

Underground Tank Technology Update

Vol. 20, No. 3 May/June 2006



uttu.engr.wisc.edu

Department of Engineering Professional Development

Underground Tank Technology Update is an electronic bimonthly publication of the University of Wisconsin-Madison, Department of Engineering Professional Development. *UTTU* supplies useful information to federal, state, and local officials working with groundwater technology and to other interested technical specialists.

UTTU is funded by the U.S. EPA under cooperative agreement No. 82933001 to the University of Wisconsin-Madison, which is responsible for its preparation. Mention of trade names or commercial products does not constitute endorsement or recommendation for use.

Comments and suggestions are welcome and may be directed to [Phil O'Leary](mailto:philoleary@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:jpullman@wisc.edu) (pullman@wisc.edu) or call 608-249-0509.

Advisory Board

Gilberto Alvarez, Environmental Engineer
OUST, U.S. EPA, Region 5, Chicago, Illinois

Bruce Bauman, Research Coordinator
Soil/Groundwater, API, Washington D.C.

Joseph Vescio, Grants Project Officer, OUST, U.S. EPA,
Washington D.C.

Louis Fournier, Ph.D., Chemist and President
STAR Environmental, Inc., Chadds Ford, Pennsylvania

Jeff Kuhn, DEQ, Petroleum Section, Helena, Montana








John T. Quigley, Emeritus Professor, Department of Engineering
Professional Development, UW-Madison

Gerald W. Phillips, U.S. EPA, Region 5, Chicago, Illinois

Staff

Phil O'Leary	Project Director
Jaime Pullman	Science Writer
Darrell Petska	Copy Editor
Debbie Benell	Program Assistant

Brief article summaries

-  **Anaerobic MTBE biodegradation..... 2**
Researchers investigated the process of MTBE natural attenuation. They focused on MTBE's biodegradation under anaerobic conditions and its relationship to TBA levels.
-  **Ethanol: the new oxygenate..... 4**
Scientists studied ethanol as a ground water contaminant. Ethanol's increased use in place of MTBE makes ethanol spills or leaky underground storage tank contamination from ethanol more likely.
-  **DNAPL co-solvent recovery 7**
Researchers examined dense non-aqueous phase liquid areal recovery by alcohol pre-flood and co-solvent flood in dipping aquifers.
-  **Human health risks of polycyclic aromatic hydrocarbons (PAH)..... 10**
Scientists in Taiwan explored the relationship between polycyclic aromatic hydrocarbons and risk of cancer in adults, children and infants based on time, mode and likelihood of exposure.
-  **Petroleum fractions-contamination 13**
Researchers examined the soil and water contamination resulting from an oil storage and distribution station in north-central Mexico. They noted differences between contaminated soil and water in terms of TPH, gasoline and diesel fractions, BTEX, PAH, MTBE and some metals.
-  **Calculating petroleum hydrocarbon plume growth..... 15**
Scientists studied the relationship between aquifer Fe(III) levels and BTEX contaminant plume expansion. Their research resulted in a growth-rate-estimation method.
-  **Reader forum 18**
Readers write in with questions for their fellow UST and remediation specialists.

Free Subscription To receive this electronic newsletter, e-mail [Debbie Benell](mailto:Debbie.Benell@epd.engr.wisc.edu) (benell@epd.engr.wisc.edu) or call 608-263-7428. There is no cost to subscribers. Your e-mail address will not be shared with other organizations.

You can access back issues of *UTTU* from 1998 to the present by visiting the archives at <http://uttu.engr.wisc.edu/issueindex.lasso>



Anaerobic MTBE biodegradation

Researchers investigated the natural biodegradation of methyl-*tert*-butyl ether (MTBE) at a gasoline station in Parsippany, New Jersey. At the site, it had been observed that decreased MTBE concentrations appeared with increased concentrations of *tert*-butyl alcohol (TBA). The scientists constructed microcosms to examine the processes of MTBE attenuation, a subject important because “many states have selected monitored natural attenuation as a remedy for organic contaminants in ground water” (Wilson and others, 2005). They focused on biological transformation as a dominant MTBE attenuation process.

Site

The site under investigation was a retail service station with gasoline contamination from a compromised underground storage tank. The contamination was first detected in 1990. Remediation efforts began with removal of the tank and monitoring well installation. Researchers acquired sediment samples in 2000 and determined that the contaminated wells were characterized by

- methane concentrations near 5 mg/L
- depleted sulfate

With this information and the sediment samples, scientists designed a microcosm study.

The site of investigation was characterized by the following:

- alternating layers of medium to coarse sand extending down 0.9 m
- a layer of silty clay with traces of coarse sand extending 0.9 to 2.1 m
- a layer of coarse sand extending 2.1 to 3.3 m

- a clay layer extending from 3.3 to 4.6 m below land surface
 - a ground water depth varying from 0.30 to 1.22 m
- Microcosm sediment samples were obtained from 0.61 to 1.22 m and 1.22 to 1.83 m below land surface with a water table of 1.22 m below land surface.

Monitoring wells were screened from 0.6 to 4.6 m below land surface. The direction of ground water flow varied from the northwest to the southeast, with predominant direction of ground water flow being to the east. “At the time they were installed, four wells at the site produced water with relatively high concentrations of BTEX (benzene, toluene, ethylbenzene, and xylenes) compounds as well as MTBE and TBA.” The well with the highest concentration (MW-5) was 20 meters west of the tank pit containing the leaking underground storage tanks (USTs). The other wells (MW-6, MW-10, and MW-11) were north of MW-5 and west of the tank pit. The most contaminated wells were upgradient from the source. There were screened in an area having residual oily phase gasoline (Wilson and others, 2005).

Concentrations

Scientists observed persistent BTEX and toluene concentrations at wells MW-5, MW-6, and MW-11. Wilson and others (2005) explained, “This implies that residual gasoline in the proximity of these wells acted as a continuing source of BTEX compounds to ground water. The reduction in concentration of toluene was first order on time, as would be expected if the concentration of toluene were controlled by the dissolution and mass transfer of toluene from residual gasoline to the flowing ground water.” TBA concentrations in 2000 “were consistently manifold higher than the concentrations of MTBE.” The monitoring wells’ “relative concentration of TBA increased with distance away from MW-5. The concentration of TBA also increased over time in

individual monitoring wells. This is anecdotal evidence that the TBA in the ground water was produced from biodegradation of MTBE and not from TBA that was originally present in the gasoline” (Wilson and others, 2005).

Methods

Microcosms

Researchers began by obtaining sediment samples from “near MW-6 because it occupied an intermediate position in the plume and because the field data suggested that natural biodegradation of MTBE at that location in the plume was extensive but was not complete. The sediment was collected and stored in 1-L glass jars. To protect the anaerobic microorganisms that might be present in the samples from oxygen in the atmosphere, the headspace above the sediment was replaced with ground water from MW-6 immediately after collection” (Wilson and others, 2005).

Researchers performed microcosm preparation in an anaerobic glove box. An oxygen meter ensured that the gas in the glove box had less than 1 ppm oxygen by volume. They created microcosms by adding MW-6 ground water to the sediment to create a slurry and then loading the slurry into 25-ml glass serum bottles. They sealed the microcosm samples with a Teflon-faced gray butyl rubber septum and a crimp cap and stored them at room temperature.

Analysis

Researchers determined MTBE and TBA concentrations by headspace gas chromatography/mass spectrometry, and sulfate and nitrate plus nitrite nitrogen concentrations by capillary electrophoresis. “Prior to sampling, while the microcosms were still sealed, the contents of each microcosm were mixed with a vortex mixer and then the sediment was allowed to settle. The septum was removed, and 1 mL of the standing

water was taken and diluted in 14 mL of distilled water containing 1% trisodium phosphate as a preservative" (Wilson and others, 2005). Researchers determined hydrogen and methane concentrations from sample headspaces and diluted samples. They used the Biologically Available Iron Assay to determine the concentration of biologically available iron in the sediment samples.

Results

MTBE in microcosms

Four treatments were set up with the following initial concentrations of MTBE, TBA and, in the fourth case, sulfate:

- control microcosms (constructed with autoclaved sediment), 1.3 ± 0.14 mg/L of MTBE and 1.1 ± 0.19 mg/L of TBA
- living microcosms, 2.1 ± 0.31 mg/L of MTBE and 1.0 ± 0.008 mg/L of TBA
- living microcosms, 1.8 ± 0.58 mg/L of MTBE and 1.3 ± 0.32 mg/L of TBA and 120 mg/L of sulfate

Wilson and others (2005) incubated microcosms at 0, 30, 58, 86, 177 and 199 days, analyzing three microcosms from each treatment after each period of incubation. They observed the following:

- "no significant consumption of MTBE or production of TBA in the autoclaved controls during 199 days"
- "no significant consumption of MTBE or production of TBA in the living microcosms after 30 or 58 days"
- significant MTBE removal in the living microcosms after 86 days
- MTBE concentrations below the detection limit in the microcosms after 177 days

Researchers then calculated the rate constant for removal of MTBE. The rate in the following experimental treatments was:

- MTBE, 11 ± 2.7 per year.
- MTBE and sulfate, 12 ± 2.9 per year
- TBA, 11 ± 2.3 per year
- autoclaved controls, (not statistically significant) 0.66 ± 0.96 per year

TBA in microcosms

Wilson and others (2005) reported microcosm TBA production to be twice "the amount that would be expected from the metabolism of MTBE that was present in the pore water." In addition, "The 'spike recovery' of MTBE in the dose solutions from the pore water of the microcosms was 27% and 56%. This suggested that approximately half of the MTBE in the microcosms was sorbed to the sediment. The TBA may have been produced from MTBE that was originally sorbed to the sediments used to construct the microcosms. The microcosms that were amended only with MTBE had significant concentrations of ethylbenzene plus xylenes and total trimethylbenzenes. It is likely that the sediment used to construct the microcosms contained residual non-aqueous phase gasoline and that the MTBE was partitioned to the gasoline."

