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A composite plume approach

Scientists collected site data from multiple contaminated sites and then pursued a composite plume data analysis approach. This approach would allow them to use data from incompletely defined groundwater plumes.

Researchers have tried similar approaches, using data from California, Texas and Florida (see Rice and others, 1995, Happel and others, 1998, Mace and others, 1997, Mace and Choi, 1998, and Reid and others, 1999, in Lundegard and Johnson, 2004). Large amounts of data were collected. "...each site data set was first reduced to a contaminant-specific plume length through fitting to an analytical model or through hand contouring, and then a statistical analysis of all plume lengths was performed." Limitations of this analysis type include "applicability of the fitting model to the specific sites, the spatial arrangement of wells and assumed flow directions, the concentration criterion used and the discretion of the investigator in deciding if each site is sufficiently well characterized" (Lundegard and Johnson, 2004).

Description of the approach

Lundegard and Johnson's (2004) approach uses "contaminant concentration data from multiple plume source systems within a hydrogeologically similar area. In the context of this work, source zones are those regions of the subsurface that contain NAPL in contact with groundwater. Soil moisture moving through a contaminated vadose zone down to groundwater will also be a source of groundwater contamination. Plumes derived from such vadose zone sources may have different characteristics than those derived from NAPL within the saturated zone."

The researchers' approach includes seven steps:

- "determine the approximate spatial extent of the

source zone at each site through the use of soil and groundwater concentration data, NAPL occurrences in monitoring wells and observations of soil borings

- determine groundwater flow direction and its variation
- identify those monitoring wells at each site that are most likely to lie within the dissolved plume flowpath downgradient of the source zone
- measure the distance along the flowpath between each downgradient well and the downgradient edge of the closest known upgradient source area
- compile contaminant concentration data for selected wells
- present the composite data set as a graph of concentration vs. downgradient distance from the source zones
 - analyze the graph" (Lundegard and Johnson, 2004)

Researchers did not analyze wells that they considered not to be flowing through any source areas.

Application to the Guadalupe Oil Field

Scientists tested their method at Guadalupe Oil Field. The field is characterized by

- about 900 groundwater wells, 3,000 soil borings and 400 cone penetrometer pushes used to identify source areas
- approximately 90 LNAPL source areas
 - source areas ranged in extent from a few thousand square feet to nearly 55 acres
 - source areas consisted of light nonaqueous petroleum liquid (LNAPL), primarily of C_{10} to C_{28} hydrocarbons and low concentrations of typical regulated compounds (benzene, polynuclear aromatics)
 - dissolved TPH (total petroleum hydrocarbon) in the 4 to 30 mg TPH/l range

- dissolved TPH that are anticipated to decrease with distance due to natural attenuation processes

Scientists were interested in "determining whether dissolved TPH plume behavior is similar for different source areas at this site," and if such information could be used for "developing groundwater monitoring plans" and "assessing potential impacts to water bodies or prioritizing source areas for remediation" (Lundegard and Johnson, 2004).

Procedures and considerations

To find downgradient wells, researchers used a software program that created a plan view site map. This map contained source zones, monitoring wells and groundwater equipotential lines. Researchers monitored groundwater data on a quarterly basis from October 1995 to 2001. Some results:

- each annual data set indicated a general trend of decreasing dissolved TPH concentrations with increasing distance from source zones
- mean TPH concentration declined from about 10 to 1 mg over distances of 0 to 500 feet
- beyond 500 feet, TPH concentration declines were smaller
- the groundwater flow field was fairly simple and uniform

Researchers also identified limitations of their approach:

- existence of fugitive (unknown) sources
- uncertainty considering well location, i.e., is a well actually downgradient of a known source?

Another essential consideration is the role that water plays, and in particular, recharge water and consequent water level changes. "Recharge of water through the vadose zone and to the top of an aquifer can produce either real or apparent concentration reductions with downgradient distance" (Lundegard and Johnson, 2004).

Real concentration reductions can result

- if hydrocarbon-free recharge water mixes with (or dilutes) a dissolved hydrocarbon plume
- if electron acceptors exist in the recharge water and facilitate hydrocarbon biodegradation

In addition, electron acceptors can be transported down to the plume through the vadose zone, and "their dispersion within groundwater can lead to top-down degradation of TPH in the underlying groundwater plume, resulting in what could appear with vertical groundwater sampling to be plume displacement."

If recharge occurs and mixing is limited, water accumulates on top of the downgradient-moving plume. "This could result in what appears to be a downward displacement of the dissolved hydrocarbon plume, even to the extent that all or part of the plume passes beneath a monitoring well screened across the upper part of the aquifer" (Lundegard and Johnson, 2004).

Water level changes in groundwater can "spread, or smear the mobile separate-phase contamination up and down the soil column through the saturated zone and capillary fringe and, therefore, disrupt the vertical profile of TPH in groundwater flowing through the source zone." The resulting dissolved TPH profile is a function of the relative position of the screen interval and the distribution of TPH. The groundwater plume will tend to be thicker where there has been greater smearing of diluent in source zones. "This will tend to result in higher measured TPH concentrations at a given distance downgradient. This effect may be expressed in groundwater data collected downgradient of the larger source areas" (Lundegard and Johnson, 2004).

