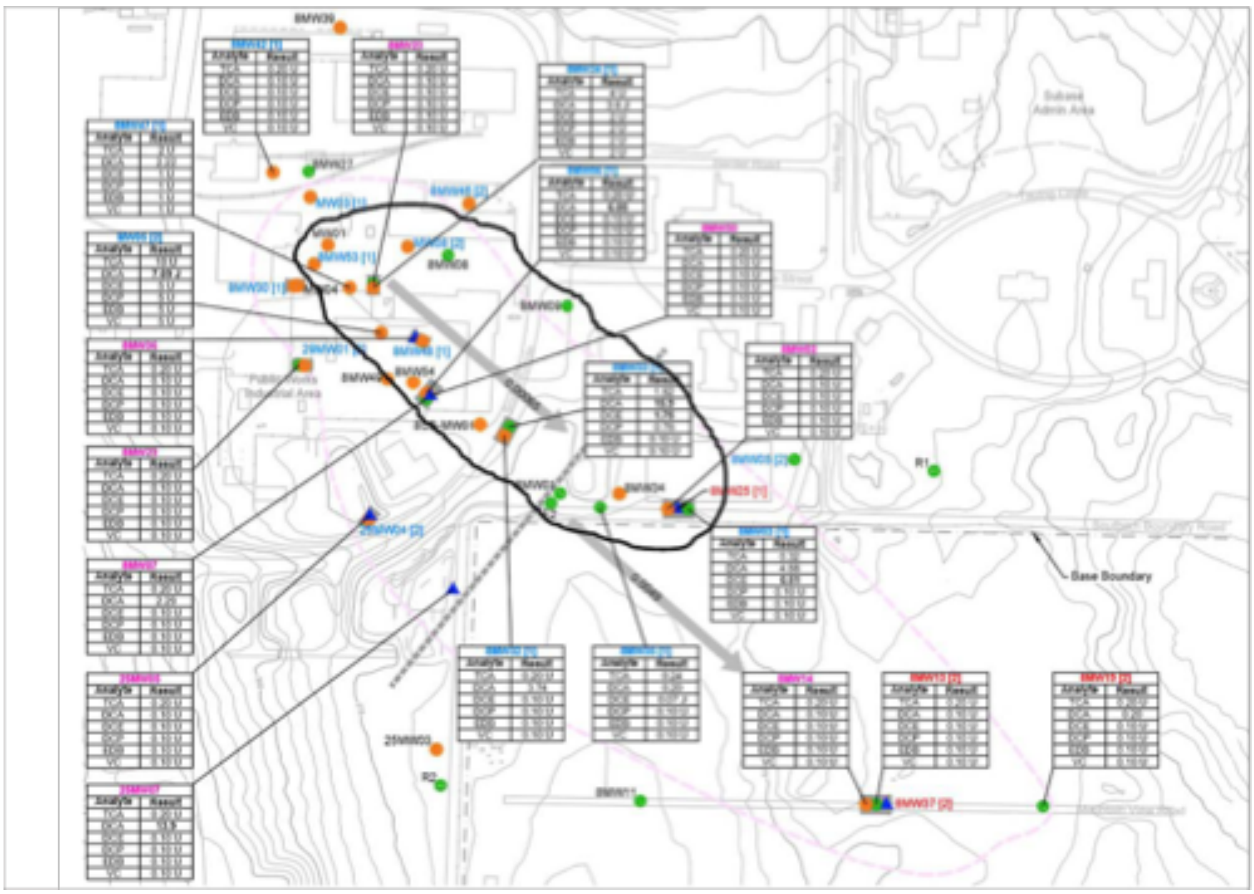
monitoring wells were installed to define the vertical and lateral extent of contamination, and a gasoline (free product) recovery system was installed. Free product refers to actual gasoline that floats on top of groundwater (also referred to as the saturated zone) because it is less dense than water. Between 1986 and 1998, approximately 22,800 liters (6,000 gallons) of free product was recovered. Residual free product and dissolved phase gasoline remains onsite and partially overlaps a small portion of the existing chlorinated solvent ("solvent") plume, which is the focus of this discussion.

