



Underground Tank Technology Update

Vol. 17, No. 1 January/February 2003



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 [John T. Quigley](#), Project Director, 432 N. Lake St., Madison, WI 53706. Tel 608-265-2083. To comment on an article, or to suggest topics for *UTTU*, please e-mail [Pat Dutt](#) or call 607-272-3212.

Advisory Board

Shushona A. Clark, Project Officer, OUST
U.S. EPA, Washington D.C.

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

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

James Davidson, President, Alpine Environmental, Inc.
Fort Collins, Colorado

Lynn DePont, 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

Joseph Odencrantz, Principal
Tri-S Environmental, Costa Mesa, California

Phil O'Leary, Professor, Department of Engineering Professional
Development, UW-Madison

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

Hal White, Hydrogeologist, OUST, U.S. EPA, Washington D.C.

Staff

John T. Quigley	Project Director
Pat Dutt	Geologist/Writer
Darrell Petska	Copy Editor
Debbie Benell	Program Assistant

Brief article summaries

Ethanol modeling 2

Researchers performed several modeling simulations to depict ethanol's effect on benzene persistence in gasoline-contaminated aquifers. A key finding was that ethanol consumes oxygen, reducing the benzene biodegradation rate.

Contaminated soils management 4

This article summarizes how Minnesota's Department of Transportation (Mn/DOT) manages its petroleum-contaminated soil. The contamination can originate from many sources including LUSTs, leaks from failed hydraulic systems, and spillage from rail yards.

Biodegradation information from hydrogen isotopes 7

Scientists can estimate how much a hydrocarbon spill has biodegraded by examining contaminant and electron acceptor concentrations. However, concentration reductions could also be a result of physical processes such as volatilization, sorption, and plume dilution. A drawback to this strategy is the difficulty of obtaining accurate mass balances of contaminants and electron acceptors. Biodegradation degree estimated from hydrogen isotopes, however, does not rely on accurate mass balances of contaminants and electron acceptors.

Research notes 8

Summaries of published papers are presented.

Information sources 11

Information sources give phone numbers/Web sites of recently published material.

Free Subscription To receive this electronic newsletter, e-mail [Debbie Benell](#) or call 608-263-7428. There is no cost to subscribers.



Ethanol modeling

Researchers performed several modeling studies depicting ethanol's effect on benzene persistence in gasoline-contaminated aquifers (Molson and others, 2002). A key finding was that ethanol consumes oxygen, reducing benzene biodegradation rate.

Previous studies

A summary of efforts undertaken to study ethanol in groundwater follows:

- a 2-D analytical model and first-order degradation rates were used to compare benzene plume lengths under ethanol and ethanol-free conditions; dynamic effects of co-transport were not considered; benzene degradation was activated only once; ethanol concentrations decreased above a certain threshold while benzene plume length was predicted to increase 17 to 34 percent
- another researcher used MODFLOR/MT3D to simulate ethanol impacts on benzene; assumptions include a dissolved benzene plume as the source, but dissolution from a residual source was not considered; dynamic interactions between benzene and ethanol were also not considered
- a Monte Carlo approach was used to obtain probability distributions of benzene concentrations downgradient of the source area; the influence of retardation factors and competitive substrates was not evaluated; first-order degradation rates were assumed with the conclusion that ethanol would increase benzene plume length by less than a factor of two
- a simulation of m-xylene and ethanol from a gasohol pool into a 2-D aquifer system again restricted the influence of ethanol to a cosolvency role; sorption

and biodegradation were not considered; researchers found ethanol increased benzene travel distance by 10 percent

Model and assumptions

Researchers in this study used the model BIONAPL, which models groundwater flow, multicomponent dissolution from a residual gasoline or gasohol source, advective-dispersive transport, oxygen-limited competitive biodegradation and microbial growth. There is a cosolvency effect (researchers included this effect when devising their model) because when the aqueous volume fraction of ethanol becomes greater than 0.1, the effective solubilities of the remaining gasoline components can increase significantly as they preferentially dissolve into the water-ethanol solution.

Assumptions for the model Molson and others (2002) used include the following:

- the source is dissolving at equilibrium, which assumes ideal component behavior and a large contact area between the residual NAPL and the groundwater (source heterogeneities and non-ideal component behavior can lead to apparent or real non-equilibrium dissolution at field contamination sites)
- the aquifer flow system is saturated, isotropic, homogeneous, and at steady state
- contaminant concentrations are dilute and density effects are not considered (buoyancy effect of a high-concentration ethanol plume is neglected)
- the residual gasoline source is immobile (valid for low pressure gradients and gasoline saturations < 0.1)
- interfacial tension changes due to ethanol are assumed insignificant

- BTEX sorption is assumed linear and reversible and is not affected by ethanol
- dissolution of the residual gasoline occurs at equilibrium according to Raoult's law
- a single electron acceptor (oxygen) and a single (immobile) microbial population are present; although additional electron acceptors may be present, oxygen is the most significant for BTEX components; anaerobic ethanol degradation is assumed minimal, but a fermentation pathway in which degradation by-products will be more persistent oxygen depleters exists
- substrate inhibition is neglected; preferential ethanol degradation assumes $k_{\text{ethanol}} > k_{\text{benzene}}$ and all components simultaneously move to where they compete for the available oxygen
- only the dissolved (aqueous) phase organics can biodegrade, not the sorbed phase organics
- the reaction stoichiometries assume complete organic degradation to CO_2 and H_2O

