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Plant lipids influence on aromatic solutes sorption

Scientists at the University of Virginia investigated the sorption of soluble aromatic compounds by grasses and the role of plant lipids in sorption. Barbour and others (2005) reported, "The contamination of soil and subsurface water by petroleum hydrocarbons, industrial chemicals, and pesticides can result in subsequent plant contamination. Pollutants enter the plants through the root system and can be translocated to other parts of the plants, causing a potential human health risk if the plants are used for foods. Interest in this topic has increased in recent years as scientists and engineers have proposed using plants to remediate shallow soil, wetlands, stormwater runoff, and groundwater systems (e.g., phytoremediation) and to document groundwater contamination."

The scientists explained, "For passive transport of poorly water soluble organic compounds, it has been noted that the single most important plant characteristic is the plant lipid content. Organic solutes in water enter the plant through root hairs and then pass through the permeable cortex cell walls and the capillary void spaces between cortex cells. Water and organic solutes must then pass through the Casparian strip, which is a waxy (lipid) material that is formed around the anticlinal walls of specialized endodermis cells. After crossing the Casparian strip, water and solutes are transported to the stems and leaves via the plant's vascular system by a fluid potential gradient. Water and solute that are not metabolized or sequestered by the plant are eventually released into the atmosphere through stomatal pores on the leaves. During transport through the plant, some organic solutes partition into plant lipids and other components, retarding their transport through the plant" (Barbour and others, 2005).

Materials and methods

The three aromatic hydrocarbons studied were:

- benzene
- 1,2-dichlorobenzene
- phenanthrene (dissolved in methanol)

The plants used for lipid and sorption investigation included:

- annual rye (*Lolium multiflorum* Lam.)
- tall fescue (*Lolium arundinaceum*)
- red fescue (*Festuca rubra* L.)

Baby spinach (*Spinacia oleracea*) was studied for intermediate lipid content. Procedure verification plants were:

- iceberg lettuce (*Lactuca sativa*)
- chives (*Allium schoenoprasum*)

Liquid quantification

The scientists bought the spinach, lettuce and chives for the study from a local grocery. All other "plants were grown hydroponically with 3 mm glass beads as the growth medium for a period of two weeks." Scientists fed the plants a solution of "0.5 ml Scott's Miracle-Gro all-purpose plant food/L of water," which "was circulated through the growth medium at a rate of 2.5 ml/min. The seeds were sown at a density of approximately 7 seeds/cm² and received 12 hours of light per day" (Barbour and others, 2005).

The plants were removed from the glass beads, "separated into root, shoot, and seed components, and weighed. The root and shoot materials were then frozen at the temperature of liquid nitrogen (77K), dried for 24 hours in a vacuum chamber, and reweighed to determine the moisture content. The dried roots and shoots were then ground (separately), and 0.3-0.5 g samples were placed in 15 ml centrifuge tubes filled with 2:1 (v/v) chloroform/methanol. The tubes

were placed on an orbital shaker at 200 rpm for 10 minutes. The supernatant was then filtered through Whatman no.1 filter paper. The plant material was extracted twice more in this manner. The combined extract was then evaporated under a stream of liquid nitrogen and weighed. Finally, the lipid material was removed from the tubes by two sequential chloroform extractions. The tubes were reweighed, and the mass of lipids was determined by difference. All lipid analyses were performed in triplicate. This procedure used the same principles employed in other common extraction methods and was verified with two plants (iceberg lettuce and chives) listed in the U.S. Department of Agriculture Nutrient Database. This procedure does not quantify lipids or lipid-like materials that are not chloroform-soluble" (Barbour and others, 2005).

Sorption studies

In centrifuge tubes, researchers combined:

- freeze-dried plant material
- water
- ¹⁴C-labeled solute

Tubes were sealed with Teflon-lined caps. The plant masses selected for each hydrocarbon were intended to "allow between 25% and 75% of the added solute to be sorbed at equilibrium," and "water volumes were chosen to minimize headspace in each batch study" (Barbour and others, 2005). Initial solute concentrations for each were:

- benzene: 15.2-1042 mg/l
- 1,2-dichlorobenzene: 12-123 mg/l
- phenanthrene: 0.11-1.55 mg/l

Researchers assayed solute concentrations and used measurement results to calculate plant phase solute concentrations. For each isotherm experiment, blank and background reactors were prepared for quality

assurance. Kinetic sorption experiments were completed to determine the time required for equilibrium studies. Organic solute concentrations in a subset of water samples for each solute/plant combination were also quantified by gas chromatography to confirm that no transformation of the compound had occurred. It was assumed that any degradation products formed in the plant would be in equilibrium with the water and could be detected in this manner" (Barbour and others, 2005).

Results

Observed lipid contents versus USDA Nutrient Database values were:

- iceberg: $0.11 \pm 0.003\%$ vs. $0.11 \pm 0.026\%$
- chives: $0.61 \pm 0.001\%$ vs. $0.73 \pm 0.11\%$

Researchers noted, "The ages of the chives in our test and those reported by the USDA are unknown, but it is possible that age differences contributed to the observed variability" (Barbour and others, 2005).

Researchers observed minor variation between grass shoot lipid contents in dry comparisons, but "the roots of annual rye were shown to have a lipid content one-fourth that of shoots of the same age and plant type. The lipid content (dry basis) of annual rye shoots decreased with age. However, when only the lowest 8 cm of the shoots was tested, the lipid content was approximately constant, with some inconsistency among the four-week samples."

The lipid contents (dry basis) for plant materials used in batch sorption studies were:

- annual rye roots: $2.2 \pm 0.04\%$
- annual rye shoots: $7.9 \pm 0.28\%$
- tall fescue shoots: $6.7 \pm 0.36\%$
- red fescue shoots: $7.7 \pm 0.67\%$
- baby spinach shoots: $5.3 \pm 0.21\%$

Researchers also observed comparable 1,2-dichlorobenzene and phenanthrene kinetic plant sorption results, "reaching equilibrium in 12-24 hours, while the benzene uptake reached equilibrium within the first hour" (Barbour and others, 2005). They also noted:

- blank reactor recovery average: 96%
- background reactor: "normal background radiation"
- mass balance recovery: > 94%
- linear "sorption isotherms for the above three compounds onto roots and shoots of annual rye"

Experimental values for the plant-water partition coefficient (plant concentration versus concentration data in a best fit-line) for annual rye were:

- benzene/shoots: 22.5 ± 2.1
- 1,2-DCB/shoots: 259 ± 5
- 1,2-DCB/roots: 105 ± 1
- phenanthrene/shoots: 4601 ± 1
- phenanthrene/roots: 1988 ± 27

Discussion

Barbour and others (2005) reported their results supported indications "that lipid-water partitioning is the predominant uptake mechanism of these three aromatic compounds." Additional supporting evidence for lipid partitioning includes:

- "linearity and magnitude of the sorption of the three solutes to annual rye and other plants for the range of concentrations studied"
- "an absence of competitive effects"
- "a positive correlation between the lipid contents of the plants and the plant-water partition coefficients for 1,2-dichlorobenzene"

- "the partition coefficients for annual rye shoots increased inversely with the solute aqueous solubility"

Researchers calculated the lipid-water partition coefficients using the experimental sorption data for "each solute/plant combination" and surmised that, "even though lipids make up a small fraction of the plant mass (2.2-7.9%), they can account for 95.9% (benzene) to 99.9% (phenanthrene) of the solute storage capacity of the dry plant" (Barbour and others, 2005). Also, since the lipid-water partition coefficients calculated were nearly "twice as large as the corresponding octanol-water partition coefficients," it may be further deduced that, "the lipid-water partition coefficients and octanol-water partition coefficients exhibit similar relations to solute solubility. On the basis of the data for 1,2-dichlorobenzene and phenanthrene, the root lipids may be more hydrophobic than the shoot lipids" (Barbour and others, 2005).