Solvents were first identified in 1993. A groundwater pump and treat (P&T) system was installed in 1997 and operated until 2000. The primary objective of the P&T system was to reduce solvent concentrations and prevent further contaminant movement across the Naval base boundary, which was accomplished. A gasoline additive, 1,2-dichloroethane (DCA), is the most prevalent solvent in the plume; others include 1,1,1-trichloroethane (TCA) and 1,1-dichloroethane (DCE).

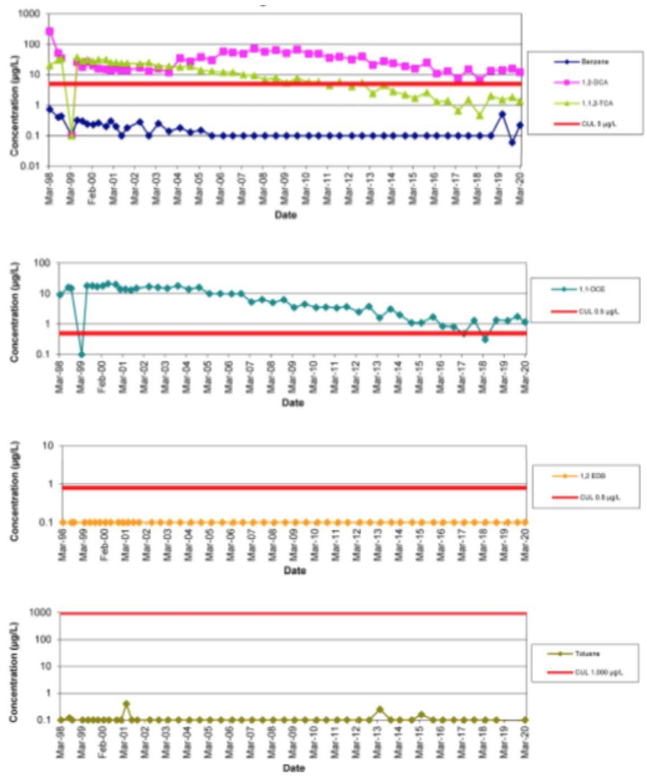
The current extent of the solvent plume is within the dark circular area in Figure 8-9, and the original extent of the solvent plume is shown by the faint pink circle.

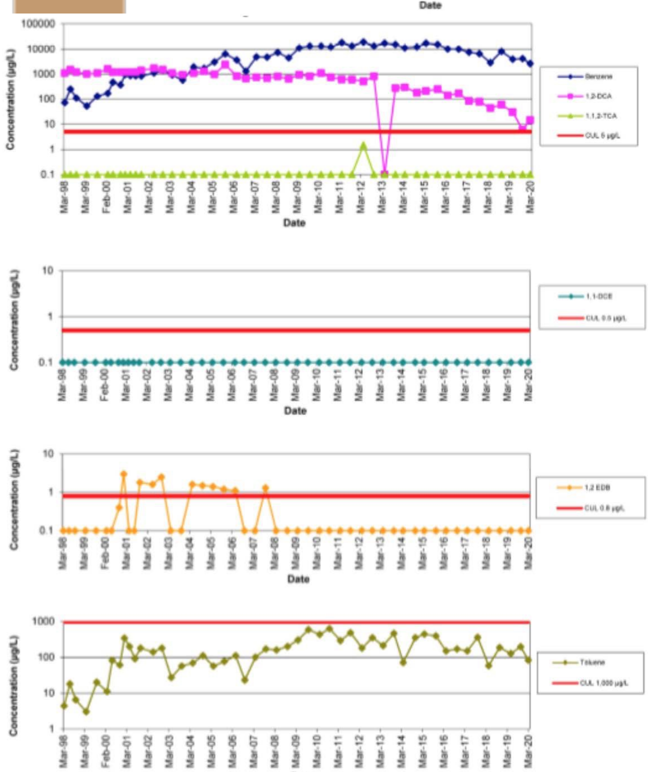
3.2.3. Bioremediation Implementation

Injections of emulsified vegetable oil (EVO) into four closely- spaced wells (not shown) immediately south of 8MW05 were completed in 2010, 2012, and 2017 (Figure 8-9) (SES, 2018). In addition to biostimulation, bioaugmentation was also



