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Brief article summaries

TPH (total petroleum hydrocarbon) analysis is based on the gas chromatography-flame ionization detection (GC-FID) technique to detect hydrocarbons. Many states still use the total petroleum hydrocarbon (TPH) analysis to analyze for dissolved hydrocarbons, even though the TPH strategy appears to be flawed. Scientists who analyze groundwater samples are predominantly interested in dissolved, mobile petroleum hydrocarbons. TPH measures more than just the dissolved, mobile petroleum hydrocarbons.

Researchers created an air sparging column apparatus in a lab to determine the potential contributions of volatilized versus biodegraded benzene in a real air sparging situation. Air sparging relies on a gas, usually air, that is injected into the subsurface below the contamination. The injected air ideally rises and dissolved-phase and free-phase contaminants partition into the vapor phase. The gases rise into the vadose zone and are captured by treatment equipment aboveground.

Researchers recently tested a molecular genetic technique that could potentially be an accurate and rapid method for detecting microorganisms capable of degrading certain aromatic hydrocarbons. The method relies on catechol 2,3-dioxygenase (C23DO) genes that occur in bacteria and can biodegrade compounds such as benzene, toluene and xylene under appropriate conditions. Researchers tested this technique in the lab and at two LUST sites in Indiana.

Several years ago, eight car rental agencies united to design and produce a fueling facility at San Francisco's International Airport. The agencies involved in this endeavor included the U.S. EPA, California Water Resources Control Board, California Air Resources Board, San Mateo Country Environmental Health Department and the San Francisco International Airport Commission. This article describes the efforts that went into designing and building the storage system.

Research notes review articles that describe direct push electrical conductivity logging, MTBE and cyclodextrins, lead contamination, volatile emissions, and VOC diffusion and sorption.

Limitations of TPH analysis

TPH (total petroleum hydrocarbon) analysis is based on a gas chromatography-flame ionization detection (GC-FID) technique to detect hydrocarbons. Many states still use TPH analysis to analyze for dissolved petroleum hydrocarbons, although the TPH strategy appears to be flawed. Scientists who analyze groundwater samples are predominantly interested in dissolved, mobile petroleum hydrocarbons. TPH measures more than the dissolved and mobile constituents.

The problem with TPH analysis

TPH analysis for groundwater poses a problem because the technique measures not only dissolved petroleum hydrocarbons but, in addition, "nondissolved petroleum or polar nonhydrocarbon compounds. Nondissolved petroleum is frequently entrained within a sample when sampling groundwater within affected soil, and polar nonhydrocarbons are present in groundwater as a result of petroleum biodegradation or other factors. The TPH analysis lacks the steps that remove the nondissolved petroleum, or a silica gel cleanup step that would remove polars. Therefore, TPH measures compounds other than the intended dissolved petroleum hydrocarbons, and the validity of these results for regulatory purposes is questionable. This is particularly problematic at sites that have not achieved closure because TPH levels exceed regulatory standards" (Zemo and Foote, 2003).

Background on chemistry of crude oil and other petroleum products

To predict what fraction of a petroleum product will dissolve in groundwater, researchers first need to identify the composition of a petroleum product. Hundreds to thousands of hydrocarbons (non-polar molecules composed exclusively of carbon and hydrogen atoms) and minor nonhydrocarbons (polar molecules containing nitrogen, sulfur or oxygen in their structure, called NSOs or hetero-atoms) make up crude oil and petroleum products. Gasoline will commonly contain

- 35 to 70 percent total C_4 to C_{12} alkanes
- 25 to 55 percent total aromatics
- 5 to 10 percent alkenes

Kerosene and jet fuel are typically

- 70 to 85 percent total C_8 to C_{18} alkanes
- 10 to 20 percent total aromatics
- 1 to 4 percent alkenes

For diesels and fuel oil #2, percentages are commonly

- 50 to 80 percent C_{10} to C_{24} alkanes
- 20 to 35 percent total aromatics
- 2 to 5 percent alkenes
- 1 to 5 percent nonhydrocarbons NSOs

High-boiling-point products like fuel oil #4 and #6 are typically

- 20 to 60 percent C_{20} to C_{40+} alkanes
- 20 to 40 percent total aromatics
- unknown amounts of alkenes
- 30 to 50 percent NSOs/residuals

Lubricating oils typically contain

- 70 to 90 percent C_{20} to C_{30} alkanes
- 10 to 30 percent total aromatics

Reviewer's comment: In addition to these bulk constituents, there are usually small percentages of various additives added to commercial products, most of which are proprietary. These additives may be organic or inorganic in nature.

Water-soluble fraction

The portion of crude oil or product that is soluble and will dissolve into water is known as the water-soluble fraction, WSF. It consists of fewer compounds than the original product, and its composition "is controlled by the effective solubility of each constituent in the mixture." Each constituent's effective solubility will be dependent on its

- pure-compound solubility
- mole fraction within the mixture
- partitioning coefficient between water and other organics in the mixture

The presence or absence of other compounds and/or minerals may impact on constituent solubility.

The WSF of the petroleum mixture follows Raoult's law, which gives "a conservative estimate of the effective solubility of petroleum hydrocarbons in water." Zemo and Foote (2003) state that "...the measurable WSF should be limited to a few petroleum constituents out of the thousands that make up the petroleum product or crude oil, and the equilibrium concentrations of each constituent within the WSF should be significantly less than its pure-compound solubility. For example, the theoretical maximum concentration of dissolved benzene in groundwater in equilibrium with fresh gasoline would be about 18 mg/l, assuming that benzene is 1 percent of the gasoline (1,780 mg/l x 0.01) and ignoring partitioning effects." One study cited in Zemo and Foote (2003) demonstrated "theoretically that only the C_6 to C_{14} aromatics had the potential to be dissolved in groundwater at concentrations of 0.005 mg/l or greater." Other laboratory studies found that the WSFs of fresh crude oil and fresh products were primarily composed of the following:

- C_6 to C_{11} monoaromatics (BTEX and the alkylated benzenes)

- C_{10} to C_{14} PNAs (naphthalene, alkylated naphthalenes, acenaphthene, fluorene, phenanthrene and anthracene)
- smaller amounts of alkanes with six carbons or fewer

Zemo and Foote (2003) report that "The discrete constituents in the WSF can be reliably identified and quantified by routine GC-MS methods. The recognition of the petroleum hydrocarbon constituents within and the chromatographic character of the WSF of various fresh products has great significance for interpretation of TPH analytical results from groundwater samples."

It is important to note that polar blending agents or additives such as oxygenates have relatively high pure-compound solubilities and large mole fractions and can be a large part of the WSF.

Other studies found that the maximum aggregate concentration of the WSF of fresh products (excluding additives such as oxygenates) is as follows:

- about 100 mg/l for gasolines
- 3 to 40 mg/l for diesels and fuel oils
- 15 to 65 mg/l for jet fuels
- about 6 mg/l for Bunker C (heavy fuel oil)

As the product weathers, its constituents change. Some soluble constituents are leached out or biodegraded and their mole fractions change. Other studies found that "...most aggregate WSF concentrations of the weathered crude oil or product were reduced to about 1 mg/l or less, regardless of the original WSF concentration associated with the fresh oil or product. Accordingly, aggregate concentrations of dissolved petroleum hydrocarbons in groundwater at sites affected by weathered crude oil or products would not be expected to exceed about 1 mg/l in most cases" (Zemo and Foote, 2003).

Reviewer's comment: This is a powerful statement since it suggests that natural attenuation will "clean up" most sites to regulatory-acceptable levels with no remedial action!

