



Underground Tank Technology Update

Vol. 19, No. 5 September/October 2005



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 (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 Pat Dutt (pdutt@twcny.rr.com) or call 607-272-3212.

Advisory Board

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

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

Kristin Underwood, 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

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
Pat Dutt	Geologist/Writer
Darrell Petska	Copy Editor
Debbie Benell	Program Assistant

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.

Brief article summaries

-  **Anaerobic biodegradation of BTEX and ethanol2**
Aerobic BTEX biodegradation often requires not only oxygen and nutrients to stimulate aerobic biodegradation but also the proper distribution of oxygen and nutrients. The biodegradation process can be further complicated by BTEX that contains ethanol; such plumes could be "technically difficult and prohibitively expensive" to remediate.
-  **Modeling small-volume releases of ethanol3**
Lahvis modeled the transport of a small volume of gasohol in the vadose zone to determine the risk of such releases to groundwater. Small-volume releases are those that occur during routine fueling operations, during equipment repair and at leaky joints and connections.
-  **Material delivery5**
Nyer and Page predict that scientists "will solve most of the chemical, biochemical and geochemical problems associated with destroying or immobilizing" our present contaminants. They predict that most remedial techniques-existing or to be developed-will help remediate an aquifer; however, delivering "effectively the necessary material to the point of contamination in the aquifer" may still be a problem.
-  **PAH biodegradation in river sediments6**
Scientists conducted batch experiments on polycyclic aromatic hydrocarbons (PAHs) from river sediments, under aerobic and anaerobic conditions, to better understand the "interactions between the biodegradation of natural humic-like organic matter and the fate and dissipation of PAHs..."
-  **Humic acids in soil remediation.....8**
To compare the efficiency of humic acids (HAs) to that of some common surfactants, scientists examined extraction procedures of two soils. One soil was rich in PAHs and the other was rich in thiophenes.
-  **The City of Los Angeles Former Gas Station Sites Program, part V9**
This section of the brownfields report addresses funding sources for remediation of former gas station sites. Sources include federal funding sources, Community Development Block Grant funds, revolving loan funds and cleanup grants and funding sources specific to California.
-  **Research notes..... 11**
Research notes review articles on the effect of water contact with petroleum and a groundwater circulation well alternative.



Anaerobic biodegradation of BTEX and ethanol

Aerobic BTEX biodegradation often requires not only oxygen and nutrients to stimulate aerobic biodegradation but also the proper distribution of oxygen and nutrients. The biodegradation process can be further complicated by BTEX that contains ethanol; such plumes could be “technically difficult and prohibitively expensive [to remediate]. Specifically, ethanol would be present at much higher concentrations than BTEX, which would significantly exacerbate the biochemical oxygen demand (BOD) and nutrient requirements of the system, and possibly contribute to clogging due to excess microbial growth on ethanol if (high-yield) aerobic conditions are maintained. Therefore, anaerobic bioremediation strategies should be considered for the cleanup of gasohol releases, especially near the source zone, which is invariably anaerobic” (Da Silva and others, 2005).

Da Silva and others (2005) sought to address the question of how to enhance anaerobic bioremediation of BTEX and ethanol. Their idea was to increase the electron acceptor pool by adding sulfate, chelated Fe(III) or nitrate. Scientists compared concentration profiles “along the length of flow-through aquifer columns to investigate the geochemical transitions and spatial variation in biodegradation efficiency before and after biostimulation. The role of molecular oxygen as an adjunct electron acceptor under microaerophilic conditions was also addressed.

Anaerobic bioremediation

As opposed to aerobic bioremediation, anaerobic bioremediation has

- relatively inexpensive anaerobic electron acceptors
- chemically more stable electron acceptors

- smaller biomass accumulation and fewer clogging problems

Experimental approach

The scientists’ laboratory experiment consisted of

- four glass aquifer columns with six sampling ports, continuously fed with BTEX and ethanol, and dissolved in synthetic groundwater
- a control column
- columns packed with aquifer material from a BTEX-contaminated site in Travis Air Force Base
- columns amended with K_2SO_4 , Fe(III)-EDTA or $NaNO_3$
- chelated Fe(III) added to facilitate distribution and enhance BTEX bioavailability
- electron acceptor concentrations added that “were equivalent on an oxidation capacity basis...and exceeded the theoretical stoichiometric requirements for the mineralization of the added BTEX”

Flow velocities were in the typical range of groundwater flow velocities. One day was required to displace one pore volume, and after three pore volumes had been exchanged, scientists measured BTEX and ethanol biodegradation efficiencies. Da Silva and others (2005) analyzed the column for the following:

- BTEX
- ethanol
- methane
- acetate
- sulfate
- nitrate
- dissolved Fe(II)

Columns were tested in each of two phases: natural attenuation and biostimulation.

Results and conclusions

For phase one, natural attenuation, Da Silva and others (2005) found BTEX and ethanol losses were small (< 20 percent) in the poisoned (control) column, thus, “implying that high removal efficiencies in non-sterile columns were mainly due to biodegradation.” In addition, “BTEX biodegradation efficiencies decreased significantly following the addition of ethanol. The preferential biodegradation of ethanol near the inlet rapidly consumed the dissolved oxygen that could have been...available for BTEX biodegradation, and relatively high BTEX concentrations were detected in the effluent even after 80 days of acclimation. The high electron acceptor demand exerted by the ethanol created strongly reducing conditions, decreasing the ORP (oxidation-reduction potential)... Lower ORP represents decreased thermodynamic feasibility of BTEX oxidation” (Da Silva and others, 2005).

