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Comments and suggestions are welcome and may be directed to [Phil O'Leary](mailto:proleary@epd.engr.wisc.edu) (proleary@epd.engr.wisc.edu), Project Director, 432 N. Lake St., Madison, WI 53706. Tel 608-262-0493. To comment on an article, or to suggest topics for *UTTU*, please e-mail [Jaime Pullman](mailto:pullman@wisc.edu) (pullman@wisc.edu) or call 608-249-0509.

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Using push-pull tests to measure degradation via phytoremediation

Researchers from Virginia Polytechnic Institute and State University recently investigated phytoremediation as a contributing mechanism in the remediation of polycyclic aromatic hydrocarbons (PAHs). They proposed that PAHs “are subject to two primary phytoremediation mechanisms” including:

- “direct plant uptake of contaminants and subsequent accumulation of either the contaminant or nontoxic metabolites within the plant tissue
- rhizosphere degradation, which involves both (a) the stimulation of microbial activity and transformation of xenobiotic contaminants caused by the release of enzymes and exudates into the rhizosphere, and (b) enhanced mineralization of contaminants by microrhizal fungi and rhizosphere microbial consortia” (Pitterle and others, 2005)

The researchers employed push-pull tests (PPTs) to calculate in-situ aerobic respiration rates as an assessment of degradation. “PPTs involve the injection of a well-mixed solution consisting of a nonreactive, conservative tracer and a reactive, biodegradable tracer (electron donor and/or electron acceptor) into the saturated zone. Following injection, extraction of groundwater from the well occurs. The conservative tracer is subject only to advection and dispersion, whereas the other reactive solute(s) are additionally presumed to be subject to constant, irreversible attenuation processes. Solute concentrations are measured throughout the injection and extraction phases, and the resulting concentration breakthrough curves are used to quantify degradation rates”

(Pitterle and others, 2005). Of particular interest to the researchers were degradation rates in treed areas versus nontreed areas and the seasonal variation in degradation rates.

Experiment

Site characteristics

In 1997, a phytoremediation system consisting of 1146 hybrid poplar trees, *Populus deltoides* x *nigra* DN34, was implemented at a creosote-contaminated site in Oneida, Tennessee. Pitterle and others (2005) described the site as “underlain by an unconfined aquifer consisting of sand and sandy clay to a depth of 3.0-3.5 m below land surface. Over the past seven years, researchers conducted biannual groundwater and annual soil-boring monitoring of 10 PAHs including 2-, 3-, 4-, and 5-ring PAHs that are representative of the contaminants detected in the initial site characterization.” The site has seen significant drops in PAH concentration levels and plume size since the phytoremediation system was installed. Naphthalene makes up “about 65 percent of the PAHs found in the groundwater at the Oneida site.”

Investigation methods

Scientists installed 10 push-pull wells, one pair at each of five locations. One in each pair was set at a shallow depth (S) and its partner at a deeper depth (D). The wells were set in the following areas:

- S1/D1, uncontaminated, nontreed
- S3/D3, contaminated, treed
- S4/D4, contaminated, treed
- S5/D5, contaminated, nontreed

The researchers did not perform tests at well pair S2/D2.

A sterilized hand auger was used to drill into bedrock for the construction of wells, which “consisted of 2.54-

cm-diameter PVC with well screens 30.5-cm long. The annulus of each well was filled with approximately 45 cm of filter sand followed by 30 cm of bentonite clay, and backfilled to the surface with a mix of soil and bentonite. Newly constructed wells were conditioned by injecting 50 liters of clean water at a flowrate of approximately 0.5 L/min. Soil samples corresponding to the screened depths for the shallow and deep pairs were collected for later microcosm construction” (Pitterle and others, 2005).

Researchers injected and monitored the following through the PPT:

- bromide
- dissolved oxygen
- naphthalene

These were also sampled for analysis in triplicate prior to injection. The injected amount, 35 liters, was added at 0.5 L/min.

The researchers did not use naphthalene for rate determinations “because of the high background concentrations of naphthalene in most of the wells; however, the compound was included in the injectate for consistency in the test procedure. The effect of naphthalene on aerobic respiration rates was evaluated by excluding naphthalene from the solution in two PPTs. Before the feed tank was sealed with Parafilm to prevent volatile losses, a submersible mixing pump was placed in the injection solution container to ensure the solutes were well-mixed” (Pitterle and others, 2005).

Scientists took injection samples of bromide, DO and naphthalene every 10 minutes. With each injection completion, extraction began. “Extraction was initiated at a flowrate ranging from 250 to 400 mL/min. Extraction samples for analysis of bromide and DO were taken every 10 to 20 minutes. Extraction continued until either three times the injected volume was collected or until the DO stabilized to background levels.”

Researchers then calculated the normalized solute concentrations and the “data were then analyzed to determine first-order degradation rates” (Pitterle and others, 2005).

Results and conclusions

The PPTs at wells D3, S5 and D4 yielded detectable naphthalene, “in respective order of increasing magnitude. Recovery of bromide was typically 90 percent or greater, while the percent recovery of DO was variable.” Researchers noted, “the approach used here does not require complete mass recovery of either tracer” (Pitterle and others, 2005).

Pitterle and others’ (2005) findings included:

- “little to no consumption of oxygen” at the control, nontreed
- “substantial DO consumption” at the contaminated, treed
- “percent recovery of mass for each tracer was nearly identical” at control
- “mass recoveries of bromide and DO in the contaminated well were 96.0 and 53.9%, respectively”
- greater oxygen consumption overall at treed versus nontreed areas
- D3-June PPT, “the DO decreased from an injection concentration of 6.45 mg/L by approximately 90 percent within the first 60 minutes of the extraction phase of the test”
- S5-February, “DO concentration measured during extraction...remained above 10% of the injection concentration through the first 150 minutes. The concentration of bromide decreased to approximately 10% of the injection concentration within the first 130 minutes and the first 170 minutes, respectively.”

Seasonal variation

Researchers conducted PPTs in the winter, spring and summer at the control well, D1, and did not observe any significant oxygen respiration levels in those tests. “Control well results indicate that aerobic respiration rates did not require any adjustment for consumption of natural organic carbon or inorganic species” (Pitterle and others, 2005).

At well D3, the researchers ran four PPTs to measure seasonal variations in degradation rates. They found that “rates increased by a factor of 4 from nonactive winter months to active summer months. The lowest rate (0.30 hr^{-1}) occurred in the winter, and the highest rate (1.25 hr^{-1}) occurred in June when the poplar trees are most active. Spring PPT rates for D3, conducted on different days in April under similar weather conditions, did not vary significantly (0.77 and 0.60 hr^{-1} , respectively), demonstrating that results can be replicated. A comparison of the results from the April PPTs shows that the inclusion of naphthalene in the injection solution had no significant impact on the rates” (Pitterle and others, 2005).

Researchers reported an increase in groundwater temperatures, from 10°C to 17°C and 20°C “at D3 from December to April and then to June, respectively.” They evaluated temperature effects and concluded that, “temperature effects on biological activity alone do not account for the differences in rates from winter to spring to summer. The apparent influence of trees on aerobic respiration rates is demonstrated by comparing results from wells D4 and D5 to rates from well S5... First-order winter rates from PPTs in treed areas (D4 and D5 December) were greater by a factor of 3-5 when compared to PPTs in a nontreed area (S5-February). For these winter rates, it is interesting to note that the difference in rates ($D4 > D3 > S5$) did not appear to be related to difference in the background concentration of

naphthalene where $D4 \approx S5 > D3$ ” (Pitterle and others, 2005).

The field rates researchers reported “represent maximum rates for conditions where the electron acceptor concentration was nonlimiting. In this research, the zones targeted with PPT wells (depth = 1.75-2.53 m) were exposed to both highly reducing conditions in the winter and to mildly reducing and aerobic conditions in other seasons when the water table was lower... For purposes of comparing rates in different areas of the site, and also for ease of measurement, oxygen was selected as an electron acceptor. Aerobic conditions produce the least limiting conditions for microbial degradation, thereby eliminating variability associated with the use of different electron acceptors. This technique will also produce the highest respiration rates at hydrocarbon-contaminated sites, which can be interpreted as the peak respiration rate when DO concentrations are at their highest level” (Pitterle and others, 2005).

Scientists concluded that PPTs can distinguish between treed and nontreed areas, as well as “show seasonal variations in the rate of oxygen uptake. The largest first-order rate occurred in June at D3, located adjacent to the largest trees at the site. This may suggest that not only will the presence of trees increase naphthalene degradation, but it is probable that the size of the tree is an important factor, likely because larger trees will have a more extensive root system. The seasonal variation in degradation rates at the same PPT well in a treed area increased by a factor of four from winter to summer. This is important because microcosm tests conducted in a controlled temperature environment would not be expected to differentiate between rates from soils collected during different times of the year. This finding also suggests that poplar-tree-based phytoremediation systems remain active, but at a lower rate, during months of the year when transpiration is inactive”

(Pitterle and others, 2005).