Physiological processes

Researchers' examination of the plume found the following:

- plume edges contained low methane concentrations, nitrate concentrations over 0.8 mg/L, and sulfate concentrations over 20 mg/L
- the inner plume was depleted of sulfate and accumulated methane
- throughout the plume nitrate concentrations were < 0.1 mg/L

Researchers noted, "In 1999, the concentration of iron II in MW-5 was 18 mg/L. Dissolved oxygen was not detected. Natural biodegradation in the plume must

occur under anaerobic conditions and specifically under iron-reducing, sulfate-reducing, or methanogenic conditions" (Wilson and others, 2005).

The researchers postulated that MTBE might be degraded by iron-reducing bacteria, though other degradation possibilities could include acetogenic bacteria, which combine MTBE with carbonate and molecular hydrogen to produce acetate and TBA. They also suggested the possibility that "the organisms that degrade MTBE at the Parsippany site act by a direct hydrogenation of the ether bond in MTBE to TBA and methane. In this process, MTBE would serve as an alternate electron acceptor. In either case, degradation of MTBE would require molecular hydrogen as a source of reducing power and carbonate as either a co-substrate or a growth substrate" (Wilson and others, 2005).

MTBE degradation

Wilson and others (2005) reported:

- alkylbenzenes degraded before MTBE
- anaerobic biodegradation of alkylbenzenes to methane and carbon dioxide produced molecular hydrogen
- molecular hydrogen concentrations "were usually at least an order of magnitude lower than the concentrations that would be expected from the metabolism of the alkylbenzenes initially present in the pore water of the microcosms," which may be due to the consumption of hydrogen during anaerobic biodegradation of MTBE

Researchers also found that "The microcosms that contained aquifer sediment contained appreciable concentrations of methane; concentrations ranged from 11.7 to 13.7 mg/L... In the plume, the highest concentration of TBA (2.3 mg/L) was associated with the highest concentration of methane (6.6 mg/L).

Only 0.51 mg/L of methane would be expected from production of 2.3 mg/L of TBA. This is 8% of the methane actually present in the ground water at field scale. Methane may have been produced during anaerobic metabolism of MTBE to TBA, but the amount of methane produced by metabolism of MTBE was inconsequential compared to methane produced by other processes, such as the anaerobic biodegradation of BTEX compounds" (Wilson and others, 2005).

"The postulated processes of MTBE carboxylation (degradation by acetogenic bacteria) and direct MTBE hydrogenation (MTBE as an alternate electron acceptor), as well as chemolithotrophic methanogenesis, all consume hydrogen and lead ultimately to the production of methane... The calculations suggest that in the microcosms, the free energy for chemolithotrophic methanogenesis, MTBE carboxylation, and MTBE hydrogenation is roughly equivalent. The free energy is lower than would be expected for processes using conventional soluble electron acceptors such as oxygen, nitrate, and sulfate. The calculations also suggest that under conditions to be expected in the aquifer, the free energy for MTBE carboxylation and MTBE hydrogenation is greater than the free energy for chemolithotrophic methanogenesis, and that MTBE-degrading organisms may have a competitive advantage over chemolithotrophic methanogens" (Wilson and others, 2005).

Wilson and others (2005) summarized, "The physiological mechanism of anaerobic MTBE biodegradation at the Parsippany site is still unclear... Enrichment with sulfate and nitrate failed to produce MTBE-degrading cultures. Enrichment with hydrogen produced cultures that degraded MTBE to TBA and produced methane. The methane could have been produced directly by an organism that hydrogenates MTBE or could have resulted from further metabolism of acetate produced by an MTBE-carboxylating organism.

At present, the enrichments are mixed cultures, and it is impossible to distinguish the two processes."

MTBE anaerobic biodegradation

Scientists noted that, "biodegradation of MTBE in water from well MW-5 was limited. At most, only 16% of the MTBE had degraded." However, the percent MTBE degraded was 60 or greater at MW-6, 7, 10 and 11 (Wilson and others, 2005).

Conclusion

Scientists concluded that, "In three experimental treatments in this microcosm study, the rate of MTBE transformation to TBA varied from 11 ± 2.3 per year to 12 ± 2.9 per year... The microcosm study documented that the aquifer harbored organisms that were capable of rapidly degrading MTBE under anaerobic conditions. Considering the usual residence time of ground water at UST spill sites, these rates are effectively instantaneous. To date, most field studies of MTBE have been conducted on large plumes that show little indication from their behavior that natural biodegradation is an important mechanism." In contrast the site of study was small, with rapid ground water flow and a decade-old spill where "the plume of ground water contamination could be hundreds of meters long. The direction of ground water flow varied from the northwest to the southeast, with the predominant direction of ground water flow being east. Despite the opportunity for transport of MTBE, there is little evidence of transport of MTBE to the west, to the north, or to the east of the perennial source area of MTBE in ground water. Rapid biotransformation of MTBE to TBA would confine MTBE in ground water to the region where the plume is being continually generated by dissolution of fuel components from residual gasoline in the aquifer. In the plume at field scale and in the microcosm study, MTBE was degraded to TBA. There was no evidence for natural biodegradation of TBA in the laboratory

microcosm study, and TBA accumulated in the downgradient portion of the plume at field scale."

Reference

Wilson, J.T., Adair, C., Kaiser, P.M. and R. Kolhatkar, "Anaerobic biodegradation of MTBE at a gasoline spill site," *Ground Water Monitoring & Remediation*, Vol. 25, No. 3, Summer 2005; www.ngwa.org

UTTU thanks Dr. John Wilson, Wilson.JohnT@epamail.epa.gov, for his help on this article.



Ethanol: the new oxygenate

Scientists at the University of Nebraska-Lincoln investigated contamination from ethanol spills and leaks from underground storage tanks (LUSTs). Such occurrences are expected to increase with the growing use of ethanol in the place of methyl *tert*-butyl ether (MTBE) as a fuel oxygenate.

Zhang and others (2006) reported, "MTBE degradation is slow and the transformation products are potentially more toxic than MTBE. In laboratory studies ethanol was rapidly mineralized to nontoxic products in both aerobic and anaerobic conditions. Since 1990 ethanol releases at fermentation plants, distribution facilities, and from both truck and rail tankers in Nebraska have ranged from a few to 30,000 gallons. Ethanol diesel and ethanol gasoline releases also have been documented. Gasohol releases from LUSTs have been reported in Kansas ground water." Small ethanol releases, compared to MTBE releases, have been shown to have little to no impact on ground water "unless the releases occur in very shallow water table areas (< 100 cm to ground water)," but the impact of large ethanol releases is not yet understood. "Ground water concentrations of ethanol typically are not reported at LUST sites because ethanol is

an unregulated contaminant, has low toxicity and persistence and is difficult to measure in trace amounts." The researchers sought to "evaluate the fate and transport of ethanol under transient conditions in a sand and gravel aquifer and to simulate the results with a commonly used 3-dimensional (3-D) solute transport model" (Zhang and others, 2006).

Materials and methods

Site

Zhang and others (2006) conducted their research at a site in Merrick County, Nebraska. The site consisted of:

- "furrow-irrigated farmland used for corn production and previously for an amended denitrification study using ethanol or acetate as carbon sources"
- unconfined primary aquifer, 12.2-meters-thick fluvial sand and gravel
- water table 3.1 meters below land surface
- ground water pH of 6.5
- aquifer sediments containing "indigenous microbes capable of degrading ethanol"

The aquifer contained vertically uniform concentrations of the following:

- 40 mg $\text{NO}_3\text{-N L}^{-1}$
- 60 mg $\text{SO}_4^{2-} \text{L}^{-1}$
- 6 mg L^{-1} dissolved oxygen
- bromide and ethanol, 0.3 to 0.5 mg/ L^{-1}

Researchers employed a screened 10-cm-diameter injection well (IW) and a screened 15-cm-diameter extraction well, 12.2 meters apart. Multilevel samplers (MLSs) four through eight comprised "the first fence downgradient from the injection well" while MLSs one through three made up the second downgradient fence. The scientists constructed the MLSs from "0.94-cm high density polyethylene (HDPE) tubing with stainless steel

screens held in place with a HDPE ferrule fastened to a piezometer with plastic bundle ties at appropriate intervals." The piezometer was "2.5-cm-diameter schedule 40 PVC pipe with a 0.6 meter slotted interval capped at the bottom." The MLSs facilitated "the collection and analysis of spatial and temporal data that characterize the fate and transport of the solutes" (Zhang and others, 2005).

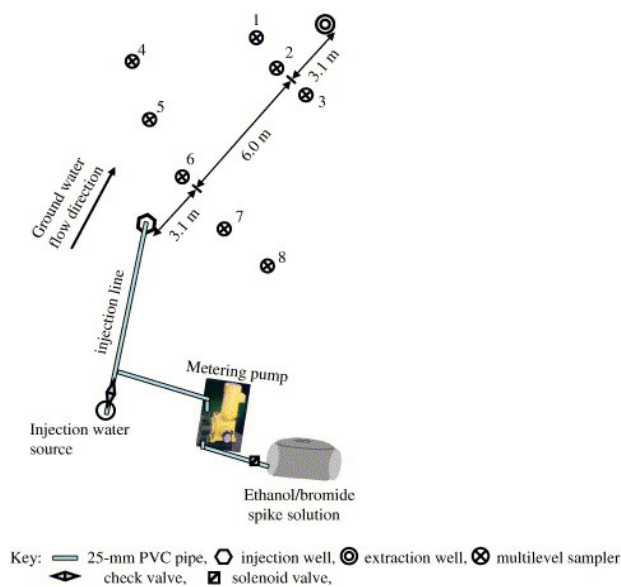


Figure 1: Plan view of ethanol study site (From Zhang and others, 2006).