Other results for phase one, natural attenuation, include:

- acetate, a common by-product of anaerobic ethanol biodegradation, biodegraded along with methane
- acetate, which served as a substrate for methanogenesis, led to methane accumulation
- under methanogenic conditions, BTEX biodegradation is slow; furthermore, “the ubiquity of anaerobic BTEX degraders in methanogenic consortia has not been established”

During phase two—anaerobic biostimulation—researchers added nitrate, sulfate or Fe(III)-EDTA (EDTA is a crystalline acid and a chelating agent) to methanogenic columns. Researchers found the following:

- benzene biodegradation increased from an average of 32 percent during phase one to greater than 70 percent for all biostimulated columns

- oxygen role is unclear, "although it is unlikely that sufficient oxygen was available to completely oxidize to CO₂ all influent benzene"
- perhaps an "anaerobic electron acceptor such as sulfate, chelated Fe(III) or nitrate could enhance benzene biodegradation, even in the absence of anaerobic benzene degraders, by accelerating the mineralization of ethanol or other substrates that are available under anaerobic conditions"
- toluene was the only hydrocarbon to disappear (> 99 percent) in sulfate- and nitrate-amended columns
- toluene was the most biodegraded (85 percent) under Fe(III)-reducing conditions
- benzene biodegradation efficiencies decreased (< 30 percent) after purging oxygen from the media; some benzene loss was due to increased volatilization
- electron acceptor utilization was rapid near the inlet and coincided with the highest ethanol biodegradation activity
- "In all cases, electron acceptor amendments fully inhibited methanogenesis, thus eliminating a potential risk of explosion"

Researchers concluded that

- "anaerobic benzene biodegradation is not always observed, and when it occurs it is often after acclimation periods greater than one year"
- this research was consistent with other research in that sulfate and nitrate could stimulate in-situ toluene biodegradation but not benzene biodegradation; "unlike benzene, toluene has a methyl group that is electrophilic; this apparently facilitates nucleophilic attack by water or by anaerobic catabolic enzymes such as benzylsuccinate synthase"
- under conditions typical of natural systems, sulfate,

- ferric iron and nitrate are thermodynamically more favorable electron acceptors than CO₂
- "sulfate, iron (III) and nitrate have different advantages and limitations for anaerobic biostimulation purposes; sulfate can accept more electrons than the other tested compounds, and its injection has been shown to increase benzene biodegradation in groundwater contaminated with petroleum hydrocarbons"; sulfate's use could be restricted given its impact on water taste, odor and potential laxative effects
 - Fe(III) by virtue of its high oxidation potential can enhance benzene mineralization; however, because of its low electron assimilation capacity, large quantities of Fe(III) may be required to be injected and the "EDTA chelator could affect microbial activity or act as a competing carbon source that hinders degradation of target pollutants" (Da Silva and others, 2005)
 - nitrate, which has the highest oxidation potential, is efficient at stimulating alkylbenzene biodegradation in situ, but nitrate may be regulated because of its potential to cause methemoglobinemia
 - "...multiple electron acceptors could be combined to increase the electron acceptor pool while meeting regulatory limits for drinking water... Whether this would result in synergistic interactions that improve the biodegradation efficiency of BTEX-ethanol mixtures remains to be determined" (Da Silva and others, 2005)
 - "A potential negative effect of biostimulation is the accumulation of biomass or precipitates that decrease aquifer porosity and permeability, hindering nutrient delivery and mass transport... occasional clogging was experienced in the column amended with EDTA-Fe(III), but not in the columns augmented with nitrate or sulfate. Apparently,

iron precipitation caused a significant decrease in effective porosity that hindered permeability, which represents a serious practical limitation for the injection of chelated Fe(III) as a biostimulatory compound" (Da Silva and others, 2005)

Da Silva and others (2005) ascertain that anaerobic biostimulation, through the addition of nitrate, sulfate, or chelated Fe(III), is a practical approach for cleanup of ethanol and some BTEX compounds such as toluene. This approach also alleviates the system's BOD demand and allows for "more efficient biotransformation of any residual BTEX in a subsequent aerobic (polishing) stage." Remediators need to examine the local groundwater chemistry to determine the potential for clogging due to mineral formation and precipitation. Other considerations include the accumulation of inhibitory by-products such as NO₂⁻ and H₂S.

Reference

Da Silva, M.L.B., G.M.L. Ruiz-Aguilar and P.J.J. Alvarez, "Enhanced Aerobic Biodegradation of BTEX-Ethanol Mixtures in Aquifer Columns Amended with Sulfate, Chelated Ferric Iron or Nitrate," *Biodegradation*, Vol. 16, 2005; <http://www.environmental-expert.com/magazine/springer/biod/>

UTTU thanks Dr. Alvarez, Alvarez@rice.edu, for his help on this article.



Modeling small-volume releases of ethanol

Lahvis (2003) modeled the transport of a small volume of gasohol in the vadose zone to determine the risk of such small-volume releases to groundwater. Small-volume releases are those that occur

- during routine fueling operations

- during equipment repair
- at leaky joints and connections

Lahvis used the computer model R-UNSAT (Lahvis and Baehr, 1997 in Lahvis, 2003) "to predict potential impacts of EtOH- (ethanol) blended gasoline and benzene as a function of

- distance between the source and groundwater
- soil type
- biodegradation
- groundwater infiltration rate

The computer model accounts for diffusion, groundwater infiltration, adsorption, and biodegradation processes, variable soil-moisture content and equilibrium partitioning among the solid, aqueous and gaseous phases" (Lahvis, 2003).