Pitterle and others (2005) noted, "At most remediation sites, the time to completion of the remediation process is an important consideration in the selection of the remediation method." Estimating this has been largely impossible for phytoremediation sites, however, "due to both the lack of extensive monitoring data and the inability to quantify rates of contaminant loss associated with the various mechanisms attributed to phytoremediation processes. The PPT results from the Oneida site, coupled with" previous research, "suggest that these rates can be estimated, at least for moderately to highly contaminated sites. Our data also indicate that winter rates of degradation are significant, although the rates could be impacted more at colder locations. Our data permit estimation of in situ microbial degradation rates of naphthalene over the year."

"Results from our site show that poplar trees are effective in ameliorating PAHs, particularly naphthalene, which is supported by site data showing enrichment of the PAH plume with higher molecular weight compounds over time, as well as increased degradation rates in contaminated regions. Results from this study indicate that push-pull test results show enhanced microbial activity during the winter period compared to control areas, indicating that benefits of phytoremediation using poplar trees are not limited to growth seasons. Further, by using the data from treed and nontreed locations, a comparison of phytoremediation with natural attenuation without intervention can be made" (Pitterle and others, 2005).

References

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Widdowson, M.A., Robinson, S.L., Anderson, R.G. and J.T. Novak. "Remediation of polycyclic aromatic hydrocarbon compounds in ground water using poplar trees," *Environmental Science & Technology*, Vol. 39, No. 6, 2005; <http://pubs.acs.org/>

UTTU thanks Mark Widdowson, mwiddows@vt.edu, for his help on this article.



Energy Policy 2005-The Underground Storage Tank Compliance Act

The Energy Policy Act of 2005 was signed into law on August 8, 2005. The policy amends portions of Subtitle I of the Resource Conservation and Recovery Act. Title XV - Ethanol and Motor Fuels, Subtitle B - Underground Tank Compliance, includes changes that will influence federal and state UST programs considerably, as well as owners and operators. The following is a summary of this section of the Energy Policy Act of 2005, Public Law 109-58.

The policy states that the Administrator must distribute funds via an allocation process from the LUST Trust Fund to the State, applicable by subsection requirements, for:

- "corrective actions taken by the State"
- "necessary administrative expenses, as determined by Administrator, that are directly related to State fund or State assurance programs"
- "enforcement, by a State or local government, of State or local regulations pertaining to underground storage tanks"

The funds supplied are "not to be used by the State to provide financial assistance to an owner or operator to meet any requirement relating to underground storage tanks" and may not be distributed "to any State that

has diverted funds from a State fund or State assurance program for purposes other than those related to the regulation of underground storage tanks...with the exception of those transfers that had been completed earlier than the date of enactment of this subsection."

General amendments:

- Withdrawal of Approval of State Funds: "After an opportunity for good faith, collaborative efforts to correct financial deficiencies with a State fund, the Administrator may withdraw approval of any State fund or State assurance program to be used as a financial responsibility mechanism without withdrawing approval of a State underground storage tank program."
- Ability to Pay: "An inability or limited ability to pay corrective action costs must be demonstrated to the Administrator (or the State pursuant)" and "shall take into consideration the ability of the owner or operator to pay corrective action costs and still maintain its basic business operations, including consideration of the overall financial condition of the owner or operator and demonstrable constraints on the ability of the owner or operator to raise revenues." The owner or operator may "provide the Administrator (or the State pursuant) with all relevant information" needed for the decision and "the Administrator (or State pursuant) shall consider alternative payment methods as may be necessary or appropriate if the Administrator (or State pursuant) determines the owner or operator cannot pay all or a portion of the costs in a lump sum payment."

Inspection

Amendments to inspection requirements:

- All regulated tanks not inspected since December 22, 1998, must undergo on-site inspection "to

determine compliance with this subtitle and the regulations under this subtitle" within two years of the enactment of this subsection.

- Following the completion of the aforementioned inspections, "the Administrator or State that receives funding under this subtitle, as appropriate, shall conduct on-site inspections of each underground storage tank regulated under this subtitle at least once every three years to determine compliance with this subtitle and the regulations under this subtitle or a requirement or standard of a State program."
- "The Administrator of the Environmental Protection Agency, in coordination with the State, shall gather information on compliance assurance programs that could serve as an alternative to the inspection programs under section 9005 (c) of the Solid Waste Disposal Act and shall, within four years after the date of enactment of this Act, submit a report to the Congress containing the results of such study."

Operator training

Amendments to operator training will occur "not later than two years after the date of enactment of the Underground Storage Tank Compliance Act, in consultation and cooperation with States and after public notice and opportunity for comment" when "the Administrator shall publish guidelines that specify training requirements" for owners, operators, maintenance workers, and emergency response employees. State-specific training requirements must be developed within two years of the Administrative guideline publication and be in accordance with those guidelines. These requirements also must "be developed in cooperation with tank owners and tank operators, take into consideration training programs implemented by tank owners and tank operators as of the date of enactment of this section and be appropriately

communicated to tank owners and operators." States will receive financial compensation for developing and implementing their plan, training requirements being mandatory.

Oxygenated fuel contamination remediation

"Corrective actions with respect to a release of a fuel containing an oxygenated fuel additive that presents a threat to human health or welfare of the environment" may be funded by section 9014 of the Trust Fund "and in the case of a State" will be carried out "in accordance with a cooperative agreement entered into by the Administrator and the State."

In terms of release prevention and compliance, the Trust Fund grants may be used to:

- conduct inspections
- issue orders
- bring actions by the Administrator or the State for regulated tanks

Compliance report

For government-owned tanks, States will be required to complete a State Compliance Report detailing the "location and owner of each underground storage tank," the status of compliance, and "the date of the last inspection" and a description of "the actions that have been and will be taken to ensure compliance" within two years of "the date of enactment of this subsection." States that develop reports may be awarded additional funds.

States will be required to keep a public record, at least annually updated, of:

- "the number, sources, and causes of underground storage tank releases in the State"
- "the record of compliance by underground storage tanks in the State"

- "data on the number of storage tank equipment failures in the State"

Delivery, deposit and acceptance

"Delivery to, deposit into, or acceptance of a regulated substance" into an underground storage tank which is not in compliance with State or Administrative regulations will be prohibited "beginning two years after the date of enactment... Within one year after the date of enactment of this section, the Administrator shall, in consultation with the States, underground storage tank owners, and product delivery industries, publish guidelines detailing the specific processes and procedures they will use to implement the provisions of this section." Special consideration may be given to situations involving rural areas. "Any person making or accepting a delivery or deposit of a regulated substance to an underground storage tank at an ineligible facility in violation of section 9012 shall also be subject to the same civil penalty for each day of violation." Persons shall only be held accountable if they were given proper notice concerning compliance failure and ineligibility.

Federal accountability

Federal departments and agencies are subject to the same regulations as all others concerning underground storage tanks. Exemptions may be made only by the President. Twelve months following the enactment of the Underground Storage Tank Compliance Act, "each Federal agency that owns or operates one or more underground storage tanks, or that manages land on which one or more underground storage tanks are located, shall submit to the Administrator, the Committee on Energy and Commerce of the United States House of Representatives, and the Committee on the Environment and Public Works of the Senate a compliance strategy report that":

- “lists the location and owner”
- “lists tanks that are not in compliance”
- “specifies the date of the last inspection by a State or Federal inspector”
- “lists each violation...respecting any underground storage tank”
- “describes the training that has been provided to the operator and other persons having primary daily on-site management responsibility for the operation and maintenance of underground storage tanks”
- “describes the actions that have been and will be taken to ensure compliance for each underground storage tank”

Tanks on tribal lands

Within one year of enactment, Indian tribes and the Administrator must “develop and implement a strategy giving priority to releases that present the greatest threat to human health or the environment, to take necessary corrective action in response to releases from leaking underground storage tanks” and “to implement and enforce requirements concerning underground storage tanks” which are located “wholly within the boundaries of an Indian reservation or any other area under the jurisdiction of an Indian tribe.” A status report of implementation and enforcement will be required within two years following the enactment of this section.

Groundwater protection

New requirements for tank installation include:

- New tanks or “piping connected to any such new tank, installed after the effective date of this subsection, or any existing underground storage tank, or existing piping connected to existing tank, that is replaced after the effective date of this subsection, shall be secondarily contained and monitored for leaks if the new or replaced

underground storage tank or piping is within 1,000 feet of any existing community water system or any existing potable drinking water well.”

- “In the case of a new underground storage tank system consisting of one or more underground storage tanks and connected by piping,” the abovementioned requirement “shall apply to all underground storage tanks and connected pipes comprising such system.”
- “In the case of a replacement of an existing underground storage tank or existing piping connected to the underground storage tank,” the abovementioned requirement “shall apply only to the specific underground storage tank or piping being replaced, not to other underground storage tanks and connected pipes comprising such system.”
- “Each installation of a new motor fuel dispenser system, after the effective date of this subsection, shall include under-dispenser spill containment if the new dispenser is within 1,000 feet of any existing community water system or any existing potable drinking water well.”
- “Repairs to an underground storage tank, piping, or dispenser that are meant to restore a tank, pipe, or dispenser to operating condition” do not apply.