Spiking

Researchers created a 605-L spiking solution containing:

- 15.64 L ethanol
- 0.68 kg bromide
- extracted groundwater

They injected for 27 hours, during which "the spiking solution was fed through a diaphragm pump at a flow

rate of $0.02 \text{ m}^3 \text{ h}^{-1}$ and mixed with water extracted at a rate of $1.85 \text{ m}^3 \text{ h}^{-1}$ from a nearby 35.3-m-deep well which tapped the secondary aquifer. Water from the deep well was anaerobic and contained no detectable nitrate, 20 mg $\text{SO}_4^{2-} \text{L}^{-1}$ and 340 mg L^{-1} as CaCO_3 alkalinity. The resulting injectate contained 220 ± 7.4 mg ethanol L^{-1} and 16 ± 1.8 mg bromide L^{-1} " (Zhang and others, 2005).

In situ injection

Researchers set the IW with an inflatable packer 11.6 meters below ground. The packer was set to "inject 50,000 L ethanol/bromide solution into the bottom 3.1 m of the primary aquifer. The pressure injection forced the injectate to move immediately into the aquifer formation through the 3.1 m section of well screen. A hydraulic gradient to the extraction well was established by pumping the extraction well at the rate of $9.1 \text{ m}^3 \text{ h}^{-1}$ for 2 days prior to the injection. During injection the extraction well pumped at a rate of $4.5 \text{ m}^3 \text{ h}^{-1}$ to initially direct plume toward the multilevel fence." When injection was complete, researchers turned off the well. "Initial pumping of the extraction well combined with pressurized injection created a hydraulic condition in which the plume was transported under forced gradient flow; however, this gradient dissipated quickly when injection and extraction ceased and natural flow conditions resumed" (Zhang and others, 2006).

Sampling and analysis

With a peristaltic pump, scientists collected ground water samples from depths of 10.6, 12.2, 13.4 and 14.6 meters at five downgradient MLSs. They monitored the plume for 2.5 months, collecting samples daily during the first three weeks and twice a week after. Zhang and others (2006) kept samples in an ice cooler at 4°C until analysis. They used 40 ml VOC vials to collect ethanol samples. They analyzed the samples using solid-phase microextraction and gas

chromatography/mass spectrometry. They collected samples for bromide, nitrite, nitrate and sulfate with 40 ml polyethylene bottles, then filtered and analyzed them using ion chromatography.

Transport model

Scientists employed a modular three-dimensional transport model (MT3D) "in conjunction with MODFLOW to simulate the transport of the bromide/ethanol plume under transient conditions... Ground water head data by MODFLOW were used to compute ground water flow velocities, which then were used in MT3D to compute contaminant transport and degradation" (Zhang and others, 2006).

Zhang and others (2006) explained, "The 150 × 150 m area was divided into 1.5 × 1.5 m grids. The aquifer depth was divided into two layers to account for partial penetration of the injection well. The top layer extends 9.1 m below the water table, while the bottom layer containing the well's screened interval is 3.1 m thick. Constant heads were assigned to the upgradient (515.2 m) and downgradient (515.9 m) boundaries of the model area. The top and bottom domain boundaries were oriented parallel to the direction of regional groundwater flow. Given the small volume of solution/water injected into and extracted from the aquifer, the boundaries had no effect on the flow condition in the central part of the domain where the injection and extraction wells were placed."

Results

Researchers found that the breakthrough curves showed virtually equivalent transport times for ethanol and bromide. They attributed variance in flow velocities between the first and second fences to "transient conditions associated with the initial pumping of the extraction well. Velocity differences with depth at a multilevel sampler appear related to aquifer heterogeneity" (Zhang and others, 2006).

Zhang and others (2006) determined that the core of the plume was "centered on an axis" between the inner fence at ML-6 and the outer fence at ML-1. Injectate concentrations were greatest at depths with the highest groundwater velocities. They observed the following:

- ML-5 and 6: bromide and ethanol breakthrough appeared after 1.5 days, not detected after day 16.
- ML-1: the plume centroid arrived at 12.2 m after 15 days, with maximum bromide and ethanol concentrations of 12 mg L⁻¹ and 4.35 mg L⁻¹, respectively

These results may be explained by preferential flow in that it "resulted in differently shaped bromide and ethanol breakthrough curves and variable peak breakthrough transport times at the second MLS fence."

Scientists also found that "peak bromide concentrations occurred in ML-2 15 days after appearing at ML-1. Unlike ML-1, ML-2 did not appear to be in an immediate hydraulic connection with transport from the injection well. Bromide arrived on day 25 at the 12.2 m depth and on day 16 at a 13.4 m depth. Peak ethanol concentrations at these depths were 4.28 and 1.2 mg L⁻¹, respectively. Although bromide persisted, ethanol was rapidly degraded throughout transport from the injection site, and about 97% of the initial ethanol was depleted when the plume left the second fence of MLSs" (Zhang and others, 2006).

The scientists also determined that the relative-core bromide concentration was 0.9 at ML-6 and 0.75 at ML-1. They reported, "The observed decrease was due to dispersive mixing of the injectate with 10% ambient ground water at the first fence and with 25% ambient ground water at the second fence. Mixing of injectate plume with the ambient ground water containing 40 mg NO₃-N L⁻¹, 60 mg SO₄²⁻ L⁻¹, and 6 mg dissolved oxygen L⁻¹ resulted in total deoxygenation, denitrification and sulfate reduction within 20 days

at ML-1. In order to estimate the amount of ethanol metabolized in these three reduction processes, concentrations of dissolved oxygen, nitrate and sulfate in the plume were input into stoichiometric equations." Researchers determined that ML-6 bromide dispersion resulted in the following:

- 10% reduction in ethanol concentration in the plume's core
- 13% ethanol consumption during deoxygenation (0.2%), denitrification (8.3%), and sulfate reduction (4.5%)
- "The remaining ethanol (77%) appears to have been transformed in anaerobic processes such as fermentation, methanogenesis, and cell growth."

Researchers noted that "anaerobic degradation of ethanol to acetic acid (acetogenesis) and methanogenesis are the major processes for ethanol degradation in anaerobic plume cores. After the ethanol was depleted, nitrate and sulfate concentrations rebounded to background levels in ML-1" (Zhang and others, 2006).

For the transport simulation, researchers based bromide breakthrough curve simulations on "a uniform hydraulic conductivity and uniform dispersivities throughout the domain. Therefore, the model lacked the ability to reproduce the demonstrated tailing in the field data. Tailing appeared dependent on transport time and was considerably more pronounced at the second fence. In order to more closely match the simulated bromide concentrations with the field data, adjustments would be necessary for heterogeneity within the three-meter-thick injection zone" (Zhang and others, 2006).

For ethanol breakthrough curves, researchers created simulations by varying the ethanol *k* from 0.2 to 0.5 per day, vertically as well as transversely ranging from 0.25 to 0.4 d⁻¹ and averaging 0.32 d⁻¹. "The sensitivity of the simulated ethanol to change in dispersivity was

assessed by simulating the degradation constants for a set of varying longitudinal and transverse dispersivities. The ethanol varied by a factor of approximately two and was more sensitive to changes in longitudinal dispersivity." Researchers also evaluated the simulated ethanol's sensitivity to horizontal aquifer hydraulic conductivity using simulated values for fine sand versus very coarse sand and gravel. "Analysis of sensitivity of the simulated ethanol to changes in porosity indicated that a 5 percent change in porosity did not significantly impact transport" (Zhang and others, 2006).

Conclusion

Zhang and others (2006) concluded, "At the first and second fences, relative bromide concentrations in the plume centroid were 90% and 75% of the injectate, respectively. Ethanol degraded rapidly with a first-order rate constant of 0.32 d^{-1} . Most of the ethanol appeared to be transformed by anaerobic processes such as fermentation and methanogenesis. Ethanol transport was not retarded. Field data and simulations indicated that ethanol did not migrate a substantial distance beyond the injection well, and 97% was biodegraded after one month. Simulated ethanol degradation rates are dependent upon using representative hydraulic conductivity and longitudinal and transverse dispersivity in the model."

Reference

Zhang, Y., Kahn, I.A., Chen, X. and R.F. Spalding, "Transport and degradation of ethanol in groundwater," *Journal of Contaminant Hydrology*, Vol. 82, p. 183-194, 2006; www.elsevier.com/locate/jconhyd



DNAPL co-solvent recovery

Researchers used a two-dimensional (2D) laboratory model to evaluate gravity's effect on "areal recovery of a representative dense non-aqueous phase liquid (DNAPL) contaminant by an alcohol pre-flood and co-solvent flood in dipping aquifers." Previous research indicated that injected alcohol and co-solvent solution may reduce "in-situ the density of DNAPL globules and displace the contaminant from the source zone. However, contact with aqueous alcohol reduces interfacial tension and causes DNAPL swelling, thus facilitating risk of uncontrolled downward DNAPL migration." Scientists also sought to examine the relationship between dip angle on areal displacement and DNAPL recovery efficiency during in-situ treatment (Boyd and others, 2006).

Materials and methods

Boyd and others (2006) used perturbation (fingering) analysis "to evaluate fluid and flow conditions that affect the stability of a flood front in an ideal aquifer at the horizontal and dip-angle orientations." They reported, "When an aquifer has a dip angle, the density difference between the displacing fluid and the displaced fluid will have a pronounced effect on the growth of the perturbation with time. The efficiency of the displacement process will be affected by the relative positions of the displacing and displaced fluids as well as the direction of flow. A dip angle therefore will affect the development of fingers and consequently affect the areal recovery efficiency for a given hydraulic condition." The resulting figures, used with Darcy's equation, allowed researchers to calculate the pressure in the displaced and displacing phase.