Conceptual flow model

The conceptual flow model is based on the Borden aquifer, which is shallow, unconfined and sandy. Other flow properties include

- hydraulic conductivity of 10^4 m/s
- porosity of 0.35
- average hydraulic gradient of 0.003
- groundwater velocity of 0.03-0.1 m/d
- aquifer recharge of 0.2 m/y

Researchers modeled two conceptual models with different spill scenarios. The first model consisted of a four-component gasoline mixture composed of benzene, toluene, ethylbenzene and xylenes. In this scenario:

- alkanes and cycloalkanes were treated as a single equivalent compound
- a single electron acceptor, oxygen, was selected
- a dynamic microbial population was included
- the gasoline selected was mixed with a 10 percent volume fraction of ethanol

In the second scenario, the basic source geometry and chemistry are the same; however, pure ethanol was spilled into an existing BTEX source.

Model 1

Initial conditions for model 1 consisted of a clean aquifer with a background oxygen concentration of 3.8 mg/l. Dispersivities of 1.0, 0.02 and 0.01 were modeled. Researchers applied the fermentation pathway (fermentation of ethanol to CO₂, organic acids, H₂ and CH₄) for the anaerobic degradation portion of this reaction. Cosolvency was not considered for this model because ethanol concentration in the source area was at or below 2,000 mg/l.

In model 1, "Because of ethanol's high solubility and limited mass in the gasohol source, all the ethanol is dissolved instantaneously and is completely flushed from the source within one pore volume, or about 320 days. The addition of ethanol to the gasoline causes a small reduction in the mole fraction for BTEX and the remaining components at an early time. This reduces their effective solubilities and source concentrations but does not significantly impact plume concentrations because ethanol is rapidly flushed from the source. The effective solubilities of the remaining components then return to the levels of the ethanol-free case." Other results from model 1 show that

- after 20 years, biodegradation has removed most of the benzene mass, leaving only a small amount of the plume from 100 to 140 m; in the ethanol-free benzene plume, degradation is quite rapid

- "the addition of ethanol has extended the benzene plume migration distance by about 135 percent at 20 years... the difference increases to 150 percent at 21.5 years" (benzene is competing with ethanol for available oxygen)
- the presence of ethanol stretched and split the benzene plume into two lobes
- most of the benzene remains in the source area after the ethanol has been completely flushed
- a significant fraction of the benzene plume mass never comes in contact with the ethanol plume
- the mass of the aqueous benzene plume also increases in the presence of ethanol because less benzene is biodegraded
- biodegradation occurs at a significant rate only in the fringe areas of the plume where the organics can mix with oxygen

Researchers also ran this model using a higher retardation factor for benzene, of $R = 1.1$ to $R = 1.5$. Ethanol was assumed to be unretarded. "In a simple reactive system, increasing the retardation factor slows the plume advance and decreases the plume extent. In a bioreactive system, however, a higher retardation factor also reduces the effective biodegradation rate since the sorbed phase is assumed nonbiodegradable. These processes will have opposite effects on the size of the benzene plume. In the ethanol-free case at 20 years, for example, the higher retardation factor has almost doubled the plume length" (Molson and others, 2002). For this higher benzene retardation case, researchers found that

- adding ethanol increased benzene plume travel distance
- the apparent advance of the plume is retarded, but only slightly because the slower travel velocity is offset by the lower effective biodegradation rate

(the sorbed phase is not biodegrading); the benzene plume persists for 27 years

- benzene plumes from the gasohol source advance more rapidly relative to those from the gasoline plume because they are co-transported with the oxygen-consuming ethanol plume
- aquifers rich in organic matter are more likely to be protected against ethanol's influence on benzene plume travel distances

A scenario with low background O₂ (reduced from 3.8 to 2.0 mg/l) showed

- a reduction of benzene degradation, producing a larger, ethanol-free benzene plume
- aerobic degradation rate of ethanol is also reduced, increasing duration of overlap between ethanol and benzene plumes
- an increase in benzene plume length of 64 percent at 20 years (relative to an ethanol-free benzene plume), to 100 percent at 25 years
- aquifers low in dissolved oxygen are potentially more susceptible to benzene persistence whereas those aquifers rich in oxygen are not

In a multiple spill scenario (spill of gasoline and gasohol once per year over a 10-year period) the "ethanol plume is repeatedly flushed through the benzene plume, but the lower mass flux of ethanol into the aquifer consumes less oxygen, leaving more available benzene" (Molson and others, 2002).

Model 2

"In this conceptual model, pure ethanol is spilled into the remaining source mass and the existing 5-year ethanol-free gasoline plume from the base case scenario of conceptual model 1" (Molson and others, 2002). Cosolvency, an increase in solubility, is important. The ethanol...causes a sharp increase in effective

solubilities and source concentrations of the gasoline components. As ethanol disperses from the source area and concentrations decline, the cosolvency effect is reduced and the effective solubilities for TEX and the remaining components return to pre-ethanol spill levels. Benzene source concentrations continue to drop following the addition of ethanol because the source becomes depleted of benzene and the mole fraction declines" (Molson and others, 2002).