Barbour and others (2005) concluded, "Although performed with dried plants, this study also has implications for uptake of solutes by living plants... Solute uptake by living plants is more complicated than the uptake by nonliving plants. In living plants, solutes must pass through the Casparian strip before entering the vascular system and may be metabolized, sequestered, or released to the atmosphere. However, it is likely that the equilibrium distribution of solute in living plants is at least partially controlled by partitioning that occurs between the transpiration stream and the lipid reservoirs of the plant... However, for the aromatic hydrocarbons in this study, it may be more accurate to use the lipid-water partition coefficient (or, alternatively, the triolein-water partition coefficient). The lipid-water partition coefficients derived herein may not be applicable to plants that differ significantly from those used in this study as there may be differences between the nature of the lipids from one plant type to the next.

Further testing is required to determine the variability of the lipid behavior with plant type. Additionally, long-term uptake experiments are needed to determine the relation between the equilibrium sorption to nonliving plants and the equilibrium uptake of a solute through the roots of a living plant."

Reference

Barbour, J.P., J.A. Smith and C.T. Chiou, "Sorption of Aromatic Organic Pollutants to Grasses from Water," *Environmental Science and Technology*, Vol. 39, No. 21, 2005; <http://pubs.acs.org/about.html>

UTTU thanks Jason Barbour, jpb3h@virginia.edu, for his help on this article.



MTBE contamination of public and private wells

Scientists from the United States Geological Survey (USGS) recently studied the presence of methyl tert-butyl ether (MTBE) in private and public wells in southeastern New Hampshire, specifically, Rockingham County. The county has the second greatest population and the largest groundwater service in the state and is therefore most at risk for MTBE contamination. "The occurrence of MTBE in groundwater is greatest in New Hampshire counties where reformulated gasoline (RFG) usage is mandated. As of 2004, there is no federal standard for MTBE in public water supplies, but a federal health advisory of less than 20-40 $\mu\text{g}/\text{l}$ was issued in 1997. Several states have developed their own standards, including New Hampshire, which has a standard of 13 $\mu\text{g}/\text{l}$. Data from the New Hampshire Department of Environmental Services indicate that the percent of public wells with MTBE greater than 0.5 $\mu\text{g}/\text{l}$ in Rockingham County has risen from 20.3% in 2000 to 23.1% in 2002. This compares to an increase from 12.7

to 15.1% statewide for the same period" (Ayotte and others, 2005).

Source waters for public water suppliers are not regularly monitored, and private wells are tested most often when owners deem it necessary, though seldom for MTBE. Therefore, the number of MTBE-contaminated wells has remained undetermined, a figure Ayotte and others set out to investigate.

Well geology

Scientists considered the geology of New Hampshire where, "In 1990, over 75% of private wells were reported as drilled into fractured crystalline bedrock aquifers. The majority of public wells are also drilled into bedrock, although the largest withdrawals for public supply are often from unconsolidated aquifers" (Ayotte and others, 2005).

Ayotte and others report area geology as:

- fractured crystalline bedrock aquifers
 - underlie much of New England
 - range in depth from a few meters to 100+ m
 - are dense, relatively impermeable
 - have low porosity
 - range in age from Cretaceous to Precambrian
 - are predominantly made up of igneous and metamorphic rocks
 - display fractures formed by stress of erosion of overlying rock, tectonic activity, cooling associated with igneous intrusions, and unweighting due to melting of continental ice sheets
- unconsolidated aquifers
 - consist primarily of discontinuous sand and gravel deposits that overlie bedrock
 - were formed during last glacial retreat

- typically occupy valleys and plains
- generally are less than 30 m thick but can be 100+ m in deep valleys
- are highly transmissive
- often yield great quantities of water

Contamination of aquifers has previously been found in wells of metropolitan Boston and in 11.3% of sampled Northeast and Mid-Atlantic region wells.

Experimental approach

Researchers randomly chose wells from all public supply wells and from a record of private wells, sampling a total of 120 of the former and 103 of the latter.

Between May and August of 2003, Ayotte and others (2005) took water samples in accord with USGS protocols using 40-ml glass septum vials and stainless steel flow-reducing port to collect samples. They used clean Teflon lines with stainless steel fittings or took samples directly from existing plumbing when the flow-reducing port was not possible. All sample sites were field-located using global positioning system (GPS) to an accuracy of approximately 30 m. Water quality parameters measured in the field included:

- temperature
- pH
- specific conductance
- dissolved oxygen concentration

All samples were analyzed by the New Hampshire Department of Environmental Services Water Quality Laboratory "for MTBE using gas chromatography/mass spectrometry techniques via purge-and-trap procedures (GC/MS) according to a modification of the U.S. EPA Method 524.2. No other compounds were analyzed. The laboratory reporting level (LRL) for the study was 0.2 $\mu\text{g}/\text{l}$. Samples were chilled immediately and analyzed within 14 days of collection" (Ayotte and

others, 2005). For quality control, scientists used the following:

- blanks
- spikes
- replicates

Researchers used statistical analysis, Geographic Information Systems (GIS), and supplementary data, including the following, to assist in analysis:

- aquifer type
- population statistics
- high-resolution land-use data
- Soil Survey Geographic (SSURGO) database
- lithology and lithochemical character of near-surface bedrock in New England
- Topologically Integrated Geographic Encoding and Referencing (TIGER) road data
- proximity to USTs and related tank information
- water sample temperature, pH, specific conductance, and dissolved oxygen

Results and conclusions

Ayotte and others (2005) ascertained in their study of Rockingham County groundwater that 40% of the public wells and 21% of the private wells sampled contained MTBE in concentrations above 0.2 $\mu\text{g}/\text{l}$. "Public and private wells have significantly different MTBE occurrence rates and public wells have higher MTBE concentrations than private wells... None of the 103 private bedrock wells has an MTBE concentration that exceeded either the state drinking water criteria of 13 $\mu\text{g}/\text{l}$ or the state action level for notification of adjacent well owners of 5 $\mu\text{g}/\text{l}$. For the public wells, however, four exceeded both the 5 $\mu\text{g}/\text{l}$ and 13 $\mu\text{g}/\text{l}$ levels" (Ayotte and others, 2005).

Researchers also concluded that MTBE contamination

of private wells was most strongly and positively correlated with population and housing density, road and urban land use. "Because many of the factors are themselves correlated, they collectively point toward increasing concentrations with increasing urbanization. In addition, MTBE concentrations are positively correlated to the specific conductance of the water sample, which may be another indication of urbanization" (Ayotte and others, 2005).

Public well MTBE contamination levels were found to vary considerably with the type of water supply establishment. "Public wells that were used for residential supply (including apartment complexes, condominiums, and mobile-home parks) had the highest rate of occurrence. Public residential well MTBE concentrations were significantly higher than for schools; commercial wells, including those at restaurants and service stations, and large community systems were not significantly different from any of the other establishment types" (Ayotte and others, 2005). In the three categories of public systems compared, MTBE was found to occur in concentrations greater than 0.2 $\mu\text{g}/\text{l}$ in:

- community water systems: 53%
- nontransient, noncommunity water systems: 27%
- transient, noncommunity water systems: 35%

"Unlike other categories, owners of transient noncommunity supplies are not required to submit routine monitoring samples of MTBE, although data from this study show that these supplies have similar occurrence rates to other public well categories" (Ayotte and others, 2005).