Map showing 2019 solvent concentrations in wells, the footprint of the solvent plume before bioremediation (faint pink circle), and the current solvent footprint (black circle) (SES, 2020)





Time-series plots of well 8MW06 before and after biostimulation. Injection of nutrients was conducted in 2010, 2012 and 2017 (SES, 2020)

Time-series plots of well 8MW33 before and after biostimulation. Injection of nutrients was conducted in 2010, 2012 and 2017 (SES, 2020)

conducted in 2010 and 2012 by introducing the anaerobic microbes Dehalococcoides spp. and Dehalobacter spp., which are known to be effective in dehalogenation (dechlorination) and to fully metabolize the solvents to harmless constituents.

Wells 8MW03, 8MW06 (Figure 8-10) and 8MW33 (Figure 8-11) are located hydraulically downgradient of the EVO injection wells, and demonstrate decreasing solvent concentrations that are primarily attributable to the biostimulation events.

Some degree of volatilization of the solvents has occurred since the solvent release in the 1980s, but the groundwater monitoring and attendant laboratory analysis conducted over time since initiating cleanup indicates that bioremediation has significantly accelerated the cleanup by destroying contaminant mass and overall lowering solvent concentrations. For example, in 8MW06 (Figure 8-10), which is about 30 meters downgradient and relatively close to the EVO injection wells, the pink DCA time-series plot shows a pronounced downward trend particularly from 2017 to 2020, likely due to the nutrient injection.

Based on aquifer pump tests conducted in the mid-1990s (FWENC, 1999), pumping rates were established where the groundwater levels remained relatively constant during the pump and treat operation to address the solvent contamination. Given the progress seen by bioremediation in reducing solvent concentrations to below drinking water cleanup levels in a portion of the plume, it is concluded that wells 8MW03 and 8MW33 would be viable candidates as pumping wells for either drinking water or industrial use. Further pumping tests in 2012 (SES, 2018) combined with earlier pump test data indicate that a pumping rate of ~ 172 liters per minute (lpm) (45 gallons per minute) would be effective within a radius

of influence of about 12 meters around each pumping well.

Based on the previous work, periodic biostimulation into the injection wells, or wells downgradient with residual contamination, will be effective every five years and would cost about $0.15 million dollars USD.