Modeling parameters included

- a gasoline containing 10 percent by volume EtOH, released at a rate of 120 g/d (0.04 gal/d liquid equivalent, which is assumed to be a conservative rate for small releases (Young and Golding, 2002 in Lahvis, 2003))
- a gasoline containing benzene, and a composite hydrocarbon (to account for transport of all other gasoline species, less benzene and EtOH)
- a three-meter-thick vadose zone with various release points
- coarse-grained and fine-grained soil
- depth-dependent soil moisture
- variable biodegradation rates
- groundwater infiltration rates of 0, 10 and 20 cm/y

Lahvis simulated EtOH biodegradation using a first-order decay model based on laboratory data, while benzene was simulated with a dual-Monod kinetics model. Modeling indicated that benzene

biodegradation was sensitive to O_2 concentration. In this model, the capillary zone was simulated using a soil moisture distribution based on vadose zone properties and steady infiltration.

Conclusions

Lahvis (2003) concluded that EtOH and benzene effects on groundwater are not expected to be significant for most small-volume releases; the exception is when the source is less than 100 cm from groundwater, or if benzene biodegradation is limited. Furthermore, for equivalent transport conditions, the impact of MTBE-blended gasoline could be significant. For ethanol:

- "biodegradation is the most critical factor affecting EtOH transport"
- at low biodegradation rates, EtOH migration is sensitive to soil type; this is related to the effective diffusion coefficient; sensitivity to biodegradation increases in coarse-grained soil at half-lives > 14 days
- using a highly conservative biodegradation rate (half-life of 69 days), biodegradation limits downward EtOH migration to approximately 100 cm from the source
- only when EtOH biodegradation is extremely limited is groundwater infiltration (rate of 20 cm/yr) likely to enhance EtOH vertical migration; "results are based on assuming a constant infiltration rate"; actual rates could be greater depending on infiltration parameters
- soil moisture significantly retards EtOH transport and travel time to groundwater; travel time is dependent on soil type, biodegradation rate, and depth to groundwater

For benzene:

- biodegradation can significantly affect benzene transport to groundwater; however, biodegradation is "critically dependent on O_2 availability"
- "where O_2 is readily available, benzene transport is limited and the potential for a groundwater impact is small"
- where O_2 is limited (i.e. aerobic biodegradation), either because of "competing sources or restrictions on O_2 diffusion" (related to diffusion through porous media), benzene impact on groundwater can be significant
- benzene transport is highly sensitive to soil type: "in sand, infiltration occurring at 20 cm/yr has a negligible effect on benzene transport because of the compound's relatively low aqueous solubility; benzene migration can, however, be affected by infiltration under conditions where vapor diffusion is limited"
- in fine-grained soils, because aerobic biodegradation is limited below the source, benzene migration to groundwater is enhanced
- the presence of EtOH biodegradation "has only a minor effect on benzene transport; in coarse-grained soils (e.g. sand), benzene migrates far ahead of EtOH, precluding any limitations caused by EtOH degradation near the source; in fine-grained soil (e.g. sandy clay) the effects of preferential EtOH biodegradation are eclipsed by limitations on O_2 availability associated with biodegradation of benzene and other reactive gasoline constituents"
- the potential for benzene to impact groundwater is primarily dependent on depth to groundwater, and extent of biodegradation in the vadose zone

Reference

Lahvis, M.A., "Evaluation of Small-Volume Releases of Ethanol-Blended Gasoline at UST Sites," *American Petroleum Institute*, October 2003, No. 19; <http://www.api.org/bulletins>

UTTU thanks Dr. Bruce Bauman, bauman@api.org, for sending us this article, and Matthew Lahvis, matthew.lahvis@shell.com, for his help.



Material delivery

By Evan K. Nyer and Gregory B. Page

The main remediation problem that scientists will face over the next decade is material delivery. We predict that researchers will solve most of the chemical, biochemical and geochemical problems associated with destroying or immobilizing existing contaminants. In addition, the techniques we have, and will develop, will work in the aquifer; thus, in-situ treatment methods will be available for every contaminant. Nevertheless, how to effectively deliver the material to the aquifer's point of contamination will remain problematic.

Think of an aquifer as the United States and the U.S. Postal Service's need to deliver mail. The main problem is to use the correct combination of cars and boats etc. to deliver a letter, or a specific reagent to the clay sand lens where tetrachloroethene (PCE) resides, for instance. PCE enters the aquifer from the clay sand lens and contaminates our monitoring well. We have performed a series of tests showing that if we add this chemical (specific reagent) to the PCE-contaminated area, we will stimulate natural bacteria and degrade the PCE. The real problem is that we do not have a reliable method that delivers our letter (chemical) to the mailbox (clay sand lens).

To make our point a little stronger, we'll go through the current state of practice. Problems exist with even the most soluble, noninteracting reagents we possess, and they are compounded when the reagent or material interacts with the aquifer solids.

Delivery of soluble material

Anytime we use a well to inject material into an aquifer, some of the material is pushed into the aquifer. That means injection rate and material volume injected will have a significant effect on how far into the aquifer the material is pushed before the aquifer's natural water movement takes over and distributes our reactive agents—hopefully where we desire. Modeling the aquifer water's natural movement without the initial push would help us understand how our reagent would move in the aquifer.

The natural movement of oxygen in a gravelly sand aquifer occurs by constant diffusion from the well. Several technologies use diffusion from a single well as their method of delivering oxygen to the aquifer. In our model, the oxygen does not interact with the aquifer solids (a good assumption) and does not get used by the bacteria (a bad assumption).

In our model, oxygen would have a delivery of only two to three feet on each side of the well. Vertical spatial distribution would be even less. Thus, we would need to install wells every six feet to get complete coverage of the aquifer. Unless the aquifer were very shallow, that would not be a practical or cost-effective design. The bottom line is that we cannot simply rely upon the aquifer to distribute our soluble material.

It only gets worse from here. In the real world, our reagents do interact with aquifer solids, geochemistry and bacteria. If we are lucky, only a simple interaction occurs with the aquifer solids and the reagents do not move as fast as the water. Reagent movement would be retarded and have a small delay before reaching

the desired location. In general, simpler compounds produce smaller retardation. As reagents are retarded, diffusion has a larger effect on their movement and they produce a wider spread across the aquifer. Many reagents, however, interact with bacteria and are eliminated before they reach the desired location.