In both public and private wells, a significant relationship was observed between MTBE well concentrations and urbanization. A strong positive correlation was found in public well samples with "some urban factors (such as population density, housing

density, and specific conductance) but not with others (such as percent urban or percent of developed land)" (Ayotte and others, 2005). Well characteristics such as well depth and other, environmental, factors were also significantly related. For example, the following correlations, observed for public wells but not private wells, were:

- strong, positive correlation of well depth and MTBE concentrations
- inverse correlation of MTBE concentration and distance to fuel UST
- inverse correlation of MTBE concentration and pH of water sample

Researchers explained, "The negative coefficient for pH indicates increasing MTBE concentrations with decreasing pH. In bedrock wells in eastern New England, the pH of groundwater is related to the estimated age of the recharge water to that well" because typically "younger groundwater is less chemically evolved than groundwater with longer residence times." Therefore, younger groundwater "is more directly influenced by activities at the land surface and, thus, is more likely to come into contact with sources of MTBE. Conversely, high-pH groundwater is more likely to be relatively old and may predate the introduction of MTBE to the local groundwater system" (Ayotte and others, 2005).

Scientists were surprised by the strong relationship between MTBE concentration and public well depth. They suggested this result could be explained by well construction and bedrock well depth.

Well construction: Fractures in well construction may intersect open boreholes at any location, and some wells may be supplied by one major fracture whereas others may be supplied by numerous fractures. Direct leakage from the overburden to the well may be

a dominant source of water to low-yield bedrock wells. The degree of bedrock fracturing may vary by formation type for the rocks in the study area, and it is possible that this could affect MTBE concentrations; however, based on state-scale geologic data, MTBE concentrations did not vary by geologic formation or groups of formations" (Ayotte and others, 2005).

Bedrock well depth increasing for lower yields: With increasing populations, more wells are being drilled and drilled deeper to reach adequate water supplies than in previous years. Generally, drilling ends "...when an adequate supply is found; if an adequate supply is not found, drilling often continues (to exploit available drawdown of water in the well), and relatively deep wells with relatively low yields often result" (Ayotte and others, 2005). These lower-yielding wells then carry higher MTBE concentrations due to several explanations:

- Previous research suggests increased pumping rates decrease contaminant concentrations "...because the ratio of clean water to contaminated water increases and the contaminated water that reaches the well is diluted. The same concept can be applied to low-yield wells. For the deep, low-yield, public bedrock wells in this study, MTBE captured by the well has less opportunity for dilution than high-yield wells" (Ayotte and others, 2005).
- The source(s) of water may dominantly be surface leakage. "The transmissivity of the bedrock may be so low that the dominant contribution of water (and MTBE) to the well is leakage from overlying unconsolidated materials near the casing/bedrock boundary" (Ayotte and others, 2005).
- "Contributing areas to deep wells are sensitive to the vertical transmissivity of the aquifer—lower transmissivity at the recharge boundary (bedrock surface) results in a decrease in the recharge

rate and a corresponding increase in the size of the contributing area to the well. For a given pumping rate, low-yield wells would have a larger contributing area and thus a greater chance of intersecting an MTBE plume than a high-yield well" (Ayotte and others, 2005).

Ayotte and others (2005) suggest other factors relating to MTBE well contamination, including:

- cumulative effects of minor spills
- urban atmosphere
- well pumping style
- subsurface vapor releases of MTBE associated with gasoline UST air vapor recovery systems
- relatively high average linear groundwater velocities for fractured crystalline bedrock

In the last case, contaminants may then travel through the bedrock aquifer system at a greater rate than within unconsolidated aquifers. "This would, in turn, result in a relatively short aquifer contact time, potentially affecting processes such as biodegradation, adsorption, and dispersion and diffusion" (Ayotte and others, 2005).

"In southeastern New Hampshire, population growth continues at a rapid rate, and there is an increasing demand for groundwater resources from bedrock aquifers. Low dilution potential coupled with potentially large contributing areas and direct overburden source water suggest that low-yielding public bedrock wells in southeast New Hampshire may be at greater risk for MTBE contamination than other wells" (Ayotte and others, 2005).

Reference

Ayotte, J.D., D.M. Argue and F.J. McGarry, "Methyl tert-Butyl Ether Occurrence and Related Factors in Public and Private Wells in Southeast New Hampshire," *Environmental Science and Technology*, Vol. 39, No.1,

2005; <http://pubs.acs.org/about.html>

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Pulsed air sparging for remediation

Yang and others (2005) recently assessed "the performance of a field-scale pulsed air-sparging system during a short-term pilot test and during long-term system operation." Previous laboratory research has suggested air-sparging systems activated in pulsed mode are more effective in remediation than continuously activated systems.

In-situ air sparging (IAS or ISAS) is a technique growing in use because, as laboratory studies have shown, it is effective in treating "immiscible-phase source zones and dissolved contaminant plumes and as a barrier to contain dissolved plumes" as well as for its "significant potential for very soluble, but slowly degrading fuel oxygenates, such as MTBE" (Yang and others, 2005).

IAS involves injecting air into the saturated zone. Pulsed mode IAS is thought to improve contaminant removal compared to continuous mode IAS because injected air displaces "groundwater in the largest pores and creates temporary groundwater flow around the sparging wells, thus creating non-steady-state conditions and inducing groundwater circulation as the air channels form and collapse during each cycle." Then "the less-treated water flows into the air channels and mixes with the treated water when the air injection is temporarily turned off, thus introducing contaminated water to the vicinity of the air pathways as the channels form and collapse during each cycle. The groundwater mixing reduces the degree to which chemical mass transport in groundwater governs contaminant removal, resulting in an increase in contaminant mass removal by pulsed air sparging" (Yang and others, 2005).

Methods

The study took place in Kalkaska County, Michigan at the site of a decommissioned production well with shallow groundwater contaminated with BTEX. The site included 32 sparging points operated continuously from their 2001 installation until the study began in 2003. Scientists installed 22 shallow groundwater-monitoring wells (MWs) to track sparging system function.

The sparging system was designed to "inject air 113 l/min per sparging well. Five vapor monitoring points (VMPs) had been installed, each consisting of a shallow sampling location, at 4 m above groundwater table, and a deep sampling location, at 0.9 m above the groundwater table" (Yang and others, 2005).

From May 2001 to September 2003, the sparging system had been operated in a continuous mode. In an April 2003 sampling at five monitoring wells, BTEX concentrations were substantially higher than site cleanup guidelines and had not decreased to a significant degree in the two years of continuous IAS. Researchers also found that "a thin layer of light nonaqueous phase liquid (LNAPL) existed in MW-1 and MW-2" (Yang and others, 2005).

The pilot test included measurement of:

- MWs: groundwater pressures and dissolved oxygen (DO)
- VMPs: volatile hydrocarbon, carbon dioxide, and oxygen concentrations
- groundwater and soil vapor parameters

The data were noted every 30 seconds.

Researchers began in September 2003 by conducting "24-hour baseline measurements of the soil vapor and groundwater parameters... while the air sparging system was operated in the continuous mode. Then, the air sparging system was shut down for 24 hours. Continuous measurements of those parameters were

conducted until the trapped air within the saturated zone was fully released. The system was then restarted and the groundwater and soil vapor parameters were monitored continuously until the groundwater/air flow reached steady state. Steady-state conditions were determined in the field by analyzing the changes of groundwater pressures and DO and soil vapor hydrocarbon concentrations" (Yang and others, 2005).

From the information gleaned, researchers determined an optimum pulsing cycle for oxygen dissolution and hydrocarbon volatilization of 4 hours on and 4 hours off. The 4-h on period was selected to make the most of DO and hydrocarbon concentrations, while a 4-h off period was chosen to give the groundwater time to recover completely (Yang and others, 2005).