3.3. Nitrates in Groundwater

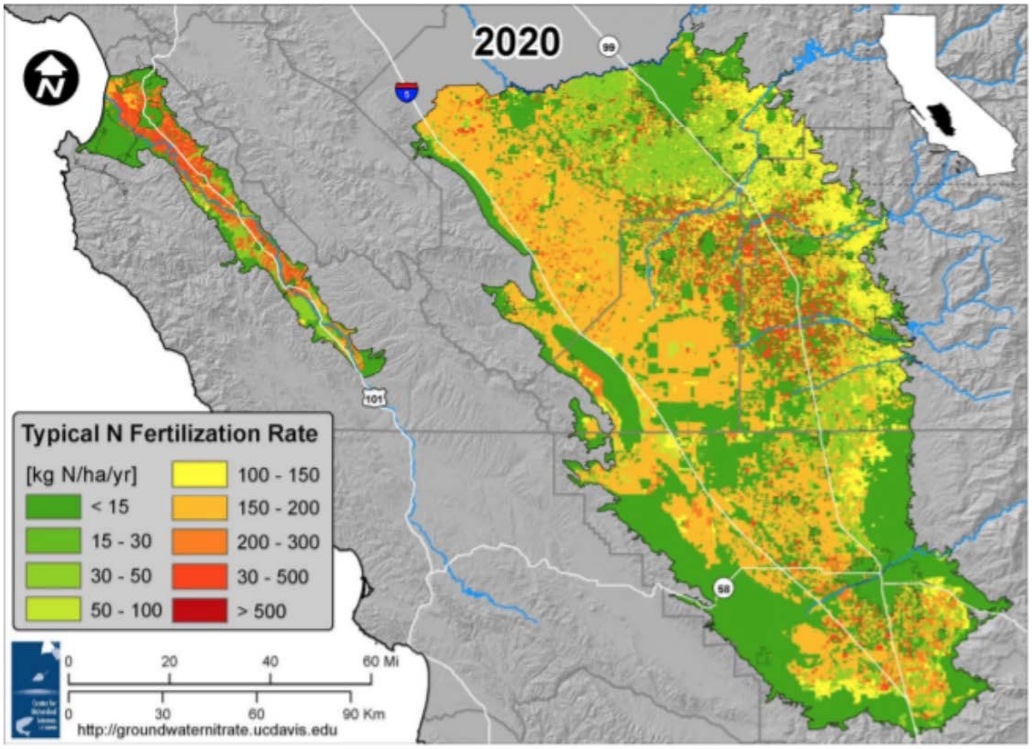
Nitrates are the most common groundwater pollutant worldwide (Ross, *et al*., 2010), and the principal sources are fertilizers, followed by human and animal waste. Nitrogen, phosphorus and potassium are the main constituents of fertilizers, and nitrogen from fertilizers is the main source of nitrate pollution (Vance *et al*., 2015). Nitrate is the dissolved form of dissolved nitrogen, which is the main source of nitrogen for plants.

3.3.1. Pump and Fertilize Remediation, Tulare Lake Basin and Salinas Valley, California, USA

Summary Statement: Two large agricultural basins in Central California have extensive nitrate groundwater contamination. Conventional treatment methods (pump and treat using reverse osmosis and ion exchange or biological treatment) are cost prohibitive. Therefore, given the ongoing agricultural activities, it is acknowledged that achieving drinking water nitrate levels (45 mg/L; for comparison, 50 mg/L in European Union) are unnecessary. The focus has become efficient use of the nitrate-bearing groundwater as the basis of application of fertilizer plus animal waste. Nitrate concentrations and nitrate mass are being lowered by pumping and using the existing nitrate-bearing groundwater, adding measured fertilizer and manure, and recirculating the optimally amended water.

3.3.2. Background

The Tulare Lake Basin (TLB) and Salinas Valley (SV) are located in California's Central Valley, USA (Figure 8-12). An ongoing thirty year



Estimated 2020 nitrogen fertilization rate, Tulare Lake Basin and Salinas Valley, California, USA. (UC Davis, 2017)

pilot program in agricultural sub-basins of the TLB and SV is assessing the effectiveness of conservatively applying nitrate-bearing groundwater as irrigation water, which is amended with annual additions of fertilizer and animal waste before actual application. The most intensive soil and manure applications occur in an area roughly 4,100 km^2 (Figure 8-12). Formerly, the volumes of water plus fertilizer and manure mixtures were inconsistently or haphazardly applied with minimal forethought, leading to nitrate overloading of soils and substantial leaching to groundwater.

Legislation has been passed that requires all dairy farmers to monitor wells via sampling and analytical testing to help control nitrate loading from manure (CWB, 2013). Funding is being allocated to improve the currently inadequate basin-wide data collection program by developing a nitrate mass balance tracking and reporting system by both cropland farmers and dairy farmers (CWB, 2013).

