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Review of stable isotope work

This article is a summary of laboratory and field studies devoted to assessing contaminant biodegradation by stable isotope analysis.

The problem

Conventional means of assessing organic contaminant biodegradation have limitations. For instance, monitoring decreasing contaminant concentration from the source is problematic because several processes such as adsorption, dispersion, dilution, chemical transformation or biodegradation can alter concentrations of compounds being investigated. Moreover, "if the monitoring transect is not oriented to the direction of groundwater flow and samples are taken only at the plume edges, the decreasing concentrations might give an incorrect impression that biodegradation is occurring" (Meckenstock and others, 2004).

Other techniques to assess biodegradation include

- measurement of contaminant concentrations with depletion of electron acceptors for aerobic (oxygen) or anaerobic respiration (nitrate, sulfate)
- detection of metabolites; however, concentration can be low and some metabolites may not be detected
- GC-MS fingerprinting of the chemical composition of contaminant plumes along the groundwater flow; however, peak interpretation can be difficult
- direct evaluation of aerobic biodegradation by microcosm studies
- molecular techniques such as PCR or fluorescence in-situ hybridization
- quantification of mRNA
- isotopic composition of individual contaminants

This article will describe the process of stable isotope analysis to assess biodegradation.

Stable isotope basics

Organic compounds are made up of mostly carbon, hydrogen, nitrogen, oxygen, sulfur and sometimes chlorine. "These elements have at least two stable isotopes that can be distinguished mass spectrometrically. With the exception of artificial isotopically enriched compounds, organic compounds consist of mixtures of isotopomers with carbon, hydrogen, oxygen and chlorine as the important elements of anthropogenic contaminants. Although the chemical and physical properties of stable isotopes are nearly identical, slight differences arise from a quantum mechanical effect depending on different zero-point energies of the heavy and light isotopes. The higher zero-point energy of the lighter isotope means that a chemical bond formed by a lighter isotope is weaker than one by the heavier isotope. This principle controls the reactivity of the individual stable isotopes in the environment and induces isotope fractionation. The extent of isotope fractionation during synthesis of organic compounds leaves a fingerprint in terms of isotope composition, providing clues that may be used to identify sources, transformation reactions and sinks of organic compounds in the environment" (Meckenstock and others, 2004).

Other facts about stable isotopes:

- about 99 percent of all carbon on earth consists of the stable carbon isotope ^{12}C and approximately 1.11 percent of the stable isotope ^{13}C
- the average abundance of the stable isotopes on earth is close to the reference materials used for stable isotope measurements
- isotope ratios in naturally occurring compounds vary

due to kinetic isotope effects during their production, which are understood as equilibrium isotope effects in processes without net reactions

Isotopic fractionation principles

The following section is taken verbatim from Meckenstock and others (2004). "Equilibrium chemical reactions (e.g. dissolution of CO_2 in water) are accompanied by equilibrium isotope effects. Unidirectional reactions—such as biodegradation—are often accompanied by significant kinetic isotope effects. These isotope effects depend on different reactivities of the isotopomers containing heavier or lighter atoms at the reactive site of a molecule, which leads to an unequal isotopic distribution between substrates and reaction products. The energy differences in the dissociation or formation of bonds in the transition state of a chemical reaction determine the isotope fractionation. Chemical bonds containing the heavier isotope are stronger to a minute extent and the activation energy for their cleavage is higher. Therefore, in biological systems usually the lighter isotopes are preferentially reacted. However, enzymatic catalysis changes the transition state of chemical reactions and lowers the activation energy, which changes the kinetics of a reaction. As isotope fractionation is the product of a different kinetic turnover rate of the lighter and heavier isotopes, the isotope fractionation will change when catalysis changes the kinetics of a reaction. A given type of reaction does not always generate the same extent of isotope fractionation. For example, an experimental study on anaerobic toluene degradation showed that the same type of enzyme reaction can lead to slightly different extents of isotope fractionation." In addition, kinetic isotope fractionation can be divided into primary and secondary effects:

- a primary effect involves a heavy atom that is cleaved or forms a bond
- in a secondary effect, the molecule is not isotopically heavier and is not involved in the reaction, but it influences the reaction

Some other facts about stable isotope fractionation:

- "Atoms that are directly involved in the molecular reaction are subject to kinetic isotope fractionation whereas atoms that are not involved in the reaction remain isotopically stable"
- "One of the most important processes determining the carbon isotopic composition of organic matter is the strong isotope fractionation upon CO²-fixation by plants, because most living organisms on earth depend on organic carbon from photosynthesis; the extent of the isotope effect depends on the CO²-fixation pathway used by different types of algae and plants "
- "Early analytical approaches on stable isotope analysis of compounds in biology were based on their purification, total combustion and subsequent mass spectrometric analysis of the evolved CO²"
- "Instruments for CSIA (compound-specific spectrometric isotope analysis) became commercially available for hydrogen, carbon, nitrogen and oxygen isotope analysis"
- "Molecular hydrogen is by far not as ionizable as carbon dioxide, for example, and therefore hydrogen isotope analysis is less sensitive than carbon isotope analysis and has a typical reproducibility between 2 and 5 percent, which is to a certain extent compensated by the usually higher isotope fractionation effects observed with hydrogen"

Laboratory isotope fractionation studies

Aerobic degradation of aromatic hydrocarbon studies revealed the following:

- oxidation of hydrocarbons resulted in enrichment of ¹³C in the residual substrate fraction
- crude oil aerobically biodegraded in seawater, and carbon isotope ratios of the residual, non-degraded contaminant fraction were measured; findings showed that the aromatic fraction exhibited no isotope shift, but there was a distinct isotope fractionation upon degradation of the aliphatic fraction
- another study found that aerobic degradation of toluene by undefined enrichment cultures did not lead to carbon isotope fractionation
- sometimes the extent of isotope fractionation can be explained by enzyme reactions involved; however, a given enzyme did not always lead to comparable isotope effects
- depending on the respective substrate and biochemical reaction, isotope fractionation can range from very strong to non-detectable

Anaerobic degradation of hydrocarbons (alkanes) in a seawater enrichment produced significant isotope shifts in the residual fraction; the alkane monooxygenase reaction (usually the primary step in aerobic alkane degradation) produces significant isotope effects.

Meckenstock and others (2004) report that the number of cultures known to degrade aromatic hydrocarbons is increasing, and "isotope fractionation in the course of biodegradation can now be determined for almost all BTEX compounds under various redox conditions."

Toluene is the most intensively studied aromatic hydrocarbon. Its ¹³C isotope effects have been studied with strains using sulfate, nitrate or ferric iron. "However, similar to the aerobic degradation with oxygenases,

the extent of fractionation during turnover of different substrates by an identical enzyme reaction can vary significantly."