Thus, we cannot simply rely upon the aquifer to deliver the reagents. Current methods for soluble reagent delivery are mainly driven by contaminant location and/or site-specific characteristics. These methods include surface applications, conventional wells, recirculating wells, direct push points/temporary wells, borings, trenches, fractured emplacement and infiltration galleries. Delivery operation can be one-time applications, periodic manual or automated injections, or closed-loop recirculation systems. A grid or a successive curtain configuration is often used to address the plume. Regardless of reagent or delivery, the establishment of any reactive zone is never instantaneous and may take months to develop fully.

Delivery of solid (nonsoluble) material

Problems arise when we try to distribute material that is solid and that interacts with the aquifer solids. Most research, which involves bacteria injection into an aquifer, has shown that bacteria do not travel well through aquifers. The best recovery was about 2 to 3 percent and diminished from there depending on bacteria size, shape and charge, and aquifer type.

The work of Harvey and others (1989, in Nyer and Page, 2004) illustrated two problems with overall delivery of bacteria to the aquifer. First, the total amount of recovered bacteria was 2.6 percent. The more interesting result, however, was that all of the recovered bacteria came out in a very short period of time. That time period was the same as the bromide tracer. After that initial slug of bacteria, no more bacteria were recovered. Even with the huge reservoir of bacteria that

was placed into the aquifer, no more bacteria traveled to the recovery well.

Harvey and others' followup work (1997, in Nyer and Page, 2004) examined bacteria size. Scientists took bacteria from the aquifer and grew large quantities in the laboratory. They found that bacteria grown under natural conditions are smaller compared to the laboratory-propagated bacteria. The bacteria increased in size by a factor of three to four, and subsequent tests showed this had a significant effect on their mobility in the aquifer.

Becker (2003 in Nyer and Page, 2004) studied the effect of bacteria shape and charge in movement through fractured bedrock. Gram-negative rod bacteria had the best recovery at 3.5 percent. The rest of the shapes had < 1 percent recovery, and this is in a fractured bedrock.

These data sets are not too surprising. Before working on contaminated sites, we designed wastewater treatment systems, which included designing sand and multimedia filters. The main removal mechanism for filtration is solid-solid contact, not straining. The solid particle you want to remove comes into contact with the large sand particle in the sand filter, and the two get stuck to each other. Aquifers are one big sand filter and tend to be very efficient at removing solid particles. The difference between the negative- and positive-charged bacteria is that most of the sand is negatively charged. Opposites attract.

This makes bacteria the ultimate retarded material (material that travels very slowly). While the reactions may take place in the laboratory and microcosms, they will not take place throughout the aquifer unless we develop new delivery techniques.

Conclusions

We have already developed some great in-situ remediation technologies. Data show that we can now treat most compounds that affect our aquifers. Other new chemicals and methods being studied will extend the compound types that are treated and the environments in which they can be treated. The missing link is delivery of these magical chemicals and/or bacteria.

Sugars will have the easiest time being delivered due to their solubility and low retardation. Nevertheless, flow patterns in models show that delivering these compounds by injection wells will be severely limited. When we add interaction between the material that we want to inject and the aquifer solids, the problems multiply. With higher retardation, compound distribution within the aquifer becomes more problematic. Injection materials that are solid particles, such as bacteria, exhibit the greatest retardation.

This does not mean that any of these materials should be excluded: each one has specific problems related to its physical/chemical nature. But we need new delivery techniques. As we mentioned, "The main problem we will face in remediation over the next decade is delivery." The argument should not be over which is better: bacteria or sugars. The argument should be: what is the best delivery method.

Reference

Nyer, E.K. and G.B. Page, "Special Delivery," *Ground Water Monitoring and Remediation*, Vol. 24, No. 1, 2004; <http://www.ngwa.org>

Reprinted with permission from the National Ground Water Association.

UTTU thanks Thad Plumley, tplumley@ngwa.org, for his help on this article.



PAH biodegradation in river sediments

Scientists conducted batch experiments on PAHs (polycyclic aromatic hydrocarbons) from river sediments. Experiments were performed under aerobic and anaerobic conditions. The purpose of this work was "to study and define the relations and interactions between the biodegradation of natural humic-like organic matter and the fate and dissipation of PAHs in a river sediment" (Quantin and others, 2005).

PAHs

PAHs are hydrophobic compounds with two or more benzene rings. They can be naturally present in ecosystems or result from activities associated with coke and gas production, and petrochemical and oil industries. They can, by virtue of their hydrophobicity and recalcitrance, accumulate in sediments in high concentrations, and this is especially true as a PAH's molecular weight increases.

Disappearance of a PAH is by volatilization, photooxidation, chemical oxidation, sorption, leaching or biodegradation. Most sediments "commonly contain some PAH-degraders... The literature offers abundant information on PAH degradation by pure cultures of microorganisms in spiked soils and sediments, but comparatively less is known about the degradation by autochthonous communities in contaminated sediments. And while biodegradation processes and pathways of PAHs are well known under aerobic conditions, studies on their degradation under anaerobic conditions are scarce. Freshwater sediments can be oxic (e.g. under rapid aerated flow streams), but they are frequently characterized by extensive anoxic zones. Anaerobiosis occurs when the flow stream is low and at sites where

O₂ consumption is high and exceeds its supply by diffusion. Under such conditions, other terminal electron acceptors than O₂, e.g., nitrate, manganese, iron, sulfate or organic compounds, can be used by anaerobic or facultative anaerobic microorganisms. The availability of electron acceptors would then be crucial in controlling the biodegradation of organic matter. Moreover, river sediments continuously receive fresh organic matter like plant residues, detritus of dead algae and diatoms, etc., representing a valuable source of carbon and energy for microorganisms, and stimulating biological activity and O₂ consumption" (Quantin and others, 2005).