The sparging system was then restarted and operated in pulse mode at the selected pulsing frequency. "The groundwater and soil vapor parameters were continuously monitored for 72 hours to evaluate the mass of hydrocarbon volatilized and biodegraded and to verify that the optimum pulsing frequency was chosen. The air-sparging system was set to operate in the pulsed mode after the pilot test was completed. Selected operational parameters were measured 2, 8, and 12 months after the start of the pulsed air sparging to evaluate the long-term performance" (Yang and others, 2005).

Results

Researchers predicted pulsed mode air sparging would increase sparging effectiveness because "pulsing the air injection induces back-and-forth groundwater flow in the formation, which increases the oxygen and hydrocarbon mass transfer rates in the groundwater and promotes groundwater mixing; therefore, hydrocarbon volatilization and degradation should improve during the pulsed air sparging" (Yang and others, 2005).

Immediately after air introduction, scientists observed:

- groundwater pressure spiked with a maximum increase of 12 cm H₂O in 15 minutes, slowly decreasing and reaching steady state approximately 4 hours later, with an abrupt fall in pressure when air injection ceased, recovering in 4 hours
- DO jumped to a peak of 2.4 mg/l within an hour, reducing to 0.5 mg/l in 7 hours
- a 2-hour "lag of soil vapor hydrocarbon concentration changes" but "lag time depressed to half an hour after three pulsing cycles" (Yang and others, 2005)
- hydrocarbon concentration at VMP-1 Deep of 20 ppmv prior to air, peaking at 800 ppmv in 3 hours, then slowly decreasing

During sparging, researchers used monitoring equipment above the water table to ensure volatilized hydrocarbon transport from the saturated zone and to "measure the extent of the hydrocarbon volatilization" (Yang and others, 2005). They observed "the thin layer of LNAPL hydrocarbons, which had existed in MW-1 and MW-2 during the continuous air-sparging operation, was not detected when the groundwater was sampled in October 2003, 45 days after start of the pulsed air sparging." Once the LNAPL was removed, the benzene concentrations dropped (October 2003 to October 2004):

- MW-1: from 0.87 mg/l to 0.412 mg/l
- MW-2: from 4.2 mg/l to 0.54 mg/l
- MW-3 and MW-5: declined under 0.001 mg/l detection limit, later increased to 0.01 mg/l, leading to "dissolution of the benzene from the vadose zone" (Yang and others, 2005)

Average hydrocarbon concentration in samples from November 2003 to May 2004 to September 2004 ranged from:

- VMP-1: 530 ppmv to 919 ppmv to 371 ppmv
- VMP-2: unmonitored due to malfunction in November to 271 ppmv to 30 ppmv

Scientists observed, "Operating the air-sparging system in a pulsing mode significantly boosted the hydrocarbon volatilization rate. The concentrations at those locations dramatically dropped in September 2004 as the mass of remaining hydrocarbons decreased...the pulsed operation [also] promoted oxygen dissolution into the groundwater." Pulsed air-sparging "significantly elevated the DO" compared to continuous air-sparging, "presumably because in the continuous mode air channels developed, limiting oxygen mass transfer to the groundwater...The dissolved oxygen dissipated rapidly in the off periods, likely as a result of biological activity in the groundwater. The steady increase of DO suggested that the pulsed air sparging sustainedly oxygenated groundwater" (Yang and others, 2005).

Scientists monitored carbon dioxide and oxygen concentrations at deep VMPs to "measure the rate of hydrocarbon biodegradation." They observed in November 2003:

- VMP-1 Deep and VMP-2 Deep increased to 0.96% and 1.42%, respectively
- oxygen concentrations fell to 18.7% and 18.3%, respectively
- DO increased in the groundwater, which encourages biological activity

The researchers found the biological activity to be somewhat affected by season, with slight increases in the summer and decreases in the winter months, though "the hydrocarbon mass loss from the site might be the main reason for the depressed CO₂ and increased O₂ in the vadose zone in 2004... The pulsed air-sparging operation reduced the hydrocarbon mass in the saturated zone, and consequently, the magnitude

of hydrocarbon biodegradation decreased" (Yang and others, 2005).

Researchers calculated the mass removal of hydrocarbons via volatilization and biodegradation during the on periods only because measuring the off periods in the field was problematic. The final calculated estimate during pulsed air sparging, therefore, is likely lower than the actual mass of hydrocarbon volatilized and biodegraded. The total removal rate was "defined as the hydrocarbon mass removed during the on period divided by the length of a pulsing cycle (including both on and off periods). The calculated values only represent the mass removal rates by air sparging around VMP-1 and VMP-2" (Yang and others, 2005).

Scientists observed that the total hydrocarbon mass removal rate increased by 3 times with the onset of pulsed air sparging. They noted, "the role of biodegradation became relatively less important in the total mass removal as the volatilized hydrocarbon mass decreased, probably because of the hydrocarbon mass loss from the site... but the total removal rate [of hydrocarbons] was still higher than it had been with continuous operation" (Yang and others, 2005).

Conclusions

Yang and others (2005) concluded that pulsed air sparging

- increased dissolved oxygen in the saturated zone
- increased hydrocarbon removal rate via volatilization and biodegradation
- increased reduction rate for dissolved benzene in the source zone
- increased volatilization in the vadose zone

In light of their results showing that pulsed mode sparging is more effective than continuous mode sparging, scientists deduced that their field study

supported previous pulsed air sparging research conducted in laboratories. "Because benzene is the risk driver at most petroleum hydrocarbon-contaminated sites, pulsed air sparging could specifically reduce risk faster than continuous air sparging... It is expected that the remediation time will be lessened as a result of the pulsed approach to air sparging" (Yang and others, 2005).

Scientists added, "It is useful to note that the main objective of pulsed air sparging was to create non-steady-state air and groundwater flow in the formation, thereby enhancing chemical mass transport in groundwater and promoting hydrocarbon removal. Additionally, pulsed operation cut the electricity cost by 50%, and these savings on energy cost were just an added benefit of the technique" (Yang and others, 2005).

Reference

Yang, X., D. Beckmann, S. Fiorenza and C. Niedermeier, "Field Study of Pulsed Air Sparging for Remediation of Petroleum Hydrocarbon-Contaminated Soil and Groundwater," *Environmental Science and Technology*, Vol. 39, No. 18, 2005; <http://pubs.acs.org/about.html>

UTTU thanks Xiaomin Yang, xiaomin.yang@bp.com, for his help on this article.



BTEX diffusion and sorption

Scientists at Queen's University in Kingston, Ontario, investigated temperature change effects on the diffusion and sorption of contaminants with geosynthetic clay liners (GCLs). They studied "the diffusion and sorption characteristics of benzene, toluene, ethylbenzene, and xylene (BTEX), compounds which represent the lighter hydrocarbons and more mobile components of Arctic

diesel (jet fuel A-1), for the GCL used as a part of the barrier wall." Their particular focus was on differences between "the typical laboratory temperature of 22°C and the average summer temperature at the Arctic site of 5-7°C" (Rowe and others, 2005).

Methods

Researchers carried out diffusion, sorption/immersion and batch sorption tests.