The fuel oxygenate, MTBE, can be degraded under oxic and anoxic conditions. Two pathways have been proposed: direct transformation to tert-butyl formate (TBF) where acetaldehyde is released; and TBA (tert butyl alcohol) formation via TBF (tert-butyl formate). "The carbon isotope fractionation factors determined for aerobic MTBE degradation by the pure culture strain PM1, an enrichment culture, and in microcosm experiments, were all in the same range. In addition, significant stable hydrogen isotope fractionation was documented in experiments with pure and enrichment cultures. Carbon isotope fractionation upon aerobic TBA degradation, which is proposed to proceed via intermediate formation of 2-hydroxy-isobutyrate (HIBA), was twice as large as upon MTBE degradation. Carbon isotope fractionation in microcosm experiments under anoxic conditions was surprisingly high...which might be useful to detect biodegradation of MTBE and TBA in-situ and in the range frequently determined for anaerobic TBE degradation" (Meckenstock and others, 2004).

Quantification of biodegradation

Scientists set up microcosm studies to simulate field conditions and define rates of isotope fractionation. When toluene and o-xylene were supplied to a column with anoxic, contaminated aquifer material, and using degraded sulfate as the electron acceptor, both compounds showed significant isotope fractionation. Researchers found "The calculated concentrations matched the measured concentrations, which indicates that under steady-state conditions (constant flow and equilibrium between biodegradation and substrate supply) isotope fractionation factors from batch experiments can be used to calculate biodegradation,

based on the initial substrate concentration and the isotope shifts observed" (Meckenstock and others, 2004).

In another study, scientists examined an anoxic aquifer contaminated with tar oil and toluene that degraded by more than 95 percent. "In contrast, indane and indene exhibited constant isotope values along the groundwater flow path although their concentrations also decreased in steep gradients. This is an important indication that the passage through the aquifer matrix and the interaction with the aquifer matrix do not affect the isotope values to a significant extent" (Meckenstock and others, 2004).

Other work with petroleum-contaminated aquifers showed that "contaminant concentrations calculated with stable isotope fractionation analysis generally were very reliable for aromatic hydrocarbons..." (Meckenstock and others, 2004).

Conclusions

Meckenstock and others (2004) conclude that "Qualitative observations of isotope shifts in single compounds along the groundwater flow path can in most cases be taken as a qualitative indicator of biodegradation. Even more promising is the quantification of biodegradation based on laboratory-derived isotope fractionation factors, which is, so far, the only direct method to quantify biodegradation of contaminants in-situ. The quantification of biodegradation is possible for well-investigated compounds with known biodegradation pathways: currently anaerobic toluene degradation and some BTEX compounds as well as chlorinated ethenes."

It is possible that stable isotope fraction analysis, SIFA, may become routine for future risk assessments. "The research on stable isotope fractionation should be extended to more environmentally relevant compounds, and the underlying principles of stable isotope

fractionation during contaminant degradation need to be further investigated. The goal should be to establish a reliable database to judge whether biodegradation of certain contaminants can be analyzed with SIFA, and if or under what circumstances the evaluation could be performed qualitatively or even quantitatively" (Meckenstock and others, 2004).

Meckenstock contends that major research needs still exist, as "the method is still restricted to rather high analyte concentrations."

Reference

Meckenstock, R.U., Morasch, B., Griebler, C. and H.H. Richnow, "Stable Isotope Fractionation Analysis as a Tool to Monitor Biodegradation in Contaminated Aquifers," *Journal of Contaminant Hydrology*, Vol. 75, 2004; <http://www.elsevier.com/locate/jconhyd>

UTTU thanks Dr. Meckenstock, rainer.meckenstock@gsf.de, for his help on this article.



Using ¹⁴C analysis to determine carbon sources

Scientists wanted to determine if a microbial community in a salt marsh was degrading petroleum residues from a 1969 oil spill, or if the microbes preferred consuming the natural organic materials. To accomplish this, they examined ¹⁴C concentrations. They specifically examined ¹⁴C from microbial phospholipid fatty acids (PLFA) and δ¹³C content and distribution to determine what carbon sources the microbial community was "actively respiring" (using). They sought to "exploit the large disparity in the ¹⁴C content of petroleum (¹⁴C-free) and of natural organic matter in salt marsh sediments (modern or near-modern ¹⁴C content) to constrain the carbon source of microbes currently active at a petroleum-contaminated site" (Slater and others, 2005).

Researchers had two goals:

- to establish compound-specific ¹⁴C as an investigative tool for contaminants
- to apply this approach to petroleum-contaminated salt marsh sediments from Wild Harbor, Massachusetts, where oil was spilled in 1969

Most hydrocarbons do not contain ¹⁴C, and thus, scientists can use the radiocarbon as a natural inverse tracer of contaminant carbon in the environment. ¹⁴C analysis of individual microbial phospholipid fatty acids (PLFA) can characterize carbon sources used by microbes in salt marsh sediments.

According to Slater and others (2005), "Measurements of concentration changes in products or reactants are further complicated by concurrent degradative and nondegradative processes of mass loss (i.e. sorption). Although culturing of organisms can provide insights into the identity and metabolic capabilities of organisms at a site, differences in conditions between laboratory cultures and environmental systems introduce large uncertainties concerning the relevance of this information to the field. Addition of tracers can identify in-situ processes occurring at a site but often require long times for a resolvable signal and in some cases have been shown to behave differently to native contaminants" (Slater and others, 2005).

Why use ¹⁴C ?

Most of the fossil-fuel-based contaminants, because of their age, lack ¹⁴C; thus, ¹⁴C can be used as an inverse tracer of contaminant carbon. When microbes begin to biodegrade a fossil fuel such as petroleum, ¹⁴C concentration of the microbial components will decrease relative to other microbes that utilize only natural organic matter, and that contain ¹⁴C. Scientists analyze the phospholipid fatty acids (PLFA) of microbes because they are an integral part of cell membranes

and "are labile and hydrolyze within weeks after cell death. Consequently, they are ideal for study of carbon sources of active microbial populations. The isotopic composition of in-situ microbial PLFA can thus reveal a near-instantaneous snapshot of the carbon source of the active microbial community at a site" (Slater and others, 2005).

Identification of fractions in marsh sediments

The first part of this analysis involved an inventory of existing petroleum hydrocarbons using comprehensive two-dimensional gas chromatography (GC x GC). They found the marsh site environment to be basically anaerobic. In addition:

- n-alkanes were completely degraded
- all other compounds usually found in No. 2 fuel oil had not degraded

Other studies (Reddy and others in Slater and others, 2005) did find degradation of No. 2 fuel oil compounds, and Slater and others (2005) sought to address this discrepancy by a more detailed analysis of the marsh site sediments.

Scientists obtained a 30- by 30-cm core from the intertidal marsh and sectioned it at 2-cm intervals. They discarded the outer section to avoid using sediments that may have been potentially cross-contaminated. They followed standard extraction procedures. To identify the various fractions, scientists used the following:

- a flame ionization detector to quantify TPH
- a gas chromatograph to identify and quantify microbial PLFA
- a gas chromatography-isotope ratio mass spectrometry (GC-IRMS) system to analyze the PLFA for compound-specific carbon isotope

- a gas chromatograph for concentrated solutions of PLFA, from which carbon dioxide was obtained and purified; "about 10 percent of the carbon dioxide was reserved for $\delta^{13}\text{C}$ analysis by isotope ratio mass spectrometry" (Slater and others, 2005).