Responsibility

Manufacturers of underground storage tanks or UST piping and those who install USTs are “required to maintain evidence of financial responsibility... in order to provide for the costs of corrective actions directly related to releases caused by improper manufacture or installation unless the person can demonstrate themselves to be already covered as an owner or operator of an underground storage tank.”

States and the Administrator must “require that a person that installs an underground storage tank system” be

qualified by:

- certification or license “by tank and piping manufacturer”
- certification or license “by the Administrator or a State, as appropriate”
- UST installation “certified by a registered professional engineer with education and experience in underground storage tank system installation”
- UST installation “inspected and approved by the Administrator or the State, as appropriate”
- compliance “with a code of practice developed by a nationally recognized association or independent manufacturer’s instructions or compliance with another method as determined by the Administrator or a State, as appropriate, to be no less protective of human health and the environment”

These changes will have a significant effect on the UST community. For more information on the policy and compliance, visit the EPA’s Web site, http://www.epa.gov/swrust1/fedlaws/nrg05_01.htm.

Reference

EPA, http://www.epa.gov/swrust1/fedlaws/nrg05_01.htm

Energy Policy Act of 2005, Government Printing Office, Public Law 109-58, August 8, 2005; http://frwebgate.access.gpo.gov/cgi-bin/getdoc.cgi?dbname=109_cong_public_laws&docid=f:publ058.109.pdf

UTTU thanks Joe O’Keefe for suggesting this article.



Biodegradation, mineral weathering and conductivity

Researchers from the University of Missouri-Rolla investigated “geochemical and stable carbon isotope data from closely spaced vertical intervals in a hydrocarbon-impacted aquifer” and used the data “to assess the relationship between biodegradation, mineral weathering, and enhanced bulk conductivity zones” (Atekwana and others, 2005).

Scientists used high resolution vertical profiling of bulk conductivity zones to direct groundwater sampling. They aimed to:

- “provide geochemical and stable carbon isotope evidence for biodegradation in a hydrocarbon-contaminated aquifer
- provide evidence of enhanced mineral weathering in the contaminated aquifer
- investigate the relationship between major ion chemistry, total dissolved solids (TDS), and bulk conductivity”

They argued that, “geophysical methodologies may provide complementary technology for the assessment of intrinsic biodegradation,” and therefore geophysical investigations should be included “as part of natural attenuation assessment programs” (Atekwana and others, 2005).

Investigation site

Researchers examined a site in Carson City, Michigan. As a former petroleum refinery, the site underwent hydrocarbon release in the form of crude oil, jet fuel and diesel from storage units and pipelines, resulting in contamination of soil and groundwater for more than 50 years. The researchers recognized two phases of hydrocarbon contamination:

- the plume fringe: “regions where dissolved hydrocarbon in groundwater is from residual-phase hydrocarbons”
- the plume core: “regions where dissolved hydrocarbon in groundwater is from free-phase hydrocarbons”

According to Atekwana and others (2005), the aquifer was composed of glacial outwash with characteristics including the following:

- predominantly quartz, with minor calcite, albite, anorthite, gypsum and dolomite mineralogy
- a variable thickness (approximately 4.6 to 6.1 m)
- an unsaturated (vadose) zone of fine- to medium-grained sands
- a saturated zone of medium-sized sands and gravels underlain by a clay unit
- a variable ground water table
- a west to southwesterly ground water flow
- a ground water flow velocity of 1.68 m/day under a hydraulic gradient of 0.0015

Methods

Researchers installed vertical resistivity probes (VRPs) and multi-level piezometers (MLPs) for groundwater sampling one meter apart at five locations. These locations were named:

- VRP9/MLP9: uncontaminated location
- VRP10/MLP10 and VRP3/MLP3: plume fringe location
- VRP1/MLP1 and VRP5/MLP5: plume core location

Atekwana and others (2005) built the VRPs of:

- 3.8-cm-inner-diameter polyvinyl chloride (PVC) pipe
- 1.3-cm-long stainless steel screws (electrodes) installed at 2.5-cm intervals along the pipe length

Researchers installed screws through the pipe because screw heads created an “electrical connection with the geologic formation, while the threaded ends inside the pipe allow for collecting apparent resistivity data.” They obtained apparent resistivity “using a 5.0 cm Wenner array incremented at 5 cm intervals. Measurements were carried out with a Syscal R2 resistivity meter” (Atekwana and others, 2005).

Atekwana and others (2005) constructed MLPs of PVC tubing fitted with screens. They installed them “approximately 30 cm apart from the base of the aquifer into the vadose zone to accommodate seasonal fluctuations of the water table. Water from each MLP was pumped to the surface using a peristaltic pump. The water was passed through a flow cell into which a HydroLab™ downhole Minisonde was immersed” to measure:

- water temperature
- pH
- specific conductance
- total dissolved solids

Total alkalinity was determined immediately after water sampling by acid titration. The researchers then collected water for total petroleum hydrocarbons (benzene + toluene + ethyl benzene + xylenes) determination, in which:

- water was collected in pre-acidified 40-mL glass vials fitted with Teflon-lined screw caps without headspace
- vials were cooled to 4°C on ice
- vials were transported to a commercial laboratory for analysis using EPA Method 2020

In addition, Atekwana and others (2005):

- filtered water samples for major anions and cations analyses

- collected water in 250-ml polyethylene bottles (pre-acidified for cations)
- cooled the bottles to 4°C on ice
- transported the bottles to the laboratory

Researchers used ion chromatography for analysis of nitrate, sulfate, sodium, calcium, and magnesium, colorimetry for analysis of silica, and an inductively coupled plasma-atomic emission spectrometer (ICP-AES) for the analysis of total iron (Fe(II)) and manganese (Mn(II)). They also collected and analyzed "water for dissolved inorganic carbon (DIC) and the carbon isotope ratio of DIC" (Atekwana and others, 2005).

Results

Bulk conductivity

Researchers observed variability in the bulk conductivity at both uncontaminated and contaminated locations. These bulk conductivity variations included the following:

- at MLP9, "3.6 milliSiemens per meter near the water table increased to 18 mS/m at 50 cm below the water table, and remained nearly constant at 16 mS/m to the base of the aquifer"
- 15 to 32 mS/m at VRP1 and VRP5 compared to 10 to 25 mS/m at VRP10 and VRP3
- lower values were measured "near the top of the aquifer but showed enhanced (greater than background) bulk conductivity bulges at 50 to more than 100 cm wide" for vertical profiles
- at VRP10, values were not significantly different from background values
- at VRP3, VRP1 and VRP5, values were "up to two times higher than values measured at the background location at VRP9"

Researchers also found that saturation was not a factor

in bulk conductivity. Rather, grain size distribution was determined to be useful "as a proxy of the petrophysical properties of the aquifer." However, they observed that "the vertical bulk conductivity profiles do not match grain size changes, especially the increase in percent silt and clay, which is expected to enhance surface conductivity and thus increase the bulk conductivity" and concluded that "the poor correspondence between bulk conductivity and grain size distribution can be used as evidence that the enhanced bulk conductivity measured in the contaminated portion of the aquifer is not due to variations in petrophysical properties" (Atekwana and others, 2005).

Biodegradation evidence

Researchers found microbes to be useful indicators for contaminant mass reduction in hydrocarbon-contaminated aquifers. They were able to isolate "microbes capable of degrading hydrocarbon... from sediments and groundwater in the study aquifer, suggesting active microbial degradation of hydrocarbon at this site" (Atekwana and others, 2005).

Background location

Scientists did not find "measurable hydrocarbon in the background location at MLP9" and therefore determined that "the distribution of chemical and isotope parameters are due to the natural evolution of groundwater" (Atekwana and others, 2005).

Within the plume fringe

Atekwana and others (2005) found locations MLP10 and MLP3 "at depth intervals with higher TPH" to contain:

- depleted NO_3^- and SO_4^{2-}
- elevated Fe(II) and Mn(II)
- increased bulk conductivities "compared to the background location"

They suggested that the variability may be due to "utilization during hydrocarbon degradation" for NO_3^- and SO_4^{2-} and the "dissolution of Fe(III) and Mn(VI) from aquifer solids coupled to microbially mediated hydrocarbon degradation. In vertical profiles, zones with higher Fe(II) and Mn(II) are coincident with zones of higher TPH and broadly overlap with zones where bulk conductivity was enhanced. The $\delta^{13}\text{C}_{\text{DIC}}$ data also are consistent with microbial hydrocarbon degradation in the plume fringe."