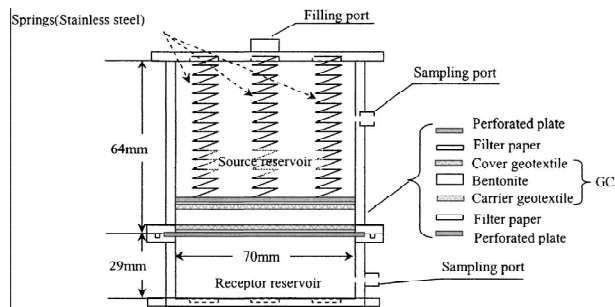


Figure 1: Schematic of diffusion cell (Rowe and others, 2005)

Diffusion tests

Researchers used stainless steel to create the diffusion cells, shown in Figure 1. "Three stainless steel springs were used to apply a confining stress of 9.5 kPa to the GCL during hydration and diffusion testing; this corresponded to the typical confining stress anticipated for the field application being examined... Two 1.25-mm-thick perforated stainless steel plates were used to support the GCL sample and allow the application of a uniform confining pressure" (Rowe and others, 2005). To prep each cell:

- Distilled water was added to hydrate the GCL sample under hydraulic gradient
- BTEX-containing solutions were added to the source reservoir and initial concentrations were noted
- Source reservoir and receptor reservoir samples were taken

Sorption/Immersion tests

Researchers then began sorption/immersion tests to determine BTEX compound partitioning effects at the differing temperatures for the cover and carrier geotextiles, by

- inserting BTEX-methanol stock into capped 250 ml glass serum bottles filled with distilled water (Rowe and others, 2005)
- adding a GCL sample to a vial of BTEX solution (solid:solution 1:40)
- monitoring contaminant concentrations until equilibrium was reached

Batch sorption tests

Rowe and others (2005) completed batch sorption tests for bentonite only at 22°C because the temperature could not be changed for the centrifuge. The tests entailed the following:

- glass tubes were filled with BTEX solution and bentonite, solid:solution 1:10
- tubes were shaken, left to equilibrate, centrifuged, left to equilibrate
- aqueous concentrations were noted

Researchers used a Varian gas chromatograph/mass spectrometer to analyze results for the diffusion and batch sorption tests.

Results

Scientists found a change in contaminant concentration "with elapsed time for a sorption/immersion test at 22°C... Similar results were obtained for 5°C except that it took longer for the containment concentration to reach equilibrium at 5°C rather than at 22°C" (Rowe and others, 2005).

The scientists found, as a result of needle-punching, that "the bentonite layer in the GCL includes some geotextile

fibers. Although the mass of geotextile fiber in the bentonite layer is small, the partitioning coefficients for the geotextile are much larger than for bentonite alone. Thus it is appropriate to consider sorption onto the geotextile fibers in the bentonite layer when assessing equivalent partitioning coefficients for the bentonite layer," though bentonite with fibers has relatively low sorption parameters (Rowe and others, 2005). Calculations for determining partitioning coefficients were done using the Arrhenius equation.

To prevent inaccurate results, "Blank tests were conducted using the diffusion apparatus without any GCL present to allow an assessment of the mass loss due to sorption onto the Teflon-coated stirrers or cell. The concentration of benzene decreased by about 10% at 22°C and by 3% at 7°C. Modeling was conducted to assess the effect of these mass losses on the interpretation of the diffusion test results for each contaminant" (Rowe and others, 2005). The modeling of diffusion included these layers:

- upper perforated plate
- cover geotextile
- bentonite layer with geotextile fibers
- carrier geotextile
- lower perforated plate

Scientists observed that some bentonite, though small, was able during hydration to cross the boundary from the cover and carrier into the geotextiles. As a result, "the effective diffusion coefficient of the BTEX compounds through the geotextile pores was considered to be bracketed by... the assumption of negligible bentonite in the geotextile and assuming the bentonite was uniformly distributed throughout the entire thickness of the GCL at the same void ratio" (Rowe and others, 2005).

Analyses of diffusion and sorption in cover geotextile, bentonite and carrier geotextile were performed separately and results were combined to identify factors contributing to sorption of the GCL.

Rowe and others (2005) presented results that "toluene, ethylbenzene, and xylenes were obtained assuming that the ratio of diffusion coefficient for the different contaminants to that for benzene was the same as for the free solution... These parameters give values that give good visual fits and low summation of square error (SSE) values," which "indicates the diffusion coefficient measured for one BTEX compound can be used to predict that of the others (assuming the same ratio in free solution at 25°C) and that equations" may be "effective for estimating the diffusion coefficients and the partitioning coefficients at different temperatures."

The researchers also observed that "mass transport to the receptor compartment was slower at 7°C than at 22°C despite...the partially compensating effects of a decrease in diffusion and sorption parameters... While it is recognized that in practice one would never get combinations of parameters such as for curves, a theoretical examination of these cases does show the effect of changes in diffusion and sorption (due to temperature) on mass transport. Thus...it can be seen that the reduction in sorption alone (due to a drop in temperature) gives rise to an increase in mass transport to the receptor. In contrast, when diffusion alone changes, there is a large decrease in mass transport through the GCL. The combined effect of reducing both diffusion and sorption due to a decrease in temperature results in a decrease in mass transport through the GCL to the receptor, demonstrating that the change in diffusion coefficient due to a change in temperature dominates over the effect of the change in partitioning coefficient" (Rowe and others, 2005).

Conclusions

Researchers found, "The sorption/immersion test indicated that the partitioning coefficients for the carrier geotextile were greater than those for the cover and that the sorption onto the geotextile component of the GCL dominated over sorption by the bentonite component. Thus, sorption by a GCL will be greater than for a similar amount of bentonite alone. These results also suggest that sorption will be product specific and may change from one product to another (even for the same manufacturer) depending on the type and amount of geotextile used."

From their investigation, Rowe and others (2005) concluded the following:

- Both diffusion and sorption depend on temperature "and both parameters were lower at 7°C than at 22°C. The effect of a lower diffusion coefficient dominated over the effect of a lower sorption coefficient and resulted in lower mass transport across the GCL at 7°C rather than at 22°C."
- The use of equations "to predict diffusion and sorption parameters at 7°C based on parameters obtained at 22°C results in a good fit to the experimental data at 7°C."
- "The diffusion coefficients for the BTEX compounds through the GCL followed the order benzene, toluene, ethylbenzene, and xylene and correspond to the order of the diffusion coefficients in free water."
- "The BTEX partitioning coefficients for the entire GCL followed the order xylene, ethylbenzene, o-xylene, toluene, and benzene."

Researchers added that since the BTEX compounds had diffusion coefficients determined under the low confining pressure (9.5 kPa), those coefficients "are expected to be near the upper end of the range of the diffusion coefficients for BTEX compounds likely to be

experienced in practical application involving the use of GCLs as barrier" (Rowe and others, 2005).

Reference

Rowe, R.K., T. Mukunoki, and H.P. Sangram, "BTEX Diffusion and Sorption for a Geosynthetic Clay Liner at Two Temperatures," *Journal of Geotechnical and Geoenvironmental Engineering*, Vol. 131, No. 10, 2005; <http://scitation.aip.org>

UTTU thanks Kerry Rowe, kerry@civil.queensu.ca, for his help on this article.



Bioscrubber treatment of contaminated gas stream

Scientists investigated the use of a two-phase partitioning bioscrubber (TPPB) in the place of biofiltration as a "treatment option of waste gases contaminated with volatile organic compounds (VOCs)." This system "was originally developed to address some of the inherent limitations of biofiltration through a design that could provide protection from high concentrations of toxic compounds, as well as enhanced rates of VOC absorption" (Nielsen and others, 2005).

The two-phase bioscrubber includes "a cell-containing aqueous medium and a second, often immiscible organic phase which functions as a repository for high concentrations of toxic substrates, controlling the aqueous-phase concentrations at subinhibitory levels. Substrate will partition through mass transfer equilibrium to the aqueous phase according to the metabolic requirements of the cells" (Nielsen and others, 2005). The second phase also includes the use of *n*-hexadecane, and the benzene is treated with *Achromobacter xylosoxidans* Y234.

Researchers sought to ensure dynamic stability of the

design because fluctuations are likely to regularly take place during field application. When fluctuations occur and the treated compounds are toxic, the “increasing substrate concentrations may surpass the level that is inhibitory to the biocatalyst, inducing performance instabilities that may lead to process failure and emissions to the environment” (Nielsen and others, 2005). Fluctuations in the following were considered:

- concentration
- flow rate
- composition

Researchers examined “the dynamic response of a TPPB to a transient benzene feed, focusing on fluctuations in concentration and flow rate, in the form of both spikes and step changes. The response to different modes of shutdown and restart have also been investigated, as this represents a type of dynamic variation and a practical aspect of operation that will be important in most applications” (Nielsen and others, 2005). The researchers used biofiltration as a basis for comparison.