Scientists found a peak TPH concentration of 4.5 mg/g dry weight. They also determined mole percentage of microbial PLFA in sediments for depths from 0 to 20 cm at 2-cm intervals. They found "no significant observable relationship between PLFA distribution and TPH concentration" (Slater and others, 2005). They did find, however, a change in PLFA carbon chemistry that indicated a transition to anaerobic conditions at deeper levels.

^{14}C measurements

Scientists selected the samples for ^{14}C analysis "that made up a majority of the microbial PLFA and were thus present in sufficient quantity for collection and analysis... Radiocarbon analysis of microbial PLFA was performed on the 0-2-, 2-4- and 4-6-cm horizons, below which decreasing PLFA concentrations necessitated combining of sections, and analysis was only possible for the 8-12-, 12-16- and 16-20-cm intervals. The PLFA collected for ^{14}C analysis represented > 75 percent of the PLFA mass for all samples and > 80 percent of all but one of the samples."

"The results from compound-specific radiocarbon analysis of the microbial PLFA are compared with the in-situ $\Delta^{14}\text{C}$ of the total organic carbon (TOC) and solvent extracted sediment residues (EXT-RES) from White and others, 2005 (in Slater and others, 2005). EXT-RES reflects the ^{14}C content of the residual organic carbon remaining in the sediments after removal of petroleum hydrocarbons since White and others (2005) determined that the TPH were completely removed during the solvent extraction. We therefore interpret EXT-RES $\Delta^{14}\text{C}$ values as indicative of the naturally occurring

organic matter at this site. In contrast, TOC values represent the $\Delta^{14}\text{C}$ of both the natural organic carbon and petroleum hydrocarbons" (Slater and others, 2005).

The TOC and EXT-RES data show an increasing trend of $\Delta^{14}\text{C}$ with depth; $\Delta^{14}\text{C}$ is a record of the changes of ^{14}C of atmospheric CO_2 , and this is associated with thermonuclear weapons testing in the 1950s and 1960s. The contaminated zone shows an offset between extracted and unextracted samples because of a contribution of radiocarbon-free TPH to the latter samples. Microbial PLFA ^{14}C should be depleted if the microbial community is using petroleum as a carbon source. Indeed, microbial PLFA $\Delta^{14}\text{C}$ values "are similar to all samples at each depth interval, indicating a consistent carbon source for the members of the microbial community" (Slater and others, 2005).

Conclusions

For this site, scientists concluded

- the microbial communities "are not significantly metabolizing petroleum hydrocarbon residues...but instead are using the naturally occurring organic matter as a carbon source" because of their availability and energetic favorability"
- using PLFA $\Delta^{14}\text{C}$ gives greater resolution of C usages than does using $\delta^{13}\text{C}$
- "the use of $\delta^{13}\text{C}$ values is further complicated by uncertain and potentially variable isotopic fractionations associated with biosynthetic production of PLFA from carbon substrates"
- caution is advisable when interpreting $\delta^{13}\text{C}$ values to determine microbial carbon sources
- the coherence of $\Delta^{14}\text{C}$ and $\delta^{13}\text{C}$ values of PLFA at a given depth indicates that "the entire microbial community...is using a similar carbon source"

- the form of the microbial carbon source is likely “incorporation of carbon...via initial metabolism of organic compounds to either dissolved inorganic carbon or acetate”
- the TPH, “which make up a maximum of about 9 percent of the TOC...are less polar than most of the natural organic matter, rendering them more strongly sorbed to matrix material and potentially less bioavailable for the microbial community”
- an abundant and more easily accessible carbon source—the carbon from organic matter at this site—“may remove any pressure for microbes to utilize a niche carbon source such as petroleum contaminants”
- if the natural carbon supply at the site could be limited, then microbes might metabolize the petroleum hydrocarbons

Scientists also explored the possibility that electron acceptors, such as sulfate, were limited and might be responsible for limited petroleum degradation; however, sulfate reducers were found throughout the core.

Slater and others (2005) conclude that “the presence of microbes capable of carrying out metabolism of a contaminant may not be sufficient to ensure that degradation takes place... [Furthermore] the presence of naturally occurring organic carbon may result in differences in the order and rates of degradation of components of a petroleum mixture as has been defined in laboratory studies. In cases where there is more than one potential carbon source, the pattern of degradation of an oil spill may differ from a situation where only petroleum carbon is present. Therefore interpreting the extent of petroleum degradation may require consideration of the other organic material present... Compound-specific ¹⁴C analysis of microbial

PLFA has unequivocally shown that no significant metabolism of the residual petroleum hydrocarbons is presently occurring in Wild Harbor salt marsh sediments. In the absence of future changes in the local geochemical conditions at the site, we speculate that hydrocarbon contamination at this site will not be subject to significant further degradation, leading to its persistence in the sediments indefinitely.”

Reference

Slater, G.F., White, H.K., Eglinton, T.I. and C.M. Reddy, “Determination of Microbial Carbon Sources in Petroleum-Contaminated Sediments Using Molecular ¹⁴C Analysis,” *Environmental Science & Technology*, Vol. 39, No. 8, 2005; <http://pubs.acs.org/journals/esthag>

See also “Isotopic Constraints on the Fate of Petroleum Residues Sequestered in Salt Marsh Sediments,” White, H.K., Reddy, C.M. and T.I. Eglinton, *Environmental Science & Technology*, Vol. 39, No. 8; 2005; <http://pubs.acs.org/journals/esthag>

UTTU thanks Dr. Helen White, hwhite@whoi.edu, for her help on this article.



Effect of benzene on bacterial diversity and structure

Fahy and others (2005) spent two years collecting and analyzing clean and benzene-contaminated groundwater samples in an effort to define how benzene affects an indigenous microbial community at an operational petrochemical manufacturing plant.

Site characteristics

The petrochemical manufacturing site, known as SIReN (Site for Innovative Research in Natural Attenuation), is located in the United Kingdom. Characteristics of this well-known site include

- an area of 180 acres
- a major sandstone aquifer
- shallow (2.8 to 8.5 m) groundwater flow
- deep (below 8.5 m) groundwater
- a major contaminant, styrene
- other contaminants including BTEX
- two benzene plumes
- 76 monitoring wells at more than 26 locations
 - BTEX was detected in 37 wells
 - concentrations declined in 25 wells
 - 4 wells showed an increase in BTEX
 - 8 wells showed no trend

Researchers collected groundwater samples for two years from both clean and contaminated areas. They then “compared bacterial communities from groundwaters with the highest BTEX contamination on the site ($> 1.8 \times 10^4 \mu\text{g/l}$) with communities from clean groundwater ($\leq 2 \mu\text{g/l}$) or with a low level of contamination ($7\text{-}14 \mu\text{g/l}$). Benzene was the predominant component of total BTEX in the wells with a high level of contamination” (Fahy and others, 2005). In all, they analyzed samples from 12 wells at seven locations. Sampling procedures are described in more detail in the text.