Within the plume core

Researchers found locations MLP1 and MLP5 "at depth intervals with higher TPH" to show:

- depletion of NO_3^- and SO_4^{2-}
- elevated Fe(II) and Mn(II)

They attributed the "variability and lower values of NO_3^- and SO_4^{2-} in the vertical profiles... to utilization by microbes during hydrocarbon degradation" while the increased levels of Fe(II) and Mn(II) "indicate dissolution of Fe(III) and Mn(VI) from aquifer solids coupled to microbially mediated hydrocarbon degradation. At MLP1, vertical distributions of Fe(II) and Mn(II) show similar patterns, with higher values at the top of the aquifer decreasing to mid-aquifer where peak bulk conductivity occurred and remaining nearly constant to the base of the aquifer. However, depth profiles of Fe(II) and Mn(II) at MLP5 have similar patterns that increase from the water table to peak values overlapping with zones of enhanced bulk conductivity, before decreasing to the base of the aquifer" (Atekwana and others, 2005).

Mineral weathering evidence—biodegradation

Scientists noted, "In natural aquifers, mineral weathering is attributed to carbonic acid formed from CO_2 dissolved in recharging waters. Linking mineral weathering to biodegradation in hydrocarbon-

contaminated aquifers requires evidence of CO₂ generation, which should be reflected in DIC and alkalinity." Thus, they found "In the background location, DIC and alkalinity increase continuously with depth, although bulk conductivity values peak in mid-aquifer before slightly decreasing with depth. In the contaminated portions of the aquifer, DIC and alkalinity increase to mid-aquifer before decreasing with depth. Except for MLP10, zones with peak DIC and alkalinity overlap with depth intervals where bulk conductivity was enhanced... Acidic conditions that should enhance mineral weathering in the contaminated portions of the aquifer are reflected in pH values that range from 6.1 to 7.1 compared to 7.0 to 7.3 for uncontaminated groundwater" (Atekwana and others, 2005).

Scientists used the Ca/Mg ratio to "assess enhanced mineral weathering related to hydrocarbon biodegradation in contaminated portions of the aquifer." They observed that "peak values of Ca/Mg ratio within the zones with enhanced bulk conductivity are higher compared to lower portions of the aquifer." The researchers also used dissolved silica concentrations as a proxy for weathering of quartz and feldspars. "Although silica depth trends are not similar in groundwater from the plume core and plume fringe, overall higher silica values compared to the background location indicate enhanced weathering of silicates due to biodegradation in the contaminated groundwater" (Atekwana and others, 2005).

TDS, mineral weathering, and bulk conductivity

The scientists observed greater total dissolved solids (TDS) values in contaminated locations at depths 50 centimeters and below compared to the uncontaminated location where "TDS increased continuously with depth, similar to DIC and alkalinity" (Atekwana and others, 2005).

Researchers determined that "If the petrophysical

properties of the aquifer do not control the bulk conductivity as seen in the grain size distribution, then changes in fluid conductivity at full aquifer saturation should be the dominant variable controlling bulk conductivity. Pore fluid conductivity is directly linked to TDS in groundwater because most dissolved solutes in natural waters are ionic and conduct electricity. Therefore, the relationship between TDS and major ions released into groundwater from weathering of aquifer minerals in contaminated locations is a key step in linking TDS to bulk conductivity." A positive correlation was calculated between TDS and "the sum of the major ions, suggesting that TDS is related to ionic enrichment resulting from enhanced mineral weathering in contaminated groundwater." Scientists noted, "In general, bulk conductivity increases with increase in TDS. However, some scatter exists in the data especially at contaminated locations" (Atekwana and others, 2005).

Conclusions

Atekwana and others (2005) found that "TDS in groundwater and bulk conductivities of sediments are generally higher at locations contaminated with hydrocarbon and undergoing intrinsic biodegradation compared to uncontaminated locations. The higher TDS in the contaminated groundwater was due to elevated calcium and alkalinity, consistent with the weathering of carbonates, gypsum, and calcium feldspars in the aquifer, suggesting that the higher bulk conductivity may in part result from higher groundwater TDS."

In addition, they reported, "This study showed considerable variability in horizontal and vertical geochemical and stable carbon isotope parameters in groundwater, which is probably controlled by local geological and biogeochemical conditions. Despite this, zones of enhanced bulk conductivity broadly overlap with redox-sensitive parameters, DIC, alkalinity,

and major ions, suggesting that the subsurface expression of microbial hydrocarbon degradation is apparently recorded in the bulk conductivity measurements. Thus, electrical conductivity is an intrinsic property of the sediment media, is responsive to both electrolyte and solid-fluid interface chemistry, and may be ideally suited for discerning changes in bulk water chemistry based on total solute concentrations, and physical changes imparted to the aquifer groundwater and sediments during biodegradation." They therefore concluded, "the zones of higher conductivity indicate zones of active biodegradation and may be used to help guide sediment and water sampling for microbiological and geochemical investigations, such that the process of biodegradation may be more effectively studied." As a result, "the link between the electrical properties of contaminated aquifers and the groundwater chemistry within a framework of microbially induced degradation processes has implications for the use of geophysical methods to assess the potential of biodegradation at hydrocarbon-contaminated sites" (Atekwana and others, 2005).

Reference

Atekwana, E.A., Atekwana, E., Legall, F.D. and R.V. Krishnamurthy, "Biodegradation and mineral weathering controls on bulk electrical conductivity in a shallow hydrocarbon-contaminated aquifer," *Journal of Contaminant Hydrology*, Vol. 80, p.149-167, 2005; <http://www.sciencedirect.com>

UTTU thanks Estella Atekwana, atekwana@umr.edu, for her help on this article.



Humic acid toxicity in PAH-contaminated soil

Scientists from Utah State University investigated soil contamination at the Libby Groundwater Superfund Site in Libby, Montana. They assessed the “toxicity of humic extracts isolated from a biologically treated contaminated soil with the Aboatox flash toxicity assay” because a “continued understanding of the ecological effects of bound and sequestered contaminants that remain after biologic treatment will aid in the risk assessment of treated soils with regard to sustainable soil reuse” (Nieman and others, 2005).

Nieman and others (2005) reported, “the aging of contaminated soils and biologic activity result in sequestration of parent compounds and production of bound residues for polycyclic aromatic hydrocarbons (PAHs) and chlorophenols, including pentachlorophenol (PCP), the primary soil contaminants” at the site of investigation. Previous studies have shown biologic degradation to be restricted by the sequestration of organic compounds. At sites of bioremediation, in concert with sequestration, the bioavailability, mobility and toxicity of contaminants significantly decreased. Therefore, some scientists have considered bound residues to be a biologic endpoint for soil decontamination though they may still be detectable.

Scientists used the Aboatox flash toxicity assay because of its rapid toxicity assessment of solid or colored samples... The test uses the bioluminescent bacteria *Vibrio fischeri* as do other acute toxicity tests, but it gives a response that is not dependent on sample color or turbidity, thus allowing for rapid assessment of whole soil samples and colored soil extracts such as soil humic materials” (Nieman and others, 2005).

Methods

Nieman and others (2005) used the following chemicals:

- radiolabeled pyrene
- ¹²C pyrene
- potassium hydroxide
- sodium hydroxide pellets
- high-performance liquid chromatography (HPLC)-grade acetonitrile
- acetone
- hexane
- acetic acid
- HCl
- HPLC-grade methanol
- Purified XAD-8 resin

Soil analysis

Researchers took soil samples from the Libby site, where bioremediation treatments had been applied to soil contaminated with PAHs and PCP during wood-treating operations. These remediation treatments had reduced contaminant concentrations to regulatory limits. At this remediation site, researchers completed the following:

- spiked ten 10 g soil samples with [4,5,9,10-¹⁴C]pyrene and nonradiolabeled pyrene each and incubated at 30°C for 396 days
- adjusted soil moisture to 85% of field capacity before incubation
- periodically rehydrated microcosms during the incubation
- spiked a second 10 microcosms with nonradiolabeled pyrene
- set up “a third set of 10 microcosms... with no amendments and no moisture addition as nonamended controls”

“Collection and counting of carbon dioxide traps (1 mL 0.5 N NaOH) in the radiolabeled microcosms indicated biologic activity and the ability to mineralize the added pyrene during the course of the incubation. At the conclusion of the incubation period, the 10 radiolabeled samples were divided into two groups of five based on biologic activity. Triplicate samples poisoned with 1000 mg/kg HgCl₂ were also incubated” (Nieman and others, 2005).