Modeling also showed

- ethanol rapidly disperses (high retardation coefficient and higher diffusion coefficient) and begins consuming oxygen ahead of the BTEX plumes
- ethanol spill has increased the benzene plume travel distance by 112 percent at 20 years (relative to the ethanol-free plume) because of two factors
 - a 5-year delay in the ethanol release allowed the benzene plume to degrade at relatively higher rates at an early time, thereby reducing benzene concentrations at the leading edge
 - a 5-year delay also increases degree of overlap between the ethanol and benzene plumes; when overlapped, ethanol is preferentially consumed
- benzene travel distance increases 140 percent at 40 years (over a non-ethanol case)
- a late accidental release of pure ethanol, for instance, combined with enhanced benzene solubility, can lead to even longer benzene travel distances

Conclusions

Molson and others (2002) concluded the following:

- ethanol in gasoline can increase benzene plume travel distances by at least 50 percent, relative to ethanol-free plumes
 - increase is most pronounced with low background

oxygen, low retardation and with a multiple gasohol spill

- the influence of ethanol on benzene persistence depends primarily on the degree of overlap between benzene and ethanol plumes
 - lower benzene retardation and low background oxygen concentrations increase plume overlap, which gives ethanol more time to deplete oxygen, which decreases benzene biodegradation rate, causing the plume to travel farther
- aquifers of greatest susceptibility to increased benzene plume length have low sorption capacity (low organic carbon content) and low dissolved oxygen
- the effect of enhanced benzene solubility due to ethanol cosolvency is expected to be small because of its short duration
- a 2-D approach will significantly overpredict plume migration distances, therefore 3-D simulations are necessary to "correctly represent the biodegradation process which occurs predominantly in the mixing zone around the surface of the plume"
- this study indicates a minor influence of ethanol on benzene mass loss whereas laboratory and microcosm studies have indicated a pronounced reduction of benzene degradation in the presence of ethanol

Reference

Molson, J.W., Barker, J.F. and E.O. Frind, "Modeling the Impact of Ethanol on the Persistence of Benzene in Gasoline-Contaminated Groundwater," *Water Resources Research*, Vol. 38, No. 1, 2002; <http://www.awra.org>

See also "The Fate, Transport and Remediation of the Gasoline Additive Ethanol," by James M. Davidson and

Daniel N. Creek, Alpine Environmental, Inc., *Proceedings of the Conference on Petroleum Hydrocarbons and Organic Chemicals in Ground Water*, Anaheim, California, 2000, NGWA; <http://www.ngwa.org>



Contaminated soils management

This article summarizes how Minnesota's Department of Transportation (Mn/DOT) manages its petroleum-contaminated soil. Mn/DOT can encounter petroleum contamination at state-owned facilities and along state right-of-way during highway construction projects. Contamination sources can include LUSTs, leaks from failed hydraulic systems, and petroleum spills on highway right of way or on properties acquired by Mn/DOT, such as former rail yards.

"What to do with petroleum-contaminated soil has become more complicated over the past years. Historically, the regulatory approach to soil petroleum contamination has ranged from requiring removal of all impacted soil for ex-situ treatment to leaving it in place to naturally biodegrade—and every option in between. Available treatment options to remediate the impacted soil have been influenced by technological advances and changing regulatory philosophies, usually with an emphasis by regulators on utilizing the most recently developed remediation technique. In addition to technical issues, another factor that has determined the treatment methodologies promoted by environmental regulators has been public comment, which if vocal enough, has dictated policy" (Kamnikar, 2001).

Changing philosophies as well as local politics influence cleanup technology selection. Even within the same agency, practices can vary. In the 1980s and early 1990s, ex-situ technologies achieved prominence.

Soils were excavated with the intention of removing all impacted soil. Ex-situ techniques include thinspreading, landspreading, thermal treatment and, beginning in the early 1990s, biomounds.

Thinspreading and landspreading

"Thinspreading applies to excavated quantities of contaminated soil that are less than 7.6 m³ (10 yd³). The soil is spread as thinly as possible at the site where it was excavated, preferably over a grassy area. Petroleum contaminant concentrations are reduced through volatilization or natural degradation. As long as the soil is not saturated with petroleum, permission can be granted to thinspread the soil on-site. Until the mid-1990s, approval to thinspread soils...usually required only verbal approval from a regulator. As the public became more sensitive to issues related to contaminated soil handling, this process became more formalized, requiring written approval from state regulators and notification of local government" (Kamnikar, 2001).

Landspreading involves tilling the contaminated soil into the upper soil horizon, making the petroleum more available to petroleum-consuming soil bacteria. Hydrocarbons are also removed by volatilization involved with handling and degraded by exposure to the sun's radiation. The landspread site must meet certain criteria, which include

- a minimum depth to groundwater: not less than 1.2 m (4 ft)
- appropriate soil type: organic soils with sufficient nutrient content to support high soil bacteria populations
- minimum slope: not greater than 4 percent
- adequate setback distances to surface waters, property boundaries, water supplies, drain tiles and habitable buildings

Other restrictions apply:

- most approvals stipulate single-use, e.g., the site can only be used once for land treatment; there are, however, a small number of commercially operated multiple-use landspread sites
- a maximum allowable spreading thickness of 10.1 cm (4 inches) of contaminated soil, which could require large areas of land

The cost of thinspreading is estimated to be about \$15/m³ (\$11.5/yd³). The technique has several limitations:

- Mn/DOT cannot always find suitable landspreading sites
- negative public opinion, generated presumably by citizens not involved sufficiently early in the process, often persuades local governments not to accept the landspreading idea
- multiple sampling events are usually required to ensure that soil is being remediated