Experimental method

Researchers collected highly contaminated sediment from a river; upstream of the collection point is an active petrochemical plant. Samples were placed in airtight jars and stored at 4°C. In the laboratory:

- centrifugation separated sediment and water
- sediment was dried and sieved at 2 mm
- sub-samples were taken for chemical analysis and experiments
- the main PAHs present were phenanthrene (PHE), fluorine (FLU), fluoranthene (FLT) and pyrene (PYR)
- three-ring compounds represented 51 percent of total extractable PAH
- four-ring compounds represented 36 percent of total extractable PAH

Batch incubations used 50 g of dry sediment (or 25 g for the abiotic controls). Researchers added distilled water and two different sources of organic matter:

- natural organic matter, the sole source of carbon (NOM treatment)
- shredded Whatman 40 cellulose fibers

Treatments were incubated under either biotic or abiotic

conditions. To evaluate bacterial activity, researchers measured organic carbon mineralization. They used a total carbon analyzer to measure DOC (dissolved organic carbon), determined soluble Fe²⁺ concentration colorimetrically and quantified total Fe.

Results

Scientists wanted to distinguish between biotic and abiotic dissipation of PAHs in polluted river sediments and "quantify the extent of these processes affected by O₂ availability" (Quantin and others, 2005). Scientists found in the abiotic treatments:

- "aerobic metabolism is more efficient for oxidation of organic molecules than anaerobic metabolism due to the abundance of O₂ serving both as an electron acceptor and a source of oxygen"
- when O₂ availability is limited, biological activity is hampered
- very slow PAH degradation (mostly easily degradable 3-ring PAHs) occurs under anaerobic conditions; this is likely due to incapacity of anaerobic bacteria to degrade PAHs because many TEA (terminal electron acceptors) were present
- insignificant extent of co-oxidation during Fe⁻ and sulfate reduction
- the major abiotic processes of PAH transformation of oxidation and sorption (only non-volatile compounds were assessed)
- production of degradation intermediates like phenanthrenol, anthraquinone and fluorenone that "may mediate the introduction of an oxygen-containing functional group on a PAH molecule, but not the cleavage of the ring structure"

From the biotic treatments, scientists found:

- between 25 and 70 days of incubation created an

increase in PAH extractability, which is related to substantial degradation of the natural organic matter "to which PAHs were adsorbed" or incorporated

- PAH can increase temporarily up to 150 percent due to PAHs "mobilized by the microbial interactions with the matrix sequestering non-extractable PAHs"
- "neoformation of PAHs upon incubation of humic substances and nutrient substrates, like plant material, may exceed PAH mobilization and account for increases of several hundred percent"
- "...abiotic dissipation of 3-ring PAHs reached 65 percent, suggesting that biodegradation constituted no more than 32 percent of PAH dissipation, irrespective of cellulose addition..."

In general, researchers concluded that

- in some instances, Fe- and Mn-oxides can be catalysts for chemical oxidation of organics
- free radicals and O₂ could have oxidized PAHs
- the added carbohydrates increased the potential electron donors and acted as potential co-substrates; "cellulose addition led to the development of a cellulolytic microflora, and, as a consequence, of a fermentative one; cellulose appeared to be a competing substrate for microorganisms; it is possible that under such conditions inorganic nutrients like N and P limited the degradation"

"The impact of introducing O₂ in situ may have a positive effect on degradation, but it is still highly questionable as it entrains the risk of mobilizing the pollutants and transporting them to less polluted areas downstream; this would surely enhance the exposure of PAHs to a wide range of biota and ultimately to humans. Alternative approaches including dredging, deposition on land and incorporation of O₂, either through bioventing or composting/landfarming, thus

appear to be a better solution, as such degradation is far more efficient, particularly when prior tests have shown that the sediments contain pollutants that are bioavailable and degradable under aerobic conditions. Nevertheless, this solution has to be carefully performed for mixed-contaminated sediments, particularly for dredged sediments containing metal sulfides that can be oxidized and then release associated metals" (Quantin and others, 2005).

Reference

Quantin, C., E.J. Joner, J.M. Portal and J. Berthelin, "PAH Dissipation in a Contaminated River Sediment Under Oxic and Anoxic Conditions," *Environmental Pollution*, Vol. 134, 2005; <http://www.elsevier.com/locate/envpol>

UTTU thanks Dr. Quantin, quantin@geol.u-psud.fr, for his help on this article.



Humic acids in soil remediation

Conte and others (2005) sought to compare the efficiency of humic acids (HAs) to that of the common synthetic surfactants, sodium dodecylsulphate (SDS) and Triton X-100 (TX100). They examined extraction procedures (soxhlet and sonication) in two soils:

- soil A, rich in PAH (polycyclic aromatic hydrocarbons) with a coarse sand fraction of 21 percent, fine sand 35 percent, silt 40 percent and clay 3.6 percent
- soil B, rich in thiophenes with a coarse sand fraction of 13 percent, fine sand 39 percent, silt 44 percent and clay 5 percent

The soils were taken from an industrial area of Cengio in Northern Italy.

Extraction procedures

The common liquid procedures used to extract pollutants from soil samples are soxhlet and sonication methods. Removal characteristics are dependent on soil characteristics, especially soil texture. "It is widely accepted that a fine-sized textured soil is a main factor for the hydrophobic adsorption of organic matter on the surface of fine colloidal soil particles, thereby favoring the associations of micro- into macroaggregates. Concomitantly, the organic material trapped into the macroaggregates is physically protected from biodegradation and becomes hardly extractable by common extraction procedures, unless the soil macroaggregates are disrupted by applying either mechanical or sonication energy... Conversely, coarse-sized soil particles are less prone to form larger soil aggregates mediated by organic matter. Thus, organic compounds are located only on the surface of the coarse-sized fractions and are removable with the same efficiency by both soxhlet and sonication" (Conte and others, 2005).