What GC-FID TPH measures

The TPH analytical methods based on GC-FID were developed in the late 1980s and early 1990s and replaced EPA Method 418.1. TPH analysis using GC-FID measures "the amount of volatile (purgeable) or semi-volatile (extractable) organics that elute within selected boiling ranges; these data are compared to petroleum product standards such as gasoline, diesel and motor oil for quantitation as TPH. The method does not specify quantitation method (which relies on boiling ranges and a response integration protocol), so methods among laboratories can vary greatly. The TPH analysis is fundamentally an aggregate rather than a constituent-specific analysis and transmits no direct information about which constituents are present in the sample" (Zemo and Foote, 2003).

The GC-FID TPH method does not include a silica gel cleanup step that would remove polar nonhydrocarbons. Therefore, polars are measured and the analysis represents a total organics measurement rather than a total petroleum hydrocarbon measurement. EPA Method 8015, on which the TPH analysis is largely based, indicates that "if this method is used for the analysis of petroleum hydrocarbons, it is limited to analysts experienced in the interpretation of hydrocarbon data" (EPA, 1996).

The shortcomings associated with using GC-FID for TPH analysis include

- interference problems
- quantitation range inconsistencies
- product identification problems
- poor interlaboratory repeatability

What it should and what it does measure

For groundwater samples, TPH should measure only dissolved, and therefore mobile hydrocarbon compounds. Thus, the TPH analytical results should show

- C_6 to C_{14} aromatics (BTEX and small PNAs) and alkanes with six or fewer carbons
- a chromatogram that should be composed of discrete peaks with lower boiling points than C_{14} and have no UCM (unresolved complex mixture) or "hump"
- TPH concentrations not exceeding the range of aggregate WSF for the type of product (about 100 mg/l for fresh gasoline to 6 mg/l for fresh bunker fuel)
- concentrations not in excess of about 1 mg/l for a weathered, high-boiling product release

Groundwater samples that show TPH concentrations from constituents "other than alkanes with six or fewer carbons, or aromatics with 14 or fewer carbons" and/or a TPH chromatogram with a hump indicate interferences, and likely they would be

- nondissolved petroleum that is included within water samples during sampling
- polar nonhydrocarbons resulting from petroleum biodegradation or other factors

The authors suggest that if TPH must be used, analysis should be modified to address the interferences. "...all of these studies demonstrate that the TPH analysis is imprecise and unreliable for the measurement of dissolved petroleum hydrocarbons in groundwater. In many cases, the entire reported TPH concentration represents nondissolved petroleum or polar nonhydrocarbons."

Zemo and Foote (2003) report that for extractable-range TPH analyses, glass-fiber filtration prior to extraction and silica gel cleanup of the extract could be used to mitigate interferences from nondissolved petroleum and polar nonhydrocarbons, respectively. They found that following filtration and silica gel cleanup, TPH concentrations in groundwater decreased by one to two orders of magnitude. They also noted that developing procedures to mitigate these same interferences in samples analyzed for purgeable TPH was an area requiring more research.

Use of TPH

Regulatory requirements for petroleum in groundwater vary widely across the country. A 2002 study (Nascarella and others, in Zemo and Foote, 2003) indicated that

- approximately 19 states still use TPH to regulate groundwater quality; half of these states have site-specific action levels while the others have action levels predominantly between 0.1 and 2 mg/l
- 22 states have adopted a constituent-specific, risk-based approach and do not use TPH
- about seven states used a "fractionated" TPH analysis in a hybrid risk-based approach

Zemo and Foote (2003) assert that "It is beyond the scope of this paper to debate the appropriateness of the concentrations that are used for TPH regulatory criteria; however...the scientific basis for many of these criteria appears to be the properties of the dissolved petroleum hydrocarbons (and possibly NSOs) associated with fresh oil or product. Accordingly, it is critical that the TPH quantification of groundwater samples reflects dissolved petroleum hydrocarbons to make a correct comparison to regulatory criteria... The TPH analysis is imprecise and frequently does not represent dissolved petroleum hydrocarbons, but rather represents nondissolved petroleum or polar nonhydrocarbons resulting from biodegradation or other sources. The concentration of these interferences measured as TPH routinely exceeds the typical 0.1 to 2 mg/l TPH action levels and therefore inhibits site closure because of this incorrect comparison" (Zemo and Foote, 2003).

Reviewer's comment: Many states recognize the limitations of the TPH analytical procedure and use TPH as an "indicator parameter," not as a regulatory parameter. That is, if a TPH analysis is low, the state knows that there is not a plume to contend with.

Conclusions

Zemo and Foote (2003) conclude that the TPH analysis

- is imprecise
- "should not be used to assess or regulate dissolved petroleum hydrocarbons in groundwater"
- "frequently represents nondissolved petroleum and/or polar nonhydrocarbons; in many cases, the entire reported TPH concentration may result from these interferences"
- data "should not be compared to existing TPH regulatory criteria that are based on dissolved petroleum hydrocarbons"

The authors recommend using a constituent-specific rather than TPH analysis. If TPH analysis must be used, samples analyzed for extractable TPH should be cleaned with silica gel to remove polars, and measures should be taken to remove turbidity if present (e.g., glass-fiber filter, low-flow purging). If certain polar nonhydrocarbons are of concern, these constituents should be identified with GC-MS or other constituent-specific methods, rather than TPH.

Reference

Zemo, D.A. and G.R. Foote, "The Technical Case for Eliminating the Use of the TPH Analysis in Assessing and Regulating Dissolved Petroleum Hydrocarbons in Ground Water," *Ground Water Monitoring & Remediation*, Vol. 23, No. 3, 2003; http://www.ngwa.org

UTTU thanks Dawn Zemo, dazemo@msn.com, and Gary Foote, gfoote@geomatrix.com, for their help on this article.

Benzene biodegradation

Adams and Reddy (2003) designed an air sparging column lab experiment to estimate the potential contributions of volatilized versus biodegraded benzene in an authentic air sparging situation. In air sparging, a gas, usually air, is injected into the subsurface below the contamination. The injected air ideally rises and dissolved-phase and free-phase contaminants partition into the vapor phase. These gases rise into the vadose zone and are ideally captured by treatment equipment aboveground.

Reviewer's comment: This is a familiar concept that may or may not apply to the real world. It is possible that gases are re-adsorbed onto soil or adsorbed onto soil or organic matter in the saturated zone just above where they are stripped. In the laboratory these kinds of tests have been done over and over and whether or not they duplicate what happens in a field situation varies from site to site.

The injected air increases the dissolved oxygen concentration in the subsurface, stimulating aerobic microbes and resulting in increased degradation of organic contaminants. This type of air sparging is often referred to as biosparging. "To take advantage of the ability of subsurface microbial populations to degrade organic compounds, air sparging may be implemented in a manner different from a traditional air sparging application. This includes a low, continuous air injection of a high injection rate for a brief period of time followed by a long period of injection cessation. When the second option is used, a large volume of air is supplied to the subsurface, and as the trapped air bubbles or channels gradually collapse, more oxygen is released, sustaining the availability of electron acceptors" (Adams and Reddy, 2003).

Reviewer's comment: In biosparging, air is injected continuously but at a lower injection rate than normal air sparging so that in-situ biodegradation is enhanced while physical volatilization of organics is minimized. In addition, it is true that sometimes one sparges periodically rather than continuously, the purpose being to establish new air channels, and these channels may or may not be beneficial.

Experimental materials

Researchers set up air sparging columns in the lab with the following components:

- benzene, the representative hydrocarbon for this study
- an activated sludge from a wastewater treatment facility which functioned as the active biomass culture
- a column filled with coarse sand

Researchers poured the biomass culture into the column, placed soil into the column through a top opening, then injected benzene via a peristaltic pump. "The mass of placed benzene solution was calculated, and the initial soil contaminant profile was determined by sampling pore water and analyzed using gas chromatography" (Adams and Reddy, 2003).