Data analyses and results

Researchers used terminal restriction fragment length polymorphism (T-RFLP) profiles (from 16S rDNA), which gives a “visual representation of the diversity and evenness of each community” (Fahy and others, 2005). They found that “The bacterial community in Ti [one of the wells investigated], a clean well, was diverse... In contrast, the bacterial community in a well with high contamination, Pi, was dominated by few groups of organisms...”

Researchers assert that “the presence of benzene exerted a large influence on the community composition and structure. To investigate the main factors affecting bacterial community structures, a principal component analysis (PCA) of the geochemical characteristics of the groundwater was carried out, followed by a canonical correspondence analysis (CCA) combining this geochemical data with the bacterial community profiles.” The factors measured for the PCA included

- dissolved oxygen
- methane
- carbon dioxide
- pH
- alkalinity
- suspended solids
- total organic carbon
- benzene
- chloride
- calcium
- magnesium
- sodium
- potassium
- aluminum
- sulfate
- nitrate
- dissolved iron
- dissolved manganese

For the CCA, researchers examined benzene and factors related to anoxic conditions, such as oxygen, carbon dioxide, methane, sulfate, nitrate, dissolved iron and manganese.

The CCA can distinguish between direct and secondary effects of benzene on community structure by “subtracting the impact of benzene from the parameters relating to anoxic conditions, namely oxygen, carbon dioxide, methane, sulfate, nitrate, dissolved iron and manganese... The partial CCAs reveal that these eight parameters accounted for 77 percent of the total variance, of which 7.7 percent are attributed to benzene and 60.3 percent to the anoxia-related parameters” (Fahy and others, 2005).

Researchers used the results from the PCA and CCA to link the communities to the groundwater’s geochemistry.

When benzene biodegrades, it depletes oxygen. “This in turn results in a succession of microorganisms able to degrade benzene microaerophilically, or with different terminal electron acceptors, such as nitrate, manganese-IV, iron-III or sulfate, or by methanogenesis. Generally, each of these processes is carried out by a different group of organisms, and the extent to which each of these processes occurs depends on the stage of the succession and environmental conditions. The partial CCAs show that anoxia is the main factor determining the structure of bacterial communities of the wells sampled here, accounting for 60.3 percent of the 77 percent variability explained by both anoxic parameters and benzene concentration.”

From these analyses, researchers determined that

- benzene was the single variable accounting for most of the variance (16 percent)
- 14 percent of the variance was due to aluminum, total organic carbon, oxygen, pH, methane and alkalinity

The multivariate analysis carried out indicated

- salinity and a high pH had an impact on certain wells
- aluminum concentration accounted for 14 percent of the variability of community structure (Al^{3+} can be toxic in acidic environments)
- well waters were not vertically mixed
- benzene reduced bacterial diversity; benzene metabolism changes redox potential

Conclusions

Researchers found that bacterial diversity in contaminated wells was half of that in clean wells. This is significant because “A species-poor environment is less well-equipped to respond to future impacts...”

Organic pollution has been shown to reduce diversity of microbial communities.

Benzene may lower diversity because

- benzene affects cell membrane integrity
- benzene can inhibit growth if its concentrations are between 80 and 150 mg/kg
- a breakdown product of benzene, catechol, may be more toxic than benzene
- benzene and its metabolites are carbon and energy sources for some microorganisms, so when present in high concentrations, “benzene degraders will out-compete other microorganisms for available resources, thereby reducing species richness” (Fahy and others, 2005)

Benzene clearly drives the microbial community structure. Although the microbial community structure was only moderately influenced by the toxic and stressful effects of benzene, the change in redox potential reduction brought about by benzene actions clearly lowered microbial community diversity.

Reference

Fahy, A., Lethbridge, G., Earle, R., Ball, A.S., Timmis, K.N. and T.J. McGenity, “Effects of Long-Term Benzene Pollution on Bacterial Diversity and Community Structure in Groundwater,” *Environmental Microbiology*, Vol. 7, No. 8, 2005; <http://www.blackwellpublishing.com>.

UTTU thanks Dr. Fahy, afahy@essex.ac.uk, for her help on this article.



Biosolid, carbon supplementation and MNA comparison

To better define the factors that control MNA (monitored natural attenuation) in biosolid- and fertilizer-amended soils, scientists set up an experiment to examine microbial populations and nutrient concentrations. Scientists sought to determine if biosolid addition could enhance "hydrocarbon bioremediation by promoting biostimulation in a diesel-contaminated, carbon-poor soil" (Sarkar and others, 2005). Ultimately scientists compared these two (biosolid- and fertilizer-amended) biostimulation methods with MNA.

Bioremediation can be defined as "the use of living organisms to remove environmental pollutants from soil, water and gases" (Sarkar and others, 2005). Bioremediation of petroleum contaminants—ideally, microbes degrade petroleum to carbon dioxide and water—became a more common remedial technique after the Exxon Valdez oil spill in 1989. The biochemical processes of microorganisms, under aerobic or anaerobic conditions, metabolize organic compounds. There are two types of bioremedial processes:

- bioaugmentation
- biostimulation

Bioaugmentation involves introducing microorganisms cultured to degrade specific hydrocarbon chains. The microorganism source can be from the contaminated soil or a stock of proven contaminant-degrading microbes.

Biostimulation "introduces additional nutrients in the form of organic and/or inorganic fertilizers into a contaminated system," and this increases the microorganism indigenous population or microbial biomass" (Sarkar and others, 2005). Because two

food sources are available, however, the indigenous microorganisms may choose not to degrade hydrocarbons.

Biostimulation and biosolids

Traditionally, nutrients added for the purposes of biostimulation have focused on N (nitrogen) and P (phosphorus). "Because C (carbon) is a major constituent of petroleum fuels, its traditional role in bioremediation research has typically been as an index to determine the amount of N and P that need to be added to reach the optimal C:N:P ratio. More recently, the role of C supplementation in hydrocarbon biodegradation has been investigated with the use of glucose, biosolids and composts... However, these experiments did not isolate C as a nutrient supplement but measured the effects of a combination of nutrients from various sources, C being one of them. Moreover, the role of C supplementation in hydrocarbon bioremediation in low-organic-matter or otherwise C-poor soils has never been investigated" (Sarkar and others, 2005).

Nutrient sources that have been used in the past include

- inorganic fertilizer
- urea
- sawdust
- compost
- manure
- biosolids

Biosolids are solid, semisolid or liquid residues that are generated during treatment of domestic sanitary sewage and that have been deemed acceptable for land application. Biosolids have various C, N and P ratios, but "the nutrient availability for vegetative growth (i.e., bioavailability) in these biosolids (used in the testing here) is mostly inorganic, 90-95 percent, with a small organic percentage, 5-10 percent."