Following incubation, researchers:

- placed samples in 40-mL Teflon centrifuge tubes
- tumbled samples with 15 mL 0.5 N NaOH for 17 hours
- centrifuged samples at 10,000 g for 10 minutes
- removed supernatant containing humic and fulvic acid
- repeated extraction twice, “once with 15 mL and once with 10 mL 0.5 N NaOH for 4.5 hours and 6 hours, respectively, and these extractions were added to the first”
- acidified humic extract and centrifuged
- dissolved the precipitated humic acid in 10 mL 0.1 N NaOH

“Aliquots of humic acid and fulvic acid were taken for liquid scintillation counting to assess associated ¹⁴C. Nonincubated, nonradiolabeled Libby soil samples were similarly extracted under an atmosphere of nitrogen to evaluate the toxicity of humic extracts isolated under anoxic conditions,” Nieman and others (2005) reported. In addition they,

- extracted residual soil
- decanted and sampled solvent for liquid scintillation counting
- air-dried remaining soil and combusted samples, which “allowed for trapping and scintillation

counting of $^{14}\text{CO}_2$ associated with unextracted ^{14}C in the soil solid phase"

- purified fulvic acid extracts by adding the 40-mL combined supernatant to 0.5 g purified XAD-8 resin that had been wet with 1.5 mL methanol
- allowed fulvic acid to sorb to the resin by shaking in a Teflon centrifuge tube overnight
- decanted the supernatant, and desorbed the fulvic acid from the resin with 2 mL 0.5 N NaOH for 5 minutes
- diluted NaOH and separated the resin by centrifugation

Researchers adjusted sample pHs "to between 7.6 and 8.0 with HCl and NaOH before toxicity testing. Uncontaminated soils from the Libby site, Kaysville, UT, and Fort Ellis, MT, were similarly extracted for use as controls" (Nieman and others, 2005).

PCP extraction and analysis

Scientists also isolated humic acid from unincubated Libby soil to test for PCP. The isolated humic acids were solvent extracted and PCP analysis was conducted on a Shimadzu 10A HPLC system. Another set of unincubated soil samples was extracted with solvent prior to humic acid extraction to evaluate the effects of extraction order on humic acid toxicity. Total PCP concentration in the soil was evaluated by extracting ten-gram samples with acetonitrile under sonication followed by HPLC analysis (Nieman and others, 2005).

Bacterial toxicity

Scientists analyzed the microbial toxicity of isolated humic and fulvic acids with a Aboatox flash toxicity assay. Nieman and others (2005) explained, "The flash toxicity test involves using the sample of interest to challenge the luminescent marine bacteria *V. fischeri*. Humic acid samples were prepared as described previously. Whole-soil samples were prepared for

the toxicity assay by making 20% (wet-weight basis) suspensions of soil in 2% NaCl and agitating for 15 minutes before testing. During the test, a 0.5-mL aliquot of active bacteria was added to a 0.5-mL suspension of the soil or humic acid sample. The bacterial light output was monitored on a luminometer with continuous mixing for a period of 30 seconds after the sample and bacteria were combined. The light output after 30 seconds of exposure was then compared with the peak light output immediately after addition of the sample. The ratio of the 30-second value to the peak value was calculated (r_{30}) and used as an indicator of acute bacterial toxicity. Values of $r_{30} > 0.8$ were considered to indicate little or no toxicity, whereas values of $r_{30} < 0.8$ were considered to display a toxic response."

Results

Nieman and others (2005) observed significant carbon dioxide and polar metabolite production "accumulated in the fulvic acid fraction" by biologically active microcosms. For carbon dioxide, production varied from 2 to 27 percent "of the added radiolabel." Mass balance results for the inactive microcosms were similar to the poisoned treatments with the majority of the added radiolabel being solvent extractable from the remaining soil after the initial humic extraction. Unlike the increase in radiolabel found in the fulvic acid fraction of active microcosms, association of ^{14}C with the humic acid fraction was similar regardless of biologic activity."

Flash toxicity analysis results "showed that all of the humic acid samples extracted from the microcosms containing contaminated soil displayed acute bacterial toxicity. Values of r_{30} ranging from 0.15 to 0.3, indicative of a 70% to 85% decrease in bacterial light output during 30 seconds of exposure, were observed for all samples. Subsequent tests of contaminated soil humic acid extracted under anoxic conditions also showed similar toxicity. The addition of pyrene to the

contaminated soil before incubation did not appear to have an effect on humic acid toxicity. Humic acid extracts of three uncontaminated control soils (Libby, Kaysville, and Montana) resulted in r_{30} values ranging from approximately 0.7 to 0.8, values generally considered to indicate a lack of toxicity. Flash toxicity of the whole soil before incubation or humic acid extraction also indicated a lack of toxicity and often displayed an increase in bacterial light output with time. Toxicity did not appear to correlate with the apparent organic carbon concentration of the sample... Fulvic acid extracts did not show a toxic response, and all fulvic acid extracts had r_{30} values between 0.83 and 1.03" (Nieman and others, 2005).

Nieman and others (2005) observed results indicating that:

- "extracted residues were readily bioavailable to the indigenous microbial community"
- "humic acid associated toxicity did not appear to inhibit further degradation"
- "toxicity can be removed when the isolated humic acid is extracted directly but tends to persist when soil is solvent-extracted before humic acid isolation" and may be "dependent on the moisture status of the humic acid during extraction"
- "PCP, a known contaminant of the Libby soil, was present in the isolated humic acid and was a likely contributor to the observed toxicity"
- "a positive correlation exists between the concentration of PCP extracted from the sample and the decrease in toxicity. This correlation was also observed with the more polar unidentified peaks, but the observed presence of PCP associated with the humic acid extracts suggests that it is a likely contributor to the observed toxicity."

Discussion and conclusions

Nieman and others (2005) found, despite bioremediation, that "sequestered and bound contaminants can result in persistent residual toxicity of humic acid extracts. The finding that the humic acid isolated from the treated Libby soil had a toxic response in the flash assay was unexpected given that aqueous slurries of the whole soil displayed no toxicity in the assay and often displayed a hermetic effect of increasing light output. Also unexpected was the finding that the fulvic acid, a potential sink of biologically produced polar metabolites of pyrene and other organic contaminants, displayed no toxicity in the flash assay."

They proposed that several factors contribute to toxicity, including the presence of residual PCP "that had become sequestered and essentially nonbioavailable during the field treatment of the soil and subsequent 396 days of incubation and was apparently made more labile by the base extraction to remove humic and fulvic acids from the soil matrix... This finding is significant in that the parent contaminant was released from the soil matrix, thus indicating that neither degradation nor binding (humification) had occurred" (Nieman and others, 2005).

The scientists acknowledged that remaining toxicity may not "present a significant risk under normal circumstances" but "mixed-use industrial sites, where a variety of chemicals may potentially cause contamination, or sites that have changed in historic use could potentially release residual contaminants if soil and groundwater chemistry were drastically altered." Therefore, they concluded, the risks to "human health of residual PCP and PAH contamination in treated soils are likely low under most potential exposure scenarios. The effects of residuals are more likely to be observed on soil microbial populations and other plant and animal populations that come into intimate contact

with the soil. Addition of the toxic humic acid extracts back into the soil matrix did not appear to inhibit the indigenous microbial population. This population has been exposed to PCP and PAH contamination and may be adapted to it. Other studies have shown shifts in microbial populations caused by PAH contamination and decreased soil ATP content caused by PCP residues, but the long-term effects of residual contamination in treated soils are not well defined... If contaminated sites, sediments, and soils that have undergone biologic treatment are to be returned to productive uses, these long-term ecologic effects should be better understood" (Nieman and others, 2005).

Reference

Nieman, J.K.C., Sims, R.C., Sorensen, J.E. and J.E. McLean, "Humic acid toxicity in biologically treated soil contaminated with polycyclic aromatic hydrocarbons and pentachlorophenol," *Archives of Environmental Contamination and Toxicology*, Vol. 49, No. 3, 2005; <http://springerlink.metapress.com>

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MTBE and TBA sorption to synthetic resins

Bi and others (2005) conducted kinetic and equilibrium sorption experiments on four synthetic resins. "Recent developments suggest that synthetic resin sorbents may be economically competitive with other more established treatment technologies" for the removal of MTBE, which is often difficult because of "its high water solubility, low Henry's law constant, and the commonly relatively low concentrations in the environment. Groundwater contaminated with MTBE is also frequently contaminated with TBA - a contaminant

in some fuel grade MTBE and a major intermediate in MTBE degradation. TBA removal from water, however, is even more difficult because it is more polar and has a lower Henry's law constant than MTBE. It has been suggested that some resins may have a relatively high sorption affinity for TBA; this may result in economical removal of TBA from ground water" (Bi and others, 2005).

Researchers also investigated the biological possibilities of resins because they "may also be an important amendment during biological treatment in order to reduce contaminant concentrations below toxic levels." Their goal "was to evaluate the sorption affinity and to elucidate the sorption mechanism of MTBE and TBA to selected resins in order to provide data for the potential applications" (Bi and others, 2005).