Researchers then

- injected air into the column for 5 minutes
- halted air injection for 24 hours (cessation)
- used activated carbon filter tubes to collect aqueous-phase benzene, which was the benzene removed through volatilization
- replaced the carbon tubes, after halting the air injection, and characterized the contaminant profile using pore water sampling and analysis
- injected air for 5 minutes, followed by 24 hours of cessation
- analyzed the soil profile's spatial distribution of biomass

Researchers completed five tests:

- the first test used clean homogeneous coarse sand: manufactured, washed sand without microorganisms and no visual traces of organic matter
- two tests used biomass solutions with concentrations of 115 mg/l and 230 mg/l
- two tests used benzene concentrations of 100 mg/l and 300 mg/l

For all tests, benzene concentrations were measured at seven ports, each port separated by 5 to 10 cm, with the bottom port, port 1, closest to the air sparging source.

Results

The first test, a baseline test, used clean, coarse sand with 100 mg/l of benzene. Benzene was monitored at ports 2, 3, 4, 5 and 7. Results showed

- after 5 minutes, benzene concentrations at the ports ranged from 25 to 75 percent of the original concentration
- at later times, concentrations tended to fluctuate
- ports at the ends of the column had lower benzene concentrations than those in the middle
- injected air forced the contaminant to migrate vertically, increasing concentrations at a higher level
- water level fluctuations may also have affected benzene concentration
- after the initial 5-minute injection period, there were no air injections for another 24 hours; during the second 5-minute injection period, benzene concentration was reduced to 40 percent of its original mass
- the third 5-minute period of air injection removed 20 percent of the original benzene mass
- additional injection removed only 10 to 20 percent of the original mass
- all soil used was clean, e.g., no microorganisms were added, therefore, all benzene reductions occurred through volatilization

The second test used coarse sand with 100 mg/l of benzene and 115 mg/l of biomass, giving the soil an organic content of 0.0014 percent, a significantly lower organic soil content than those typical of remedial sites, 0.017 to 0.15 percent. Results showed:

- after 5 minutes of air injection, 45 percent of the initial benzene still remained in the column
- benzene degradation appeared to be uniform throughout the profile
- higher concentrations were detected at ports 3, 4 and 5
- ports 2 and 7 became benzene-free after 5 minutes of injection followed by the 24 hours of cessation
- ports 3, 4 and 5 had concentrations of $\leq$ 10 mg/l after the second 5 minutes of air injection
- after the first 24-hour period of injection cessation, only 10 percent of the initial benzene mass remained, indicating biodegradation was occurring; researchers calculated a biodegradation rate of 1.38 mg/l/hour
- contaminant tailing occurred at all ports until 5,400 minutes, when all ports were benzene-free

The third test used a biomass solution of 230 mg/l with a benzene concentration of 100 mg/l. Results showed:

- after the first 5 minutes of air injection, benzene concentration was 25 mg/l at ports 2, 3, 5 and 7 and 50 mg/l at port 4
- after the second 5-minute air injection, all port concentrations were ≤ 10 mg/l
- after the first 5 minutes of injection, about 50 percent of the original benzene mass remained in the soil profile, and following the 24-hour cessation period, 17 percent of the benzene remained, indicating biodegradation had occurred
- the profile was benzene-free after 4,500 minutes
- almost 20 percent of benzene biodegraded during the first 5-minute injection period, corresponding to a degradation rate of 240 mg/l/hour
- during the next 24-hour cessation period, benzene reduction was also about 20 percent, although "It is possible that a large portion of the degradation occurred over a much smaller time frame than the 24-hour cessation period; it appears that dissolved oxygen could be a rate-limiting factor for degradation; in other words, if efficient aerobic biodegradation is to occur, ample oxygen must be supplied to the subsurface" (Adams and Reddy, 2003)

Researchers determined that "...the dissolved-oxygen concentration can be useful in determining the extent of biodegradation during the use of air sparging. Dissolved oxygen depletion may be the rate-limiting factor for degradation within the subsurface; without adequate subsurface dissolved oxygen, degradation rates become prohibitive for efficient removal" (Adams and Reddy, 2003).

In addition, "During the first period of injection cessation, the two biomass-infiltrated soils experienced reductions ranging from 10 to 15 percent of the initial benzene mass. The curves representing the two biomass concentrations were nearly identical throughout testing, indicating that, in the range of these biomass concentrations, remedial efficiency was independent of biomass content within the soil." Benzene was removed from the clean soil, but at a much slower rate than that from biomass-infiltrated soils. Furthermore, "While the biomass-infiltrated soils were characterized by a substantial tailing period followed by complete benzene removal, about 20 percent of the initial benzene mass remained within the clean soil. This demonstrates the importance and added benefit of biodegradation to the efficiency of air sparging" (Adams and Reddy, 2003).

The fourth test involved a biomass concentration of 115 mg/l and benzene concentration of 300 mg/l. Results indicated:

- after 5 minutes of air injection, benzene concentrations ranged from 25 mg/l to a high of 75 mg/l; about 45 percent of the original benzene was removed
- removal from biodegradation for the following 24-hour period ranged from 25 to 50 mg/l; data from ports showed tailing effects similar to tests 2 and 3, with the highest concentrations detected at ports 4 and 5
- during the 24 hours of cessation, about 10 percent benzene was removed by biodegradation, a rate of about 1.13 mg/l
- the second 5-minute air injection removed only 3 percent of the initial benzene mass
- the second period of cessation removed only 5 percent of the initial benzene mass
- the soil profile was benzene-free after 6,700 minutes
- in the two soil tests (numbers 2 and 4) with similar biomass and different initial benzene masses, similar percentages of initial benzene masses were removed during the first 5 minutes of air injection (45 percent of the 100 mg/l test, 55 percent of the 300 mg/l test); during the 24-hour cessation, however, similar benzene masses were removed
- after the second 5-minute air injection, large reductions in the remaining benzene mass occurred for both the 300 mg/l and 100 mg/l tests

The fifth test used a biomass solution of 230 mg/l and benzene solution of 300 mg/l. Results indicated:

- after the first 5 minutes of air injection, benzene concentrations at the ports ranged between 40 mg/l to 125 mg/l, and 52 percent of the initial benzene mass was removed
- during the first 24 hours of injection cessation, only 30 percent of the original benzene mass remained, corresponding to a degradation rate of 2.13 mg/l/hr
- after the second period of air injection, 10 percent of the initial benzene mass remained
- little degradation occurred during the rest of the test; most of the subsequent removal occurred during air injection periods, i.e., through volatilization, followed by tailing

Adams and Reddy (2003) attribute the tailing—an indication of difficult benzene removal—to "inadequate oxygen delivery and the slow diffusion of the contaminant from zones that were not as saturated with air. In addition, there may have been an uneven distribution of the microbial colonies or a reduction in the number of microorganisms using benzene as a substrate."

A comparison of the two tests that had the same initial benzene concentrations (300 mg/l) but different biomass concentrations (tests 3 and 5) indicated that injection and cessation periods removed similar amounts of benzene. "Therefore, within the range of tested soil biomass content, removal rates due to biodegradation and volatilization appear to be independent of biomass concentration."

Reviewer's comment: For all tests, researchers need to take into consideration how much dissolved benzene was removed by sorption onto the sand column. Benzene decreases cannot be arbitrarily attributed to either in-situ biodegradation or volatilization unless the off-gases are, at a minimum, captured and analyzed.