Conclusions

Lundegard and Johnson (2004) state that the composite plume concept "is an alternative to the use of single site metric (i.e., plume length) when performing collective

data set analyses." This approach

- uses data from groundwater plumes "that are both densely sampled and sparsely sampled by monitoring wells"
- gives "results that are not influenced by the selection of fitting models and are less dependent on subjective decisions concerning data sufficiency"
- "is highly data-driven, [and] anomalies and potentially biased data are generally evident"
- "may be especially suited to the analysis of large sites or regions with multiple source areas with similar hydrogeological settings"

A limitation of this approach is data; "To be useful, a minimum of tens of monitoring well locations are probably necessary." Researchers also note that "data from sites with drastically dissimilar conditions should be analyzed separately. A cautious approach would be to make separate plots for groups of sites with reasonably similar conditions and then to compare those plots before deciding which groups should be merged" (Lundegard and Johnson, 2004).

Reference

Lundegard, P.D. and P.C. Johnson, "A Composite Plume Approach for the Analysis of Dissolved Contaminants in Ground Water vs. Distance from Source Areas," *Ground Water Monitoring & Remediation*, Vol. 24, No. 3, 2004; <http://www.ngwa.org>.

Summarized with permission from the National Ground Water Association, <http://www.ngwa.org>.

UTTU thanks Dr. Lundegard, pdlundeg@unocal.com, for his help on this article.



Earthworm bioassay for assessing soil ecotoxicity

Y.J. An (2005) used a representative soil invertebrate—the earthworm—to assess soil ecotoxicity of MTBE. The goal of this research was twofold:

- to "characterize the acute ecotoxicity of MTBE in two earthworm species, *Perionyx excavatus* and *Eisenia andrei*, using filter paper, OECD (Organization for Economic Cooperation and Development) artificial soil, and natural soil tests
- to test a modified OECD Guideline 207 for analyzing MTBE

Dr. An determined the median lethal concentration (LC50), and examined "abnormal morphology of earthworms exposed to MTBE."

Soils

The natural soil selected for testing, a sandy loam with pH 5.2, 0.3 percent organic matter, consisted of the following components:

- sand, 59 percent
- silt, 20 percent
- clay, 21 percent

The artificial soil (pH 6.0 ±0.5, 95 percent peat moss as organic matter), in contrast, contained

- sand, 69.5 percent
- kaolin clay, 20 percent
- sphagnum peat moss, 10 percent
- CaCO₃, 0.5 percent

Earthworm characteristics

The two species of earthworms used for this analysis are common vermiculture earthworms found in Korean breeding grounds. The culture *P. excavatus* fed daily

on sludge cake while *E. andrei* fed on cow excrement. The weight range of an adult earthworm, selected for testing, was 400 to 600 mg. Three hours prior to use, "workers separated earthworms from the cultures and rinsed them with distilled water, and kept them on damp filter paper at 25° C in darkness to remove gut contents" (An, 2005).

Testing procedure

Preliminary tests conducted with earthworms involved putting them in a capped test unit to prevent potential MTBE volatilization out of the unit. Scientists added 10 grams of dry soil (OECD artificial soil or field soil) to each test unit, which was then spiked with specific MTBE concentrations.

"Concentrations prepared were 0.0, 0.25, 0.5, 1, 1.5, 2 and 4 percent MTBE solution (corresponding to 0, 0.04, 0.09, 0.18, 0.26, 0.35 and 0.7 mg/cm²). Researchers used a micropipette to add one milligram of solution to each test unit. One milligram of distilled water was pipetted into the control vial. Each test unit contained an earthworm, and the test was done with 10 replicates. Our preliminary test showed that earthworms could survive up to 4 days in the closed test unit" (An, 2005). Following incubation periods of 24, 48 and 72 hours, scientists examined earthworms for mortality and abnormality. "Earthworms were presumed dead when no response to light or/and the mechanical stimulus by needle was observed" (An, 2005).

Test results

Results from the paper contact method indicated that MTBE was toxic to both *P. excavatus* and *E. andrei*. Mortality increased with increasing MTBE concentrations. "The LC50 values for *P. excavatus* exposed to MTBE for 24, 48 and 72 hours were 0.418, 0.240 and 0.079 mg MTBE/cm², respectively, and the LC50 values for *E. andrei* were 0.471, 0.354 and

0.282 mg MTBE/cm², respectively. This indicates that *P. excavatus* is more sensitive to MTBE than *E. andrei*...and would be a better indicator species for MTBE pollution in soil" (An, 2005).

Dr. An also found that when exposed to MTBE, earthworms became "immediately restless, and response to light became slow... General symptoms [of morphological abnormalities] included abnormal swelling, soiling, curling and fragmentation. Bleeding and mucous secretion were observed in all treated earthworms compared to control earthworms" (An, 2005).

Conclusions

From this study, An (2005) concluded

- earthworm survival was adversely affected by MTBE
- MTBE is more toxic in OECD artificial soil than in field soil because the soil's physicochemical properties (organic matter content, soil pH) influence contaminant bioavailability
- earthworms stayed on the top layer of the field soils and burrowed into the OECD soils, and this behavior may have increased overall routes of exposure in the OECD soils
- *P. excavatus* is a better indicator species for MTBE pollution in soil than *E. andrei*
- use of the earthworm bioassay "can be a good protocol to test the ecotoxicity of VOCs such as MTBE"

Reference

An, Y.J., "Assessing Soil Ecotoxicity of Methyl tert-Butyl Ether Using Earthworm Bioassay: Closed Soil Microcosm Test for Volatile Organic Compounds,"

Environmental Pollution, Vol. 134, No. 2, 2005; <http://www.elsevier.com/locate/envpol>

UTTU thanks Dr. Youn-Joo An, anyoo@konkuk.ac.kr, for sending us this article.