3.3.3. Pump and Fertilize Remediation

In order to reduce future groundwater contamination, improving nitrogen and water management on croplands is critical, given that widespread application of synthetic nitrogen fertilizers is a foundation for California's robust agricultural economy. The five counties that comprise the TLB and SV are among the most agriculturally productive in the United States

Nutrient, soil, and water management practices capable of reducing the impacts of croplands on groundwater quality include optimizing application rates and timing of water, fertilizer, and manure applications
to better align with crop need, adjusting

crop rotation strategies, improving storage and handling of fertilizers and manure, and tracking manure-nitrogen in order to reduce inorganic nitrogen applications as appropriate (UC Davis, 2012).

Data collection is in progress from the ongoing pilot test regarding the effectiveness of pump and fertilize remediation. Therefore, existing data from nitrate loading from fertilizer and manure, and associated wells, was used to model and predict the impact of existing and future nitrate applications (UC Davis, 2012).

25 (%)

20 15 10

5 0

Salinas Valley

Tulare Lake Basin

In order to reduce future groundwater contamination, improving nitrogen and water management

on croplands is critical

Percent Reduction in Nitrate Load to Groundwater

Percentage reductions in net revenue estimated from different levels of reduction in loading to groundwater, Tulare Lake Basin and Salinas Valley, California, USA (UC Davis, 2012)

Percent Reduction in Net Revenues

The model was designed to assess the economic impact
on farmers of policies that reduce nitrate loading from croplands. Because nitrate loading to groundwater in irrigated cropping systems is mainly a function of nutrient and water management, the model is based on economic and environmental consequences of changes in nutrient use and irrigation efficiency. It is assumed that better management costs more money.

The model also assumes that the mass of nitrate leaching to groundwater from irrigated croplands is a function of two pieces of information: 1) the amount of nitrogen applied, times 2) the quantity of water moving beyond the rootzone. The model allows producers to adopt changes to both or either factors.

An important aspect of the model is accounting for nitrate leaching potential, which is based on two metrics: nitrogen use efficiency (NUE), and nitrogen surplus. NUE is defined as the recovery of nitrogen by the crop and nitrogen surplus is the amount of nitrogen that is left behind in soil and becomes available to subsequent crops.

Modeling results indicates that small reductions in nitrate loading to groundwater from croplands can be made at relatively low costs, which is consistent with other studies (Vickner *et al*., 1998; Knapp *et al*., 2008) (Figure 8-13).

The cost of reducing nitrate loading to groundwater from irrigated crop farming appears to more significantly increase with reductions of nitrate volumes of more than 25 percent (Figure 8-13), depending on the true costs of implementing efficiency improving management practices involving: a) changes in nitrogen use efficiency, b) changes in irrigation efficiency, and c) changes in cropping patterns (UC Davis, 2012). Again, the model assumed that better management will be more expensive due to increased infrastructure cost, labor cost, and costs for information and education, but will reduce total nitrate loading from croplands.

The predicted costs to reduce nitrate loading in the TLB and SV can be illustrated if it is assumed an agricultural or dairy farm operation occupying 200 hectacres (500 acres) has a net annual revenue of $100,000 USD. A 15 percent decrease in loading to groundwater will cost $3,000 annually; a 25 percent decrease will cost $7,000; and a 50 percent decrease will cost $17,000 (UC Davis, 2012). The added costs are in large part due to the need to distribute the amended irrigation water more efficiently and involve operation and maintenance labor, additional well installation, and pumps and piping.

Pump and fertilize costs were compared to pump and treat (P & T) costs for a nitrate-contaminated plume area of similar size (500 acres) with similar well depth (75 meters), where biological treatment with P & T is employed (UC Davis, 2012a). A P & T system would require an initial capital outlay of $2,000,000 USD or more, and would require operation for several years (depending on factors such as number of extraction wells in operation and pumping rates) to remove contaminant mass to a level similar to that achieved by the

pump and fertilize method of 50 percent loading reduction (UC Davis, 2012a; Gander, 2020). The expected annual operation and maintenance (O & M) costs for the P & T system would be $50,000 - $100,000 USD (Gander, 2020). Although profoundly more expensive, drinking water levels would be achieved, or nearly so, within five to ten years in at least a portion of the plume. Thereafter, a combination of nitrate source control and a reduced pump and treatment scheme would have to be operated to maintain or further reduce the nitrate mass.