Methods

Scientists used the following:

- millipore water
- MTBE
- TBA
- TBA-d₁₀

The studied resins included:

- Ambersorb 563
- Dow Optipore L493
- Amberlite XAD4
- Amberlite XAD7

Bi and others (2005) completed the following:

- washed the resins with ethanol and millipore water
- placed sorbent into a conical flask
- added the ethanol (or water)
- stirred the resin for 10 minutes with low intensity
- removed the ethanol (or water) by a water-jet vacuum pump

- removed retained water and trace ethanol by heating in an oven
- heated Ambersorb 563 (specified utilization temperature range: 0-60°C) at 55°C for 24 hours
- heated the remaining resins at 110°C for 90 ± 2 hours

Researchers pretreated resins to “remove residual compounds from the sorbent matrix, which is important for the potential use of resins in a bacteria cultivation experiment.” They used both the pretreated and the untreated Ambersorb 563 “in sorption experiments, in order to study the impact of pretreatment on the sorption affinity” (Bi and others, 2005). Scientists then estimated the theoretical maximum sorption capacity of each resin micropore.

Using N₂ porosimetry, the scientists measured:

- Brunauer, Emmett, and Teller (BET) surface area
- microporosity

They used a gas chromatography-flame ionization detector and direct aqueous injection-gas chromatography/mass spectrometry to analyze:

- MTBE
- o-xylene
- TBA

MTBE sorption kinetics experiments consisted of

- 0.01 g Ambersorb 563 (both treated and untreated) added to the vials
- 0.06 g XAD4, XAD7, and L493 added
- an initial MTBE concentration of 11.5 mg/L
- 10 mL of MTBE solution in 20-mL crimped headspace vials

TBA sorption kinetics experiments consisted of

- 0.06 g of all sorbents
- an initial TBA concentration of 7.71 mg/L

- 10-mL screw-top vials filled with TBA solution

The o-xylene sorption kinetic experiments were carried out with the initial concentration of 17.4 mg/L, and the solution volume in 20-mL crimp-top headspace vials was 10 mL. The mass of XAD7 added into each vial was 0.06 g, and for the other resins 0.01 g. All vials were shaken on a horizontal shaker” (Bi and others, 2005).

For sorption isotherm experiments (equilibrium sorption) involving MTBE, 10 mL solutions (concentration range 0.57-177 mg/L) were added into 20-mL crimp-top headspace vials. The sorbent amount was 0.06 g of XAD7 or 0.01 g of the other sorbents. The speed of the horizontal shaker was 160 rpm. For TBA sorption experiments, initial concentrations of 0.154-86.9 mg/L were used, and the screw-top 10-mL vials were filled with TBA solution and shaken on a reciprocating shaker with a speed of 100 rpm. In each vial, 0.2 g XAD7 or 0.06 g of the other sorbents were added. For binary experiments, the initial concentration of o-xylene was 43.5 mg/L in all samples. Researchers noted that different vials were used due to the different analytical methods applied for MTBE and TBA determination.

MTBE sorption kinetics to equilibrium concentration occurred in approximately the following speeds:

- XAD4, 4 hours
- L493, 24 hours
- XAD7, 24 hours
- Ambersorb 563 (untreated), 24 hours
- Ambersorb 563, 40 hours

TBA sorption kinetics to equilibrium concentration occurred in approximately the following speeds:

- XAD4, 24 hours
- L493, 24 hours
- Ambersorb 563 (treated and untreated), 48 hours
- after 24 and 48 hours, XAD7, no change in concentration

Bi and others (2005) reported that “due to the high sorption rate and affinity of untreated Ambersorb 563, the aqueous concentration of o-xylene was below the detection limit within three hours. For the other sorbents, aqueous o-xylene concentrations became very low (<0.5 mg/L) after 3 hours, and there was no detectable change in concentration after 24 hours.”

Scientists used the following to calculate results:

- Freundlich isotherm, to evaluate sorption at high concentrations
- Langmuir isotherm
- Toth isotherm
- Langmuir-Freundlich isotherm
- Dubinin-Astakov (DA) isotherm, to “describe sorption to carbonaceous resin and the results were interpreted based on a micropore-filling mechanism”
- Langmuir-Freundlich two-site isotherm, to evaluate partitioning

Results and discussion

Single-solute solution

Researchers determined “that Ambersorb 563 has the highest sorption potential and XAD7 has the lowest,” a result that agrees with the results of previous studies. They surmised, “these results show that the pretreatment slightly reduced the sorption affinity of Ambersorb 563 and XAD4. XAD7 has the lowest sorption affinity. XAD4 has the highest sorption rate but a relatively low affinity” (Bi and others, 2005).

Binary solution

For o-xylene, researchers observed greatest sorption for untreated Ambersorb 563 and least for XAD7. “Binary sorption results imply that the sorbents preferentially sorb o-xylene over MTBE. Consequently, presence of o-xylene decreases the sorption of MTBE to sorbents.”

This inhibition of MTBE sorption is significant for Ambersorb 563, XAD4 and XAD7, but is insignificant for Optipore L493, "which may indicate additional mesopore filling" (Bi and others, 2005).

Bi and others (2005) reported that future study of two synthetic zeolites (all-silica β Zeolite and Mordenite) would be useful because they "have a much higher affinity for MTBE than all other investigated sorbents" and because "there are still some shortcomings for their practical application" including the following:

- "there is no data on desorption characteristics (i.e., reversibility) of TBA and MTBE from zeolites"
- the zeolites "are not commercially available, and thus reproducibility of batches might be limited"
- no competitive sorption study has been carried out for MTBE
- zeolites might be rather specific for certain compounds and sorption data for TBA have not yet been reported"

Sorption mechanism

Scientists used the Langmuir-Freundlich two-site isotherm "to evaluate the contribution of partitioning in the MTBE sorption process to L493." An examination of the results suggested partitioning to be ultimately negligible. "An adsorption mechanism of MTBE to sorbents is also consistent with the observed competition between MTBE and *o*-xylene sorption" (Bi and others, 2005).

They drew several conclusions from this information, including:

- likely "there is another sorption mechanism in addition to micropore-filling, at low concentrations"
- "adsorption to specific sorbent sites of high adsorption energies" is a possible sorption mechanism

Bi and others (2005) explained, "In the binary

sorption, *o*-xylene molecules preferentially occupy most of sorbent-specific sites, even fill into part of the micropores... Compared with Ambersorb 563, the other sorbents have higher ratios of surface area to microporosity, which means the contributions of adsorption to specific sites to the total sorption are higher at low concentrations. This is shown by the underestimation of sorption affinities of the other sorbents by DA isotherms in binary sorption."

They continued, "The competitive sorption between *o*-xylene and MTBE reflects molecular interaction in the water-sorbent system. The sorption processes include two major steps:

- sorbate molecules released from bulk water phase
- adherence to specific site and filling into the micropores of sorbent phase

The energy involved in the second step should be similar for MTBE and *o*-xylene, since van der Waals interactions with the hydrophobic resin surface will be dominant. Therefore, preferential sorption of *o*-xylene suggests that the energy of the whole sorption process is dominated by the first step. As an apolar organic compound, *o*-xylene requires a high amount of free energy to accommodate it in the bulk water phase. Consequently, *o*-xylene is favorably released from water and sorbed to the sorbents. MTBE, which is a strong H-acceptor, can easily form H-bonds with surrounding water molecules. Therefore, MTBE can partition into water favorably due to a higher energy gain when inserting MTBE into cavity in bulk water phase" (Bi and others, 2005).

TBA

Researchers used the Freundlich isotherm for TBA isotherm modeling and found a "lower potential for removal of TBA from the solution compared with MTBE" for all the considered sorbents. For the resins

considered, sorption affinity was:

- highest for Ambersorb 563
- lowest for Amberlite XAD7

For the binary experiments, "*o*-xylene was removed" to yield sorption:

- "below detection limits" for Ambersorb 563 and XAD4
- of 0.018-0.023 mg/L and 0.03-0.23 mg/L for L493 and XAD7

For binary experiments, TBA removal was inefficient by XAD4 and XAD7 and "there is little effect of the presence of *o*-xylene on the sorption affinity of TBA to Ambersorb 563, L493, and XAD4. Due to the presence of *o*-xylene, the sorption of XAD7 is negligible." They reported, "TBA is both H-donor and H-acceptor, so its molecular interaction with water is energetically more favorable than that of MTBE, and lower partitioning to sorbents is the consequence. This is a rationale for the fact that TBA is less competitive than MTBE in the binary sorption experiments with *o*-xylene and the equilibrium concentration of *o*-xylene is low in the solutions, i.e., *o*-xylene concentration below detection limit (0.01 mg/L) for Ambersorb 563 and XAD4, 0.02 mg/L for Optipore L493, and 0.17 mg/L for XAD7... In the experimental concentration range, TBA sorption mechanisms include both adsorption to the specific sites of sorbent and the micropore-filling. At low concentrations, the superposition of these two mechanisms can be well represented by the Freundlich isotherm. At high aqueous concentrations, the Langmuir-Freundlich isotherm or combined two-site isotherm gives a better representation of the experimental isotherm" (Bi and others, 2005).