MTBE toxicity testing for plants

MTBE is classified as a potential human carcinogen, but according to animal exposure studies of algae, bacteria, fish, amphibians and invertebrates, MTBE is classified as a carcinogen. Dr. An and others (2002) undertook a study to gather toxicological information on plants exposed to MTBE. The plants considered were

- wild oats, *Avena sativa*
- sweet corn, *Zea mays*
- wheat, *Triticum*
- lettuce, *Lactuca sativa*

The toxic levels measured were

- LC50, the median lethal concentration
- EC50, the median effective concentration
- NOAEC, the no-observed-adverse-effect concentration
- LOAEC, lowest-observed-adverse-effect concentration

Soil microcosm setup and protocol

"Acute toxicity tests were conducted in a closed canning jar test unit at an ambient mean laboratory temperature of 24±1° C. The light used was continuous from a blue plan light lamp with a GE 65W reflector bulb... The lamp was used to accelerate seedling growth during the 120-hour incubation period. Wide-mouth glass canning jars with lids...were used as the test containers."

Experiment criteria are as follows:

- each MTBE concentration was prepared with three replicates
- soil used was a sandy loam with soil moisture 20 percent by weight and soil pH of 5.0 ± 0.36
- seeds were planted just below the surface
- each test unit had 0.1 kg (dry weight) of soil and 0.02 liter of test solution with a specific MTBE concentration
- MTBE test solutions were evenly distributed drop-wise to the soil top
- lids were tightened to prevent volatilization
- jars were placed in an air exhaust hood, with temperature recorded daily
- after 120 hours, plants were separated from the soil
- seeds were checked for germination; growth was measured by shoot and root length
- MTBE concentrations tested were with 0, 193, 321, 536, 893 and 1,488 mg/kg soil
- MTBE concentrations used with lettuce were 0, 4, 7, 15, 30, 60 and 119 mg/kg
- the control was distilled water without MTBE

Dr. An and others (2002) describe in their paper the U.S. EPA statistical computer program and other data manipulation techniques used for this analysis.

Results and conclusions

Dr. An and others (2002) report that

- the effect of MTBE on germination was species specific
- lettuce was the most sensitive, followed by wild oats, wheat and sweet corn

- at the low concentration of 193 mg MTBE/kg soil (dry weight), lettuce germination was reduced to approximately 20 percent of that in the control treatment
- effect of MTBE on germination in all species (lettuce, wild oats, wheat and sweet corn) was noted and was concentration dependent
- wheat and corn were affected by only the highest exposure concentrations
- plant growth was expected to be a more sensitive endpoint than seed germination; seedling growth for all species was affected by MTBE
- MTBE toxicity was "in general agreement with that reported in previous studies involving other contaminants in terms of the relative order of the sensitivity rankings"
- typical MTBE concentrations detected in groundwater are generally low (e.g., $< 20 \mu\text{g/l}$), and..."may be too low to have an adverse influence on the plants when utilized for agricultural purposes over a short time"
- "lower levels of MTBE may show chronic adverse effects after long-term exposure"

Reference

An, Y.J., Kampbell, D.H. and M.E. McGill, "Toxicity of Methyl tert-Butyl Ether to Plants (*avena sativa*, *sea mays*, *triticum aestivum* and *lactuca sativa*)," *Environmental Toxicology and Chemistry*, Vol. 21, No. 8, 2002; <http://entc.allenpress.com/entconline/?request=get-current-issue>.

UTTU thanks Dr. Youn-Joo An, anyoo@konkuk.ac.kr, for assistance with this article.



Modeling: BTEX vs. benzene

Suarez and Rifai (2004), wanting to simulate the fate and transport of fuel hydrocarbons in groundwater, used Bioplume III to model natural attenuation of BTEX and benzene. Ultimately they wanted to estimate cleanup times and evaluate model confidence level.

Modeling limitations

Limitations of modeling BTEX include the following:

- modeling cannot account for selective or competitive biodegradation of hydrocarbons
- models that use instantaneous reaction are "limited to when the microbial biodegradation kinetics are fast relative to the rate of groundwater flow that mixes electron acceptors with dissolved contaminants"
- because compounds are not modeled separately, there is no accountability for the various compounds' differences in mobility and sorption tendency

Limitations of first-order kinetic modeling for individual components include these:

- site-specific information, such as availability of electron acceptors, may not be accounted for
- first-order decay rates, determined in the laboratory, do not readily transfer to field situations

Cleanup goals identified

For the benzene cleanup goal, scientists used the maximum contaminant level (MCL) in drinking water, 0.005 mg/l. The cleanup goal for BTEX was 5 mg/l, which included the following MCLs:

- toluene, 1 mg/l
- ethylbenzene, 0.7 mg/l
- xylene, 10 mg/l

Site description and contaminant history

The site modeled, located along a coastal area of the United States, is an industrial facility that was active from the 1950s until 1985. Geology consists of two units:

- an upper alluvial deposit zone of sands, silty sand, clay and gravel
- a limestone of Tertiary age

Other site characteristics:

- underlying the limestone is a silty clay that appears to limit contamination
- the water table is 1.0 to 5.5 m below ground surface, and flow is southward
- hydraulic conductivities of alluvial deposits range from 3.3×10^{-7} to 2.3×10^{-3} m/sec
- groundwater flow has no significant seasonal variations
- horizontal gradients vary between 0.0008 and 0.002 m/m for the dry and rainy seasons respectively
- using average hydraulic conductivity (with a gradient of 0.002 m/m) of 1.9×10^{-5} , and assumed effective porosity of 0.2, the average seepage velocity is about 1.0×10^{-7} m/sec

In terms of contaminant history:

- contamination occurred over an area of about 60 acres
- off-site and on-site sources contributed to contamination
- the first contaminant incident was a ruptured pipe in 1977 that resulted in a 300,000-gallon spill of BTX, of which 70 percent was benzene; 270,000 gallons were recovered
- between 1965 and 1975, cloudy, white water was discharging into a nearby creek

- between 1989 and 1995, the creek sustained several oil spills
- wells in the northeastern part of the facility have LNAPLs, light nonaqueous phase liquids, with plume thicknesses varying from 0.02 to 0.7 m and consisting mostly of xylene
- another contributing contaminant is a NAPL plume adjacent to the facility with a thickness up to 1.5 m

Present characterizations of the two plumes follows:

- dissolved organic contamination has been monitored since 1979
 - benzene concentrations ranged from 1,780 mg/l to < 1 mg/l across the site
 - BTEX concentration was 1,893 mg/l, reduced to 570 mg/l in 2000
- plume lengths declined from 550 to 305 meters between 1979 and 1996, but have not changed substantially since then
- benzene and BTEX plume extents are similar, suggesting parallel behavior of benzene and BTEX compounds

Natural attenuation monitoring

In 1999 and 2000 researchers took several geochemical measurements:

- dissolved oxygen
- temperature
- conductivity
- redox potential
- pH
- alkalinity
- ferrous iron
- nitrate
- sulfate

- chloride
- methane

The patterns identified were similar to those found at other natural attenuation sites. "That is, highly contaminated areas had depleted electron acceptors (dissolved oxygen and nitrate) and a high concentration of byproducts (ferrous iron and methane). Sulfate concentrations, however, did not follow the expected trend..." (Suarez and Rifai, 2004).

Modeling

For input parameters for Bioplume III, researchers used site-specific data, and when this was not available, they made reasonable estimates. Researchers monitored the contaminated zone as "a shallow, continuous unconfined aquifer comprised of silty clay and sandy silt across the site. The modeled aquifer had a variable thickness ranging from 2.1 to 5.5 m" (Suarez and Rifai, 2004).

In terms of bodies of water that influence site conditions:

- the ocean is nearby
- two canals transport sea water and have a significant impact on groundwater levels
- a creek exists on the eastern side of the site

Tides and seasonal water fluctuations also affect groundwater levels.

For site hydrology simulation, researchers introduced pumping wells and used measured hydraulic conductivity values to develop a hydraulic conductivity distribution across the site. Flow conditions were calibrated to 1996 data.

BTEX and benzene models

Assumptions and/or criteria for the BTEX plume model included

- instantaneous reaction kinetics was used for BTEX biodegradation

- base year was 1978
- an initial dissolved plume was assumed
- contaminant sources were represented by 11 injection wells
- source concentrations and rates were assumed variable
- initial electron acceptor concentrations were estimated from field data

Assumptions and/or criteria for the benzene plume included

- use of a first-order reaction
- use of seven wells to model sources

Other issues addressed included

- calibration
- sensitivity analysis
- predictions

Calibration. Researchers calibrated the Bioplume III model and determined groundwater level and extent of the BTEX and benzene plumes. Details are given in the text.

Sensitivity analysis. Because aquifer characteristics and contaminant concentrations are spatially variable, and sufficient data is often difficult and costly to obtain, "much uncertainty is associated with groundwater contamination depiction." To assess these uncertainties, researchers commonly rely on stochastic modeling or sensitivity analysis. Researchers found that biodegradation rate had the most significant effect on plume length for both benzene and BTEX models.

Predictions. Modeling two different scenarios, researchers

- had injection rates and concentrations decreasing with time, using a line of best fit of source data between 1978 and 1999

- assumed 20 percent annual reduction in LNAPL volume

"For each scenario, six criteria were evaluated: maximum concentration, average concentration across the site, distance to downgradient edge from well D-11, total dissolved mass, plume length, and time to reach cleanup goal. This was defined as the time required to achieve concentrations lower than 5 mg/l in 95 percent of the cells for the BTEX plume and 0.005 mg/l for the benzene plume" (Suarez and Rifai, 2004).

Conclusions

Researchers concluded that

- "natural attenuation models can be used to simulate BTEX plumes using instantaneous biodegradation, and one-component plumes using first-order kinetics"
- with use of the instantaneous kinetic model, input parameters most sensitive are source definition, hydraulic conductivity and assimilative capacity
- with use of the first-order kinetic simulation, the model is most sensitive to changes in biodegradation rate and source definition
- "simulated plumes using a first-order model for the site were longer than those obtained using an instantaneous reaction model"
- "biodegradation is a key parameter for both scenarios, whether for instantaneous or first-order kinetics"
- for first-order kinetics, "the Bioplume III model was most sensitive to hydraulic conductivity when looking at plume length"
- according to model predictions, "if no source is removed, cleanup goals will be achieved by the years 2206 and 2106 for the BTEX and benzene plumes, respectively"
- "removing the LNAPL at an annual rate of 20

percent will shorten the remediation time for the BTEX plume by 50 years, but it will not have an impact on the benzene remediation time"

- "cleanup times may differ because of maximum concentrations, cleanup goals and calculated decay rate"
- "natural attenuation cleanup times using BTEX and assimilative capacity are 47 percent to 90 percent higher than those for benzene alone"
- "...the uncertainty analysis for model predictions showed similar plume length and distances traveled by the leading edge for both the benzene and BTEX plumes"

Reference

Suarez, M.P. and H.S. Rifai, "Modeling Natural Attenuation of Total BTEX and Benzene Plumes with Different Kinetics," *Ground Water Monitoring & Review*, Summer 2004; <http://www.ngwa.org>.