Experimental procedure

Nielsen and others (2005) employed the following:

- *Achromobacter xylosoxidans* Y234 for benzene degradation
- TPPB: 2 liters of aqueous medium and 1 liter of *n*-hexadecane within a 5-liter New Brunswick BioFlo III bioreactor

Researchers agitated the TPPB continually and maintained conditions at:

- pH 6.6
- 30°C
- 800 rpm

“The nominal operating point from which fluctuations were imposed included aeration at a combined feed gas flow of 60 l/h” (Nielsen and others, 2005).

Researchers then:

- induced feed stream perturbations
- returned the feed to its nominal condition

Researchers also measured and noted the following:

- “(every 12-24 hours), 10-ml liquid samples of the reactor contents, drawn into 15-ml centrifuge tubes prior to phase separation by centrifugation (15 min at 4°C and 3400 rpm)”
- benzene in *n*-hexadecane, by GC/FID
- “aqueous benzene levels, estimated using an experimentally determined equilibrium partitioning coefficient”
- dissolved oxygen levels
- “biomass concentrations in the aqueous phase, determined by optical density measurements”
- culture purity

Fluctuations

Nielsen and others (2005) applied fluctuations in spikes, steps, shutdown and restart following TPPB steady-state biomass concentration. Spikes and steps included the following characteristics:

- 5-minute-long spikes and 4-hour-long steps in the feed rate created by “increasing the enriched benzene feed stream flow rate while maintaining the total aeration rate”
- spikes in the benzene feed concentration of approximately 4, 8, and 20 times the nominal value introduced
- step changes of approximately 2, 4, and 10 times the nominal value introduced
- system response to “a 2-fold step change in the loading rate” due to a 4-hour flow rate increase at constant concentration

Shutdown and restart investigations included:

- “stoppage of the benzene feed from its nominal value for 24 hours while maintaining makeup aeration at 60 l/h.”
- “halt of all air flow to the bioscrubber for 24 hours”

The system was continually agitated and monitored for 24 hours following restart “to investigate stability. Dynamic experiments were performed in the following order:”

- spike
- step changes (constant flow rate)
- step changes (constant concentration)
- shutdowns

“The different magnitudes of each type of feed dynamic were performed in randomized order. Biomass concentrations were measured prior to each dynamic experiment” (Nielsen and others, 2005).

Equilibrium

Nielsen and others (2005) estimated Henry’s law coefficients “for the distribution of benzene between the gas and each of the aqueous (same composition as used in the bioscrubber) and organic (*n*-hexadecane) phases at 30°C to aid in analysis.” They also:

- injected liquid benzene into 125 ml amber serum bottles containing 45 ml of aqueous medium or *n*-hexadecane and capped them with Teflon-lined septa
- analyzed headspace samples for benzene content via gas chromatography (1-hour equilibrium)
- tested the equilibrated gas-phase concentrations in the range of 1-20 g/m³ for each liquid phase
- calculated liquid-phase benzene concentrations by material balance

“The performance of the bioscrubber unit was assessed by instantaneous measurement of the apparent

elimination capacity (EC) and the apparent removal efficiency (RE)" (Nielsen and others, 2005).

Results

Researchers found, "During the preliminary stage of the experiment, a steady-state biomass concentration of 5.8 ± 0.2 g (CDW)/l was attained after approximately 200 hours of operation. An average apparent elimination capacity of 61.6 ± 6.4 g/(m³ h) (average of all instantaneous measurements) was achieved throughout, representing an average removal efficiency of over 99%. Dissolved oxygen (DO) levels were maintained relatively constant at $89.4 \pm 1.4\%$ of saturation, well above the limiting conditions. This steady state served as the condition from which all dynamic fluctuations were imposed" (Nielsen and others, 2005). Researchers observed:

- during spikes, "the process was able to operate with no change in removal efficiency during the initial period after the spike was introduced"
- after spikes, "removal efficiency dropped temporarily, with the magnitude of the decrease reflecting the spike size"
- higher loadings yielded increased benzene absorption, "leading to greater benzene retention in the liquid phases. The elevated benzene content in the system promotes increased bioactivity and, thus, higher consumption rates of DO"
- larger spikes equaled larger DO consumption rates
- larger spikes required longer recovery time
- "aqueous-phase benzene concentrations remained low throughout dynamic fluctuations"
- return to nominal value yielded stripping of "excess absorbed benzene from liquid phases, resulting in higher off-gas benzene concentrations and decreased measured instantaneous removal efficiency"

Researchers reported, "The most dramatic decrease in removal efficiency resulted after the 20-fold spike; however, it did not decrease below 92%, corresponding to a maximum emitted off-gas benzene concentration of only 0.4 g/m³. This off-gas concentration, assumed to be in equilibrium with the liquid phases of the bioscrubber, would correspond to an aqueous-phase benzene concentration of approximately 1.2 g/m³, well below the inhibitory threshold of this organism" (Nielsen and others, 2005).

The step increases imposed were monitored and researchers reported that "The TPPB handles each of the step change inputs well, adapting to the temporary load changes to achieve average elimination capacities of up to 650 g/(m³ h) while continuing to maintain removal efficiencies above 99% throughout. Periods of reduced performance, observed after each of the spike experiments due to stripping of absorbed benzene, were not observed after any of the step changes returned to the nominal conditions."

Nielsen and others (2005) also applied "a step change in loading capacity at constant feed gas benzene concentration by changing the total feed gas flow rate." They observed:

- "DO levels remain higher through the dynamic period"
- "removal efficiency briefly plunges to 97% as higher rates of stripping from the bioscrubber are experienced due to the higher airflow" after onset
- system recovery to 99% removal efficiency, "then maintained throughout the duration of the experiment"

In the two shutdown experiments, the bioscrubber performed without need for a reacclimation period. Researchers observed that shutdown one yielded increased DO levels from an average value of 86% to 90% saturation. Without the benzene feed, "the

offset in dissolved oxygen from 100% saturation is associated with the dissolved oxygen requirements for the endogenous activities of the cells." Shutdown two yielded reduced DO levels which dropped "abruptly as all residual absorbed benzene was quickly consumed and then gradually over the following 15 hours. A constant rate at which dissolved oxygen was consumed in the bioscrubber is thought to be characteristic of the culture's endogenous requirements during total starvation. Even after a 9-hour period of total dissolved oxygen limitation experienced during the second shutdown, the bioscrubber immediately reestablished its original performance at high removal efficiency" (Nielsen and others, 2005). Both of the shutdowns yielded:

- reduced biomass levels "of approximately 14% by the time of restart"
- subsequent recovery of biomass after return to nominal condition, "approaching the characteristic steady-state level of 5.8 ± 0.2 g (CDW)/l over the course of 48 hours after the feed was reinitiated"

Conclusions

Researchers concluded that the bioscrubber was adaptable to dynamic periods, particularly longer dynamic periods, "by using the excess substrate to produce more cells (Nielsen and others, 2005)." They observed:

- "benzene feed spikes of 4-8 fold had little effect on effluent concentrations and removal efficiencies remained high"
- no inhibition of *A. xylooxidans* Y234 "as low aqueous benzene concentrations were maintained through partitioning into the organic phase"

They noted that, in response to loading changes, biofilters "have typically been found to require an intermediate period of bed acclimation" whereas

"the TPPB was able to adapt to each of the loading changes studied" relatively quickly, "ensuring that absorbed benzene concentrations in the TPPB were low and that no excessive stripping would occur after the transient period ended." Nielsen and others (2005) observed that the TPPB:

- "is less susceptible to flow rate changes because its enhanced mass transfer characteristics and well-mixed design translate into highly effective absorption, thus requiring much shorter residence times"
- "experienced no loss of performance after restart, responding almost immediately with no observable reacclimation periods required"
- had no oxygen limitation

Oxygen limitation has been observed to impede toluene-degrading biofilter performance. Scientists reported in their bioscrubber investigation that, "as additional substrate becomes available during transient loads, the adapting cells rapidly respond by consuming additional oxygen. As the magnitude of the perturbations increased, correspondingly greater decreases in the dissolved oxygen levels were observed... Although dissolved oxygen levels never reached critically low levels under the conditions examined, the possibility of such limitations (and the poor performance that would result) in response to even larger fluctuations is a valid concern."