Researchers developed and tested a biodegradation model from batch reactor tests that "may be used to predict degradation rates and compare with the actual measured rates of degradation during air sparging... The model overpredicted degradation rate. Model parameters were determined based on the batch reactor tests in which the biomass, benzene, dissolved oxygen and nutrients maintained intimate contact. Additionally, the parameters were measured during a time period in which benzene, oxygen and nutrients were in ample supply. Within the column tests, however, rate-limiting factors existed, including dissolved oxygen concentration, and at later times, benzene concentration."

Researchers note that the "nature of the porous media prevented full contact at all times between the biomass, benzene, nutrients and dissolved oxygen... Uneven spatial distributions of the necessary constituents as well as transport limitations prevent theoretical degradation rates from being achieved. It is interesting to note the deviation between actual and predicted degradation rates at later times. As the benzene is removed, transport and distribution become greater factors, preventing larger rates of removal from occurring" (Adams and Reddy, 2003)

Reviewer's comment: If air addition is ceased, then the dissolved oxygen content must decrease, so oxygen supply to the microbes cannot be said to be constant. Because dissolved oxygen decreases, the rate of biodegradation must decrease such that it can never be comparable to "theoretical."

Conclusions

Researchers concluded the following:

- during air sparging, biodegradation removes substantial amounts of benzene, but the dominant removal mechanism is partitioning of NAPL and aqueous-phase benzene into the vapor phase
- benzene biodegradation ceased in the absence of adequate dissolved oxygen levels
- when intimate contact among biomass, dissolved oxygen, aqueous-phase benzene and nutrients is prevented, as in the soil column tests, biodegradation rate is inhibited *(Reviewer's comment: This is one reason why duplicating field conditions in the laboratory is so difficult.)*
- biodegradation rates were independent of initial aqueous-phase benzene concentration and biomass concentrations
- dissolved oxygen concentration was the rate-limiting factor for biodegradation—not biomass concentration *(Reviewer's comment: This experiment began with a large concentration of biomass whereas, in the field, one has to "grow biomass.")*

Reference

Adams, J.A. and K.R. Reddy, "Extent of Benzene Biodegradation in Saturated Soil Column During Air Sparging," *Ground Water Monitoring & Remediation*, Vol. 23, No. 3, 2003; http://www.ngwa.org

Reviewer's comment: In cooperation with the U.S. EPA, I have conducted tests to determine how much jet fuel was volatilized into the vadose zone at an airport site contaminated with jet fuel when a horizontal air sparge system was used for remediation vs. how much mass was retained in the saturated zone and biodegraded therein. In our tests, approximately 15 percent of the total jet fuel present volatilized into the vadose zone, but 85 percent of the initial mass did not and was biodegraded instead. The values would vary from site to site and from hydrocarbon product to hydrocarbon product and would depend on the remediation system design, use of horizontal vs. vertical sparge wells, and other factors.

Bioremediation monitoring with a catabolic gene probe

Researchers recently tested a molecular genetic technique that could potentially be an accurate and rapid method for detecting microorganisms capable of degrading aromatic hydrocarbons. The method relies on catechol 2,3-dioxygenase (C23DO) genes that occur in bacteria and biodegrade compounds such as benzene, toluene and xylene. Researchers tested this technique in the lab and at two LUST sites in Indiana.

Background

Until recently, the effectiveness of aerobic bioremediation and monitored natural attenuation was, for the most part, determined by indirect methods such as plume shrinkage. Cultivation-based methods that exist "detect less than 10 percent of microbial populations. Direct analysis of DNA, however, eliminates the need to cultivate cells." Mesarch and others (2004) developed a molecular genetic method, gene probe, a "direct technique for monitoring aerobic BTX biodegrading microorganisms." Analysis of a catabolic gene—the gene probe—can shed light on a microbial community's biodegradation potential. The technique scientists developed uses PCR, polymerase chain reaction, a DNA identification method, which is described below.

How PCR/real-time PCR works

The following section is reported verbatim from the Lawrence Livermore National Laboratory site.

"Developing a way to rapidly identify DNA by real-time polymerase chain reaction (PCR) was a breakthrough event in the mid-1990s that launched Livermore's biodefense program. At the time, PCR was a well-established technique for identifying specific regions of DNA. PCR worked by making multiple copies of a particular segment (referred to as the amplicon) of the DNA in the sample. When the sample is heated, the double-helix of DNA separates into two single complementary strands. When the sample is cooled, single, short (18- to 25-nucleotide) strands of DNA, called primers, attach to the ends of the target region to be amplified. Subsequently, a heat-stable enzyme (*Taq* DNA polymerase from *Thermus aquaticus*, a bacterium isolated from hydrothermal vents) replicates the region of DNA bracketed by the primers. With each heating-cooling cycle, the amount of DNA doubles. Eventually, after 20 cycles, a single target would be amplified a millionfold.

"A dramatic advance in PCR technology was the development of real-time PCR, which allows for rapid quantification of specific genes. In addition to the specific primers used in conventional PCR, real-time PCR also includes a probe (typically 20 to 35 nucleotides long) that specifically binds to a region of the target DNA that is bracketed by primers. [Nucleotide sequences of catabolic genes for the microbial degradation of many environmental pollutants are known (Mesarch and others, 2004).] The probe is labeled with fluorescent dyes at each end. One dye quenches the fluorescence of the other when the probe is intact. The real-time PCR method relies on the exonuclease activity of *Taq* DNA polymerase that cleaves on the probe, resulting in fluorescence. The amount of fluorescence is proportional to the amount of replication, which in turn is proportional to the number of initial target DNA copies. By performing real-time PCR with specific DNA standards, a calibration curve is obtained to calculate the amount of target DNA in the environmental DNA extract" (http://www.llnl.gov/str/September03/Beller.html).

Catabolic genes

"Catabolic genes determine the biodegradation potential of the microbial community... This information has been used to create gene probes for direct detection of toluene, methane, alkane, PCB, and naphthalene catabolic genes."

First, researchers needed to find an appropriate target gene to monitor BTX bioremediation. They selected the C23DO gene. "C23DO genes are known to occur in bacteria that catabolize (a destructive process that breaks down larger molecules into smaller molecules) benzene, toluene, xylenes, phenol, biphenyl, naphthalene and other aromatic compounds."

Next researchers conducted laboratory tests and field experiments

- to determine if the C23DO genes could "be detected in 'wild-type' indigenous organisms, and if detection and enumeration of C23DO genes is a reliable measurement of aerobic BTX bioremediation potential"
- to monitor C23DO genes in aerobic microcosms with uncontaminated soil exposed to different aromatic hydrocarbons
- to isolate culturable aromatic hydrocarbon-degraders and test them for the presence of target C23DO genes
- to perform QC-PCR for C23DO genes "on DNA extracts from environmental samples obtained from two field sites undergoing MNA (monitored natural attenuation)"
- to determine if clays in the samples impact on DNA recovery (DNA can strongly adsorb to clay)
- to estimate the total culturable community and size of the C23DO-utilizing population; to obtain these estimates, researchers performed heterotrophic and benzoate plate counts

Thus, according to Mesarch and others (2004), "If aerobic BTX biodegradation was active, our QC-PCR assay should detect enrichment of C23DO genes resulting from exposure to aromatic hydrocarbons."