Summarized with permission from the National Ground Water Association.



Hydrocarbon biosurfactants

Biosurfactants are surface-active agents that are produced by living organisms, normally as part of their digestive processes. Surfactants alter conditions at interfaces; generally, they lower surface and interfacial tensions. A wide variety of microorganisms with different chemical structures and properties produce surfactants. "Moreover, as their chemical structures and surface properties are so different, each emulsifier probably provides advantages in a particular ecological niche... [some] bioemulsifiers enhance the growth of bacteria on hydrophobic water-insoluble substrates by increasing their bioavailability, presumably by increasing their

surface area, desorbing them from surfaces and increasing their apparent solubility. Bioemulsifiers also play an important role in regulating the attachment-detachment of microorganisms to and from surfaces" (Ron and Rosenberg, 2001).

"Surfactants are amphiphilic compounds that reduce the free energy of the system by replacing the bulk molecules of higher energy at an interface. They are used in [many applications including] soil washing or flushing due to their [potential] ability to mobilize contaminants. They contain a hydrophobic portion with little affinity for bulk medium (and concentrate at the surface) and a hydrophilic group that is attracted to the bulk medium (oriented toward the solution)" (Mulligan, 2005).

Advantages to using biosurfactants for remedial work include

- biodegradability
- low toxicity
- effectiveness at enhancing "biodegradation and solubilization of low-solubility compounds."

Surface tension

A surfactant's effectiveness is related to its ability to lower surface tension. Surface tension "is a measure of the surface free energy per unit area required to bring a molecule from the bulk phase to the surface."

Surfactants are selected based on their

- ability to lower surface tensions
- ability to increase solubility
- detergency powers
- wetting ability and foaming capacity

Desirable characteristics of surfactants include

- solubility enhancement

- surface tension reduction
- low critical micelle concentrations

Biosurfactants

Biosurfactants can be biologically produced by yeast or bacteria and substrates such as sugars, oils, alkanes and wastes. They have the following characteristics:

- they can be derived from a wide variety of microorganisms
- the CMCs generally range from 1 to 200 mg/l
- molecular mass ranges from 500 to 1,500 Da
- their advantages over synthetic surfactants include high specificity, biodegradability and biocompatibility
- pH, salt concentrations and temperatures affect properties
- solubility and surface-active properties are dependent on orientation of residues
- most are aerobic; some are anaerobic
- most are produced from hydrocarbon substrates, but some can be produced from carbohydrates

Reviewer's comment: biosurfactants have two major potential disadvantages:

- *if biosurfactants are created externally and added to a soil or groundwater system, it may be difficult or impossible to uniformly distribute the surfactant in such a way that it performs the desired task*
- *biosurfactants are often more biodegradable than the substance which they are intended to help make bioavailable; hence, the biosurfactant itself may become a more favorable food source than the contaminant to be degraded*

One group of biosurfactants, rhamnolipids, made from *Pseudomonas aeruginosa*, produces biosurfactants whose composition and yields depend on fermentor

design, pH, nutrient composition, substrate and temperature used.

Biosurfactants used in enhanced oil recovery and transportation of crude oils have been effective in

- reducing oil and water interfacial tension in-situ
- reducing oil viscosity
- removing water from the emulsions prior to processing

Rhamnolipid effect on petroleum hydrocarbons

The effect of rhamnolipids on organic contaminant biodegradation is mixed. Results from one study led scientists to propose two mechanisms for enhanced biodegradation: "...enhanced solubility of the substrate for the microbial cells, and interaction with the cell surface, which increases the hydrophobicity of the surface allowing hydrophobic substrates to associate more easily."

Another study with hexadecane degradation indicated that the "biosurfactant could enhance biodegradation if the process is rate-limited. For example, in the case of small soil pore sizes (6 nm), the hexadecane is entrapped and of limited availability. The rhamnolipid stimulates release of entrapped substrates (if mixing conditions are low such as in a column) and enhances uptake by cells (if the substrate is available). This could then become important in the stimulation of bacterial degradation under in situ conditions" (Mulligan, 2005).

Yet another study of bioremediation of n-alkanes in petroleum sludge using a bacterial consortium, nutrients and rhamnolipids indicated lower biodegradation rates as chain length increased.

"...addition of rhamnolipid produced by *Pseudomonas* sp. DS10-129 along with poultry litter and coir pith enhanced ex-situ bioremediation of a gasoline-contaminated soil. Research with another strain,

Pseudomonas marginalis, also indicated that the produced biosurfactants solubilized polycyclic aromatic hydrocarbons (PAHs) such as phenanthrene and enhanced biodegradation" (Mulligan, 2005).