The potential of biosolid use for treatment of petroleum-contaminated soils has not been studied extensively. Advantages of biosolids include

- low or no cost
- slow nutrient release
- easy availability
- minimal environmental impact, due to slow nutrient release

Disadvantages of biosolids include

- difficulty of supplying deeper soil layers with nutrients
- potential for metals contamination

Experimental setup

The soil tested was a Texas Tarpley clay, a 90 percent clay soil. Scientists analyzed the soil for moisture content, pH, nutrient concentration and total C, H, N and P. Diesel was supplied from a typical gas station, while Grade A biosolid pellets were from a sewage treatment plant in Largo, Florida. For this experiment, scientists

- added 500 grams of soil and sterile inorganic fertilizer and biosolids in each of six sterilized, 1.4 liter glass pans
- autoclaved and pulverized the biosolids to accelerate nutrient distribution to microbes
- mixed the biosolids thoroughly at two rates, low (5 percent) and high (10 percent)
- added a high-grade NH_4NO_3 fertilizer in amounts such that N and P contents approximated those of the biosolid-amended systems
- added deionized water to achieve a 60 percent soil moisture content
- added diesel fuel for an initial total petroleum hydrocarbon (TPH) concentration of approximately

4,000 mg/kg that varied between 3,350 and 4,250 mg/kg

- mixed, by hand, soil, fertilizer/biosolids, water and diesel
- covered the pans with punctured plastic wrap to permit gas exchange

After components were mixed, scientists examined the soils during the experiment's eight-week duration. This involved the following:

- establishing baselines for TPH concentration, pH, nutrient concentration and microbial population
- monitoring weekly the pH, TPH and microbial population
- determining microbial populations using 5-tube Most Probable Number
- determining TPH concentration using a gas chromatograph
- measuring bioavailable P five times
- adjusting soil moisture content

Soil, biosolid and fertilizer comparison

The native soil used in this experiment was characterized by

- a neutral pH
- low concentrations of C and N and total bioavailable P

In contrast to the soil, biosolids generally have a greater concentration of total and bioavailable nutrients.

The inorganic fertilizer

- was highly acidic, pH ~ 3
- contained the greatest concentration of N, total and bioavailable P
- did not contain any C

Results

During the first week, TPH, in MNA and biosolid treatment, was reduced as follows:

- 84.4 percent for MNA (indicating native microbes were capable of degrading hydrocarbons)
- 91.0 percent for low-rate biosolids treatment
- 90.4 percent for high-rate biosolids treatment

By week four, TPH was reduced as follows:

- 89.7 percent for MNA
- 91.9 percent for low-rate biosolids
- 90.9 percent for high-rate biosolids

By week eight (end of the experiment), TPH was reduced as follows:

- 93.8 percent for MNA
- 96.2 percent for low-rate biosolids
- 96.2 percent for high-rate biosolids

Chromatographic analysis of the diesel-contaminated soils indicated that the heavier carbon compounds did not volatilize or biodegrade.

In fertilizer-amended soils, 65.5 to 76.3 percent of TPH degraded during week 1.

By week 4, TPH removal rates were as follows:

- 92.3 percent by MNA
- 91.5 percent in low-rate fertilizer
- 93.8 percent in high-rate fertilizer

By week 8 (experiment end), TPH removal rates were

- 94.5 percent by MNA
- 95.5 percent by low-rate fertilizer
- 96.8 percent by high-rate fertilizer

Reaction rates and TPH degradation

In terms of reaction rates, "...TPH degradation in the MNA soils was described by the lowest reaction rate constants; the biosolids (both rated) and high-rate

fertilizer-amended soils had the fastest reaction rates. Rate constants of the low-rate fertilizer-amended soil were intermediate" (Sarkar and others, 2005).

The Tarpley clay soil had a high microbial population that was immediately stimulated (by 12,430 and 11,384 percent for low- and high-rate biosolids soils, respectively) when amended. These population increases corresponded to TPH decreases. Scientists attribute increases in microbial population to readily bioavailable P, N and C. MNA soils had a 57 percent increase in microbial population, and that corresponded with a TPH decrease.

The microbial population in the fertilizer-amended soils "remained relatively invariable throughout the experimental period." Researchers attribute the differences in microbe population between the biosolid- and fertilizer-amended soils to two possible factors:

- "carbon supplementation by biosolids that stimulated microbial growth"
- "the potential toxic effect of fertilizer-induced acidity (pH of the fertilizer mix was about 3)"

Studies have confirmed that N and P are the nutrients necessary for cellular production; if limited, they can hinder petroleum hydrocarbon degradation. The optimal C:N:P ratio for hydrocarbon biodegradation is 100:15:3 (33:5:1), and this assumes nutrients are bioavailable. From this study, and others, researchers found

- MNA soils had less C, N and P than biosolid-amended soils
- biosolid- and fertilizer-amended soils had similar N and P concentrations
- excess N can cause ammonia toxicity; coupled with a low pH, excess N can impact negatively on TPH degradation and cause a toxic effect on the microbial population

In addition, studies showed that the pH concentrations of MNA and biosolid-amended soils were within or near the optimum pH range, 6.5 to 8.5, for hydrocarbon degradation. The pH of the fertilizer-amended soils was around 3.

Conclusions

Sarkar and others (2005) concluded the following:

- biosolid addition enhanced petroleum hydrocarbon degradation
- after 8 weeks, biosolid- and fertilizer-amended soils degraded more than 96 percent of the original TPH whereas the MNA (control soils) degraded only 94 percent
- “the large increase in microbial population in the biosolids-amended soils suggests that carbon supplementation may enhance degradation of petroleum hydrocarbons in low-organic-matter or otherwise C-poor soils”
- “TPH degradation rate and the amount of TPH degraded in the high-rate fertilizer-treated soils, when compared to those in the low-rate fertilizer-treated soil, indicate that certain levels of N and P supplementation may be capable of stimulating hydrocarbon degradation similar to that provided by sources that contribute C to the system”
- a small difference existed in TPH degradation between MNA and biosolid- and fertilizer-amended soils
- some soils will be poor candidates and others will be excellent candidates for MNA

Reference

Sarkar, D., Ferguson, M., Datta, R. and S. Birnbaum, “Bioremediation of Petroleum Hydrocarbons in Contaminated Soils: Comparison of Biosolids Addition,

Carbon Supplementation and Monitored Natural Attenuation,” *Environmental Pollution*, Vol. 136, 2005; <http://elsevier.com/locate/envpol>



Impacts of TBA on groundwater from small releases of ethanol-blended gasoline at UST sites

By Matthew A. Lahvis

With the acceptance of ethanol (EtOH) as the replacement for methyl tert-butyl alcohol (MTBE) in reformulated gasoline, concern exists regarding whether small releases of EtOH-blended gasoline pose risks to groundwater at underground storage tank (UST) sites. Recent modeling (Lahvis, 2003) and field studies (Dakhel and others, 2003) have shown that EtOH and benzene concentrations in groundwater will be insignificant ($< 10 \mu\text{g/l}$) unless one or more of the following conditions exists:

- the source is located in close proximity ($< 0.5 \text{ m}$) to the water table
- groundwater infiltration is significant ($> 100 \text{ cm/yr}$)
- biodegradation is limited

EtOH and benzene may not be the only constituents of environmental concern in EtOH-blended gasoline, however. The fuel oxygenate tert-butyl alcohol (TBA), for example, may also be present in EtOH-blended gasoline as a result of processes used to manufacture EtOH for use in motor fuel. Further, TBA could be produced in the vadose zone through the biotransformation of MTBE if present as an impurity in EtOH-blended gasoline.