In summary, this brief cost comparison shows the two order- of-magnitude difference in these two technologies, and underscores the importance of defining groundwater use objectives and short- and long-term management goals.

04

Groundwater Pollution and Climate Change

The transport and chemical behavior of polluted surface water and groundwater has been well-studied. What has received much less attention is how climate change may alter how pollutants move in the subsurface; how they daylight

to surface water bodies or the ground surface; and how the deleterious effects of pollutants may be exacerbated in response to climate change.

The following are examples of how climate change can create pollution, or how climate change affects existing pollution:

-Rising sea levels from climate change coupled with the lowering of freshwater levels in drinking water wells results in seawater intrusion into coastal aquifers, rendering drinking water unsuitable for consumption due to high chloride concentrations. In some areas, climate change will cause drought, which will also increase the negative impact of seawater intrusion on coastal groundwater resources.

- Increased flooding from more intense storms increases the deposition of pollutants in floodplains and low-lying urban areas. This redistribution and concentration of pollutants in surface soils will increasingly leach into groundwater.
- Temperatures are rising due to climate change. Warmer temperatures increase the rate of evaporation of water into the atmosphere, in effect increasing the atmosphere’s capacity to “hold” water. Increased evaporation is causing drought in some areas and dropping water levels, but also causing increased precipitation in other areas.
- Climate change is expected to affect recharge, but the effects may not necessarily be negative or decrease in all regions worldwide (Gurdak *et al*., 2010). Recharge is projected to increase in northern latitudes and decrease

strongly (e.g., 30-70%) in some semi-arid zones (Doll *et al*., 2008); this effect may be occurring now in South Africa and neighboring countries.

- In some basins, heavy rainstorms induced by climate change have led to increased runoff and decreased aquifer recharge. However, caution must be used in applying sweeping generalizations in all climatic environments about less recharge year-over-year due to more extreme storm events due to climate change. This effect appears real in many surface water/groundwater basins but requires more region-specific study.

  Studies by Cuthbert *et al*. (2019) and Owor *et al*. (2009) present data that some aquifers in arid and semi-arid environments significantly benefit from recharge during extreme storm events, perhaps more so than all day rainfall episodes. Here, storm-related runoff is not causing as much of a decrease in

groundwater levels as may have been originally hypothesized. Thus, aquifers can show significant resiliency in capturing recharge during extreme storm events. Further, multiple studies indicate that climate change is causing fewer, but more extreme, heavy rain events (Taylor, 2020).

Regional precipitation data and water level data in wells, along with the attendant hydrogeologic setting, must be considered when drawing conclusions about the effects of climate change on recharge.

• In some geologic and climatic settings, higher groundwater levels from increased recharge from more intense heavy rainfall events induced by climate change is also associated with increased diarrheal diseases from bacteria in shallow groundwater-fed water supplies (e.g., wells 5-10 meters deep) and outbreaks of diarrheal diseases in both low- and high-income countries (e.g., Taylor *et al*., 2009).

• Sparse data suggests that overlying soils or bedrock filter some microplastics before concentrating in underlying groundwater (WHO, 2019). Less frequent but more intense monsoonal rains induced by climate change has been shown to be a major contributor to aquifer recharge events in some semi-arid to arid environment aquifers. Therefore, climate change-induced monsoonal rains can not only increase recharge but will also potentially increase the leaching of microplastics (e.g., from pesticides) to aquifers.

• Although poorly documented, the land application of biosolids from waste water treatment plants (WWTPs) serve as potential leachate sources of PFAS and microplastics. Climate change-induced monsoonal rains may increase leaching.