The limitation to biofilter use in this experiment's design primarily is the large Henry's law coefficient of benzene in water. In this case, however, researchers were able to use a smaller coefficient of *n*-hexadecane, the addition of which "to the bioscrubber not only serves to partition toxic concentrations of benzene away from the cells but also greatly enhances benzene absorption" (Nielsen and others, 2005).

Researchers concluded, "The improved mass transfer characteristics arising from organic-phase addition are perhaps most important during dynamic fluctuations where substrate loading rates may temporarily exceed the maximum elimination capacity of the organism." The organic phase keeps absorption and overall mass transfer rates high. "Optimizing" the organic phase volume fraction that will ensure a "target minimum efficiency while assuaging toxic concentrations of benzene" will translate into material cost savings and will be the focus of future work" (Nielsen and others, 2005).

"Although it is the biocatalyst that ultimately destroys target pollutants, the primary function of any biological waste gas treatment technology is to remove VOCs from the contaminated air stream... A highly active biocatalyst will minimize substrate accumulation in the media, resulting in maximal driving forces for mass transfer. Therefore, bioreactors should be designed both to provide sufficient mass transfer and to establish an environment in which bioactivity can be maintained under all conditions. Satisfying both of these objectives has allowed the TPPB to achieve success during both steady and transient operation" (Nielsen and others, 2005).

Reference

Nielsen, D.R., A.J. Daugulis and P.J. McLellan, "Transient Performance of a Two-Phase Partitioning Bioscrubber Treating a Benzene-Contaminated Gas Stream," *Environmental Science and Technology*, Vol. 39, No. 22, 2005; <http://pubs.acs.org/about.html>

UTTU thanks David Nielsen, Nielsen@chee.queensu.ca, for his help on this article.



Two-dimensional isotope analysis for MTBE biodegradation

Scientists investigated "the fate of the gasoline additive methyl tert-butyl ether (MTBE) and its major degradation product tert-butyl alcohol (TBA) in a groundwater plume at an industrial disposal site" (Zwank and others, 2005). The study was completed using compound-specific isotope analysis (CSIA) and a two-dimensional stable isotope approach that "is based on a comparison of measured field data with carbon and hydrogen isotope fractionation data reported for biodegradation of MTBE under oxic and anoxic conditions. Specifically, a novel evaluation procedure allowed for the first time the interpretation of observed empirical fractionation of MTBE in terms of theoretically based intrinsic kinetic isotope effects (KIE)." This approach allowed researchers to assess both "the nature and extent of in-situ biodegradation but also to decipher the pathway of anaerobic MTBE degradation" (Zwank and others, 2005).

The investigation used TBA, because while little is known of its biodegradation tendencies, "TBA often accumulates in the presence of MTBE and therefore has been used in field studies as an indicator of MTBE biodegradation," though instances of MTBE biodegradation without TBA buildup had also been observed. "The potential lack of TBA accumulation and the fact that TBA may be present as a constituent of spilled gasoline complicated the assessment of in-situ degradation of MTBE by a mass balance approach even under well-defined boundary conditions." Therefore, scientists were forced to consider a new approach at the field site under study, "due to the widespread contamination of the plume, the existence of multiple contamination sources, and complex biogeochemical and hydrological conditions" (Zwank and others, 2005).

Background

Researchers based their investigation on the idea that, "as bond cleavage may be accompanied by a kinetic isotope effect, the isotope signatures of the reactant and the product(s) may change during a given transformation reaction. The remaining fraction of the parent compound may thus become progressively enriched in heavier isotopes since bonds containing light isotopes are slightly less stable and thus more reactive than those with heavy isotopes." Therefore, using a series of equations, scientists were able to calculate the expected degree of biodegradation, B , and f , "defined as the ratio of MTBE concentration at well x as compared to a reference concentration of MTBE" (Zwank and others, 2005). To calculate the estimated TBA and MTBE concentrations at well x , Zwank and others (2005) assumed:

- "similar transport processes for TBA and MTBE"
- "MTBE degradation as the only source of TBA"
- "the absence of TBA biotransformation"

Researchers used corrective factors to calculate isotopic signatures because "if molecules contain more than one atom of the element for which isotope fractionation is studied, two different effects must be taken into account. One effect is the 'dilution' of the measured isotopic shift due to the presence of atoms of the studied element at non-reacting positions in a molecule... This dilution of the observed isotopic shift can be corrected by an appropriate factor where n is the total number of atoms of one element present in the molecule and x is the number of atoms of this element that are located at reactive positions" (Zwank and others, 2005).

The second effect researchers sought to correct was intramolecular competition. "Depending on the symmetry of the molecule, it is possible that the investigated element is present at z chemically equivalent, reactive positions in the molecule. In the

case of the oxidation of MTBE, this is the case for the three hydrogen atoms of the methoxy group. At low natural isotopic abundance only one of the three positions at most is occupied by deuterium. Hence, if a bond to this heavy isotope is broken, the reaction is in competition with breakage of bonds to the light hydrogen isotopes in equivalent positions (Zwank and others, 2005)." The KIE value may be calculated after these corrections are made.

Experiment

The scientists' site of study was an industrial landfill in South America. The landfill was closed but had been used for more than 20 years, until 1989, as a disposal site for phenol. MTBE, used as a chemical solvent, was deposited at the site. Open ponds were used as disposal sites, "located on a shallow hill, leading to a radial groundwater flow pattern" (Zwank and others, 2005).

The site of study was characterized by the following:

- water table between 10 and 20 m below topsoil
- shallow aquifer (10-15 m)
- low hydraulic conductivity
- underlying zone of basaltic rock of volcanic origin
- fissures in impermeable zone, allowing preferential flow to occur
- average annual groundwater temperature between 25 and 30°C

Researchers noted difficulty with assessment of the site due to the number of disposal ponds, 13, their location in relation to nearby wells, the several different types of production wastes present including BTEX, phenol, and isopropyl benzene, and the close proximity of two wetlands, located less than 600 m downstream. "To protect these wetlands from contamination, three pumping wells and two deep horizontal pumping wells"

were "installed as hydraulic barriers. The installation of these wells has changed the hydrological regime at the site, leading to potentially higher transport velocities of the contaminants. Forty-seven permanent monitoring wells have been installed at the site and are sampled semi-annually. The monitoring wells do not all extend to the bottom of the aquifer, hence varying dilution effects during sampling cannot be excluded" (Zwank and others, 2005).