The aim of this study was to predict maximum TBA concentrations that could occur in groundwater associated with a small release of EtOH-blended gasoline in the vadose zone. Conservative source and

transport assumptions were applied. The approach used is similar to that applied in previous modeling studies of Lahvis and Rehmann (2000) and Lahvis (2003) to assess potential impacts on groundwater from small releases of methyl tert-butyl ether (MTBE)- and EtOH-blended gasoline, respectively. This work has been previously published as an API Technical Research Bulletin (see Lahvis, 2005).

TBA's association with EtOH-blended gasoline

TBA may be present in EtOH-blended gasoline as a result of processes used to manufacture EtOH for use in motor fuel. TBA may be added directly to pure-grade EtOH as a denaturant (Liner, 2000), or it could be present in pure-grade EtOH as a byproduct of alcohol fermentation (Tibelius, 1996). TBA may also be associated with EtOH-blended gasoline as an impurity. According to current regulations, EtOH-blended gasoline may contain small amounts (up to 0.3 percent by volume) of MTBE (California Environmental Protection Agency, 2003), which could potentially biodegrade to TBA in the vadose zone. Prior to July 2004, the allowable fraction in reformulated gasoline (RFG) sold or distributed in California was 0.6 percent by volume. In December 2005, the allowable fraction will be 0.15 percent by volume MTBE. These percentages are well below the 11 percent by volume MTBE that RFG contained prior to the 2003 phase-out.

A small release

Small releases of gasoline, either liquid or vapor, may result from routine fueling operations, equipment repair, or leaky joints/connections in UST systems. The magnitude (volume and rate), type (liquid or vapor), and occurrence of small releases are poorly understood. To date, the only investigation undertaken to address these issues was a tracer study of recently

upgraded UST systems in California. The study found detectable levels of tracer in 61 percent of the 182 systems tested, and all but one release was believed to be vapor-related (Young and Golding, 2002). Nearly all of the releases were estimated to occur at rates < 0.04 gal/d (liquid equivalent), with a maximum rate of 0.4 gal/d (liquid equivalent); rates were well below the current liquid leak detection threshold of 2.4 gal/d (0.1 gal/h). Rate estimates, along with the actual type and frequency of occurrence, remain in doubt, however, because of order of magnitude uncertainty in mass-balance calculations and lack of field validation of compounding sources.

In the case of small liquid releases, the volume is not of sufficient magnitude for the liquid product to directly contact groundwater. Rather, individual constituents of the liquid product migrate to groundwater by diffusion and advection. Resulting effects on groundwater are a function of the magnitude of released product, its composition, the physicochemical properties of the constituents that compose the product, and the prevailing hydrogeologic conditions of the vadose zone into which the product is released.

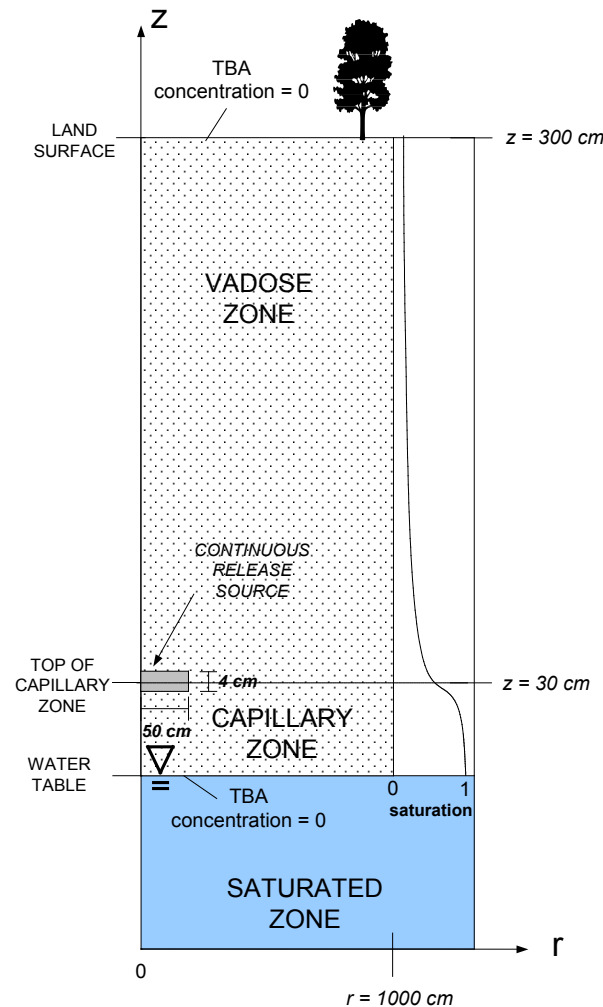


Figure 1. Model geometry and boundary conditions for simulation of a continuous small release of EtOH-blended fuel in the vadose zone.

Approach used in this study

TBA transport in the vadose zone was simulated using the computer code R-UNSAT, developed and documented by the U.S. Geological Survey (Lahvis and Baehr, 1997). The transport model accounts for diffusion, groundwater infiltration, adsorption and biodegradation processes, variable soil-moisture content and equilibrium partitioning among the solid, aqueous and gaseous phases. Gaseous-phase advection was not simulated because this process is assumed to be negligible for compounds, such as TBA, which strongly partition to the aqueous phase.

The model was applied to simulate two-dimensional (axisymmetric) steady-state transport in a variably saturated vadose zone, assuming variable (hydrostatic) moisture condition based on soil properties defined by van Genuchten (1980). Figure 1 illustrates the model geometry and boundary conditions.

Very conservative transport assumptions were applied to determine an upper-bound concentration of TBA in groundwater. In particular, the model scenario involved:

- a small-release rate of 120 gal/d (0.04 gal/d liquid gasoline equivalent); this is representative of the upper-bound rate for the vast majority of small releases occurring at UST sites (Young and Golding, 2002)
- a source consisting of 10 percent EtOH and 0.6 percent MTBE
- complete and instantaneous transformation of the MTBE to TBA by microbial degradation, resulting in a constant source concentration of 0.6 percent TBA
- no biodegradation of TBA in the vadose zone
- a sand vadose zone
- a continuous release source located just above (30 cm) the water table, representative of the top of the capillary zone

- a zero concentration boundary at the water boundary table
- a groundwater infiltration rate of 20 cm/yr

It is important to note that complete transformation of MTBE to TBA without subsequent biodegradation of TBA in the vadose zone is likely to be extremely conservative given the relatively short residence time (hours to days) for transport of MTBE to groundwater in sandy soils (Lahvis, 2000) and the potential for TBA to be biodegraded under aerobic conditions, which are predicted to exist at small-release sites where sandy soils are present (Lahvis, 2005).