Thermal treatment

Thermal treatment involves heating the soil to a high enough temperature so that contaminants volatilize or are chemically destroyed. Advantages of thermal treatment include

- immediacy
- reduced long-term liability
- a fairly easy regulatory approval process
- ability to remediate heavier-end hydrocarbons
- requirement (usually) of only one sampling event to ensure clean soil

Disadvantages include

- potentially long hauling distances, which could make thermal treatment cost-prohibitive

- treatment costs fairly high in comparison to other techniques, \$55/m³ (\$46/yd³) and significantly higher than landspreading
- minimum volume requirements for mobile units of about 1,000 m³ (1,308 yd³)
- potential liability with facilities that do not adhere to permit conditions or fully treat contaminated soil

In general, Mn/DOT uses thermal treatment when soils have high contaminant concentrations (3 or 4 percent petroleum hydrocarbons by weight) or when petroleum products include heavier-end hydrocarbons such as hydraulic oils. The number of contractors that thermally treat soils varies, but the number is expected to decrease because of additional requirements for such facilities. Kamnikar (2001) reports that use of thermal treatment has decreased over the past several years.

A changing philosophy among state and federal regulators has resulted in a reduction of the amount of contaminated soil excavated from leak sites. In Minnesota, contaminated soil is removed only if

- it is completely saturated with free product
- the total volume of contaminated soil does not exceed 115 m³ (150 yd³) and is not in contact with groundwater
- new USTs will be installed in the same basin

Rather than excavating large volumes of soil as was done in the past, regulators require owners to complete a drilling investigation and risk assessment of the leak site to determine appropriateness of excavating impacted soil.

Biomounds

Biomounds, which can be thought of as a form of composting, use native microorganisms and sometimes laboratory-developed microbial strains to degrade contaminants. This technique was first described in

UTTU in 1992 (Vol. 6, No. 5). "Naturally occurring bacteria already present in the soil usually has the ability to efficiently degrade petroleum compounds, as long as concentrations do not exceed approximately 3 to 4 percent by weight... Because aerobic degradation of petroleum compounds is more efficient than anaerobic degradation, a passive air injection system is placed within the biomound to facilitate air diffusion. The biomound is essentially sealed off from the atmosphere with polyethylene sheeting except for vertical open-ended pipes connected to the horizontal passive air injection system. The vertical pipes are the in-flow and out-flow points for the aeration system. Air flow through the biomound is driven by a pressure gradient established by the change in elevation between the pipe openings. Also, air flow is likely influenced by thermal convection within the biomound" (Kamnikar, 2001).

Passive air systems may be selected over air injection systems for several reasons:

- sites located in remote areas do not always have available electricity
- without the blowers or vacuum systems, overall equipment cost of the system is reduced
- active air injection systems could strip needed moisture from the biomound
- state regulators may be concerned that active air injection systems could volatilize hydrocarbons, releasing contaminants to the atmosphere

Other facts about biomounds:

- manure added to soil (to supply nutrients, moisture and bulk) extended treatment time during the colder months and lessened soil compaction, thereby increasing soil diffusivity
- fine-grained soils can take as long as 1 to 2 years to treat; coarse-grained soils can be remediated in less than a year

- treated soil product has been used as surface dressing along highways or in landscape berms
- hauling materials consumes a large percentage of project cost, consequently, hauling distances are critical
- cost is about \$20/m³ (\$15/yd³)
- a supply of manure, woodchips or other bulking agent increases biomound effectiveness
- the procedure is more labor-intensive than landspreading
- the biomound must be dismantled after cleanup is complete
- heavier-end hydrocarbons may not be remediated
- biomounds may require multiple sampling events

Advantages:

- site can be reused
- biomounds are usually less expensive than landfilling or thermal treatment, depending on haulage costs
- the process results in recycling of contaminated soil, low-grade woodchips and manure
- permitting is readily available
- cleaned soil may be beneficially reused onsite
- the simple design and lack of sophisticated equipment "may result in remediation of soils that otherwise might not be treated, especially in developing nations"

Other ex-situ treatment options

Other ex-situ treatment options, some of which require special permission, include

- incorporation of small quantities of petroleum-contaminated soil in cold mix asphalt
- landfilling, which is not encouraged because

landfilling doesn't result in contaminant destruction; costs also vary greatly

- use of soils as daily cover for landfills; this is considered a beneficial use, because cost is less than disposal by landfilling
- use of soil as controlled fill on another part of the construction project
- use of soil beneath parking areas at building construction sites

In-situ options

Petroleum-contaminated soils at Mn/DOT facilities have not been treated by active in-situ techniques to date. Highly contaminated soils (soils saturated with petroleum hydrocarbons) are excavated and treated ex-situ, or soils are left in-situ to biodegrade naturally. In addition, many Mn/DOT sites are in remote areas and generally not in the vicinity of sensitive receptors. Because these facilities are constructed as slab on grade and the maintenance yards are large, vapor accumulation in substructures is not a problem and any contaminated soil/groundwater is usually confined to the site. For these reasons, it is usually appropriate to allow natural degradation to reduce contamination concentrations rather than to spend limited resources to speed up degradation through active in-situ techniques.