By virtue of soil A's lower aggregate stability (larger coarse-sized fractions), both soxhlet and sonication extraction efficiencies were similar; in soil B, organic pollutants on fine particle surfaces are contained in more structurally stable macroaggregates. "Hence, the soxhlet extraction, based simply on temperature, could only wash away the fraction of contaminants mainly present on the surfaces of macroaggregates, whereas ultrasonic vibrations, caused by exerting a disaggregation energy on the macroaggregates, could also expose to solubilization the pollutants adsorbed on the surfaces of the inner fine particles. For this reason, the amount of pollutants extracted by sonication from soil B resulted in larger quantities than that obtained by soxhlet" (Conte and others, 2005).

Researchers also found that washing with water did not as efficiently remove pollutants from soil as the synthetic (SDS and TX100) or natural surfactants (HA). Synthetic surfactants can remove pollutants but "only when the surfactant solution reaches the surfaces of soil particles and the pollutants may be desorbed into the micellar phases... This work also indicates for the first time that a natural non-toxic surfactant such as humic acid removes similar amounts of contaminants from a polluted soil as synthetic surfactants" (Conte and others, 2005).

Soil washing can affect aggregate particle size; for instance, "The finer texture of soil B...and the consequent tendency of soil particles to create aggregation, may be the reason for the larger amount of pollutants removed by sonication than by soxhlet." Using synthetic or natural surfactants may increase soil structural stability "due to the aggregating action that the hydrophobicity of surfactants may exert on the solid soil particles. This may in turn affect the solubilization of contaminants during the determination procedures depending on the specific structure of pollutants."

Conclusions

Conte and others (2005) conclude that "soil texture is an important parameter to take into account to select the most appropriate analytical technique to remove and determine soil contaminants. We found that water contaminants are more quantitatively removed by sonication rather than by soxhlet when a soil is characterized by a fine texture, whereas both soxhlet and sonication give equivalent results in more coarse-textured soils. However, since sonication is faster than soxhlet (in our experimental work it took only 12 minutes versus 48 hours needed for soxhlet), the use of sonication should be recommended as a standard procedure for all kinds of soils. The disadvantage of sonication, a reported degradation of aromatic organic pollutants, is reasonably balanced by its more

quantitative removal efficiency” (Conte and others, 2005).

Researchers ascertain that “water cannot be recommended for an efficient removal of pollutants from a contaminated soil and that organic surfactants should be relied upon in soil washing procedures. However, synthetic surfactants such as SDS and TX100, which are efficient in soil washings, may become a further environmental problem because of their biological activity. We have shown here that a natural surfactant such as a humic acid solution can be used in washings of a contaminated soil with the same efficiency as that of synthetic surfactants... Humic substances can even improve biomass activity on washed soils and contribute to a further natural attenuation once the soils are disposed after an ex-situ remediation process.”

Reference

Conte, P., A. Agretto, R. Spaccini and A. Piccolo, “Soil Remediation: Humic Acids as Natural Surfactants in the Washings of Highly Contaminated Soils,” *Environmental Pollution*, Vol. 135, 2005; <http://www.elsevier.com/locate/envpol>

UTTU thanks Dr. Conte, pellegrino.conte@unina.it, for his help on this article.



The City of Los Angeles Former Gas Station Sites Program, part V

This section addresses funding sources for remediation of former gas station sites. Below is a chart listing the various sources available to owner/operators of California USTs. A description of the sources follows the chart.

	CA Petroleum UST Fund	CA Petroleum UST Fund EAR Account	U.S. EPA Brownfields Grants	U.S. HUD CDBG Funds
Amount	1.5 million/site	1.5 million/site	\$200,000*/grant	Depends on jurisdiction population
Activities covered	-Assessment ordered by regulator -Remediation from LUSTs	-Assessment -UST removal -Remediation	-Assessment -Remediation -UST removal if needed for assessment	-Assessment -UST removal -Remediation
Key eligibility criteria	Contamination identified -Funding to UST owner or operators on a reimbursed basis -Site is in compliance -Owner eligible for fund	Potential contamination indicated -Owner is either not found without funds -recalcitrant	Contamination indicated or suspected	-Site must be in a CDBG eligible census tract -Municipality must allocate CDBG funds for this purpose
Time schedule	Application to UST Fund by May is best	Application to Regional Water Quality Board by March 1	See U.S. EPA Web site (http://www.epa.gov/oust/) for application criteria and deadline	Funds budgeted by local government annually

*Applicants can request a waiver to receive up to \$350,000 for an assessment of certain contaminated sites including petroleum sites.

Community Development Block Grant funds (CDBG)

Community Development Block Grant funds are provided by the U.S. Department of Housing and Urban Development (HUD) to cities and counties to improve housing and economic development opportunities in low-income communities. The City of Los Angeles has chosen to fund a portion of its Brownfields Program through CDBG funds allocated each year for this purpose. Cities can choose to spend these funds for site assessment, remediation, agency oversight costs, legal support, and other expenses related to economic development of sites in qualifying census tracts. For details, consult with the agency in your city or county that handles CDBG funds. The HUD Web site, <http://www.hud.gov>, also has information on this program.