Microcosm laboratory study

Researchers set up microcosms using 5 g of uncontaminated sandy loam soil that had no detectable C23DO genes. Microcosms were prepared in duplicate and spiked with aromatic hydrocarbons (naphthalene, biphenyl and phenanthrene added as solids). Laboratory workers sampled the microcosms once a week, and after 4 weeks, plated aliquots (0.1 ml) of the microcosm "onto media plates vapor-fed with the substrate used in the microcosm and incubated at room temperature. Morphologically distinct colonies were picked, restreaked and grown to confirm substrate utilization. Specific hydrocarbon degraders were not isolated from the gasoline-fed microcosms. PCR was performed on 15-20 of the isolates from each substrate" (Mesarch and others, 2004).

Researchers found

- C23DO genes in aerobic *m*-xylene, *p*-xylene and naphthalene microcosms in each of the 4 weeks of testing
- "within a 1-week period, gene copy numbers increased from 10^7 genes/ml in naphthalene microcosms to greater than 10^6 genes/ml in *m*-xylene microcosms"
- "high concentrations of *m*-xylene (7,100 g/l) resulted in enrichment of quantifiable C23DO genes every week, while low concentrations of *p*-xylene (210 g/l) produced consistent signals of C23DO genes below the quantitation limit"

- at low concentrations of o-xylene or benzene, no C23DO genes were detected throughout the 4 weeks; when concentrations were increased tenfold, C23DO genes were detected
- in toluene microcosms, no C23DO genes were detected at low concentrations, yet they were at high concentrations
- no C23DO genes were detected in biphenyl-, phenanthrene- or naphthalene-amended microcosms, or in the control microcosms without added substrate

Researchers cultivated "an abundant number of degraders" from the hydrocarbon-amended microcosms. They found that "The proportion of isolates containing C23DO genes was highest among the naphthalene (19 of 20), *m*-xylene (14 of 15) and *p*-xylene (11 of 20) degrading isolates, and lower in isolates from the o-xylene (1 of 20) and toluene (1 of 20) microcosms. None of the 20 biphenyl, benzene or phenanthrene isolates tested possessed a C23DO gene detected by our primers. The gasoline isolates were not tested for the presence of C23DO genes because the primary substrate(s) used by these microorganisms could not be determined" (Mesarch and others, 2004). C23DO genes were not detected in anaerobic naphthalene microcosms or in no-substrate controls through 4 weeks.

Researchers concluded:

- "...dioxygenase enzymes require molecular oxygen to function; this clearly demonstrates that C23DO gene detection confirms the presence of both oxygen and an aromatic substrate"
- "since sites are generally contaminated with petroleum mixtures that contain *m*-xylene, *p*-xylene and naphthalene, our C23DO primers would be suitable for general monitoring of aerobic bioremediation"

LUST field sites in Indiana

Researchers obtained groundwater samples from LUST sites in Linton and Winamac, Indiana in August 1999 and April 2000, respectively. Both sites at the time were undergoing MNA, monitored natural attenuation. USTs stored diesel, gasoline, fuel oil and waste oil at Winamac while the Linton USTs stored diesel and gasoline. Groundwater was properly sampled and shipped to Purdue University for microbiological and genetic analysis. In addition, field workers obtained four soil borings from the Linton site.

The Winamac site has 12 groundwater wells in a subsurface of silty clay soil grading to sand and gravel at about 7 feet below ground level. The Linton site is mostly clay down to 16 feet, where bedrock is encountered. Field workers installed six wells here. Because the Linton site was so clayey, and DNA extraction from clayey soils is difficult, researchers tested DNA extractability from the samples.

Researchers also used heterotrophic plate counts to enumerate aerobic heterotrophic bacteria. (Heterotrophs require organic compounds of nitrogen and carbon for nourishment while autotrophs usually make their food from the sun.) For the plate counts researchers used

- benzoate, "a low-volatility aromatic compound that can be easily incorporated into agar and is an intermediate in known degradation pathways utilizing C23DO genes... benzoate plate counts (250 mg/l benzoate) were incubated for 3 weeks to enumerate bacteria capable of degrading aromatic compounds
- naphthalene plate counts (only on the Linton samples)

At the Winamac field site:

- five of the 11 wells sampled contained aromatic compounds
- DNA concentrations ranged from 1.5 to 21.5 ng DNA/l
- three of the five contaminated wells and three uncontaminated wells contained C23DO genes
- two contaminated wells did not contain any C23DO genes
- there was no significant difference between total heterotrophs or benzoate-degraders in contaminated and uncontaminated samples
- there was no correlation between heterotrophs and BTX and SVOC (semi-volatile organic compound) concentrations or benzoate-degraders and BTX and SVOC concentrations
- the highest concentration of C23DO genes occurred in a well previously contaminated with xylenes; other wells containing xylene also had the gene
- C23DO genes were also found close to a BTX plume
- the genes were not found in wells that contained only benzene or benzene and ethylbenzene; "in microcosms, benzene concentrations higher than those found in [the wells here] failed to strongly select for bacteria containing C23DO genes... in addition [these wells] occur roughly in the center of the contaminant plume, which is often anaerobic because oxygen utilization rates are greater than oxygen recharge rates"

Researchers concluded that "The pattern of C23DO detection at the Winamac site is consistent with our microcosm studies and strongly suggests that aerobic bioremediation is occurring."

At the Linton field site:

- only two groundwater wells had BTX compounds above the detection limit; no target C23DO genes were detected in the sample extracts

- all soil cores contained TPH above 100 mg/kg (note: TPH values include BTX)
- all DNA concentrations were below the fluorometer detection limit of 1 ng DNA/l
- "DNA amplification did occur in all samples using universal 16S rDNA primers, indicating DNA was present in all extracts and of sufficient quality to allow PCR amplification"
- weak amplification of C23DO was found in an uncontaminated groundwater sample and in two soil samples

Mesarch and others (2004) assert that "The Linton site contained fewer culturable aerobic bacteria than the Winamac site. There was no correlation between heterotrophs and BTX and SVOC concentrations at the Linton site... None of the Linton samples contained culturable aerobic benzoate-degrading or naphthalene-degrading bacteria. In contrast to the Linton aquifer solids, which contained culturable heterotrophs, no bacteria could be cultured from the TPH-contaminated soil from SBs" (soil bores).

"The low level of C23DO genes in the Linton aquifer samples, in combination with the absence of culturable benzoate- or naphthalene-degrading bacteria, strongly suggests that significant aerobic bioremediation was not occurring." The gene occurred in some samples that may have been near the aerobic fringe of the contaminant plume.

Researchers also point out that clay can "decrease the size and activity of microbial communities. High clay content results in low water potential and low hydraulic conductivity, limiting both nutrient and oxygen transport to subsurface bacteria" (Mesarch and others, 2004). In the Linton samples "the clay soil compromises the C23DO detection limit by as much as three orders of magnitude." Mesarch and others suggest the problem could be alleviated by modifying the DNA procedure.

Summary and conclusions

Researchers using standard culture techniques, such as plate count data, showed no correlation of BTX to bacteria; however, a strong correlation was found between the presence of xylene and naphthalenes to enriched C23DO genes. The presence of C23DO genes also indicated oxygen.

"The development of PCR primers for other catabolic genes would be useful. In addition, rapid progress is being made in developing quantitative PCR methods that can be completed more quickly than the QC-PCR technique described here. The specificity of molecular genetic techniques provides critical information about the in-situ microbial community that would be useful for monitoring the effects of subsurface aeration technology or oxygen amendments used for in-situ bioremediation. The ability to perform accurate direct microbial analysis, combined with the short time required to process samples, poises molecular genetic techniques at the threshold of future in-situ bioremediation monitoring" (Mesarch and others, 2004).