Practical application of sorbents

The desorption kinetics experiments completed by scientists used L493, "which is considered a suitable sorbent in bacteria enrichment," and "the

desorption data indicate that it takes about ten days to approach desorption equilibrium, under non-stirred and room temperature (22–23°C) conditions. Such non-stirred conditions...are necessary for using L493 as substrate reservoir in bacteria enrichment... The equilibrium concentrations were well predicted by the Langmuir-Freundlich isotherm based on mass balance calculations. This might be an indication that there is no desorption hysteresis of MTBE from L493" (Bi and others, 2005).

Scientists determined pretreatment to be unnecessary and L493 to be the most "suitable sorbent according to its sorption affinity and good desorption characteristics for MTBE (reversibility of sorption)" for bacteria enrichment experiments. "During bacteria enrichment, when the initial aqueous concentration of substrate is fixed, addition of L493 can keep this concentration in the biodegradation process for a long period... In the design of passive samplers in organic contamination monitoring, L493 is a good sorbent for sampling of BTEX and MTBE. However, for more polar compounds such as TBA, Amborsorb 563 should be applied in the sampler" (Bi and others, 2005).

Conclusion

Bi and others (2005) concluded, "In the studied concentration range, the sequence of the equilibrium sorption affinity for MTBE and TBA is Amborsorb 563 > L493 > XAD4 > XAD7. The pretreatment with ethanol causes the decrease of the sorption capacity but is necessary in case of subsequent bacteria enrichment. Bi-solute experiments indicate that all the sorbents preferentially sorb the hydrophobic o-xylene over hydrophilic MTBE and TBA. Overall, the LF isotherm fits best the data for MTBE sorption to all the sorbents, and the Freundlich isotherm fits best the data for TBA. Micropore-filling and/or another type of adsorption

mechanism dominates the sorption process in the experimental concentration range."

Reference

Bi, E., Haderlein, S.B. and T.C. Schmidt, "Sorption of methyl tert-butyl ether (MTBE) and tert-butyl alcohol (TBA) to synthetic resins," *Water Research*, Vol. 39, Issue 17, 2005; <http://www.sciencedirect.com/>

UTTU thanks **Torsten Schmidt**, torsten.schmidt@uni-tuebingen.de, for his help on this article.



Economics of combination contaminant plume management

Scientists examined the financial feasibility of employing hydraulic barriers and pump-and-treat systems together as a means of contaminant plume management. They focused their investigation on the use of conventional pump-and-treat systems (CPT). Researchers considered both operational and capital costs. They assumed that a reduction in pumping rate would reduce operational costs. "Therefore, any measure that enables a reduction in the pumping rate required to establish hydraulic containment of a given contaminated area or contaminant plume is of general interest" (Bayer and others, 2005).

Despite the increasing number of remediation technologies, Bayer and others (2005) report that, "at several sites, the prevailing conditions do not allow for methods alternative to pump and treat. Especially, hydraulic and/or hydrogeochemical site characteristics may narrow the number of applicable technologies. Innovative approaches such as enhanced bioremediation or cosolvent-supported methods represent not just ambitious but also sensible technologies, which have to be

accurately adapted to a site. Uncertainties about the structure and the properties of the subsurface may represent a considerable risk for dispersing the reagents and, consequently, for the overall success. Therefore, hydraulic containment focusing on ground water protection rather than on its cleanup is still an important means in ground water management, though technologies designed for contaminant removal should be preferred if feasible."

The investigation incorporated into a comparative cost analysis the results from a previous study by Bayer et al. (2004) in which a "comparison of...barrier-supported pump-and-treat systems (BPT) with CPT revealed that additional physical barriers may have a tremendous impact on the performance of hydraulic containment by pumping wells." Using this information, scientists created a model for economic evaluations. From the onset, however, scientists pointed out, "BPT can only represent an attractive alternative to the conventional approach if the barrier costs can be compensated by a reduction in operational cost" (Bayer and others, 2005).

BPT and CPT performance scenarios

Bayer and others (2005) created four different scenarios modeled by a two-dimensional ground water flow domain under closed conditions in which barrier settings of barrier shape, length, and location were examined for effect.

Scientists used simulation software for analysis and calculation of the scenarios. They repeatedly:

- modeled remediation system effect on ground water flow
- used a particle-tracking algorithm to determine the extent of the contaminated area captured

"The general objective of BPT is to deviate the ground water flow to achieve a reduction in the pumping rate of one well positioned downgradient of the contaminated

area. This well shall capture the contaminated area at a minimum pumping rate" (Bayer and others, 2005). Scientists examined the following in each BPT scenario:

- different settings of the barrier length, b (L)
- distance of the pumping well to the contaminated area, x (L)

Scientists analyzed each scenario and compared it to CPT in terms of required pumping rate for determination of system sensitivities and to geometrical design factors. Scenarios, which assumed homogenous flow conditions, included:

- A) remediation well only
- B) upgradient barrier
- C) downgradient barrier
- D) upgradient and downgradient barriers
- E) upgradient and side-barriers

Bayer and others (2005) observed the following:

- downgradient barriers (C) led to "lower pumping rates than upgradient barriers (B)"
- "if barrier length is longer than the width of the contaminated area, it is preferable to subdivide a given barrier length into two parts (D) with a longer segment at the downgradient edge of the area to be captured
- for a barrier length > 2.5 times the contaminated area width, the optimal solution is scenario E: a barrier that is tracked downgradient along the sides of the contamination starting from the upgradient edge"

The previous Bayer study had analyzed BPT and CPT operation, under heterogeneous flow conditions, with 500 possible realizations of the spatial transmissivity distribution. The minimum pumping rate was applied to each realization. The results of the more recent Bayer study supported those of the previous study,

for homogeneous flow conditions. Bayer and others (2005) observed overall reduced pumping rate means and variances for BPT, "reflecting that barriers can reduce the sensitivity of pump-and-treat systems to variations in aquifer heterogeneity and, by this, raise the system robustness." The "lower sensitivity and consequently higher robustness is shown by the reduced spreading of the pumping rates and not by the change in mean values, compared to CPT" (Bayer and others, 2005).

Method of economic analysis

To compare and evaluate BPT and CPT economically, scientists analyzed only

- pumping and treatment costs (onsite with GAC sorption)
- additional barrier installation costs

They considered initial and operational payments as well as inflation and discounted cash flow. Total costs were broken down into "cost elements associated with single modules of work and technical equipment" (Bayer and others, 2005). Scientists did not consider elements of comparable cost for BPT and CPT, including investigation, site infrastructure, labor, and monitoring. They considered five major cost factors, including:

- the site size
- the ground water flow rate
- the concentration of contaminants in the pumped water
- the expected time of operation
- the net interest rate for discounting future costs to net present value

Calculation

Bayer and others (2005) further broke down total remediation costs into the following divisions:

- pumping costs
- GAC filling costs
- costs for the on-site treatment facility and for BPT scenarios
- barrier construction costs

Researchers used mathematical regression "based on site characteristics and real cost values" to create cost functions. They used the functions to evaluate "unit price values that are staggered with the quantity purchased and efficiency increments" (Bayer and others, 2005).

Pumping

Researchers limited their analysis of ground water extraction costs to operational costs. These were primarily electricity costs, which depended upon pumping rate and duration due to their combined effect on efficiency. As an example, Bayer and others presented the regression-based calculation of electricity costs in detail because such an approach may "be applied to estimate the costs of any other material consumption or operation of technical devices." This is possible because, as scientists report, "the nonlinearity of a cost function may result from staggered unit costs and/or from a rise in technical efficiency with an increasing number of units processed" (Bayer and others, 2005).

GAC filling

Researchers studied the cost of GAC for aiding remediation. They considered the "direct treatment of the extracted ground water by GAC as a standard technology" though other options exist which would alter cost estimations. They used "the volume of the GAC filling and the length of the exchange period" in their evaluation of GAC cost and assumed "that the contact time within the treatment unit" was great enough to disregard kinetic sorption limitations. They used a nonlinear Freundlich isotherm to describe

"the equilibrium loading of the GAC, which depends on both the GAC and the contaminant type as well as on the concentration of the contaminant in the extracted ground water" (Bayer and others, 2005). The calculations were based upon several assumptions, including:

- a "fairly constant level of concentration over the years" in extracted ground water
- similar concentration values for CPT and BPT

On-site treatment facility and barrier construction

Scientists compiled costs for design and equipment into a flat rate. "The amount of expenditures is assumed to be a function of the rate of extracted ground water" (Bayer and others, 2005). In addition, they considered that the on-site treatment would need to be exchanged after a certain service life (here 10 years) and therefore counted facility costs as repeatedly accruing.

Similarly, "for the BPT scenarios, additional costs accrue for the construction of the hydraulic barrier. These costs are calculated using site installation costs, length of the barrier, vertical extension, and unit price for the barrier installation. It is assumed that barrier construction costs are not subject to maintenance" (Bayer and others, 2005).