Researchers used a specially designed 2D laboratory apparatus to simulate the cross-sectional ground water and contaminant flow. The apparatus consisted of:

- a stainless steel frame
- two sheets of 1.27-cm tempered glass, enclosing the frame
- 0.15-cm Viton gaskets, sealing the chamber
- two 2.03-cm-diameter steel rods, welded to the frame
- 22.1 kg of 0.45-mm glass beads, filling the chamber
- stainless steel mesh fencing, dispersing the background gradient flow

The apparatus was assembled and bolted closed. Researchers drilled the top sheet of glass with 17 symmetrically spaced ports, which were then "fitted with a 5-cm plug contained within a specially manufactured fitting and connected to control valves with 0.8-mm Teflon tubing. Flow was controlled by peristaltic pumps. Six of the ports were used to simulate a double-triangle well pattern." They used a port at each end of the chamber "to simulate a background aquifer flow. The 2D areal plane was fixed in the horizontal position or rotated and fixed at a dip angle of 15° or 30° by adjusting the rotation control handle" (Boyd and others, 2006).

Researchers used PCE, dyed red, to represent DNAPL. They prepared an aqueous isobutanol solution for a pre-flood "to reduce the density of trapped PCE. Another solution was prepared for viscosity control and used as a co-solvent flood by mixing 65% ethylene glycol and 35% 1-propanol for 24 hours prior to use. Ultra-pure water was used for all experimental work" (Boyd and others, 2006).

Experimental procedures

Researchers used liquid chromatography analysis and an UV diode array detector to find PCE concentrations. Prior to all experiments, they saturated the porous media with water, set the chamber in a vertical position and injected water through the lower port. Displaced air was released through the upper port until the chamber was filled with water. The chamber was then positioned horizontally and locked in place. Boyd and others (2006) contaminated the porous media by "releasing 50-mL or 100-mL PCE through a port located in the center of the model and driven by gravity flow. After contamination, the source zone was flooded with water to further disperse the free product until the contaminant was reduced to an immobile, trapped PCE saturation using an injection rate of 0.3 mL/min per well. This flow rate was based on a field-to-laboratory scaling parameter that relates viscous force and displacement distance to capillary force for NAPL displacement in porous media and a description of a typical NAPL remediation site. A prototype of the 2D model was used to determine maximum NAPL recovery for a range of injection flow rates."

For dip-angle experiments, researchers conducted the simulated PCE "within the center of the porous media by rotating the model chamber at an incline of 10° until the contaminant was reduced to an immobile, trapped PCE saturation." They then injected water through the central port "used for the contamination at a flow rate of 20 mL/min with recovery through the six surrounding wells. After 24 hours of water flooding, the central port was closed. Trapped, immobile PCE saturations after water flooding were calculated in the range of 6% to 14% of the pore volume using the PCE volume divided by the pore volume of the contaminated source zones" (Boyd and others, 2006).

For chemical pre-flooding, scientists pumped aqueous isobutanol "across the PCE source zone using three

injection wells and the double-triangle well pattern at an injection rate of 1.2 mL/min per well. This aqueous isobutanol pre-flood was used to pre-condition trapped PCE by reducing its density. For inclined experiments, the model was rotated to the desired dip angle at the start of the aqueous isobutanol pre-flood. After 24 hours of operation, the pumps were turned off and the aqueous isobutanol solution was allowed to stand for another 36 hours. Next, the source zone was flooded by injecting 4 L of a solution of ethylene glycol/1-propanol for 4 hours at a rate of approximately 5.5 mL/min per well. Thereafter, for the remainder of the simulated cleanup operation, water was pumped through the contaminated source zone at an injection rate of 5.5 mL/min per well for approximately 4-6 hours. For the duration of the experiment, the background gradient flow was maintained with constant head across the 2D model." Upon completion of each experiment, scientists flushed the chamber with methanol, followed by ultra-pure water (Boyd and others, 2006).

Scientists performed each remediation experiment at least twice. Samples collected from the extraction wells were analyzed for PCE using Hewlett Packard liquid chromatography (HPLC) within 48 hours of collection, and 10% "were selected randomly and analyzed in duplicate for quality control" (Boyd and others, 2006).

Horizontal orientation

For the three experiments involving horizontal orientation of the chamber, scientists performed two scenarios with 50 mL spilled neat PCE. "In the first scenario, injection was performed opposite to the direction of the background gradient flow. In the second scenario, injection was performed in the same direction as the gradient flow. A third scenario was studied by spilling 100-mL PCE and injecting opposite to the direction

of the background gradient flow" (Boyd and others, 2006).

For dip-angle orientation experiments, researchers inclined the 2D model "at 15° or 30° to investigate effects of gravity on areal PCE recovery efficiency. Contamination was simulated by spilling 50-mL PCE, and injections were all performed in the same direction as the background gradient flow." The background influent and injected flooding solutions were applied from the elevated end and recovered from the lower end of the model (Boyd and others, 2006).

Boyd and others (2006) also conducted sensitivity experiments "to evaluate effects of the alcohol pre-flood on PCE mobilization and areal recovery efficiency. Instead of injecting aqueous isobutanol for 24 hours followed by 36 hours of contact, these sensitivity experiments were performed by allowing trapped PCE contact with the background gradient flow for 60 hours after completing the water flood stage of the remediation scheme. Experiments were conducted with the 2D model oriented in the horizontal position, at the 30° dip angle with downward flow and at the 30° dip angle with upward flow."

Results and discussion

Researchers found "minimal PCE recovery (0.1-0.3%) occurred during the water flood, the alcohol pre-flood and the contact stage (0-84 hours)" during horizontal orientation. "Most PCE recovery in the horizontal orientation occurred during the co-solvent flood stage (84-96 hours)." Similarly, the scientists observed minimal PCE recovery during the water flood stage (0-24 hours) for dip-angle orientation experiments. "Some PCE recovery occurred in the dip-angle experiments during the alcohol pre-flood stage (24-48 hours), but most of the PCE recovery occurred during the co-solvent flood stage (84-96 hours)" (Boyd and others, 2006).

The scientists reported, "during the alcohol pre-flood,

trapped PCE globules swelled as a result of isobutanol partitioning. Modified PCE globules were observed to coalesce and form a NAPL bank allowing some downward migration of the contaminant. The zone of contamination was visually inspected through the top and bottom glass plates and the plume was observed to expand during the alcohol pre-flood" (Boyd and others, 2006).

The scientists also observed PCE partitioning and downward migration. "In all experiments, PCE was observed to move...toward the injection ports as well as concurrent with flow to the extraction ports, regardless of the dip angle and flow direction. The observed PCE movement was attributed to preferential partitioning of PCE into the aqueous isobutanol phase... PCE also was observed to migrate downward during the alcohol pre-flood in the downward flow dip-angle experiments" (Boyd and others, 2006).

Boyd and others (2006) reported, "During the co-solvent flood stage, PCE initially was recovered from the extraction wells as free product, and then the effluent changed to milky white or pink, indicating a highly miscible displacement process. After completing the remediation process, most of the unrecovered PCE remained outside of the capture zone as viewed from the bottom as a result of uncontrolled migration and bypassing of the extraction wells. The distribution of unrecovered PCE was greater for dip-angle experiments, regardless of whether the flow was applied in the downward or upward direction." Experiments without the alcohol pre-flood yielded relatively small PCE recovery "as free product (1-2 mL) at the beginning of the co-solvent flood." After completing the remediation process, "most of the unrecovered PCE remained within the capture zone as small PCE globules as viewed from the bottom of the 2D model. No remaining PCE was visible through the top plate."

Preliminary experiments conducted by the researchers had focused on "the effects of spill volume and the relative direction of the background gradient flow on PCE recovery using the 2D model in the horizontal orientation." Results from these investigations "indicate that the maximum recovery of a 50-mL PCE spill was 86 to 93 percent of the original source zone contamination, regardless of whether the injection was oriented in the same direction or opposite to the direction of background flow." Efficiency was not influenced by plume size. Perturbation analysis by researchers indicated "that the trailing front is stable, whereas the leading front is unstable during the alcohol pre-flood and the co-solvent flood stages... Instabilities at the leading front are exacerbated at greater dip angle for the alcohol pre-flood in the downward flow direction" (Boyd and others, 2006).

In dip-angle orientation experiments in "the horizontal orientation, PCE recovery was less than 0.3% after the alcohol pre-flood and contact period. Although interfacial tension was reduced and NAPL swelling and density reduction likely occurred, free product PCE was not displaced during the alcohol pre-flood when the 2D model was oriented in the horizontal plane. PCE concentrations in the extraction wells were measured in the soluble range during the alcohol pre-flood stage" (Boyd and others, 2006).

When researchers conducted dip-angle experiments in the downward flow direction, "effluent samples collected at the extraction wells during the alcohol pre-flood included mixtures of free product and soluble PCE. When PCE swelling was combined with interfacial tension reduction and gravity, some of the modified PCE moved downward, thus causing early PCE breakthrough and bypassing of the extraction wells." Researchers found PCE recovery values to include:

- 7-13% at 15° dip-angle, after the alcohol pre-flood and contact period
- 11-14% at 30° dip-angles, after the alcohol pre-flood and contact period

Experiments in the upward flow direction yielded effluents containing free-phase mixtures. PCE recovery was 2-3% at the 30° dip-angle, after the alcohol pre-flood and contact period. "These results therefore demonstrate that the alcohol pre-flood caused uncontrolled migration of PCE in the dip-angle experiments, which resulted in reduced PCE recovery after the co-solvent flood and completion of the remediation scheme" (Boyd and others, 2006).