Scientists have tested the release of low solubility compounds from soil and other solids. "They have been found to release three times as much oil as water alone from the beaches in Alaska after the Exxon Valdez tanker spill. Removal efficiency varied according to contact time and biosurfactant concentration" (Mulligan, 2005). Another study "found that the rhamnolipids from *P. aeruginosa* UG2 were able to effectively remove a hydrocarbon mixture from a sandy loam soil and that the degree of removal (from 23 to 59 percent) was dependent on the type of hydrocarbon removed and the concentration of surfactant" (Mulligan, 2005).

A study of biosurfactants and waste hydrocarbons showed that "to degrade hydrocarbons, bacteria must adsorb onto the surfactant-oil interface which is 25-50 nm in thickness. Only approximately 1 percent of all the biosurfactant was needed to emulsify the oil" (Southam and others, 2001 in Mulligan, 2005).

Rhamnolipids were used to remove heavy metals (lead and cadmium). Researchers found that clay and iron oxide contents affected biosurfactant efficiency. "Biosurfactants could also be added as a soil washing process for excavated soil. Due to the foaming property of the biosurfactant, metal-biosurfactant complexes can be removed by addition of air to cause foaming and then the biosurfactant can be recycled through precipitation by reducing the pH to 2. Improvements in the fermentation and purification process will continue to decrease costs" (Mulligan, 2005).

Results of many studies

Based on the results of many studies, Mulligan (2005) concludes

- rhamnolipids are effective for hydrocarbon and heavy metal removal and could also be effective for removal of mixed (hydrocarbon and metal) contaminants
- low concentrations of rhamnolipids below the CMC enhance mineralization of entrapped hydrocarbons while concentrations above the CMC enhance hydrocarbon mobility
- "attempts are being made to determine nonaqueous phase liquid (NAPL) mole fraction and micelle-aqueous partition coefficients with rhamnolipids to understand equilibrium solubilization behavior in surfactant-enhanced soil remediation situations"
- biosurfactants, because they are less toxic and less persistent than synthetic surfactants, may be a better choice for oil spills (*Reviewer's comment: Because synthetic surfactants are more persistent (longer lasting), they might be more economical to use.*)
- an emulsifier produced by *Pseudomonas aeruginosa* SB30 could disperse oil into fine droplets, which could enhance bioremediation
- "despite the large amount of research on dispersants, there is very little on the use of biosurfactants as biodispersants despite their potential benefits, particularly for enhancing oil biodegradation and solubilization"
- "a strain of *Bacillus subtilis* was able to produce a biosurfactant at 45° C at high NaCl concentrations and a wide pH range... it was able to remove 62 percent of the oil in a sand pack saturated with kerosene and thus could be used for in-situ soil removal and cleaning sludge from sludge tanks... the species could release oil at low concentrations

of 0.04 mg/l from oil-saturated columns... *Bacillus subtilis* was also used to remove high levels of metals and hydrocarbons from contaminated soil and sediments "

- BOD-Balance™, a biosurfactant extracted from cactus, was able to decrease oil and grease concentrations derived from pet food
- scientists found gram-negative strains of biosurfactant producers in a hydrocarbon or mixed contaminant soil, but "much more effort is required to determine the role of biosurfactant-producing organisms in-situ and to exploit their potential"
- strains of *Bacillus* and *Pseudomonas* at hydrocarbon-contaminated sites are biosurfactant producers, and their presence should be exploited
- biosurfactants seem to enhance biodegradation by influencing contaminant bioavailability, and because of their biodegradability and low toxicity, they are promising for use in remediation

Mulligan suggests that more information "is required concerning the interaction of the biosurfactants and the contaminant, relationship of the biosurfactant structure and contaminant removal and the soil, scale-up and cost reduction for ex-situ production, and understanding of the factors influencing the bioremediation of the compounds by enhanced bioavailability. Methods to enhance the economics of biosurfactant utilization will need to be developed further" (Mulligan, 2005).

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UTTU thanks Dr. Mulligan, mulligan@civil.concordia.ca, for her help on this article.



TDR detection of organics in sandy soils

Researchers recently studied the distribution of nonaqueous phase liquids (NAPL) in sandy soils, using a TDR (time domain reflectometry) probe system and eigendecomposition method of analysis. "The proposed technique characterizes the captured signatures of the NAPLs and water contents by a number of eigenvalues calculated by autoregressive modeling and singular value decomposition methods" (Mohamed and Said, 2004). Current monitoring procedures, for the most part, rely on monitoring wells, which can be expensive and time consuming; however, TDR can offer early detection and characterization, which can save considerable time and money.

Theory

TDR, a "monitoring probe machined from a conducting rod, is connected to a pulse generator and to an oscilloscope via a transmission line (coaxial cables). The oscilloscope is used to acquire the system response through a measurement point on the transmission line.

During measurement, an electrical pulse with a fast rising edge is generated periodically by the pulse generator and launched toward the probe. The pulse signal propagating toward the probe appears on the oscilloscope as it passes the measurement point located at a known distance from the generator on the transmission line. As the pulse reaches the probe end, it reflects back on the transmission line with pulse characteristics dependent on the properties of the media surrounding the probe..." (Mohamed and Said, 2004). Essentially, the pulse measures the electrical characteristics of the media surrounding the probe.

"In eigendecomposition analysis, an orthogonal set of expansion vectors are extracted to indicate dominant variability in a collection of data points. The coordinates of the points along each vector will be an eigenvector, and the length of the projection will be an eigenvalue" (Mohamed and Said, 2004).