In the two sampling sets conducted by Zwank and others (2005), sampling consisted of the following:

- wells were pre-pumped for several hours prior to sampling
- water temperature and pH were noted on site
- oxygenation was noted using oxygen-sensitive electrode
- samples were taken in polyethylene flasks, acidified, and kept at 4°C until analysis
- 40-ml glass vials were filled without headspace with samples for concentrations of isotopic signatures of MTBE and TBA; vials were closed with Teflon-sealed screw caps and kept at 4°C until analysis

With the samples, scientists determined MTBE, TBA, and BTEX concentration via aqueous injection gas chromatography/mass spectrometry. The samples then went through the following regime:

- samples were "extracted using a solid-phase microextraction (SPME) procedure"
- extracted "analytes were thermally desorbed for 1 minute in a split-splitless injector (270°C) equipped with a deactivated SPME liner"
- "the chromatographic separation of the analytes was achieved on a gas chromatograph"
- carbon isotopic measurements: analytes were combusted after separation in a combustion interface maintained at 940°C

- resulting CO₂ was analyzed in an isotope ratio mass spectrometer
- hydrogen isotopic analysis: analytes were pyrolyzed at 1400°C
- resulting H₂ was analyzed in the isotope ratio mass spectrometer
- H₃⁺ “factor was determined daily by measuring a set of nine reference gas peaks of increasing amplitudes

After at least three replicates, researchers averaged results, yielding the isotopic signatures.

Zwank and others (2005) completed hydrolysis of MTBE to TBA under acidic conditions that included:

- 20-ml headspace vials sealed with Teflon-lined crimp caps
- vials filled with 17 ml deionized water
- addition of 1.7 ml HCL to vials
- placement of vials in agitator of a CombiPAL Autosampler at 60°C
- 1 hour equilibration
- addition of MTBE spike of 0.5 μm to reaction vials

Researchers used mass spectrometry to measure MTBE and TBA concentrations with “the mass spectrometer acquiring in the scan mode in order to verify that no additional products formed during hydrolysis. The high methanol concentrations produced during the reaction led to an overestimation of the TBA concentrations, due to a peak broadening, but since no additional products were formed, complete MTBE hydrolysis can be expected” (Zwank and others, 2005).

To identify isotopic relationships of the tert-butyl group, researchers:

- spiked a vial with 1 ml of pure MTBE of known isotopic signature
- spiked a vial with “200 ml of a methanolic solution

of a field sample from the MTBE source containing no TBA”

- kept vials “at 60°C for 5 hours” for hydrolysis
- neutralized samples “using NaOH and kept them at 4°C until analysis
- determined carbon isotopic compositions “using purge-and-trap extraction”

Results and discussion

Zwank and others (2005) reported, “As MTBE was completely transformed to TBA, which was stable under the given conditions, the carbon isotopic signature of TBA corresponds to the tert-butyl of MTBE. MTBE was hydrolyzed with an observed pseudo-first-order constant of -0.0233 min^{-1} corresponding to the half-life of 30 minutes.” Through calculation, researchers determined, “the isotopic signature of the methoxy group and the tert-butyl group of MTBE differed by more than 10 ‰. To our knowledge, this is the first indication of position-specific isotopic signatures in MTBE” (Zwank and others, 2005).

In terms of aerobic and anaerobic degradation of MTBE, aerobic co-metabolic degradation when tested in the laboratory was observed to yield a carbon isotopic enrichment. Scientists observed anaerobic biodegradation to create “substantially higher carbon isotopic enrichment as compared to aerobic conditions” which “may indicate that different reaction mechanisms are involved in aerobic and anaerobic biodegradation of MTBE and thus may be used to characterize the nature of biodegradation in the field” (Zwank and others, 2005).

Scientists observed:

- “significant isotopic enrichment of MTBE with increasing distance from the source”
- “the carbon isotopic signature of TBA was more or less invariable within the plume”

- the signature was “slightly enriched in ¹³C as compared to MTBE at the source”

Researchers suggested, “This effect can be explained by a position-specific difference in the carbon isotopic signature of the methoxy and tert-butyl group in MTBE as found for a MTBE standard. The hydrogen isotopic signature of TBA did not show a consistent trend” (Zwank and others, 2005).

Scientists did not observe an “apparent simple correlation between MTBE concentration and the carbon isotopic enrichment patterns.” They suggested, therefore, that, “other processes such as dilution and elimination processes (e.g., volatilization) that do not cause significant isotopic fractionations also have to be taken into account. To correct for dilution processes, researchers can normalize MTBE concentrations to a suitable conservative tracer. At this site, however, due to the multiple contamination sources and the long contamination history of the disposal site, no suitable conservative tracer could be identified.” Scientists therefore sought methods outside of the more traditional Rayleigh-plot method to delineate biodegradation.

The solution suggested by Zwank and others (2005) was to link *f* values calculated from measured carbon isotope ratios and hydrogen isotope ratios measured in the same sample. When applied, scientists found that “the calculation of *f* based on carbon isotopic fractionation resulted in a strong correlation suggesting that this approach allows researchers to distinguish MTBE concentration decrease associated with in-situ biodegradation from dilution or other nonfractionating processes” (Zwank and others, 2005). Using this calculation, scientists observed very low *f* values for aerobic biodegradation if microorganisms were at work, and much higher, more plausible values for anaerobic biodegradation. Therefore, Zwank and others (2005) concluded that aerobic biotransformation

of MTBE could be ruled out "as a major degradation pathway," and calculations could yield "the extent of biodegradation."

This situation, scientists reported, "illustrates the potential of using a multi-element approach in CSIA, especially in field studies. If the data of only one element were present, a quantification of in-situ biodegradation would have been impossible... This new approach relies on the combined evaluation of carbon and hydrogen isotopic data collected at the field site and allows researchers to identify (i) whether the observed isotopic enrichment of carbon and hydrogen isotopes at the site is associated with one single process, as well as (ii) the nature of this process" (Zwank and others, 2005).

When TBA concentrations were calculated, scientists often observed low results. This "general underestimation can be explained by the fact that the measured MTBE concentrations used for this calculation are not only lowered by biodegradation or dilution but by an additional process that does not yield TBA and does not change the isotopic composition of the parent compound. Owing to the relatively high temperature of the groundwater (~25°C) and the higher water-air partition constant of MTBE as compared to TBA," volatilization or evaporation may be at work (Zwank and others, 2005).

Researchers concluded that, "this approach...should only work if both isotope signatures are influenced by the same reaction." They observed the following:

- "a good correlation of the hydrogen and carbon isotopic shifts"
- "aerobic biodegradation causes a small carbon isotopic fractionation but a very strong shift in hydrogen isotopic signatures"
- "anaerobic biodegradation results in strong isotopic enrichment for both carbon and hydrogen"

- "the significant difference between fractionation patterns under oxic versus anoxic conditions is a strong indicator for the existence of different reaction mechanisms"
- "in the presence of oxygen, the most likely degradation pathway for MTBE and TBA starts with an oxidation of the methoxy group by mono-oxygenases. The thus formed tert-butoxy methanol either reacts directly to TBA and formaldehyde or is further oxidized to tert-butyl formate, which then hydrolyzes to form TBA"
- "extent of hydrogen fractionation depends on the nature of the leaving group"
- "a S_N1 reaction mechanism cannot be ruled out based on kinetic isotopic effects" but "an oxidation mechanism seems to be most plausible in the presence of molecular oxygen"

"This reevaluation of isotopic fractionation data illustrates that differing isotopic enrichments found for aerobic and anaerobic biodegradation indeed reflect the underlying reaction mechanisms and therefore can be used as a powerful tool for the qualification of in-situ biodegradation of MTBE. A major advantage of this approach is its applicability at biogeochemically and hydrologically complex field sites as it is independent of mass balances, as is illustrated by this case study" (Zwank and others, 2005).

Reference

Zwank, L., M. Berg, M. Elsner, T.C. Schmidt, R.P. Schwarzenbach and S.B. Haderlein, "New Evaluation Scheme for Two-Dimensional Isotope Analysis to Decipher Biodegradation Processes: Application to Groundwater Contamination by MTBE," *Environmental Science and Technology*, Vol. 39, No. 4, 2005; <http://pubs.acs.org/about.html>