Site scenario

Bayer and others (2005) reported that the pump-and-treat scenarios they ran were "compared with respect to total remediation costs within the framework of an example site." The scenarios were set for an operation time of 30 years. The economic model developed considered "only those cost elements that differ between scenarios... Hence, the cost estimates...should be interpreted in terms of cost differences rather than by real total cost values, which are expected to be higher than the values presented."

Researchers designed an example site, 100 m²,

contaminated by chlorinated hydrocarbons. They assumed the site was primarily dominated by *cis*-1,2-dichloroethylene (*cis*-DCE) and therefore approximated remediation costs considering only *cis*-DCE, a confined aquifer and uniform ground water flow. "The pumping well is located 50 meters downgradient of the contamination. The concentration of *cis*-DCE in the pumped water is assumed to be 500 mg/m³" (Bayer and others, 2005).

Cost function

Researchers represented:

- rate of interest, 7%
- inflation rate, 3%
- unit energy demand, 0.007 kWh/m³/m
- total dynamic head, 10 m

They created regression parameters by estimating from Sontheimer et al. (1985) literature isotherm values for GAC and information from consultants for the estimation of real cost values.

Bayer and others (2005) assumed a 10-year maintenance cycle. They installed slurry walls "over the complete aquifer thickness. Unit costs per area of wall differ depending on installation depth as well as stability and impermeability requirements. NFESC (2004) reports prices of €20/m² to more than €500/m²" (Bayer and other, 2005). They did not consider quality to be an impeding factor on overall BPT performance. As a result barrier construction was given a relatively low unit price.

Results

Economic comparison for homogeneous aquifer conditions

Researchers estimated CPT system costs in comparison to the hydraulic analysis for homogeneous aquifer conditions to total €853,000. The GAC filling

expenditures comprise 75 percent of those costs.

They found that BPT system installation was advantageous depending on barrier length and location. For each scenario, Bayer and others (2005) reported that:

- the upgradient (B) does not reduce costs "regardless of length"
- for barrier (E), costs were reduced only "for a barrier length $b > \sim 220$ m"
- for barrier C or D, reduced costs were "obtained at almost any barrier length"

The researchers found scenario E, with a 300-meter barrier, to be the most economical. "Total costs are reduced here to €498,000. The pumping rate is reduced from 54 m³/h (CPT) to 10 m³/h, and as a consequence, GAC filling costs are reduced to €86,000, which represent only 14 percent of the total costs" (Bayer and others, 2005).

Researchers reported a positive relationship between specific on-site treatment costs and "the economic benefit for a BPT application in comparison to a CPT application. Consequently, every parameter that affects the unit treatment costs will possibly affect the ranking of CPT and BPT scenarios" and "the magnitude of discounting the annual cash expenditures for on-site treatment to net present values might be crucial: the lower the discount rate (interest rate), the higher the net present value of the treatment costs for the entire operation time of the remediation system. Therefore, a low discount rate and/or a high inflation rate will favor BPT compared to CPT" (Bayer and others, 2005).

Economic comparison for heterogeneous aquifer conditions

Using hydraulic analysis, researchers also rated the economic performance of BPT under conditions of uncertain aquifer transmissivity. They found BPT setting

E to be the most economical and reliable while C and D both yielded "lower costs than the CPT scenario A. The usefulness of an upgradient barrier B, however, appears to be particularly dependent on the degree of heterogeneity. While it is the worst option for ensemble one, it is the least equivalent to CPT for ensemble two. This might be an indication for a general advantage of the application of BPT that is obtained from blocking the aforementioned high-conductivity channels, which are particularly perceptible in highly heterogeneous aquifers."

Conclusions

Bayer and others (2005) concluded that CPT pumping rates could be significantly reduced with the use of barriers "to hydraulically isolate contaminated aquifer zones" by considering "the influence of site characteristics, technology design, and performance as well as economic factors on the expenditures for remediation system design" in a cost analysis.

Researchers focused on "contamination control rather than on the extent of mass removal" with the goal of establishing "a complete capture of the plume and to treat the extracted water in a dual-bed system via sorptive removal onto activated carbon... For most of the BPT systems examined and for the greater part of the parameter spectrum analyzed, the economic benefit that arises from the pumping rate reduction is substantially larger than the additional costs that have to be paid for construction of the barriers. However, the economic benefit varies significantly depending on the location and the length of the barrier(s). High cost savings can be achieved when the barrier surrounds the contamination along the upgradient edge and at the sides (E). In general, the savings increased with

- increasing treatment costs per unit
- increasing amount of water to be treated

- decreasing net interest rate
- decreasing construction costs per unit barrier length"

In terms of the CPT and BPT analysis researchers performed for heterogeneous aquifer conditions, "the results support the findings of the analysis for homogeneous aquifer conditions with regard to the ranking of BPT and CPT," and "since an additional physical barrier tends to reduce not only the mean pumping rate but also the spread of the probability density curves, the uncertainty about the remediation costs is reduced in two ways. First, the impact of the pumping rate on total remediation costs is diminished as the part of those costs that depend on the pumping rate is decreased. Second, the uncertainty about the remediation costs arising from the uncertainty of the appropriate pumping rate to achieve a complete capture of the plume is reduced" (Bayer and others, 2005).

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Research notes

Trace analysis of methyl tert-butyl ether in water samples using headspace solvent microextraction and gas chromatography-flame ionization detection

Bahramifar, N., Yamini, Y., Shariati-Feizabadi, S. and M. Shamsipur, *Journal of Chromatography A*, Vol. 1042, 2004; <http://www.sciencedirect.com>

Researchers sought to optimize elements of headspace solvent microextraction (HSME) and use the improved methods to evaluate the detection limit and "the dynamic linear range of the proposed method" of methyl tert-butyl ether (MTBE). Improvements were made to stirring rate, temperature and volume of the sample, microdrop and addition of salt (Bahramifar and others, 2004).

Bahramifar and others (2004) carried out a series of examinations involving the variables in question. "All quantifications made in this study were based on the relative peak area of MTBE to the internal standard (toluene) from the average of three replicate measurements."

Based on previous research, scientists reported, "a direct relationship exists between the amount of analyte extracted by HSME and the initial concentration of analyte in the sample. This relationship indicates that HSME quantitative analysis is feasible in nonequilibrium situations once the HSME conditions and the sampling time are held constant" (Bahramifar and others, 2004). Researchers concluded HSME to be an attractive alternative to purge-and-trap methods of limit detection because the range is similar, it is low cost, simple,

and does not suffer from memory effect “since a fresh organic solvent is used for each extraction.” In addition, “comparison of this technique with solid-phase microextraction (SPME) for the determination of MTBE in water samples reveals that the two techniques are comparable in terms of precision, sensitivity and analysis time.” They note that while HSME is superior in many respects, SPME is advantageous in that it doesn’t yield a “solvent peak in the chromatogram” and splitless ‘injection’ may be used (Bahramifar and others, 2004).

Transgenic plants in phytoremediation: recent advances and new possibilities

Cherian, S. and M.M. Oliveira, *Environmental Science and Technology*, Vol. 39, No. 24, 2005; http://pubs3.acs.org/acs/journals/doi/lookup?in_doi=10.1021/es051134l

Great strides have been made in recent years in the use of phytoremediation, an appealing remediation technology because it is economical, effective and aesthetically pleasing. Cherian and Oliveira (2005) reviewed the recent improvements made in phytoremediation in terms of the genetic technologies that have created plant species especially adept at phytoremediation by manipulating characteristics important to phytoremediation, such as “faster growth rate, high biomass, hardiness and tolerance to pollutants.”

The scientists reported, “phytoremediation, the use of plants and their associated microbes to remedy contaminated soils, sediments, and groundwater, is emerging as a cost-effective and environmentally friendly technology. Due in large part to its aesthetic appeal, this technology has gained increasing attention over the past 10 years. Phytoremediation uses different plant processes and mechanisms normally involved in the accumulation, complexation, volatilization, and

degradation of organic and inorganic pollutants. Certain plants, called hyperaccumulators, are good candidates in phytoremediation, particularly for the removal of heavy metals. Phytoremediation efficiency of plants can be substantially improved using genetic engineering technologies. Recent research results, including overexpression of genes whose protein products are involved in metal uptake, transport, and sequestration, or act as enzymes involved in the degradation of hazardous organics, have opened up new possibilities in phytoremediation. This paper provides a critical review of the recent progress made toward the development of transgenic plants with improved phytoremediation capabilities and their potential use in environmental cleanup.” (Cherian and Oliveira, 2005).

Cherian and Oliveira (2005) considered the following phytoremediation strategies:

- rhizofiltration, root system elimination of aquatic waste material
- phytostabilization, plant reduction of the mobility and bioavailability of pollutants in the environment either by immobilization or by preventing their migration
- phytodegradation, plant and microbial degradation of organic contaminants
- phytoextraction, plant removal and concentration of metals from the soil to the harvestable parts
- phytovolatilization, the extraction of “volatile elements such as selenium and mercury (in some cases) from sludge and soils and their release through transpiration to the atmosphere as detoxified vapor”

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