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Mesarch, M.B., Nakatsu, C.H. and L. Nies, "Bench-Scale and Field-Scale Evaluation of Catechol 2,3-Dioxygenase Specific Primers for Monitoring BTX Bioremediation," *Water Research*, Vol. 38, 2004; http://www.environmental-center.com/magazine/elsevier/watres/

One of the authors, Dr. Larry Nies, comments: We have fully developed the detection of several other genes (toluene monooxygenase, toluene dioxygenase, phenol hydroxylase, ring hydroxylating monooxygenase, naphthalene dioxygenase and several biphenyl dioxygenases). Analysis for these newer genes is available (or very soon will be) to the public. Microbial Insights (http://www.microbe.com/) has licensed the technology and offers several types of modern molecular genetic detection analytical services. This is a relatively recent development.

UTTU thanks Dr. Larry Nies, nies@ecn.purdue.edu, for his help on this article.

Designing an earthquake-proof storage system at the airport in the bay

By Gene Rotter and John Hartmann

Several years ago, eight car rental agencies united to design and build a fueling facility at San Francisco's International Airport. The agencies involved in this endeavor included the U.S. EPA, California Water Resources Control Board, California Air Resources Board, San Mateo County Environmental Health Department and the San Francisco International Airport Commission.

The airport site

The San Francisco Airport was built partially on a landfill. The Bay itself forms the entire northern, eastern, and southern boundaries of the airport, and the Pacific Ocean is just 6 miles to the west. As many people know from television coverage of the earthquake we had about 15 years ago, much of the fill land in the Bay areas can be quite unstable. Additionally, the site has a very high water table, approximately 6 feet below the surface.

In addition, this project had to be coordinated with the design and building of a monorail that would connect the new car rental facility to the airport terminals. At this time, the airport was also building a new international terminal, a Bay Area Rapid Transit (BART) station, several new elevated roadways that would connect the Highway 101 freeway near the airport, and a new airport rail transit system to the new international terminal with the parking garages.

The airport commission mandated that the USTs be of triple-wall fiberglass construction because of the potential earth movement, both from the earthquakes (California has hundreds of them each month, mostly tiny ones) and the vibrations that might be caused by the monorail.

Reviewer's comment: Steel triple-wall tanks would have been better. Fiberglass tanks are notorious for leaking, and usually catastrophically.

Triple-wall tanks

Because of the requirement for triple-wall fiberglass tanks as well as the length of some of the piping runs, selection of equipment and monitoring methods posed other challenges. Many leak detection devices do not have third-party approvals for either triple wall-systems or long pipe runs. Thus, several manufacturers were consulted about their ability to customize their products for the special requirements imposed by the environmental and regulatory requirements.

Consultation with development engineers helped to determine that hydrostatically monitored, triple-wall tanks could be built. In hydrostatic monitoring, the cavity between the tank walls, sometimes called the interstitial space, is filled with a liquid brine solution. The tank maker then builds a reservoir on top of the tank where the level of the brine solution can be monitored.

In the case of triple-wall tanks, two reservoirs monitor the two interstices. Each reservoir is on the outboard side of a manway containing fittings. Able to hold up to 5 gallons of liquid, the reservoir is normally only half-filled and contains a sensor that can determine if the monitoring liquid is rising or falling.

The eight companies decided they would need 14 triple-wall tanks. Eleven of the tanks are 12,000 gallons and three are 15,000 gallons. Each tank has two manways in which all of their 4-inch openings are located. The manways are contained with 48-inch containment collars. The 48-inch diameter sumps are nearly 7 feet deep, and continuously wound for extra strength. One manway contains the fittings for the fill and vapor recovery, while the other contains fittings for the tank gauge, turbine pump, vent and vapor opening.

Tank installation

Because 14 tanks needed to be installed in one big wet hole right next to the monorail line, engineers decided that shoring would be critical. Engineers used heavy-duty interlocking zee-type steel shoring that extended as deep as 50 feet below grade in several locations around the hole.

Twelve-inch I-beams were attached horizontally at five levels around the hole. The shoring then had to be jacked apart (width-wise) so that the 12-inch-diameter steel pipe could be used as cross braces opposing I-beams. The cross braces were welded to the I-beams, which had been held in place by pressure when the jacks were released. This formed a giant steel cage into which the tanks were inserted.

Four wire braid straps anchored each tank to the lower cross braces so that the tanks would stay in place until the 12-inch concrete slab was poured above them. The straps hold the tanks in place by attaching to the cross braces that were left in place along with the shoring when the tanks were buried.

Once the slab was installed over the hole, the straps were no longer needed to hold the tanks in place. Nonetheless, abandoning the shoring and straps in place was determined to be the most effective method of installation.

From grade to the bottom of the tanks is approximately 17 feet deep. The tank hole itself was 165 feet long and about 35 feet wide at the widest point. All the tanks are 10 feet in diameter. The 12,000-gallon tanks are 23 feet, 8.5 inches long and the 15,000-gallon tanks are 29 feet, 2 inches long.

Piping installation

Once the tanks were set, the contractor faced the task of installing nearly 2.5 miles of double-wall piping. Because union labor needed to be used, a call was sent to the union hiring hall every day—and every day a new (different) crew was dispatched to the site. Each crew was trained on site by the contractor's staff. It took more than two months to connect the piping. The members of the plumber union learned their tasks quickly and provided many helpful suggestions during the installation process.

Because of its coaxial design, contractors chose a flexible piping. The double-wall pipe was installed inside a protective, corrugated PVC pipe that doubles (or triples) as an additional level of containment.

Although the longest pipe run is about 900 feet, the longest continuous length is much shorter—"only" 210 feet. The piping enters multiple four-foot-deep transition sumps along the main raceway, which itself is more than 20 feet wide.

The custom-designed transition piping sumps are 4 feet deep. This allowed the piping to accommodate fiberglass panels (that divided the interior of the sumps into separate sections) so that each pipe that entered and exited the sump could be monitored separately. Some sumps contain as many as five lines entering near the bottom and exiting more than three feet higher, with a separate discriminating sensor for each line.

Leak detection and monitoring

Twenty fueling islands with 60 dispensers are located perpendicular to the raceway. Each time a section of piping was completed (from sump to sump and sump to dispensers), the local regulators tested both the primary and secondary pipes for tightness.

Each car rental agency has its "own" fuel tanks and piping, so each is responsible for monitoring for any leaks in its own system. Therefore, each company has its own tank gauge system with leak monitoring sensors. The tanks have sensors in the hydrostatic reservoirs of the annular spaces. Every one of the 29 transition sumps has dividers installed between the individual pipe runs; each section is monitored by a discriminating sensor that can detect the presence of either water or fuel. This allows each car rental company to monitor its own tanks and piping even though the car rental companies share a common tank hole, pipe runs and sumps.

The tank and piping sensors are connected to consoles, as are both the sensors in the vapor recovery system and the sensors below the dispensers. Each car rental agency has located these consoles in their on-site office. To monitor piping, 230 discriminating sensors were required.

Hertz has the largest portion of the facility and uses four of the 14 tanks. Because its location is the farthest from the tanks themselves, Hertz has longer pipe runs and more sumps to monitor than any of the other companies. This means that Hertz needed two devices to monitor the eight interstitial spaces, four tank-level probes at more than 60 locations in the piping and vapor recovery runs, as well as the underpump dispenser sumps. When any of the sensors shows a fuel or high-water alarm, the system provides for positive shutdown of the submerged pumps. An alarm will sound only in the proper agency's office for any lines or tanks in any of the transition sumps or dispenser sumps. Other tanks in the same tank hole and other lines in the same raceway and even in the same transition sump will continue to function while the source of the alarm is checked.