Facts about TDR:

- it measures soil pore fluid concentrations for a sampling volume with a well-defined volume
- it allows for data collection of water content and salt concentration at a high spatial and temporal resolution
- success or failure "is heavily dependent on the appropriateness of the calibration procedure used"
- "characteristics of the reflecting signals are highly influenced by the electrical properties of the pore fluid, soil structure and minerals, initial placing conditions and temperature" (Mohamed and Said, 2004)

The text also describes autoregressive modeling and singular value decomposition (SVD), which will not be discussed here.

Experiment

Researchers tested a soil material consisting of sand, endeavoring to avoid clay minerals "which have a major impact on the system's performance [and] one needs to minimize such effects, especially at the stage of developing and calibrating the newly developed system." The sand used ranged in diameter from 0.1 to 1 mm, had a specific gravity of 2.53, a maximum dry density of 1.53 mg/m³, and an optimum moisture content of 10 percent.

Researchers next

- selected NAPLs:
 - neutral polar-acetone
 - nonpolar-heptane and xylene
 - hydrocarbons-benzene and trichloroethylene
- used NAPLs in various combinations with deionized water
- placed the soil in a testing column
- created a hole through the testing material with the diameter slightly less than that of the probe's
- pushed the testing probe through the soil material
- connected the probe to the oscilloscope
- took measurements; they captured and recorded reflected signals for each variation of moisture and/or NAPL fluid content

Conclusions

Mohamed and Said (2004) concluded the following:

- as NAPL content increases, reflected amplitude increases and time delay decreases (acetone content increases the soil medium dielectric constant, capacitance decreases and resistance increases)

- the TDR system allows the output signal from the pulse generator to be transmitted directly to the probe while the reflected signal is recorded on the oscilloscope
- reflected signals can be analyzed using the eigendecomposition method (although they can also be analyzed by other methods, such as Fourier spectral analysis)
- the most significant eigenvalues were identified based on their power spectrum
- the relative eigenvalue of the first mode, (E_{ow}), which is a measure of the power carried by the signal, was calculated and correlated to organic chemical type and content, and octanol water partition coefficient ($\log K_{ow}$)
- for the same NAPL content, as $\log K_{ow}$ increases, E_{ow} decreases due to increase of hydrophobicity
- for the same $\log K_{ow}$ as the organic content in soil pore fluid increases, E_{ow} increases due to decrease of dielectric properties of the pore fluids

Another study

Mohamed and Said (2005) also examined the results from a TDR study of motor oil, diesel oil, methanol and ethanol in a sandy soil. They needed to correlate eigenvalues to physicochemical properties, which requires

- identifying a characteristic property such as octanol/water partition coefficient (K_{ow}), which measures soil pore fluid hydrophobicity
- choosing a wide range of organic compounds with large variations in K_{ow}
- conducting experiments with variations in water and organic contents
- calculating the eigenvectors for each case

- using a statistical package to correlate eigenvalues with K_{ow} ; for known eigenvalues, the soil organic content would be predicted

Again, they used different combinations of deionized water and organic fluid contents. Researchers found

- as water content increases, the magnitude of the first and second eigenvalues decreases
- for motor and diesel oils, eigenvalues are the same
- ethanol and methanol have different eigenvalues because the dielectric properties of ethanol are less than that of methanol

At this time Mohamed and Said (2005) are still conducting analyses on these mixtures and refining calibration for use of TDR in sandy soils.

References

Mohamed, A.M.O. and R.A. Said, "Detection of Organic Pollutants in Sandy Soils via TDR and Eigendecomposition," *Journal of Contaminant Hydrology*, Vol. 76, 2005; <http://www.elsevier.com/locate/jconhyd>

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UTTU thanks Dr. Mohamed, Mohamed.A@uaeu.ac.ae for his help on this article.



Research notes

Laboratory comparison of polyethylene and dialysis membrane diffusion samplers

Ehlke, T.A., Imbrigiotta, T.E. and J.M. Dale, *Ground Water Monitoring & Remediation*, Vol. 24, No. 1, 2004; <http://www.ngwa.org>

Researchers conducted a laboratory study on the ability of diffusion samplers to collect volatile organic compounds and inorganic ions. To adequately describe the site geochemistry, researchers collected samples for both inorganic and organic constituents.

Researchers used diffusion samplers because "they eliminate the need to purge a well prior to collection of ground water samples, and ground water monitoring and purge water treatment costs can be reduced." Usually a minimum equilibrium time of 14 days is recommended for VOCs, but this varies depending upon the organic compound and temperature. The diffusion samplers were made from regenerated cellulose dialysis membrane and low density, flat polyethylene tubing.

Diffusion samplers that are normally made from LDPE film (low density polyethylene) are not suitable for sampling hydrophilic polar molecules or charged compounds such as inorganic ions. Even larger organic compounds may "not diffuse across an LDPE membrane. MTBE, acetone, and a few semivolatile organic compounds studied were poorly sampled with LDPE diffusion samplers."