• Decreased recharge creates a lowering of water levels in aquifers. In arsenic-bearing formations, when the saturated zone drops, the oxidation state of arsenic changes (As[III] to As[V]) due to exposure to more oxygen. In formations with the mineral arsenical pyrite, as in Bangladesh,

arsenic is released as pyrite oxidizes and dissolved arsenic concentrations are increased, creating a more severe pollution problem in groundwater.

• Certain types of groundwater remediation systems are designed to treat groundwater that is collecting contaminants that have leached to certain depths in the subsurface. When water levels drop substantially (3-5 meters or more) due to climate change, these systems may not have been designed to continue to function at lower water tables and added costs will be incurred for redesign.

05

Concluding Remarks & Policy Recommendations

Monitoring, sustaining water supply volumes, and sustaining or improving various levels of water quality, are fundamental challenges for those charged with managing water security within a limited budget. Policymakers and many water practitioners only have a vague notion of what constitutes drinking water level quality water, or how concentrations of certain naturally-occurring constituents or anthropogenic constituents can be managed or remediated to make the water usable for many agricultural or industrial applications.

This study is intended to raise awareness and educate policymakers and practitioners to ensure they have the technical underpinning to make informed decisions when managing water

security with regard to varying levels of water quality. The following are some high-level policy issues and recommendations to address them:

Issue: The transport and chemical behavior of polluted surface water and groundwater has been well-studied. What has received much less attention is how climate change may alter the way pollutants move in the subsurface; how they daylight to surface water bodies or the ground surface; and how the deleterious effects of pollutants may be exacerbated in response to climate change, as discussed in this study.

receive influent that contains PFAS from many sources.
Even if ongoing sampling and laboratory analysis is not feasible due to a lack of funding from the initial users of PFAS-bearing products, some level of baseline sampling/laboratory analysis can verify the presence of PFAS from effluent from WWTPs, and this will guide the control of effluent or restrict or prohibit land application of biosolids generated by the WWTPs.

Issue: The production of plastics is increasing (Lacy *et al*., 2019). Plastics are produced by the processing of fossil fuels, which is known to contribute to climate change. About four to eight percent of annual global oil consumption is associated with plastics, according to the World Economic Forum (Lacy *et al*., 2019). If this reliance on plastics persists, plastics will account for 20 percent of oil consumption by 2059.

Policy Recommendation: This trend must be reversed by the passage of statutory requirements in individual

Countries should move toward a policy of full cost accounting to ensure the market price of plastics reflects the cost of production as well as life cycle management

countries that mandate gradual reduction of plastics production. Countries should move toward a policy of full cost accounting to ensure the market price of plastics reflects the cost of production as well as life cycle management (clean up, recycling, reuse, etc.). This recommendation is akin to the Extended Producer Responsibility (EPR) approach, under which producers are given a significant responsibility – financial and/ or physical – for the treatment or disposal of post-consumer products.

Policy Recommendation: Policy makers need to be aware of how climate influences or exacerbates or creates pollution (see Section 5), particularly with regard to conditions in their own jurisdictions.

Issue: Although data on this subject are incomplete, PFAS (a carcinogen) is widespread in effluent from industrial processes that is discharged to either sewer systems or the natural environment. WWTPs are not analyzing for PFAS in their influent and discharge water is likewise not being analyzed, resulting in discharged PFAS leaching into underlying aquifers. Although banned in some parts of Europe, WWTPs continue to generate vast amounts of biosolids that are spread over agricultural areas or undeveloped areas. These biosolids contain PFAS and there is subsequent crop uptake of PFAS, which is poorly understood, or leaching of PFAS into underlying groundwater.

Policy Recommendation: Industrial facilities should be allocating funds to quantify, via laboratory analysis, PFAS compounds before wastewater effluent is released from their facilities. Although not a source of PFAS, WWTPs inevitably

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