Researchers report that the greatest recovery, 89-93%, occurred in the horizontal plane during the co-solvent flood stage (84-96 hours). Recovery in the downward direction was decreased at the 15° dip angle, 70-77%, and was further reduced at 30° (57-59%). "Similarly, low PCE recovery was observed for injection in the upward flow direction at the 30° inclination (57-60%). For both downward and upward flow experiments, PCE was observed to preferentially migrate and partition into the aqueous isobutanol solution phase during the alcohol flooding stage." The researchers attributed lower PCE recovery "to flooding front instabilities and partitioning of PCE at greater dip-angle orientations that occurred during the alcohol pre-flood stage" (Boyd and others, 2006).

Boyd and others (2006) reported, "Thus, when the 2D model was operated with a dip angle and the alcohol pre-flood was used as a part of the remediation scheme, gravity tended to exaggerate bypassing of PCE at the recovery wells, causing lower PCE recovery, regardless of the direction of flow. These experimental results and predictions therefore demonstrate the potential adverse effects of using an alcohol pre-flood to clean up DNAPL in a dipping aquifer."

Conclusions

Researchers concluded that PCE recovery was greatest at the horizontal orientation. "Lower PCE recovery was observed for experiments conducted at the dip-angle orientations and attributed to PCE mobilization and uncontrolled migration, and the formation of fingering at the flooding fronts. Fingering caused bypassing of the recovery wells and, as a result, more PCE migrated outside of the capture zone and yielded lower PCE recovery. Additional study results demonstrate that the use of an alcohol pre-flood improved PCE recovery in the horizontal orientation, but the alcohol pre-flood reduced PCE recovery in dip-angle experiments in both the downward and upward flow directions" (Boyd and others, 2006).

"Results of this study can be used in planning and design of chemical flooding processes for ground water remediation. Perturbation (fingering) analysis can be used to predict the stability of the chemical flooding fronts for various injection sequences and dip-angle orientations. Displacement fronts should be designed for minimal fingering, thus providing optimal areal recovery efficiency during each stage of flooding. Laboratory testing methods and PCE recovery data developed by this study also can be used as a guide for predicting the potential risk of downward DNAPL migration in dipping aquifers. And finally, results of this study can be used as a guide in selecting well locations and in designing well patterns for specific contaminated sites and remediation schemes. The design of injection and recovery well patterns should ensure sufficient capture area by considering effects of contaminant expansion during pre-flooding" (Boyd and others, 2006).

Reference

Boyd, G.R., Li, M., Husserl, J. and A.M. Ocampo-Gomez, "Dip-angle influence on areal DNAPL recovery by co-solvent flooding with and without pre-flooding,"

Journal of Contaminant Hydrology, Vol. 82, pp. 319-337, 2006; www.elsevier.com/locate/jconhyd

UTTU thanks Dr. Glen Boyd, glen.boyd@hdrinc.com, for his help on this article.



Human health risks of polycyclic aromatic hydrocarbons (PAH)

Scientists evaluated the relationship of polycyclic aromatic hydrocarbons (PAH), known carcinogens, to cancer risk in adults, children, and infants. Chen and Liao (2005) reported, "The relationship between cancer and the environment is largely conditioned by investigations involving PAH exposures. Several individual PAHs such as benzo[a]pyrene (B[a]P), chrysene, indeno[1,2,3-c,d]pyrene, and benzo[b]fluoranthene have produced carcinogenic, mutagenic, and genotoxic effects in animal experiments." The scientists developed a probabilistic risk assessment for evaluating the carcinogenic risk in industrial, urban and rural areas of PAH exposure. They considered inhalation and dermal contact as routes of exposure as well as indoor and outdoor air quality.

Materials and methods

Chen and Liao (2005) used previous research by Fang et al. (2004), and Tsai et al. (2004) that examined total PAH and particle-bound PAH concentrations as sources of empirical data. Work by Fang et al. (2004) examined Taichung Industry Park and a suburban area, Tunghai University, for PAH concentrations. "Taichung Industry Park represents the typical large-scale multiple industry with more than 800 factories. The sampling site is located on the roof of a pharmaceutical factory (18 m in height), situated at the center of Taichung Industry Park." At Tunghai University, "The sampling heights were set in the range of 1-1.5 m above ground level to

simulate the breathing zone" (Chen and Liao, 2005). Fang et al. (2004) took consecutive PAH samples for 48 hours, from August 2002 to July 2003, and monitored meteorological conditions at the industrial park and the university, as well as at a third site, located in a different area of Tunghai University than the suburban area, that represented a rural area. They determined PAH concentration and size distribution and estimated the dry deposition fluxes and health risk for August 2002 to December 2002 samples. For the industrial and suburban sites, researchers found the following:

- total 21 PAH concentration at Taichung Industrial Park, $1,560.1 \pm 1,429.4 \text{ ng m}^{-3}$
- total 21 PAH concentration at Tunghai University, $734.1 \pm 541.0 \text{ ng m}^{-3}$
- "mean concentrations of total PAHs in ambient air at industrial, urban, and rural sites in central Taichung, Taiwan were measured to be 1,652, 1,185, and 834.1 ng m^{-3} , respectively."

Work by Tsai et al. (2004) was analyzed by Chen and Liao (2005) for its inclusion of PAH measurements taken at a highway toll station. These values were used by Chen and Liao "to account for traffic pollution sources." Tsai et al. (2004) "collected 48, 35, and 33 personal PAH samples from booth attendants of the dayshift, nightshift, and late-night, respectively. Their study showed the average recovery efficiency of PAHs was 85 percent." They used the individual compound's potency equivalency factor (PEF) relative to the molecular weight of benzo[a]pyrene (B[a]P) as an estimate "of the health risk posed by multi-component PAH exposure" (Chen and Liao, 2005).

Exposure

Chen and Liao (2005) created an occupancy probability (OP) to the amount of time an individual

spends in a specific place. "We assumed that a cohort lived in a rural area and their workplace or children's school" was "nearby an industrial park and they were vulnerably exposed to PAH pollution from traffic when they went to work or school. We divided a 24-hour period into five time intervals" each representing an individual's location during a 24-hour period (rural/home, commuting, work or school). "We assumed the OP within each period followed a uniform distribution and the summation of the daily basis OP at 24 hours for rural, traffic, and industrial settings was equal to 1." They employed the " $B[a]P_{eq}$ -based PAH concentration in rural, traffic, and industrial areas" to be "associated with age-group-specific OP values at different settings" and used those values "to calculate daily exposure level through inhalation and dermal contact" (Chen and Liao, 2005).

Incremental lifetime cancer risk (ILCR)

Chen and Liao (2005) integrated "the potency equivalence factors (PEFs), human OP and the ILCR approaches to quantitatively estimate the exposure risk" for adults, children and infants. They based $B[a]P$ potency on "the 95 percent upper confidence limit of the linearized multistage model applied to the incidence of respiratory tumors after inhalation exposure in hamsters" and used "selected types of probability distribution for random variables including the inhalation risk and dermal contact risk parameters. The surface area (SA) describes the amount of skin exposed to the contaminated media. The amount of skin exposed depends upon the exposure scenarios. The adult in a commercial/industrial workplace was assumed to wear a short-sleeved shirt, long pants, and shoes; therefore, the exposed skin surface is limited to the head, hands, and forearms. We can calculate the age group SA according to the recommended value. Recommended dermal absorption fraction from soil for $B[a]P$ and other PAHs followed a lognormal distribution with a

geometric mean 0.13 and geometric standard deviation 1.26. An averaging time of $365 \text{ day year}^{-1}$ for 70 years was used to characterize lifetime exposure for cancer risk calculation."

Uncertainty analysis

Chen and Liao incorporated variability and uncertainty using a Monte Carlo simulation to improve realistic risk distribution. They also performed a sensitivity analysis that "identified the most significant parameters that were included in the uncertainty and variability analysis. The sensitivity of each variable relative to one another was assessed by calculating rank correlation coefficients between each input and output during simulations and then estimating each input contribution to the output variance by squaring the output variance and normalizing to 100%. The Monte Carlo simulation and sensitivity analysis were implemented using Crystal Ball software."

Results

PAH and exposure

Scientists found that the median total PAH and $B[a]P$ concentrations at rural, industrial and traffic settings present for inhalation exposure were estimated to include the following values, respectively:

- 645 and 18.7 ng m^{-3}
- 1,200 and 25.67 ng m^{-3}
- 10,611.28 and 158.5 ng m^{-3}

Median particle-bound PAH and median $B[a]P$ concentrations at these sites for dermal contact exposure were estimated to include the following values, respectively:

- 68.48 and 6.20 ng m^{-3}
- 107.8 and 5.48 ng m^{-3}
- 1,103.97 and 127.84 ng m^{-3}

They reported, "Data reanalysis also demonstrates that

$B[a]P$ levels in the traffic setting were much higher than those measured in rural and industrial settings" (Chen and Liao, 2005).

For adults, children and infants, Chen and Liao (2005) estimated the median $B[a]P$ concentration of inhalation exposure compared to dermal contact exposure to be:

- for adults, $1,628 \text{ inhalation ng day}^{-1}$, $7.0 \times 10^{-4} \mu\text{g g}^{-1}$ dermal contact
- for children, $1,590 \text{ inhalation ng day}^{-1}$, $8.7 \times 10^{-4} \mu\text{g g}^{-1}$ dermal contact
- for infants, $252 \text{ inhalation ng day}^{-1}$, $4.8 \times 10^{-4} \mu\text{g g}^{-1}$ dermal contact

The scientists reported, "In inhalation exposure, the $B[a]P_{eq}$ levels for adults and children are nearly closed and higher than that of infants, whereas in dermal exposure, the $B[a]P$ level of children is slightly higher than that of adults and both are higher than that of infants" (Chen and Liao, 2005).