Transport modeling provides estimates of the mass flux (or mass-loading rate) of TBA to groundwater. In the absence of biodegradation, the mass-loading rate to groundwater is proportional to rates of groundwater infiltration and diffusion across the water table (which, in turn, is proportional to the concentration gradient across the water table.) The concentration at the water table is directly proportional to the rate at which TBA enters groundwater (i.e., the mass-loading rate) and the rate at which TBA migrates laterally from the source area in groundwater. The water table concentration can be related to a groundwater concentration by assuming a dilution attenuation factor that accounts for mixing and dispersion in the saturated zone (Environmental Protection Agency, 1996).

Results

The steady-state distribution of TBA resulting from a small release of EtOH-blended gasoline occurring 30 cm above the water table is illustrated in Figure 2. Because there is no mass loss of TBA to the atmosphere or as a result of biodegradation in the vadose zone, the mass-loading rate of TBA to groundwater (0.71 gal/d) is equivalent to the release rate from the source and source concentration. TBA concentrations at the water table in the source zone corresponding to this mass-loading rate range from approximately 10 to 1,000 ppb, depending on the assumed rate of groundwater flow (Figure 3). Actual TBA concentrations observed in monitoring wells screened across the water table are likely to be substantially less than these values, depending on the amount of dilution attenuation in groundwater. For example, mixing in groundwater would increase dilution attenuation by more than an order of magnitude assuming reasonable approximations of source size (50 ft), groundwater flow (0.1 ft/d), and dissolved plume thickness (10 ft). Given that concentrations of TBA in groundwater will be approximately proportional to the source concentration, resultant concentrations of TBA in groundwater from an EtOH source containing 0.3 percent MTBE by volume will be roughly 50 percent of the concentrations depicted in Figure 3. These concentrations are not likely to be observed at most field sites, however, given the incorporation of particularly conservative modeling assumptions used to define the upper bound on small releases.

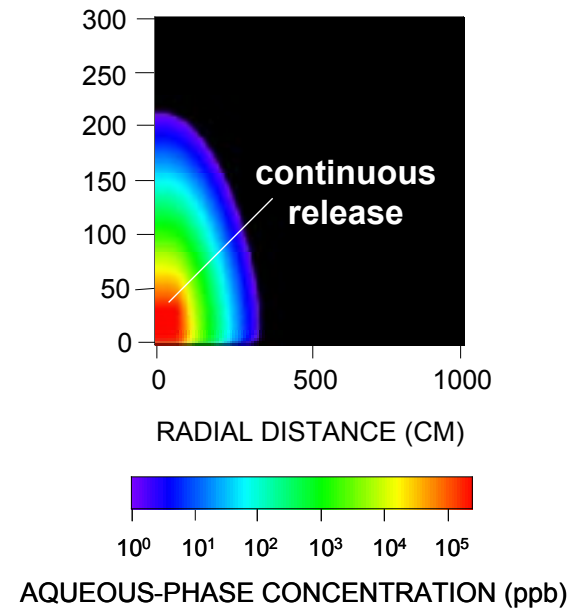


Figure 2. Steady-state distribution of TBA in sand, assuming an infiltration rate of 20 cm/yr and no biodegradation.

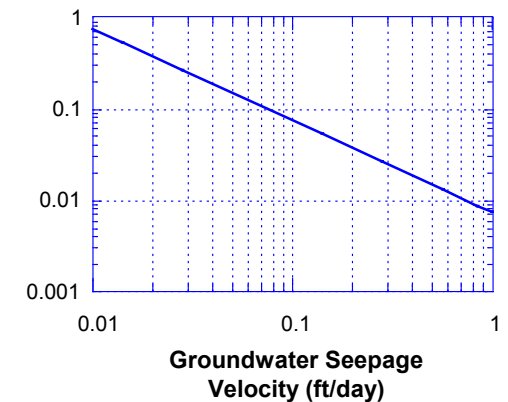


Figure 3. Dissolved phase concentrations of TBA in the source zone at the water table as a function of groundwater seepage velocity.

Potential impacts to supply wells can be simply determined from mass-discharge principles, assuming that the concentration in the supply well is proportional to the rate at which TBA enters groundwater (the mass-loading rate) and the rate at which it is extracted via pumping (Newell et al., 2002). This proportionality is only possible if the supply well completely captures the TBA plume, flow in the well is constant (rate and direction) and steady state, and no mass loss occurs between the source and the well—conditions not likely to be met at most field sites. Nevertheless, on the basis of this calculation, dissolved-phase concentrations of TBA are predicted to be below levels of detection (approximately 5 µg/l) in the vast majority of domestic or public supply wells, assuming the TBA mass-loading rate predicted by transport modeling (0.71 gal/d) and a well discharge occurring at rates > 25 gal/min.

Key parameters affecting TBA transport to groundwater

TBA partitions strongly to the aqueous phase as reflected by its extremely low Henry's constant (0.00048). Aqueous-phase transport processes (i.e., aqueous-phase diffusion and aqueous-phase advection caused by infiltrating recharge water) will thus govern TBA transport in the vadose zone. Because aqueous-phase transport processes (diffusion in particular) are also relative to vapor-phase transport processes, TBA transport to groundwater will be slow relative to benzene, toluene, ethylbenzene and xylenes (BTEX) and other more volatile gasoline constituents that favor transport in the vapor phase, especially when groundwater infiltration is limited. Further, because aqueous-phase diffusion is slow relative to aqueous-phase advection, small differences in the groundwater infiltration rate could cause significant differences in both concentrations of TBA in groundwater and travel times of TBA to groundwater (especially for sources

located well above the water table.) TBA transport to groundwater may also be sensitive to aerobic biodegradation in the vadose zone (Bradley and others, 2002) although this pathway was not evaluated in this investigation. In summary, the key processes to consider in evaluating potential TBA impacts on groundwater are depth to groundwater, groundwater infiltration and biodegradation.

Conclusions

Upper bound concentrations of TBA at the water table in the source zone predicted by transport modeling ranged from approximately 10 to 1,000 ppb for reasonable approximations of groundwater flow. Actual concentrations of TBA observed in monitoring wells are likely to be substantially less than these values due to dilution attenuation in the saturated zone. Further, the assumptions used to define the amount of TBA produced from a small release were particularly conservative. TBA concentrations observed in domestic or public supply wells are expected to be below levels of detection, unless the wells are located immediately adjacent to and directly downgradient from the source zone.

Reference

- Lahvis, M.A., "Maximum Potential Impacts of Tertiary Butyl Alcohol (TBA) on Groundwater from Small-Volume Releases of Ethanol-Blended Gasoline in the Vadose Zone," *American Petroleum Institute*, No. 22, January 2005; <http://www.api.org/bulletins>. Other references cited in the UTTU article are found in this paper.
- Lahvis, M.A., "Simulation of Small Releases of Oxygenated Gasoline," *17th Annual National Tanks Conference*, Seattle, Washington, March 14-16, 2005.