Other major decisions

In addition to the slabs covering the dispensers and piping raceway, contractors poured a 300 by 700-foot slab around the dispenser islands. The slab around the dispensers was 16 inches thick. Contractors anticipated 2.5 to 3 inches of settling during the first 2 years, most of it occurring in the first year to 18 months.

Because the settling would be uneven and unpredictable, it was not possible to use hard piping under this slab. Thus, flexible piping was selected for both product piping and vapor recovery piping.

All of the commercial dispensers are outfitted with a "balance" vapor recovery system. Shields rather than vapor-assist systems have been used to balance the systems for the last several years; this has occurred, in part, because onboard refueling vapor recovery systems (ORVR) in new vehicles tend to be incompatible with existing vapor-assist systems.

To accommodate a balance system for this project, contractors had to install and monitor vapor pots. Vapor pots are required since, with balance systems, the slope of the vapor recovery pipe cannot be maintained all the way back to the tanks. Therefore, condensation must be collected and monitored.

These vapor pots collect condensation and are connected to submerged pumps. The pumps siphon back any collected liquid into the pumping system. Engineers recommended using two CPT, constant pressure turbine, submerged pumps, and this advice was followed.

Because of the distance from the tanks to the dispensers and the number of nozzles served by those tanks, five of the 14 tanks have two turbines installed to service the same 2-inch line. It is expected that under the most adverse circumstances, flow rates of 6 to 8 gallons per minute can be maintained.

Monitoring the progress

The size of this project alone makes it unusual. Because of the triple-wall tanks and the double-wall piping contained inside of a third pipe, monitoring was an exceptional challenge. In California, the local regulatory agency (city or county), which is responsible for implementing both state and federal regulations, was therefore an integral part of the planning process. Environmental health officials from the County of San Mateo were involved in each step of the decision-making process because no other installations like this existed in the immediate area.

Regulatory and environmental agencies are expected to work together—but not necessarily private sector competitors. The most unusual aspect of this project revolved around the cooperation of the car rental agencies to accommodate the airport commission, which owns the land and is responsible to the public.

A trustee account was established for funds to be deposited by the car rental agencies in proportion to their respective market shares. When an expense was incurred, such as a bill for tanks, other equipment, concrete, labor, etc., a check was issued from the trustee account. This was done instead of forcing the suppliers to attempt to bill each agency according to their respective percentage. This allowed the eight companies to share one design firm, one equipment supplier and one contractor.

Reference

Rotter, G. and J. Hartmann, "Designing an Earthquake-Proof Storage System at the Airport in the Bay," Reprinted from the August 1998 issue of *Petroleum Equipment & Technology* magazine, published by John Hartmann, principal of John Hartmann & Associates. More than 800 articles appear on his Web site, http://www.pe-t.com, and new articles are being posted to the site regularly.

Research notes

Direct-push electrical conductivity logging for high-resolution hydrostratigraphic characterization

Schulmeister, M.K., Butler, J.J., Healey, J.H., Zheng, L., Wysocki, D.A. and G.W. McCall, *Ground Water Monitoring & Remediation*, Vol. 23, No. 3, Summer 2003; http://www.ngwa.org

Researchers evaluated the resolution and quality of direct-push electrical conductivity (EC) logging at a "well-studied research site that is underlain by highly stratified alluvial sediments." They found that "When variations in pore-fluid chemistry are small, the electrical conductivity of saturated media is primarily a function of clay content, and hydrostratigraphic features can be described at a level of detail (<2.5 cm in thickness) that had not previously been possible in the absence of continuous cores. Series of direct-push EC logs can be used to map the lateral continuity of layers with non-negligible clay content and to develop important new insights into flow transport at a site." EC logging, however, will provide little information in sand and gravel intervals with negligible clay.

Other common sources of hydrostratigraphic information include geologic logs and well-bore geophysical methods, but the methods do not have the resolution of EC logging. Well bore geophysical methods can be biased by irregular borehole diameter and drilling fluids. Researchers found that higher EC values generally indicate fine-grained material, and lower values correspond to coarser sediments. Cores and water samples, however, are necessary to help interpret EC logs.

Site-specific information garnered from EC logging includes:

- stratigraphic information on groundwater flow and transport
- lithofacies maps
- identification of fine-scale variations in geologic deposits

Researchers conclude that "The use of high-resolution direct-push logging combined with the continuity of surface geophysical surveys should yield an image of the subsurface at a level of detail that has rarely been possible. At many sites in unconsolidated settings, such detailed views of the subsurface could vastly improve the efficacy of remediation activities and the quality of contaminant-transport predictions."

Immobilization behavior of methyl tert-butyl ether by cyclodextrins

Baek, K., Yang, J.S. and J.W. Yang, *Journal of Hazardous Materials*, B105, 2003; http://www.sciencedirect.com/science/journal/03043894

Baek and others (2003) studied cyclodextrins with respect to their ability to immobilize MTBE. "Cyclodextrins (CDs) have a low-polarity cavity in which organic compounds of appropriate shape and size can form inclusion complexes. This unique property provides CDs with a capacity to significantly increase the apparent solubility of low-polarity organic contaminants such as polyaromatic hydrocarbons, herbicides, pesticides, iodine and various organics. However, for VOCs with relatively high water solubility, such as benzene and MTBE, CDs can immobilize the VOCs into the cavity in the aqueous phase."

Inclusion of MTBE in cyclodextrins is not possible in every case because the MTBE is 0.53 nm in length and 0.43 nm in width. The natural CDs are made up of α-, β-, and γ-CDs. The α-CD has a diameter of 0.5 nm in diameter and a depth of 0.8 mn, which means the MTBE molecule must be at the smaller orientation to fit into the α-CD. The β and γ-CDs have diameter cavities of 0.6 and 0.8 nm respectively, and can more successfully encapsulate the MTBE molecule.

Induction of methyl tertiary butyl ether (MTBE)-oxidizing activity in Mycobacterium vaccae JOB5 by MTBE

Johnson, E.L., Smith, C.A., O'Reilly, K.T. and M.R. Hyman, *Applied Environmental Microbiology*, Vol. 70, 2004; http://www.asm.org

Several papers have indicated that bacteria grown on alkanes have the ability to degrade MTBE. The concept of requiring growth on a primary substrate to transform a secondary compound is called cometabolism. Typically the substrate serves not only as a source of food and energy but also as an essential ingredient for turning on the production of required enzymes. The process of turning on specific enzyme production is called induction. Alkane-induced MTBE cometabolism has been proposed as an active remedial technology and has been suggested to play a role in the fate of MTBE in the presence of alkanes released from gasoline. Due to the low solubility of alkanes and their limited groundwater transport, cometabolic MTBE degradation was not thought to be important in downgradient areas of plumes.

Reviewer's comment: Industry has demonstrated that MTBE is aerobically biodegradable directly and does not necessarily need a co-metabolic material to be present.

Johnson and others (2004) demonstrate that MTBE can induce the production of alkane oxidizing enzymes responsible for MTBE transformation. In the absence of alkanes, Mycobacterium vaccae grown on sugars or organic acids does not produce these enzymes. The research shows that if MTBE is added, the MTBE transforming activity increases with time. Similar results were detected with TBA (tert butyl alcohol) and TAME (tertiary amyl methyl ether). The impact of protein synthesis and specific enzyme inhibitors supports the claim that the increase in activity is due to the induction and production of alkane-oxidizing enzymes. Growth substrates tested in the study included organic acids that have been found in contaminated groundwater. These findings provide a potential explanation why MTBE-degrading activity is detected in association with some groundwater even though it is not always possible to isolate bacteria from these sites that can grow on MTBE alone.