Cancer risk

Researchers found that adults and children had higher inhalation ILCR values than ILCR dermal contact values, while the opposite relationship was true for infants. "Percentile predictions of total ILCR personal exposure of three age groups could be determined from cumulative density functions (cdf) corresponding to probability density functions. The total ILCRs that combine dermal contact and inhalation exposure pathways are estimated to be lognormal (LN) distributions of $\text{LN}(1.66 \times 10^{-4}, 1.89)$, $\text{LN}(1.44 \times 10^{-5}, 2.13)$, and $\text{LN}(2.10 \times 10^{-7}, 2.93)$, for adults, children, and infants, respectively" (Chen and Liao, 2005).

They reported, for most regulatory programs, that "an ILCR between 10^{-6} and 10^{-4} indicates potential risk. Our results indicate that the 97.5% probability inhalation and dermal contact ILCRs for adults and children exposed to PAHs have orders of magnitude around

10^{-5} and 10^{-4} , indicating high potential carcinogenic risk. All 97.5% probabilities of $B[a]P_{eq}$ -based total ILCRs (TILCRs) are larger than 10^{-6} , indicating unacceptable probability distributions for three age groups." Personal exposure to carcinogenic PAHs for adults had a 97.5% probability, which "is outside the range of 10^{-6} - 10^{-4} , indicating a high potential health risk; whereas for children and infants" the probability was 97.5% with a TILCR of 10^{-6} - 10^{-5} (children: 7.05×10^{-5} and infants: 2.41×10^{-6}) (Chen and Liao, 2005).

Sensitivity

Scientists performed a quantitative sensitivity analysis "to evaluate the variability and uncertainty of parameters in the exposure pathway that contributed most significantly to the risk estimates." They determined that "the inhalation cancer slope factors (CSF) and daily inhalation exposure level (E_i) are the most influential variables for all three age groups, for which average contributions to output variance are 67%, 69% and 69%, respectively, for adults, children, and infants. For dermal exposure to particle-bound PAH, the particle-to-skin adherence factor (AF_d) and daily dermal exposure level (E_d) are the most influential variables for all three age groups, for which the contributions to output variance range from 59-76% and 46-56%, respectively" (Chen and Liao, 2005).

Discussion and conclusions

Chen and Liao (2005) concluded, "the study of human exposure to environmental PAH pollution sources identified the age-specific potential cancer risks. Recognition of the importance of inhalation cancer slope factor and particle-bound PAH-to-skin adherence factor in PAH exposure led to the efforts to estimate the significance of inhalation and dermal ILCRs. Sensitivity analysis indicates that to increase the accuracy of the results, efforts should focus on a better definition of probability distributions for inhalation cancer slope

factor and particle-bound PAH-to-skin adherence factor. Given the scarcity of data, most of the probability distributions were based on U.S. EPA data, and this may be a limit to the validity of the case presented." They noted that "uncertainties are inherent in quantitative risk assessment because of assumptions required to extrapolate from one species to another, from high to low situations, and because of the statistical modeling techniques required to fit data points." Furthermore, "rodent-derived risk factors may have different orders of magnitude comparing with empirical-data-derived risk estimates."

"The carcinogenic risk assessment of PAH remains difficult, particularly due to the very high number of these compounds present in mixtures to which the general population may be exposed, as well as due to the possible contemporary presence of other risk factors and to possible synergistic and/or antagonistic effects. Due to the limited number of dose-response data on carcinogenicity, and depending on the exposure route, different PEFs can be obtained." They noted, "It has also to be remembered that the $B[a]P$ concentrations used for this calculation represent an external exposure estimation of carcinogenic compounds and not the effective active concentration at the lung level" (Chen and Liao, 2005).

The scientists encouraged further research in three areas. "First, there is a need to conduct a more extensive characterization of the distribution of exposures within given population groups. This would require the collection of more detailed information on the characterization of occupation probabilities, PAH uptake in the lung and skin, and daily working logs. It would be useful to characterize better the distribution of exposures by age of individuals exposed. Second, there is a need for global sensitivity analysis using the Monte Carlo simulation model with the more detailed data sets as inputs. The ranges and

distributions of parameters can then be combined by use of the Monte Carlo simulation model to produce a response surface. Relationships between the input ranges and model output should then be assessed with stepwise regression in order to identify the relationship between output variability and input uncertainties and variabilities. Finally, on the basis of the results of the sensitivity analysis, research should be directed to those parameters that, if better characterized, could most effectively reduce variability in the results" (Chen and Liao, 2005).

Reference

- Chen, S.C. and C.M. Liao, "Health risk assessment on humans exposed to environmental polycyclic aromatic hydrocarbons pollution sources," *Science of the Total Environment*, article in press, 2005; www.elsevier.com/locate/scitotenv
- Fang, G.C., Wu, Y.S., Fu, P.C., Yang, I.L. and M.H. Chen, "Polycyclic aromatic hydrocarbons in the ambient air of suburban and industrial regions of central Taiwan," *Chemosphere*, Vol. 54, No. 4, 2004; www.elsevier.com/locate/chemosphere
- Tsai, P.J., Shih, T.S., Chen, H.L., Lee, W.J., Lai, C.H. and S.H. Liou, "Assessing and predicting the exposures of polycyclic aromatic hydrocarbons (PAHs) and their carcinogenic potencies from vehicle engine exhausts to highway toll station workers," *Atmos Environ*, Vol. 278, 2004; www.elsevier.com/locate/atmosenv

UTTU thanks Dr. Chen, f92622007@ntu.edu.tw, for his help on this article.



Petroleum fractions-contamination

Researchers investigated the contamination of a north-central Mexico oil storage and distribution station (ODSS). Their objective was to examine the contaminated soil and water in terms of total petroleum hydrocarbons (TPH), gasoline and diesel fractions, BTEX (benzene, toluene, ethyl benzene, and xylenes), polycyclic aromatic hydrocarbons (PAH), methyl-*tert*-butyl ether (MTBE) and some metals. In addition to this, they performed "measurements of the explosivity index along the ODSS" and a health risk assessment (HRA) (Iturbe and others, 2005).

The area of investigation is semi-dry, semi-hot with an average annual temperature of approximately 18.1°C. Iturbe and others (2005) reported, "The site belongs to the hydrological sub-basin of *Rio Aguascalientes* in the *Rio Verde Grande* basin of the *Lerma-Santiago* hydrological region (RH-12). The ODSS is located over an aquifer." The aquifer is made up of:

- alluvial non-consolidated material
- inter-digitized strata of irregular geometries
- a phreatic level 45 m (upper section) and 178 m (lower section) below surface

Methods

Soil sampling

Iturbe and others (2005) sampled 38 different points of the ODSS area at depths ranging from 0.45 to 1.5 meters below surface using pneumatic perforation equipment. This equipment included:

- 3-inch helicoidal tube for drilling
- 0.6-meter-long, 1.5-inch-diameter tube for sampling

- 63.5 kg hammer "having a free ball of 760 mm similar to that used for standard penetration testing (SPT)"

Soil samples were not exposed to air. They were stored at 4°C until analysis.

Scientists assessed soil samples for:

- TPH
- hydrocarbons profile, including diesel and gasoline fractions, MTBE, *tert*-amyl methyl ether (TAME)
- BTEX and "16 polycyclic aromatic hydrocarbons (PAH) considered as priority pollutants by the United States Environmental Protection Agency"
- total Zn, total and hexavalent Cr, total Pb, and total Fe

All samples were evaluated according to U.S. EPA analytical techniques (Iturbe and others, 2005).

Explosivity

For the 38 sampling points, researchers measured the explosivity index with a COSMOS XP-311 ALPHA A system.

Health risk assessment (HRA)

Researchers used a RBCA Tool Kit for Chemical Releases for the HRA. They sought the presence of contaminants including:

- BTEX
- "12 of the 16 priority PAHs proposed by the U.S. EPA (4 of the 16 were below the analytical detection limits)"
- MTBE
- chromium (VI)
- zinc

Iturbe and others (2005) defined two types of receptors for contaminant-exposed populations. These were:

- receptors within the contamination source (on-site), ODSS workers
- receptors out of the contamination source (off-site), ODSS workers, "people living in the ODSS surroundings (about 350 m downgradient from the ODSS)"

They classified individual risk within the site as acceptable for each chemical compound by class: for classes A and B carcinogenic compounds, 1×10^{-6} , "and 1×10^{-5} for class C carcinogens. The total accumulated risk considered as acceptable is 1×10^{-5} . For non-carcinogenic compounds (classes D and E), it was considered that the hazard quotient (HQ) and the hazard index (HI) had acceptable values of 1.0. When applying the model, degradation was not considered, because off-site receptors are quite close to the contamination source, so it was necessary to make it more restrictive" (Iturbe and others, 2005).

Results

Hydrocarbons

Scientists discovered the following:

- TPH at all sampling points at an interval of 47-21,093 mg kg⁻¹
- diesel fraction at 12 of the 38 sampling points, from 6.9 to 3,460 mg kg⁻¹
- gasoline fraction at eight of the 38 sampling points, from 17.38 to 993.6 mg kg⁻¹
- no incidence of TAME
- MTBE in concentrations from 0.024 to 0.645 mg kg⁻¹
- benzene at four sampling points, 0.091 to 0.156 mg kg⁻¹
- toluene at two sampling points, from 0.04 to 24 mg kg⁻¹

- ethylbenzene in concentrations from 0.091 to 0.334 mg kg⁻¹
- xylene isomers mixture in concentrations of 1.29 to 2.2 mg kg⁻¹

They also found TPHs in "high concentrations in four zones. The first corresponds to sampling points 5 to 6, located at the railway zone, reaching concentrations between 10,770 and 21,093 mg kg⁻¹. The second corresponds to sampling point 3, where 10,770 mg kg⁻¹ was detected. This point is located beneath the ODSS' laboratories. The third hot spot is located at point 35, where a maximum concentration of 11,549 mg kg⁻¹ was measured. The fourth hot spot corresponds to point 36, where a maximum concentration of 12,994 mg kg⁻¹ was found. This zone is where storage tanks are located, specifically near a diesel-product tank" (Iturbe and others, 2005).