U.S. EPA brownfields assessment, revolving loan fund and cleanup grants

U.S. EPA offers grants to local governmental agencies for assessment and cleanup of brownfields, including

petroleum sites. Additional funds are available to initiate a revolving loan program. Grants are available that will cover Phase 1, Phase II, environmental assessment (see previous UTTU Vol. 18 and Vol. 19, Nos. 1, 2 and 3), cleanup and reuse plans, cleanup costs, community involvement, purchase of environmental insurance and LUST removal, if needed to complete an assessment. The grants are available to states, local governments, tribes, and non-profit organizations. Check the U.S. EPA Web site, <http://www.epa.gov/brownfields>, under “Grants and Funding” for details and deadlines. Also consult with your local U.S. EPA Regional Office for available programs.

Targeted brownfields assessments

The U.S. EPA also assists cities, redevelopment agencies and non-profit organizations in performing Phase 1s and Phase IIs at qualifying brownfield sites. (See previous UTTU Vol. 18, No. 6, and Vol. 19, Nos. 1, 2, and 3 for an explanation of these terms.)

The U.S. EPA has various other funding sources available for brownfield projects. See their Web site for an explanation of these programs at <http://www.epa.gov/brownfields>. Also consult your local U.S. EPA Regional Office Web site.

California state funding sources

The California Petroleum Underground Storage Tank Cleanup Fund, which is administered by the California State Water Resources Control Board (SWRCB), may be thought of as an insurance program. It enables UST owners and operators to satisfy federal and state financial responsibility requirements to assist with cleanup costs of UST-contaminated soil and groundwater. The fund will reimburse up to \$1.5 million in eligible expenses per site. It provides coverage for third-party liability due to releases but does not pay for UST removal. Eligible recipients are grouped into categories that have different priorities for payment.

For a UST owner or operator to be eligible, the tanks must be in compliance with all regulations, i.e. removed or upgraded to local regulatory requirements by December 1998. Sites with USTs still in place can qualify for the fund only under a waiver provision. Consult Appendix E (<http://www.lacity.org/ead/labf>) for a summary of fund provisions, including waiver provisions. In California, UST removal contractors are familiar with the fund and can advise on site eligibility. The fund provides up to \$3,000 to pay a consultant to prepare documentation for a fund application. Fund staff can provide the names of such consultants. Consult Appendix A (<http://www.lacity.org/ead/labf>) for a resource list and how to contact the fund office. In some cases the fund also includes provisions for UST owners to pass their fund rights to future owners. Municipalities that are considering taking ownership of sites need to take great care to review all the regulations thoroughly to determine eligibility to receive fund reimbursement.

Note that this is a reimbursement program; owners who qualify for the fund may be able to find an environmental consultant who will forgo payment until the reimbursement payment is received. Otherwise, a loan may be needed.

This program can be of great benefit by providing funding for the remediation of former gas station sites, but criteria for qualification are complex. The City's Redevelopment Agency retained the services of an UST fund consultant to advise on eligibility issues. Not all expenses will meet qualifications. For example, the cleanup fund will not reimburse costs of removing USTs, and fund staff can only determine a site's eligibility after tanks have been removed and contamination has been confirmed by the lead agency.

Emergency, Abandoned, Recalcitrant (EAR) Account

This is a specific pool of money that the SWRCB allocates annually for use at sites that present an emergency situation (Emergency), at sites whose owners have no resources or cannot be located (Abandoned), or at sites whose owners refuse to undertake cleanup (Recalcitrant).

Local UST regulating agencies can nominate sites with identified contamination to receive funds under the "abandoned" or "recalcitrant" category. The local agency that oversees USTs must nominate sites to their Regional Water Quality Control Board (RWQCB) by March 1st. Regional boards submit priority sites to the SWRCB by May 1st. In July, the EAR Account Administrator will establish a statewide priority list of proposed UST lead sites and amounts to be allocated and present the list to the SWRCB for adoption. The City of Los Angeles Brownfields Program works closely with their fire department and RWQCB to prepare and submit a nomination. For more information on the EAR account, contact the EAR Account staff in Sacramento,

and see their Web site, <http://www.swrcb.ca.gov/tankpage.html>.

Loans

A bank will not always accept a property with a non-compliant UST as collateral on a loan. If contamination is found, the costs to remediate may exceed the property value. If the borrower defaults on the loan, it is difficult for the bank to recover its loan, which in turn makes it difficult to find buyers for such properties. If an owner has no other property to use as collateral, he or she is unlikely to obtain a conventional loan to pay for UST removal.

Some non-profit community development corporations, however, will provide a loan to remove USTs based on the owner's credit history and other factors. The non-profit's goal is to support redevelopment in low-income neighborhoods. To obtain a referral to a community development corporation in your area, check with the California Community Economic Development Association. In addition, the California State Department of Community Services can provide the name of an economic development agency that can refer you to a non-profit organization that makes loans to small businesses. A list of agencies is available on their Web site. Contact information on these organizations can be found in Appendix A (<http://www.lacity.org/ead/labf>).

Insurance policies

It is possible to receive payment through a business liability insurance policy held by a former site owner. Prior to approximately 1972, most general liability insurance had no exclusions related to pollution; after 1972, some policies had some exclusions. After 1986, most policies had total exclusions for pollution-related claims. At the same time, pollution insurance began to develop as a separate product, although few UST owners obtained pollution insurance. In the

1990s federal law required UST owner/operators to obtain pollution insurance. Since 1998, all UST owner/operators have been required to have pollution insurance.

One can hire an insurance archeologist who searches for old insurance policies that can be used to cover contaminant cleanup cost. The City's Brownfields Program has not tried this strategy; the cost, however, to retain the expert could be cost effective on larger sites. Appendix A <http://www.lacity.org/ead/labf> lists Web sites with more information on insurance archeology.