Reviewer's comment: MTBE biodegrades at sites normally only after all alkanes have been reduced to insignificant concentrations. Hence, it is not necessarily the alkanes themselves that support cometabolism but the reaction and/or enzymes that are generated by the alkane biodegradation process.

Lead contamination and isotope signatures in the urban environment of Hong Kong

Duzgoren-Aydin, N.S., Li, X.D. and S.C. Wong, *Environment International*, Vol. 30, 2004; http://www.elsevier.com/locate/envint

Researchers investigated the extent and sources of Pb (lead) pollution in Hong Kong's urban environment. Scientists sampled several urban settings including tunnel, commercial, residential and car park sites and analyzed samples for Pb. "Depending on the type of sample, the level of contamination varied significantly within any given setting. In general, Pb concentration of roadside topsoils and gully sediments was lower than those of the corresponding road dusts... There has been a significant decrease in Pb concentration of the overall urban environment in Hong Kong from the levels recorded in the 1970s and 1980s, which can be possibly attributed to the progressive phasing out of leaded petrol since 1986." In the United States, automotive sources were once the major contributor of Pb emissions. Today, the major contributor is metals processing.

Modeling volatile chemical transport, biodecay, and emission to indoor air

J. Parker, *Ground Water Monitoring & Remediation*, Vol. 23, No. 1, Winter, 2003; http://www.ngwa.org

Parker created a vapor concentration model that models NAPLs (nonaqueous phase liquids) and dissolved contaminants from groundwater or soil into buildings. Previous models have considered factors such as first-order decay, and although such models are "attractively simple," the "apparent rate coefficients are highly variable due to the influences of many site-specific factors" (Parker, 2003). Because of the limitations of empirical first-order decay models, more physically based electron receptor-limited groundwater biodecay models have been developed. "An analysis of oxygen-limited biodecay in the unsaturated zone...indicates biodecay rates are markedly affected by the distribution of available oxygen among multiple degrading species. Neglecting biodecay and/or source depletion over time will lead to overestimation of human health risk from vapor exposure" (Parker, 2003).

Other models developed may consider vapor soil advection and diffusion through building foundations or simple dilution with building air, but none thus far have considered "possible reductions in building intrusion from horizontal airflow beneath the building induced by wind. Further, none of the models cited consider vapor transport induced by barometric pressure fluctuations" (Parker, 2003) or barometric pumping.

Parker's model includes the following:

- a finite source mass
- vapor transport due to advection, diffusion and barometric pumping
- oxygen-limited biodecay
- building underflow

In his paper, Parker gives his theory and tests it "with data from the literature to assess competitive oxygen use in multispecies systems." He also presents example applications.

Results of his studies indicate the following:

- his model generally over-predicted mean concentrations
- model parameter uncertainty in upper and lower indoor air concentration differed by a factor of about 150
- "increasing subbase permeability will result in greater flushing of volatile COCs from under the building; this decreases the concentration of intruding air"
- "longitudinal dispersivity and relative biodecay rate accounted for 3 to 17 percent of the variance"
- "foundation pressure differential, building underpressure, source concentration and building air exchange rate each accounted for 1 to 9 percent of the variance"
- slab-on-grade construction may "be a major factor controlling vapor intrusion into buildings"
- estimates of soil permeability will affect estimate of contaminated air entering the building
- the effect of "assuming a homogeneous soil characterized by simple arithmetic average total and air-filled porosities was considered"
- the observed gradient change may also result from "a change in biodecay rate with depth... Although biodecay rates may be very small (<1 percent of the available oxygen is consumed while degrading benzene), biodecay can nevertheless have a significant effect on risk-based cleanup levels"

The diffusion and sorption of volatile organic compounds through kaolinitic clayey soils

Itakura, T., Airey, D.W. and C.J. Leo, *Journal of Contaminant Hydrology*, Vol. 65, 2003; http://www.elsevier.com/

Researchers performed laboratory experiments to derive estimates of the effective molecular diffusion coefficient (D_c) and sorption coefficient (K_d) for methyl ethyl ketone (MEK), toluene and trichloroethylene (TCE) in natural clayey soils. Results of the experiments are as follows:

- "batch-type sorption methods may overestimate K_d values because they allow soil particles to "fully contact" organic contaminants in slurry samples"
- "the f_{oc}-K_{oc} (organic carbon content-coefficient of organic carbon) method considers that the organic carbon content is the only factor to influence the sorption of organic contaminants to soils
- sorption estimations may be affected by low f_{oc} (less than 0.001), clay content, and clay mineralogy
- differing K_d values could be attributed to soil structure
- a new diffusion test (using a double reservoir diffusion testing apparatus) overcomes some of these limitations; "however, the more complicated apparatus and longer testing times may allow organic compounds to be lost due to volatility and sorption to the apparatus wall"

Itakura and others (2003) conclude that "...the accuracy of the estimated parameters is uncertain and further studies could be required to investigate whether these differences between the samples are relevant in the field... Though it is not certain at this stage which method is able to estimate the most accurate K_d values, it is necessary that more than one testing method is used to assess the transport of organic compounds."

Other papers of interest include the following:

"Aerobic Biodegradation of Methyl Tert-Butyl Ether in Gasoline-Contaminated Aquifer Sediments," Zoeckler, J.R., Widdowson, M.A. and J.T. Novak, *Journal of Environmental Engineering*, Vol. 129, No. 7, 2003; http://ojps.aip.org

"Biodegradation of Hopane Prevents Use as Conservative Biomarker During Bioremediation of PAHs in Petroleum Contaminated Soils," Huesemann, M.H., Hausmann, T.S. and T.J. Fortman, *Bioremediation Journal*, Vol. 7, No. 2, 2003; http://www.sciencedirect.com

"Bioslurping Model for Assessing Light Hydrocarbon Recovery in Contaminated Unconfined Aquifer II: Optimization Analysis," Yen, H.K. and N.B. Chang, *Practice Periodical of Hazardous, Toxic and Radioactive Waste Management*, Vol. 7, No. 2, http://ojps.aip.org

"Changes in the Molecular Composition of Crude Oils During Their Preparation for GC and GC-MS Analyses," Ahmed, M. and S.C. George, *Organic Geochemistry*, http://www.sciencedirect.com/

"Dielectric Dispersion Characteristics of Sand Contaminated by Heavy Metal, Landfill Leachate and BTEX (02-104B)," Lee, J.H., Oh, M.H., Park, J., Lee, S.H. and K.H. Ahn, *Journal of Hazardous Materials*, Vol. 105, No. 1-3, December 2003; http://www.sciencedirect.com/science/journal/03043894

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"Estimation of Potential Impacts and Natural Resource Damages of Oil," McCay, D.F., Rowe, J.J., Whittier, N., Sankaranarayanan, S. and D.S. Etkin, *Journal of Hazardous Materials*, Vol. 107, No. 1-2, 2004; http://www.sciencedirect.com/science/journal/03043894

"Evaluation of the HP 6890/5973 Bench-Top Gas Chromatograph/Mass Selective Detector for Use in Mobile Laboratories," Li, K. and M. Fingas, *Journal of Hazardous Materials*, Vol. 102, Issue 1, August 2003; http://www.sciencedirect.com/science/journal/03043894

"Impact of Random Variables Probability Distribution on Public Health Risk Assessment from Contaminated Soil," M.M. Hamed, *Journal of Soil Contamination*, Vol. 9, No. 2, 2000; http://www.sciencedirect.com/science

"Integrated Subsurface Modeling and Risk Assessment of Petroleum-Contaminated Sites in Western Canada," Chen, Z. and G.H. Huang, *Journal of Environmental Engineering*, Vol. 128, No. 9, 2003; http://ojps.aip.org/

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