Several PAHs were discovered at different sampling points. Four of the sampling points contained:

- pyrene (non-carcinogenic)
- phenanthrene (non-carcinogenic)
- anthracene (non-carcinogenic)
- benzo(a)anthracene (carcinogenic)

Fluorene (non-carcinogenic) was found at three sampling points. Two points included:

- benzo(a)pyrene (carcinogenic)
- benzo(b)fluoranthene (carcinogenic)
- acenaphthene (non-carcinogenic)

One point included:

- acenaphthylene
- naphthalene (U.S. EPA priority pollutant)
- fluoranthene (carcinogenic)
- chrysene (carcinogenic)

There were five points where PAHs were detected.

"The first is point 4, where the total amount of PAHs detected was 101.0 mg kg⁻¹. This point is located in the railway zone. The second point corresponds also to the railway zone, sampling point 5, where a total PAH concentration of 75.8 mg kg⁻¹ was detected. Note that these points were also hot spots regarding TPH presence. The third point is located at sampling point 28, with a total PAH concentration of 35.6 mg kg⁻¹. This point is located at the filling tanks zone. The fourth point corresponds to sampling point 35, where a total PAH concentration of 47.1 mg kg⁻¹ was measured. This point is located very near an American Petroleum Institute (API) separator. Finally, the last point is 36 with a total PAH concentration of 40.5 mg kg⁻¹, very near a diesel-product storage tank. This last point corresponds with a hot spot regarding TPH concentrations" (Iturbe and others, 2005).

Explosivity

Researchers observed points of explosivity to "coincide exactly with those points in which organic compounds were found... A 50 percent explosivity value was detected at point 19, while the other explosivity values ranged from 15 to 25 percent... These explosivity values, in some cases, were tightly related to the TPH or volatile organic compounds present in the subsoil; hence, explosivity measurements could be used as a preliminary assessment method" (Iturbe and others, 2005).

Metals

Iturbe and others (2005) found Zn, Cr, Fe, and Pb. Overall, they determined metals distribution to be variable and unrelated to organic compounds distribution. They also investigated "correlation factors for the relationship between organics-organics", considering "only correlation factors over 0.85" to be satisfactory. They found correlative relationships between diesel fraction and MTBE with TPHs

to be significant. They reported, "regarding the relationship between PAHs and TPHs, four compounds correlated very clearly with TPHs and diesel fractions. Acenaphthene, phenanthrene, fluorene, and benzo(a)anthracene correlated with TPH. Fluorene and benzo(a)anthracene correlated with the diesel fraction. Finally, none of the PAHs found at the ODSS correlated with the gasoline fraction." The three metals investigated also did not correlate with TPHs, diesel or gasoline fractions. "This would imply that their presence is due rather to geological issues, and not to petroleum derivatives contamination."

HRA results

Researchers found that groundwater samples were within acceptable values for accumulated risk, the hazard index (HI), individual risks and hazard quotients for on-site and off-site receptors. Conversely for soil samples, "the individual acceptable risks for benzo(a)anthracene, benzo(a)pyrene, benzo(b)fluoranthene, and chrysene were exceeded for on-site commercial land use receptors, whereas for off-site receptors only benzo(a)pyrene exceeded the acceptable risk. Besides, the accumulated risk was exceeded for on-site commercial use receptors. In regard to the exterior air exposure, the individual risks for benzo(a)pyrene and benzo(b)fluoranthene and the chrysene hazard quotient were exceeded for both on-site and off-site receptors. This was due to volatilization and particle emission from the soil to the exterior air exposition routes. For on-site receptors, only chrysene showed a hazard quotient higher than that established as acceptable. The accumulated risk for this medium was only exceeded for on-site commercial use workers and off-site receptors. Nevertheless, the hazard index (HI) established as acceptable was exceeded for the two kinds of receptors defined for this medium, including on-site construction worker activities" (Iturbe and others, 2005).

Contamination

Researchers based calculations for area and volume on sampling point TPH concentrations. "An average soil depth of 1 m was considered. Taking into account soils with TPH concentrations higher than 2,000 mg kg⁻¹, the area contaminated corresponding to the railway zone is about 12,776 m², at the south of the storage tanks about 6,558 m², and at the zone located to the south of the filling tanks about 783 m². Total area to be treated is about 20,107 m²" (Iturbe and others, 2005).

Conclusions

Iturbe and others (2005) concluded, "It seems that the diesel fraction and MTBE are quite related with TPH... None of the BTEX correlated with the diesel fraction as expected. This would imply that diesel appeared always where gasoline was present, and both were related with MTBE. This fact can be possible, considering that common pipelines are used for transportation of fuels (diesel and different gasolines). They concluded that, "All the contaminated areas are susceptible to soil washing or bioremediation using biopiles" and recommended them "as feasible technologies for the decontamination of the calculated volumes as to attain cleanup levels in the short and medium term."

UTTU thanks Luis Torres Bustillos, LTorresB@lingen.unam.mx for his help on this article.

Reference

Iturbe, R., Flores, C., Flores, R.M. and L.G. Torres, "Subsoil TPH and other petroleum fractions-contamination levels in an oil storage and distribution station in north-central Mexico," *Chemosphere*, Vol. 61, No. 11, 2005; www.elsevier.com/locate/chemosphere



Calculating petroleum hydrocarbon plume growth

Researchers examined "how plumes from persistent sources evolve over time as methanogenic conditions develop. In theory, the rate of expansion of the methanogenic zone should depend on the flux of the degradable organic carbon and the available electron acceptors in the aquifer." With this knowledge, they developed a growth-rate-estimation (GRE) "method to forecast the expansion of the methanogenic zone and associated benzene and ethylbenzene plumes and compare the results to field data. The growth-rate estimates are determined using ground water flow velocity, porosity, and the concentrations of BTEX and sediment Fe(III). The GRE method is appropriate for use in contaminant plumes where the redox state of the plume has evolved to methanogenic conditions and when the contaminant of concern is attenuated by oxidation processes outside the methanogenic zone. The method reproduces observed growth rates for two different plumes and is simple to use because it ignores the effects of sorption, dilution, and reaction kinetics." They surmised, "Insights from the GRE method can form a basis for designing monitoring strategies that minimize costs and maximize information about changes in plumes" (Bekins and others, 2005).

Sites

Scientists based their investigation at two field sites. The Bemidji, Minnesota site was contaminated in 1979 by a burst oil pipeline. Between 1992 and 1995 the 5 mg/L BTEX contour expanded at a rate of approximately 3 meters per year while the overall plume size remained steady.

Scientists reported, "Plots of the maximum concentration

of benzene and ethylbenzene observed in each vertical well cluster for the years 1988, 1992, and 1993 show that during this period, the BTEX front steepened and expanded over the region between 55 and 70 m downgradient. To determine the expansion rate between 1988 and 1993, the measured 1988 concentration at well 518A was projected downgradient to find the location where the same concentration occurs in the 1993 plot. The location of the equivalent concentration falls between two wells but is just 0.76 m downgradient from well 531A at a total distance of 11.3 m from well 518A. These data yield an average advance rate for the BTEX front of 2.3 m/year" (Bekins and others, 2005). Researchers collected data such as flow velocity and porosity for the GRE from previous studies by Essaid et al. (2003) and Dillard et al. (1997).

The second site Bekins and others (2005) examined was the Laurel Bay Exchange, located in Beaufort, South Carolina. The site was contaminated by a UST gasoline release, the date of which is unknown, "but the buried tank first failed a test for tightness on December 15, 1990." Site characteristics include:

- a surficial aquifer 10 to 12 meters thick
- a water table 3 to 4 meters below surface
- relatively homogenous aquifer sediment
- a hydraulic conductivity of 2.7 to 5.3 m/d
- a porosity of 0.30
- 15.2 to 29.5 m/year linear flow velocities
- Fe(III) concentration average value of 0.52 μmol/g
- Fe(III) values below 0.1 μmol/g within the methanogenic zone
- decreased toluene and xylene concentrations between 49 and 83 m
- benzene and ethylbenzene concentrations that do not decrease until beyond 80 m

- “Methanogenic or sulfate-reducing conditions present by 1996 in the deep wells between the source area and 60 m downgradient”

Scientists described, “By 1994, the combined benzene and ethylbenzene front had arrived at a monitoring well, located 49 m downgradient from the source. By 1996, the fronts had advanced 83 m downgradient, yielding an advance rate of 14.8 m/year for the period 1994 to 1996. By 1998, the fronts had reached a drainage ditch, 184 m downgradient from the source, giving a minimum advance rate of 50 m/year between 1996 and 1998. The rapid increase in the advance rate of the plume after 1996 can be attributed to a steepening of the water table gradient by at least a factor of five beyond 100 m downgradient from the source” (Bekins and others, 2005).

Estimation method

Researchers categorized BTEX compounds based on their migration and degradation behaviors. Toluene and xylene fractions “degrade under methanogenic conditions, whereas benzene and ethylbenzene migrate almost conservatively until they reach the iron-reducing zone, where they degrade rapidly. They considered “the rate that Fe(III) and sulfate are consumed by microbial oxidation of the reduced carbon in the plume” as a measure of the methanogenic front advance (Bekins and others, 2005).