Conclusions

Kamnikar (2001) concluded the following:

- treatment/disposal options other than those discussed in state or federal regulatory guidelines may be acceptable, and responsible parties should seek out these other options
- non-traditional treatment practices may be accepted on a site-specific or pilot project basis
- even within the same regulatory agency, different

programs may support and provide information on different remediation alternatives

- early community involvement in decision making, especially where new and innovative techniques are proposed, is crucial to develop an atmosphere of trust and goodwill
- sharing remediation experiences with regulators, other responsible parties and consultants helps all to learn from the experience

Reference

Kamnikar, B., "Managing Petroleum-Contaminated Soil: Department of Transportation Perspective," *Journal of Environmental Engineering*, December 2001; <http://ojs.aip.org/eeo>.

See also:

"Biomounds Pass Tests in Minnesota," Kamnikar, B., *Soil & Groundwater Cleanup*, May 1996; <http://www.aehsmag.com>

"Spill Plans for Transportation Maintenance Facilities: How Minnesota Complies with the Federal Rule," *Transportation Research News*, January-February 2001; <http://www.nas.edu/trb/>

UTTU thanks Brian Kamnikar, Senior Engineer, Minnesota Department of Transportation (brian.kamnikar@dot.state.mn.us) for his help on this article.



Biodegradation information from hydrogen isotopes

Scientists can estimate how much a hydrocarbon spill has biodegraded by examining contaminant and electron acceptor concentrations. Concentration reductions, however, may also result from physical

processes such as volatilization, sorption, and plume dilution. A drawback to this strategy is the difficulty of obtaining accurate mass balances of contaminants and electron acceptors.

"Recently, compound-specific isotope analysis (CSIA), or measurement of the $^{13}\text{C}/^{12}\text{C}$ or $^2\text{H}/^1\text{H}$ ratios of petroleum hydrocarbons, has been used to measure biodegradation of these contaminants. This is done by measuring the shift in isotopic composition ($\delta^{13}\text{C}$ or $\delta^2\text{H}$ values) of the residual contaminant compared to its original value. For certain compounds, as biodegradation proceeds, the residual contaminant becomes enriched in heavier isotopes (^{13}C , ^2H) and depleted in the lighter isotopes (^{12}C , ^1H) due to faster reaction rates of bonds containing the light isotopes. The result is that the isotopic signature of the residual contaminant shifts to increasingly more enriched values as biodegradation proceeds" (Mancini and others, 2002). Laboratory studies have shown that volatilization, dissolution and sorption do not cause fractionation outside of the analytical uncertainty typical for CSIA (± 0.5 percent). Isotope fractionation studies have revealed the following:

- carbon isotopes during biodegradation of chlorinated hydrocarbons indicate large and reproducible ^{13}C enrichments on the order of 10 ppm
- laboratory studies of aromatic hydrocarbons that investigated carbon fractionation (anaerobic and aerobic studies) documented significantly smaller degrees of fractionation
- one study of aerobic biodegradation of toluene that used a mixed consortium indicated no resolvable carbon isotope fractionation
- another study of aerobic biodegradation of benzene that used a mixed consortium reported a +2.0 percent carbon isotope fractionation, observed only

at a late stage of biodegradation

- anaerobic biodegradation of toluene by a mixed consortium showed a small carbon isotope fractionation of +2.4 percent and +2 percent at > 90 percent biodegradation for sulfate and anaerobic methanogenic biodegradation of benzene
- carbon isotopic shifts of < +6 percent between 90 and 98 percent degradation of toluene under nitrate, iron and sulfate reducing conditions were indicated
- aerobic biodegradation of benzene by two pure cultures gave shifts in carbon isotope values between +3.4 percent at 90 percent biodegradation and +5.5 percent at about 78 percent biodegradation
- hydrogen isotope fractionation of anaerobic methanogenic biodegradation of toluene indicated a > +60 percent fractionation; the same consortium produced a carbon isotope fractionation of only +2 percent; in the same study, hydrogen isotope enrichment of toluene became apparent at 32 percent biodegradation, unlike carbon isotope fractionation, which was resolvable only at > 90 percent biodegradation
- a study of aerobic biodegradation of 70 percent benzene showed +23 percent hydrogen isotopic fractionation
- one researcher suggested that carbon isotope analysis might be appropriate for identifying different sources of BTEX, and hydrogen isotope analysis would provide evidence of aromatic hydrocarbon biodegradation in the field

Study area

Mancini and others (2002) studied an industrial site in the southern Netherlands contaminated with benzene,

ethylbenzene, toluene, xylene and styrene. Site characteristics are as follows:

- a subsurface consisting of alternating layers of sand, clay and silt underlain by an impermeable clay
- precipitation that exceeds evaporation, resulting in a net infiltration of 100-200 mm/year
- dissolved plume of aromatic hydrocarbons that is approximately 160 m long, located in an aquifer of permeable sand between 11 and 18 m below surface
- an aquifer that is semiconfined
- average groundwater flow velocity of approximately 5 m/yr
- groundwater flow predominantly horizontal but with a downward vertical component of approximately 0.2 m/yr, determined by net infiltration rate of the study area

Sampling and analysis

Field workers took samples of temperature, pH, dissolved oxygen and electrical conductivity, dissolved inorganic carbon, dissolved methane and contaminants from 22 wells. Researchers determined that "The dissolved benzene and ethylbenzene plume is located within an anaerobic zone where methane concentrations are as high as 37 mg/l. Besides methanogenesis, sulfate reduction and iron reduction appear to be dominant redox processes for oxidation of natural sedimentary organic matter. High methane concentrations alone cannot be used as unambiguous proof of biodegradation of the aromatic pollutants, however, because natural sedimentary organic carbon may contribute to the reduction of the electron acceptors" (Mancini and others, 2002). Therefore researchers analyzed stable carbon and hydrogen isotopes of dissolved benzene and ethylbenzene to provide more conclusive evidence of biodegradation.