Regenerated cellulose dialysis membrane diffusion samplers are more advantageous than LDPE diffusion samplers because of the regenerated cellulose dialysis membrane diffusion samplers'

- ease of construction
- inexpensive cost
- ability to be constructed in any size capacity from a few milliliters to several liters
- equilibrium time for VOCs and inorganic ions (should be shorter for larger sample volumes)
- exclusion of all particulates and most colloids
- capability of sampling for both organic and inorganic ions

Disadvantages of these diffusion samplers include

- a requirement for strict handling, cleaning and storage procedures
- regenerated cellulose dialysis material's light negative surface charge in waters greater than a pH of 3
- a potential for biodegradation

Study of five discrete-interval-type ground water sampling devices

Parker, L.V. and C.H. Clark, *Ground Water Monitoring & Remediation*, Vol. 24, No. 3, 2004, <http://www.ngwa.org/>

Parker and Clark (2004) tested five discrete-interval-type ground water sampling devices: the KABIS, HydraSleeve, Discrete Interval, Pneumo-Bailer and United States Geological Survey's passive diffusion bag (PDB) samplers. The article gives a complete description of each device. Each was tested for its ability to collect volatile organics, explosives, pesticides and metals from a standpipe and trichloroethylene (TCE) from a deep monitoring well.

"The PDB sampler was the easiest to use but could only be used to sample volatile organic compounds (VOCs). The HydraSleeve and the KABIS samplers were also easy to use: these devices produced representative

concentrations of explosives, pesticides and metals in the standpipe experiments but elevated the turbidity in our monitoring well. Although there were statistically significant differences for some VOCs with both devices, these differences were generally very small (< 5 percent). The one exception was an 18 percent loss of TCE with the KABIS sampler."

Parker and Clark also tested two simple, thief-type devices: they were easy to operate but caused bubbling when sampling and elevated the turbidity in the well. In some wells, redeveloping the well may be necessary prior to using the devices.

Vertical delineation of contamination in fractured bedrock aquifer

D. Muscalo, *Ground Water Monitoring & Remediation*, Vol. 24, No. 1, 2004; <http://www.ngwa.org>

Scientists determined the vertical extent of gasoline contamination in groundwater monitoring wells at a fractured rock site in New Jersey, using samples selected from 6.1-m sections of boreholes and packer sampling methods. Contamination in this area was found as deep as 91.4 m. Field workers drilled four boreholes and samples were later analyzed in a field laboratory. Muscalo (2004) found that contaminant concentration generally decreased with depth.

"The results of this investigation demonstrate that lighter-than-water compounds can occur dissolved in fractured bedrock aquifers at great depths. As documented by this study, dissolved-phase concentration of lighter-than-water compounds may increase with depth in fractured bedrock aquifers" (Muscalo, 2004).



Information sources

U.S. EPA publications and information

Reports that can be viewed or downloaded at <http://clu-in.org/techpubs.htm> include:

- A Decision-Making Framework for Cleanup of Sites Impacted with Light Non-Aqueous Phase Liquids (LNAPL) (EPA 542-R-04-011)
- Case Study of the Triad Approach: Expedited Characterization of Petroleum Constituents and PCBs Using Test Kits and a Mobile Chromatography Laboratory at the Former Cos Cob Power Plant Site (EPA 542-R-04-008)
- Cost and Performance Report for LNAPL Characterization and Remediation: Multi-Phase Extraction and Dual-Pump Recovery of LNAPL at the BP Amoco Refinery, Sugar Creek, MO (EPA 542-R-05-016)
- Cost and Performance Report for LNAPL Characterization and Remediation: Partition Interwell Tracer Testing (PITT) and Rapid Optical Screening Tool (ROST) Characterization and Evaluation (SEAR) at the Chevron Cincinnati Facility, Hooven, OH (EPA 542-R-05-017)
- Cost-Effective Design of Pump-and-Treat Systems (EPA 542-R-05-008)
- Effective Contracting Approaches for Operating Pump-and-Treat Systems (EPA 542-R-05-009)
- O&M Report Template for Ground Water Remedies (with Emphasis on Pump-and-Treat Systems (EPA 542-R-05-010)
- Technology News and Trends

Other EPA documents include:

- A Compendium of Chemical, Physical and Biological Methods for Assessing and Monitoring the Remediation of Contaminated Sediment Sites (EPA 600-R-04-108), <http://www.epa.gov/nerleerd/108Complete.pdf>
- Consolidated CLU-IN Project Profile Search, <http://clu-in.org/databases/search>
- Remediation Technology Demonstration Project Profiles, http://clu-in.org/products/demos/search/vendor_search.cfm
- The Basics: Understanding the Behavior of Light Non-Aqueous Phase Liquids (LNAPLs) in the Subsurface (an online training course), <http://www.rtdf.org/public/napl/>
- UST-LUST Virtual Classroom, <http://www.epa.gov/oust>; click on appropriate title

Other documents

API Interactive LNAPL Guide, <http://groundwater.api.org/lnaplguide>

ITRC Overview of Groundwater Remediation Technologies for MTBE and TBA (MTBE-1), <http://www.itrcweb.org>; click on Guidance Documents

ITRC Permeable Reactive Barriers: Lessons Learned/ New Directions (PRB-4), <http://www.itrcweb.org>; click on Guidance Documents

ITRC Technical and Regulatory Guidance for In-Situ Chemical Oxidation of Contaminated Soil and Groundwater (Second Edition, ISCO-2), <http://www.itrcweb.org>; click on Guidance Documents

UTTU obtained many of these sites from TechDirect (<http://clu-in.com/techdrct>), Ground Water Monitoring & Remediation (<http://www.ngwa.org>), and other publications. We thank the editors and writers for allowing us to reprint this material.