For the Bemidji site, Bekins and others (2005) also took into account the following considerations:

- “the degradation of benzene and ethylbenzene to consumption of Fe(III) at the downgradient edge of the methanogenic zone” as an advancing reaction front
- “a constant, unidirectional flow field, by advection only,” following a plug-flow model
- negligible effect of sorption and volatilization

- “the benzene, ethylbenzene and depleted Fe(III) fronts advance together” while “a substantial amount of Fe(III) remains in the aquifer behind” the combined front

To calculate the advance rate of the combined front, researchers used “a simple computation based on mass balance. The method uses the change in concentration of available Fe(III) between the clean aquifer and the methanogenic zone together with the benzene and ethylbenzene fluxes.” Additional equations developed for this study by Bekins and others (2005) considered:

- the time required for the front to move the length of the control volume
- the hydrocarbon mass loss due to biodegradation
- the starting and ending hydrocarbon mass
- control volume
- change in Fe(III) concentration
- flux in and flux out
- distance moved by the reaction front
- the effect of electron acceptors

Application method

Researchers applied two of the developed equations to estimate the growth rates of the investigation sites. For the Bemidji site, their findings included:

- an estimated growth rate of 2.2 m/year in the methanogenic zone
- an observed advance rate of 2.3 m/year in the methanogenic zone
- a maximum growth rate 10% of the ground water flow velocity “because of the high concentration of available Fe(III) on the sediments”
- a slightly lower minimum growth rate estimate with both iron and sulfate “because dissolved sulfate concentrations are very low”

For the Laurel Bay site, the researchers found:

- an estimated growth rate range of 9.4 to 18.3 m/year
- an observed advance rate of 14.8 m/year
- a predicted maximum growth rate 60% of the ground water flow
- that sulfate reduction changes the advance rate estimate by only 10%

Scientists reported, “The observed methanogenic front at Bemidji advances at less than one-sixth the rate of Laurel Bay, even though the benzene and ethylbenzene fluxes at the two sites are comparable. The difference is due mainly to the eightfold higher concentration of available sediment Fe(III) at Bemidji” (Bekins and others, 2005).

The researchers applied the GRE method to understand the slow growth and expansion of contours at the Bemidji site.

Discussion

Bekins and others (2005) reported, “The GRE method is based on a conceptual model of a BTEX plume evolving to a stage in which methanogenic conditions prevail in the contaminated aquifer downgradient from the source. When the aquifer initially becomes contaminated, the microbial population is small, and the ability to degrade the contaminants is not yet well established. The plume advances quickly while the degrading microbial population is also rapidly growing. Once the aquifer microbial population has expanded to a value that is in equilibrium with the flux of reduced carbon, growth of the plume slows down, and the plume size appears to stabilize. As electron acceptors are depleted near the source, methanogenic conditions are established, and the BTEX components separate because xylenes and toluene degrade under methanogenic conditions, while benzene and

ethylbenzene migrate through the methanogenic zone with little degradation. Once the plume reaches a stage where the benzene and ethylbenzene front is associated with the transition from methanogenic to iron- and sulfate-reducing conditions, the method we have presented applies."

The researchers explained, "The GRE method is based on the assumption that benzene degradation is very slow under methanogenic conditions and comparatively rapid under iron-reducing conditions. A compilation of anaerobic benzene degradation rates from the literature indicates that methanogenic rates are not always slower than iron-reducing rates. However, the intrasite and intersite variations for a single redox state are comparable to the difference between methanogenic and iron reduction rates averaged over all sites. These data suggest that rate comparisons for different redox conditions should be made using nearby locations from the same site. Microcosms constructed using sediments from nearby iron-reducing and mixed iron-reducing/methanogenic locations at Bemidji show large differences in rates. A number of other field sites also exhibit limited degradation of benzene and ethylbenzene under methanogenic conditions, with rapid degradation in downgradient iron-reducing zones suggesting that these rate differences may apply more generally" (Bekins and others, 2005). The GRE method requires quantification of Fe(III) in sediments in the uncontaminated aquifer and within the methanogenic zone of the plume.

The GRE method may also be used to "account for other important electron acceptors at a site." The researchers noted, "longitudinal dispersivity controls the degree of mixing, and higher dispersivity may be due to greater flow velocity or aquifer heterogeneity. For plumes with very slow advance rates like Bemidji, the distance between the migrating benzene front and dissolved electron acceptors grows over time, and

dissolved electron acceptors become increasingly unavailable. However, in rapidly migrating plumes growing at close to the ground water velocity, such as Laurel Bay, dissolved sulfate may remain available at the benzene front. For distal portions of plumes, mixing of low-contaminant concentrations with dissolved electron acceptors is enhanced by the greater travel distance and increased surface area of the plume. Thus, the use of the GRE method with dissolved oxygen as the electron acceptor provides insight into the very slow advance rate of the 5 µg/L contour at Bemidji" (Bekins and others, 2005).

The researchers suggested the GRE method may apply to contaminant plumes beyond BTEX, "where microbially driven organic carbon oxidation reactions are coupled to reductions of electron acceptors in the aquifer. The Laurel Bay site has significant concentrations of MTBE, and this compound does not appear to degrade under anaerobic conditions at the site. Thus, the benzene and ethylbenzene plume growth method may apply even when MTBE is present. When compounds are present that degrade under one redox condition but persist under less favorable conditions, a migrating front will develop" (Bekins and others, 2005). The GRE method would not be appropriate for some situations without modification. Consideration is required for reaction kinetics, contaminant type, source strength, methanogenic degradation capabilities, and Fe(III) recycling.

Conclusions

Bekins and others (2005) concluded, "At sites where ground water is contaminated by a long-term source, BTEX contaminant plumes grow slowly over time. When removal of the source is impractical, it is important to estimate the rate of plume growth and assess its impact on downgradient receptors. The plume growth can be assessed in several ways. One way is to examine

the growth in the area contaminated with the highest concentrations of BTEX compounds. Growth in this area is associated with expansion of the methanogenic zone and minimal degradation of benzene under methanogenic conditions. A simple mass balance shows that the growth rate equals the ratio of the hydrocarbon flux to the aquifer oxidation capacity (OXC) due to iron and sulfate reduction. The GRE method presented here provides an excellent match to data for two BTEX plumes located in Bemidji, Minnesota, and Laurel Bay, South Carolina, with respective growth rates of 2.3 and 14.8 m/year. The more standard method for assessing plume growth is to watch for expansion of the 5 µg/L benzene contour. Data from the Bemidji, Minnesota, site show that this contour does not appear to expand even though the area with benzene > 5 mg/L has expanded noticeably. Using the mass balance method to estimate the growth of the 5 µg/L contour in the aerobic portion of the aquifer shows that this contour expands at only 0.26 m/year. This rate is 20 times slower than the expansion rate of the methanogenic zone and would be very difficult to see with a ground water sampling network composed of monitoring wells. The field data and analyses from the Bemidji site show that plume growth at sites with persistent BTEX sources should be monitored at the edge of the methanogenic zone. The method presented here provides a tool for projecting growth rates over the expected lifetime of the source. In some cases, projected growth rates will be much higher than that observed at the 5 µg/L contour, and the decision to use monitored natural attenuation (MNA) should be reassessed."

Reference

Bekins, B.A., Cozzarelli, I.M. and G.P. Curtis, "A simple method for calculating growth rates of petroleum hydrocarbon plumes," *Ground Water*, Vol. 43, No. 6, 2005; www.ngwa.org

Dillard, L.A., Essaid, H.I. and W.N. Herkelrath, "Multiphase flow modeling of a crude-oil spill site with a bimodal permeability distribution," *Water Resources Research*, Vol. 33, No. 7, 1997; www.agu.org/pubs/back/wr/index.shtml

Essaid, H.I., Cozzarelli, I.M., Eganhouse, R.P., Herkelrath, W.N., Bekins, B.A. and G.N. Delin, "Inverse modeling of BTEX dissolution and biodegradation at the Bemidji, MN crude-oil spill site," *Journal of Contaminant Hydrology*, Vol. 67, No.1, 2003; www.elsevier.com/locate/jconhyd.



Reader forum

These questions were sent to UTTU. If you have answers, comments or suggestions, please e-mail Jaime Pullman at pullman@wisc.edu and she will pass them along to the writer and readers who are interested.

Free-product removal

I am evaluating this question in relation to closed George Air Force Base, where there is over one million gallons of free product (FP) remaining and over 200,000 gallons removed to date. Skimming and soil vapor extraction (SVE) are currently in progress. It is understood that the formation has natural limits on what it can yield, and to some extent these conditions are being observed. Recently, the Air Force was trying to push for shutting down all active remediation (e.g. no risk, no receptors, and additional FP removal would have insignificant effect on the very long cleanup time). I said, no you can't stop because the aquifer continues to yield FP at the current rate of 600 gal per month, although removal rates are decreasing. Additional FP removal wells could be installed that would enhance removal even more - although at a cost. And even more enhancement could be observed by expanding the SVE system to focus on removing additional volatile fraction FP (instead of petroleum hydrocarbons remaining in the soil column only).

Funding constraints are forcing the government to look for ways to cut costs. At this particular time the Air Force tells us they will continue the skimming and SVE removal, although these are not as effective as they could be if enhanced. I am looking for the following to support what I believe "practicable" FP removal means (e.g. "can you still do it").

1) case histories

2) guidance documents

3) legal interpretations

My search for free product removal information to date has been futile. Can you help here?

Jehiel (Jay) Cass

Water Resources Control Engineer

Hydrocarbon assessment

We recently had the need to test some disused asphalt that was to be disposed of as "clean fill." At the same time we also tested some fresh off-spec material to provide a benchmark. We tested for total petroleum hydrocarbons and BTEX. When the results came back from the lab, I was surprised to see that the TPH levels were low and within the Australian criteria for both the aged and fresh asphalt. I asked the lab to re-test the samples as I explained that I was surprised at the outcome. They performed their normal solvent extraction of the samples and again the results were low.

You could smell the bitumen in the sample. However, I was wondering whether it might be tightly bound to the gravel and unextractable, and therefore stable? Are you able to shed some light onto why the asphalt samples did not show high levels of TPH (even the fresh one)?

Mark Rigby

Mark Rigby & Associates Environmental