Results

Basing their analysis on hydrogen isotopic evidence, researchers found that benzene and ethylbenzene came from two different source areas. "Even at a complicated site such as this one, where mixing of different contaminant sources cannot be ruled out, the substantial hydrogen isotope fractionation effects observed with respect to both source areas provide conclusive evidence of biodegradation. Results from isotope analysis at this field site indicate that while carbon isotopes have the ability to identify late stages of biodegradation, hydrogen isotopes are a more powerful tool to identify biodegradation of aromatic hydrocarbons even at low percent biodegradation, due to the larger fractionation found for hydrogen isotope values. The extent of hydrogen isotopic enrichment in the most biodegraded wells is an order of magnitude larger than carbon isotopic enrichment... Nevertheless, combined carbon and hydrogen isotope analyses provide the ability to compare biodegradation in the field based on two different parameters and, hence, provide a stronger basis for assessment of contaminant biodegradation" (Mancini and others, 2002).

Reference

Mancini, S.A., Lacrampe-Couloume, G., Jonker, H., Van Breukelen, B.M., Groen, J., Volkering, F. and B. Sherwood Lollar, "Hydrogen Isotopic Enrichment: An Indicator of Biodegradation at a Petroleum Hydrocarbon Contaminated Field Site," *Environmental Science & Technology*, Vol. 36, No. 11, 2002; <http://www.pubs.acs.org>



Research notes

Assessment of Natural Attenuation of Chlorinated Aliphatics and BTEX in Subarctic Groundwater

Richmond, S.A., Lindstrom, J.E. and J.F. Braddock, *Environmental Science & Technology*, Vol. 35, No. 20, 2001; <http://www.pubs.acs.org>

Researchers assessed the applicability of monitored natural attenuation of trichloroethene (TCE), trichloroethane (TCA) and benzene in a subarctic aquifer. The site is characterized by discontinuous permafrost and a sediment thickness of about 180 m. The regional hydraulic gradient, 1.23 mm/m, varies locally and seasonally. Depth to groundwater is between 0.3 and 5.0 m below ground surface. Aquifer porosity is 25 to 40 percent while groundwater velocity is approximately 1 m/day.

Microbiological analyses, which used glutamate mineralization potentials to indicate heterotrophic activity, indicated that microorganisms did not function optimally at this site. "The fact that heterotrophic activity was greater at 25°C implies that the microbial community present is psychrotolerant (i.e., capable of growth at colder temperatures but functioning optimally at temperatures between 25°C and 30°C). This is notable in that groundwater at this and other subarctic sites is permanently cold, varying by only a few degrees during the year. While microorganisms present in ocean floor sediments have adapted to growth at permanently cold temperatures, this apparently is not the case at this site. Further support for this interpretation is provided by microscopic examination. Although numerous cells are present, many had sporulated, and few were actively dividing. These data and observations suggest that,

even with an ample supply of readily oxidizable substrate electron acceptor and nutrients, biodegradation rates are likely to be much lower at this site than those seen in more temperate climates" (Richmond and others, 2001).

Researchers concluded: "Determining that intrinsic bioremediation is a viable treatment strategy can be difficult, as demonstrated at this subarctic site. Because of low contaminant concentration, high background concentrations of sulfate, chloride, and alkalinity, uncertain TEAP (terminal electron acceptor potential) determination, and extremely low microbial activity, this study was not able to conclusively document footprints characteristic of intrinsic bioremediation... sediment microcosms designed to examine contaminant transformation and measurement of in-situ organic acids expected from microbial contaminant transformations may provide essential data when attempting to document intrinsic bioremediation of BTEX and chlorinated aliphatics in this and other dilute systems" (Richmond and others, 2001).

Evaluation of a Cost-Effective SVOC Field Screening Technique for Use at Petroleum-Contaminated Sites

Hood, G.M., Allee, P.C. and P.G. Pucel, *Contaminated Soil, Sediment and Water*, June 2002; <http://www.aehsmag.com>

Researchers adapted the fluorescence spectroscopy laboratory technique (widely used in biochemical research laboratories) as a field screening technique for detecting SVOC (semi-volatile organic compounds). A field worker in an eight-hour day can screen 30 to 40 samples. The cost per sample is about 20 dollars. "Extraction fluorescence can provide better reproducibility than comparable VOC techniques while offering a wider dynamic range because of the technique's ability to use dilutions."

Hydrogeologic Assessment of In-situ Natural Attenuation in a Controlled Field Experiment

Devlin, J.F., McMaster, M. and J.F. Barker, *Water Resources Research*, Vol. 38, No. 1, 2002; <http://www.agu.org/wrr>

Researchers created an experiment to investigate the natural attenuation of toluene (TOL), carbon tetrachloride (CT) and tetrachloroethene (CF). They performed the experiment in a 24 m-long, 3 m-deep, three-sided sheet pile alleyway (a gate) in a pristine, unconfined aquifer at the Canadian Forces Base, Borden Province. The site was covered with a greenhouse structure, which not only protected equipment and instrumentation but prevented local recharge by rainfall or snowfall that might have affected hydraulics. "With the hydraulics tightly controlled, an experimental setting was established that made it possible to address the second objective of this study: to attempt mass balances and compare the results with biodegradation assessments based on contaminant distribution snapshots and flux differences along the flow path. A further objective was to evaluate the effects of mixed contaminants on degradation behavior" (Devlin and others, 2002).