Responsible parties

Owners who have the ability to address contamination but refuse to do so can be dealt with through enforcement actions by agencies ranging from the local UST regulators to the RWQCB, DTSC, California Department of Toxic Substances or occasionally through the U.S. EPA. For California cities that cannot undertake these actions, the EAR Account (see above) may be a beneficial resource. For sites that are in redevelopment areas, the Polanco Act can be used to gain access and force recalcitrant owners to pay. Chapter 6 (<http://www.lacity.org/ead/labf>) provides more information on the Polanco Act.

Reference

"Guide to Resolving Environmental and Legal Issues at Abandoned and Underutilized Gas Station Sites," <http://www.lacity.org/ead/labf/>

UTTU thanks Maxine Leichter, maxineleichter@yahoo.com, for her help on this article.



Research notes

Investigation of interactions between surface water and petroleum-type pollutant

Jovancicevic, B.S., M.P. Antic, T.M. Solevic, M.M. Vrvic, A. Kronimus. and J. Schwarzbauer, *Environmental Science and Pollution Research Journal*, Vol. 12, No. 4, 2005; <http://www.environmental-expert.com/magazine/ecommed/espr/>

In the aftermath of an oil spill, workers usually take oil samples from more than one sedimentary environment, from different distances from the spill, and at various times. How are all of these variables accounted for when identifying spill characteristics? Researchers sought to identify one such variable—the effect of interactions between oil contaminants and water. They focused on “the influence of the intensity of interaction between the oil contaminant and water on its chemical composition...[and] the influence of the environment, microorganisms or migration on the oil contaminants’ composition” (Jovancicevic and others, 2005). To accomplish this, “it is very important to define which part of organic matter has been analyzed. Namely, previous investigations showed that there were some differences in chemical composition of the same oil contaminant depending on the intensity of its contact with groundwater” (Jovancicevic and others, 2005).

Researchers examined four extracts of an oil contaminant taken from a waste water canal that contained effluent from a petrochemical plant and oil refinery. Extract 1, separated from the aqueous phase by decantation, had the weakest interaction with water. Water interaction with subsequent extracts increased. “Extract 2 was extracted from the remaining aqueous phase with chloroform by shaking in a separatory

funnel for 1 minute. Subsequently, extract 3 was extracted with chloroform by shaking in a separatory funnel for 5 minutes. Extract 4 [which had the strongest interaction with water], was extracted with chloroform by mechanical shaking for 24 hours” (Jovancicevic and others, 2005).

Analysis of sterane and triterpane-type polycyclic alkanes indicated that the four extracts originated from the same contaminant. However, there were differences in the extracts’ chemical makeups:

- extracts 1 and 2 had a uniform distribution of n-alkanes
- extract 3 had even-numbered members dominating the odd ones
- extract 4 showed a bimodal distribution
- extract 1 had the least negative $\delta^{13}\text{C}_{\text{PDB}}$ values of the $\text{C}_{19}\text{-C}_{26}$ n-alkanes
- extract 3 had the highest concentration of even-numbered n-fatty acids, $\text{C}_{19}\text{-C}_{24}$

“n-Alkanes and specific isoprenoids (pristane, phytane) are dominant saturated hydrocarbons in most crude oils that haven’t been exposed to microbial degradation in reservoir rocks. Therefore, it is possible to easily identify and analyze oil contaminants from the distribution and abundance of n-alkanes and major isoprenoids during the early stages of an oil spill, especially where the spilled oil is heavy and background hydrocarbon levels are low in an impacted environment” (Jovancicevic and others, 2005).

The gas chromatogram for extract 1 indicated a sample of crude oil which had not been exposed to biodegradation; extract 3 revealed a different chromatogram. “It was proven that microorganisms of the algal type (non-photosynthetic-nutritional, unicellular, sporulating algae—Pyrrophyta) were responsible for the appearance of these even-numbered n-alkanes

[in extract 3, ranging from C₁₂ to C₁₆]...and that their biosynthesis was much more pronounced in the oil contaminant and had experienced a stronger interaction with water" (Jovancicevic and others, 2005).

The chemical makeup of extract 4 may result from "the formation of inclusion compounds with colloidal micelles formed between the oil contaminant's NSO-compounds (nitrogen, sulfur, oxygen) and water" (Jovancicevic and others, 2005). Migration of heavy fuel oil, for instance, through water-wet sediments or a crushed rock environment (silicate minerals such as quartz and antigorite) and increase in depth and distance from the oil spill cause the increase in the most polar fraction, NSO-compounds..."

Researchers also report that the four extracts showed dissimilarities in carbon isotope compositions, suggesting that the four extracts may not be from the same source, making further investigation necessary.

Modeling a Ground Water Circulation Well Alternative

Elmore, A.C. and L. DeAngelis, *Ground Water Monitoring & Remediation*, Vol. 24, No 1, 2004; <http://www.ngwa.org>

An innovative zero-discharge technology, ground water circulation well (GCW), was tested at an ordnance plant site in Nebraska. The technology "involves extracting ground water through one interval in a well, treating the ground water, and recharging the treated zero net extraction and recharge. This technology has some advantages over other technologies such as in-situ bioremediation in that GCW is not negatively impacted by very high contaminant concentrations, and GCW may be applicable where the geochemical properties of an aquifer are not favorable for sustaining biological activity" (Elmore and DeAngelis, 2004).

Scientists designed, implemented and evaluated

the performance of a GCW system and compared the data obtained with the results obtained from ground water modeling (three stages of ground water modeling). "The model-predicted flow geometry compared favorably to the data obtained during the pilot study. Although reliability of the model predictions could be improved by collecting location-specific measurements of hydraulic conductivity anisotropy data, the project stakeholders' confidence in the analysis was sufficiently high to replace the previously selected pump-and-treat focused remediation with GCW-based focused remediation at the study site. The predicted reductions in remediation costs and overall remediation time offset the perception of the relatively low risk associated with the model predictions" (Elmore and DeAngelis, 2004).