Results of the experiment indicated

- low concentrations of CT, CF and TOL occurred rapidly and within a short distance of the source, < 18 m
- the manner of plume evolution suggests that in-situ microorganisms adapt to the presence of contaminants, utilize them, and then grow, causing increased mass loss rates; plume recession begins once the degradation rates exceed the influx rates
- the mere presence of degradation products is not sufficient to infer significant rates of natural attenuation

- for degradation to be quantifiable (in this study), contaminant half-life had to be 60 days or less; such a half-life corresponds to a travel distance of only a few meters; therefore, degradation must be quite rapid to be detected by this study's methods
- concentration profiles were limited by variation in source strength; plumes must be stabilized before associating instantaneous concentration distributions with short-term fluctuations
- to perform an ideal mass balance, a parcel of plume must be tracked as it passes two fences, and any losses must be calculated; "the larger the parcel, the more reliable the estimated degradation rate; although this is a preferred approach in theory, it was found to be a time-consuming method in practice that imposed limitations on which data could be considered"
- fluxes can be determined for different time intervals and at different fences and compared directly; this has the potential of greatly facilitating the analysis and shortening the data collection time

Hydrolysis of tert-Butyl Methyl Ether (MTBE) in Dilute Aqueous Acid

O'Reilly, K.T., Moir, M.E., Taylor, C.D., Smith C.A. and M.R. Hyman, *Environmental Science & Technology*, Vol. 35, No. 19, 2001; <http://pubs.acs.org>

MTBE is typically an unreactive compound, yet researchers recently analyzed the rate of MTBE hydrolysis in aqueous solutions. Near a neutral pH of 7, rate of MTBE hydrolysis "is too slow to have a significant impact on the fate of this compound; at pH 7, the half-life of MTBE is thousands of years. The observation of surface-catalyzed hydrolysis, however, may have implications for MTBE fate in some subsurface environments. The role of soils in catalyzing the hydrolysis of

organic compounds has been recently discussed" (O'Reilly and others, 2001). Results suggest that the surface acidity of clay can be 2 to 4 pH units lower than the bulk solution. "Although the acidity of clays decreases as water content increases, clays can be used as solid acids in aqueous solutions... Although the stability of MTBE at many sites indicates that abiotic transformation may not be common, the high surface area of clays, coupled with the high solids-to-water ratio of the subsurface, suggests a possibility of surface-catalyzed reactions."

Researchers believe that "one area of research that is potentially impacted by the current findings is the role of anaerobic microbial degradation of MTBE. To date, all of the isolated MTBE-degrading microbial cultures are aerobic, and this is consistent with a role for oxygenase enzymes in the initial cleavage of the ether bond." Research suggests some limited anaerobic MTBE degradation; however, the mechanism of MTBE degradation is unknown. "While anaerobic conditions obviously exclude the possibility of an oxygenation reaction directed at MTBE, an enzyme-catalyzed hydrolysis of MTBE could potentially occur under either aerobic or anaerobic conditions. The enzymes that may be involved in MTBE anaerobic degradation are not known." Authors conclude: "The results presented in this study suggest that ether oxygenated may be sufficiently susceptible to hydrolysis to be subject to enzymatic cleavage" (O'Reilly and others, 2001).

Investigation of the Vadose Zone Using Barometric Pressure Cycles

Neeper, D.A., *Journal of Contaminant Hydrology*, Vol. 54, 2002; <http://www.elsevier.com/locate/jconhyd>

This article describes an investigation of the vadose zone with respect to its ability to transmit barometric pressure variations. Such information is valuable "as

preparation for either active or passive soil vapor extraction in ash flow tuffs, where it was feared that subsurface airflow might occur mainly in fractures and consequently be ineffective for removal of volatile contaminants. The purpose of this paper is to illustrate a technique for investigation of hydrologic properties and airflow" (Neeper, 2002).

Monitoring Well Comparison Study: An Evaluation of Direct-Push vs. Conventional Monitoring Wells

Alvarez, G. and V. Kremesee, U.S. EPA, OUST, May 2002; <http://www.epa.gov/swrust1/cat/sitechar.htm>

Researchers carried out a study designed to compare data from direct push vs. monitoring wells. The study took place at two sites in Georgia and two in Ohio. Study conclusions are as follows for the two well types:

- groundwater levels measured were nearly identical
- MTBE concentrations measured were nearly identical
- BTEX concentrations measured were nearly identical at three sites; the fourth site may have had a systematic error
- total suspended solid concentrations were higher from direct push wells
- a statistical analysis of the geochemical data indicates no difference in concentrations between the two well types

Removal of NAPLs from the Unsaturated Zone Using Steam: Prevention of Downward Migration by Injecting Mixtures of Steam and Air

Schmidt, R., Gudberg, J., Sonnenborg, T.O. and K.H. Jensen, *Journal of Contaminant Hydrology*, Vol. 55,

2002; <http://www.elsevier.com/locate/jconhyd>

One-dimensional laboratory experiments have shown that steam can remove volatile or semivolatile contaminants from saturated and unsaturated porous media. Steam injection has been shown (using two-dimensional studies) to remediate heterogeneous porous media. A potential drawback of this technique would be increased contaminant mobility and possible vertical migration due to gravitational forces. Another study indicated that heating the area below the contaminant, thereby creating an underlying steam zone, could arrest contaminant downward migration.

Schmidt and others (2002) performed steam and steam-air injection experiments in a 2-dimensional sandbox to remediate unsaturated porous media contaminated by two different NAPLs. "The pure steam injection experiments demonstrated downward migration of accumulated NAPL ahead of the heat front in the unsaturated zone, suggesting the phenomenon will be a major concern with regard to field-scale operations. The steam-air mixture injection experiments showed that downward migration can be avoided when mixing steam and air as a consequence of three mechanisms:

- the noncondensable air will remove some of the contaminant and, consequently, less NAPL can accumulate
- the temperature gradient at the heat front is less steep, implying that the area where the contaminant condenses is larger
- the velocity of the evaporation front is lower than the velocity of the heat front; consequently, it is not the total mass of NAPL that accumulates at the front"

Other articles of interest include the following:

"Bioenhancement of NAPL Pool Dissolution: Experimental Evaluation," Seagren, E.A., Rittmann, B.E. and A.J.

Valocchi, *Journal of Contaminant Hydrology*, Vol. 55, 2002; <http://www.elsevier.com/locate/jconhyd>

"Electrokinetic Ion Transport Through Unsaturated Soil: 1. Theory, Model Development and Testing," Mattson, E.D., Bowman R.S. and E.R. Lindgren, *Journal of Contaminant Hydrology*, Vol. 54, 2002; <http://www.elsevier.com/locate/jconhyd>

"Evaluation of VOC Loss from Soil Samples," Sorini, S.S., Schabron, J.F. and J.F. Rovani, *Contaminated Soil, Sediment and Water*, June 2002; <http://www.aehsmag.com>

"Experimental Evaluation of Fouling Processes in Porous Polyethylene Well Screens Used for Horizontal Wells," Logan, A.J., Sigrist, R.L. and J. Munakata-Mars, *Ground Water Monitoring and Remediation*, Winter 2002; <http://www.ngwa.org>

"Influence of Rate-Limited Sorption on the Cleanup of Layered Soils by Vapor Extraction," V. Kalris, *Journal of Contaminant Hydrology*, Vol. 55, 2002; <http://www.elsevier.com/locate/jconhyd>

"Particulate Coal in Soils and Sediments: Recognition and Potential Influences on Hydrocarbon Fingerprinting and Concentration," Stout, S.A., Emsbo-Mattingly, S., Uhler, A.D. and K.J. McCarthy, *Contaminated Soil, Sediment and Water*, June 2002; <http://www.aehsmag.com>



Information sources

U.S. EPA Web sites and documents

Publications that can be downloaded from <http://clu-in.org/techpubs.htm> include

- Elements for Effective Management of Operating Pump-and-Treat Systems (EPA 542-R-02-009)

Videos that can be viewed at U.S. EPA's Web site, <http://clu-in.org/studio>, include

- Field-Based Geophysical Technologies Seminar: Part I
- In-Situ Treatment of Groundwater Contaminated with NAPL
- ITRC Phytotechnologies

Citizen's Guides, <http://www.cluin.org/products/citguide>

Economic Analysis of the Implementation of Permeable Reactive Barriers for Remediation of Contaminated Ground Water (EPA 600-R-02-034), http://www.epa.gov/ada/download/reports/epa_600_r02_034.pdf

Information on Open-Path Measurement Technologies, such as ultraviolet differential absorption spectroscopy, Fournier Transform-infrared spectroscopy and light detection and ranging, <http://clu-in.org/21m2>

Long-term Performance of Permeable Reactive Barriers Using Zero-Valent Iron (EPA 600-S-02-001), http://www.epa.gov/ada/download/briefs/epa_600_s02_001.pdf

Remediation Technologies Development Forum Update, <http://clu-in.org/download/rtdf/updt0802.pdf>

Superfund Remedy Decisions Internet Web Page, <http://www.epa.gov/superfund/action/guidance/remedy/index.htm>

Technical Approaches to Characterizing and Redeveloping Brownfield Sites: Municipal Landfills and Illegal Dumps (EPA 625-R-02-002), <http://www.epa.gov/ORD/NRMRL/Pubs/625R02002/625R02002.htm>

Other Web sites and documents

Engineering and Design: Soil Vapor Extraction and Bioventing (EM-1110-1-4001),

<http://www.usace.army.mil/usace-docs/eng-manuals/em1110-1-4001/toc.htm>

Environmental Effects and Dredging and Disposal Database (E2-D2), <http://www.wes.army.mil/el/e2d2/index.html>

Evaluating Hydrocarbon Removal from Source Zones and its Effect on Dissolved Plume Longevity and Concentration, <http://www.api.org/lnapl>

Fate and effects of gasoline oxygenates, <http://ese.ogi.edu/research.html>

IronRefs database, <http://ese.ogi.edu/research.html>, contains data on groundwater remediation application of zero-valent metals

One-Stop Shopping for USGS Information on Remediation, <http://toxics.usgs.gov/topics/remediation.html>

RODS Database, records of decision, <http://cfpub.epa.gov/superrods/>

Systematic Approach to In-Situ Bioremediation: Nitrates, Carbon Tetrachloride and Perchlorate (ISB-8), <http://www.itrcweb.org/user/isb-8.pdf>

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