UTTU thanks Matthew Lahvis, matthew.lahvis@shell.com and Harley Hopkins, Hopkins@api.org, for their help on this article.



Vapor transport of oxygenated gasoline to indoor air associated with small releases at UST sites

By Matthew Lahvis

Data from field sites and a recent tracer investigation (Young and Golding, 2002) indicate that small gasoline releases are currently more common than large-scale releases at LUST sites. Potential risks to human health and the environment posed by these releases need to be fully examined. Previous modeling (Lahvis and Rehmann, 2000; Lahvis, 2003) and field studies (Dakhel and others, 2003) focused on potential impacts to groundwater posed by MTBE, ethanol, and benzene. Potential risks associated with the vapor transport to indoor air pathways, however, have never been evaluated.

The purpose of this study is to assess potential human exposure to vapor intrusion from a small release of oxygenated gasoline in the vadose zone. The potential for exposure was defined by model calibration as the lateral offset distance at which benzene concentrations exceed a 10^{-6} risk-based screening level of 3.1 µg/m³ for shallow soil gas, assuming a slab attenuation factor of 0.1 (Environmental Protection Agency, 2002). Mass flux to indoor air is therefore not factored into the exposure assessment. This work has been previously published as an API Technical Research Bulletin (see Lahvis, 2005).

What constitutes a small gasoline release?

Small releases of gasoline may be liquid or vapor and

occur as a result of:

- routine fueling operations
- equipment repair
- leaky joints and connections

In the case of a small liquid release, the volume of product released is not sufficient for the product to contact groundwater. Contamination of groundwater occurs by migration of individual gasoline constituents to groundwater by processes such as diffusion and advection. The potential for groundwater to be contaminated will be a function of:

- the magnitude (volume and rate) of product released
- product composition
- the physicochemical properties of the product's constituents
- the hydrogeologic conditions of the vadose zone

The magnitude, type (liquid or vapor), and occurrence of small releases are poorly understood. To date, the only investigation undertaken to address these issues was a tracer study of recently upgraded UST systems in California. The study found detectable levels of tracer in 61 percent of 182 systems tested, and all but one release was believed to be vapor-related (Young and Golding, 2002). Virtually all of the small releases were estimated to occur at rates < 0.04 gal/d (liquid equivalent), with a maximum rate of 0.4 gal/d—rates well below the current liquid leak detection threshold of 2.4 gal/d (0.1 gal/h). Rate estimates, along with the actual type and frequency of occurrence, remain in doubt, however, because of order of magnitude uncertainty in mass-balance calculations and lack of field validation of compounding sources.

What approach was used in this study?

Benzene transport in the vadose zone was simulated using the computer code R-UNSAT, developed and documented by the U.S. Geological Survey (Lahvis and Baehr, 1997). The transport model accounts for diffusion, groundwater infiltration, adsorption, and biodegradation processes, variable soil-moisture content, and equilibrium partitioning among the solid, aqueous, and gaseous phases. As shown in Figure 1, the model was applied to simulate steady-state transport in one (Scenario 1) and two (Scenario 2) dimensions. Scenario 1 represents a case where vapor migration is confined between a capped surface cover (e.g., asphalt pavement) and the water table, both assumed to be impervious to vapor transport. The source is vertically distributed across the entire thickness of the vadose zone. Scenario 2 represents a case where the source is positioned at a finite depth (366 cm) below land surface, commensurate with the default basement mixing height defined in Environmental Protection Agency (2002). The far-lateral and water-table boundaries were established at distances defined from initial model simulations designed to minimize effects on the resultant vapor distribution. For assessing risk, Scenario 1 represents a very conservative case; Scenario 2 represents a more realistic case. Model assumptions for both scenarios include:

- a small release rate of 120 gal/d (0.04 gal/d liquid gasoline equivalent), assumed to be representative of the upper-bound rate for the vast majority of small releases occurring at UST sites (Young and Golding, 2002)
- a gasoline source containing 10 percent by volume EtOH and 1.4 percent by volume benzene, consistent with the composition reported in California Environmental Protection Agency (1988)

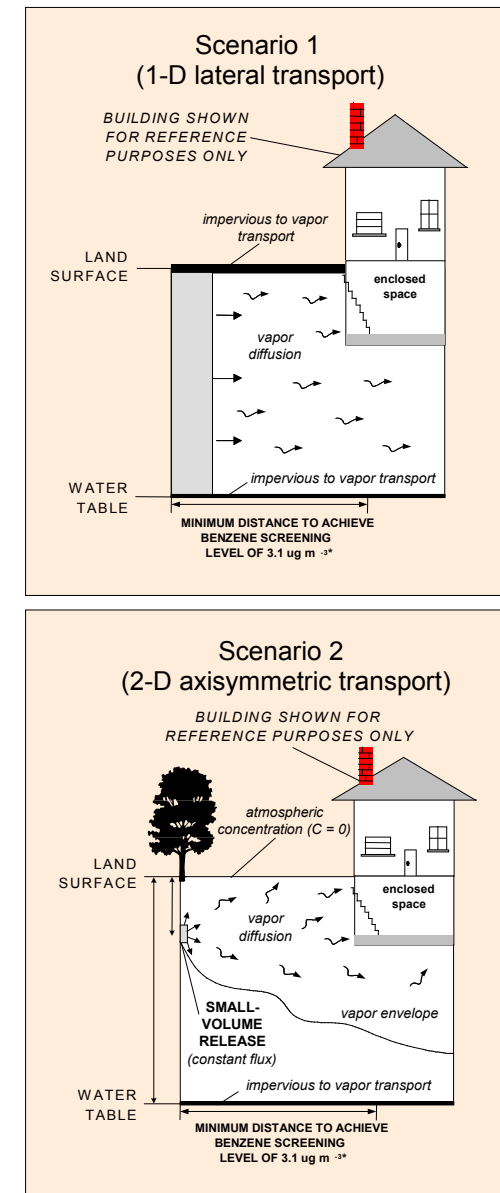


Figure 1. Model geometry and boundary conditions used in model simulations. The buildings shown in Figure 1 are used for reference only and were not part of the model simulation.

- a homogeneous vadose zone consisting of sand at a residual moisture saturation of 0.053 (a default value recommended by the Environmental Protection Agency (2002))
- variable biodegradation rates (half-lives) for benzene ranging from 0.69 - 69,000 days
- no groundwater infiltration

In Scenario 2, the lateral offset distance was defined as the minimum distance necessary to achieve a target concentration for benzene in soil gas of $3.1 \mu\text{g}/\text{m}^3$ at a typical basement depth of 366 cm (Environmental Protection Agency, 2002).

What were the results?

The potential for exposure to vapor intrusion varied depending on the model geometry (i.e. Scenario 1 or Scenario 2) and the biodegradation rate (see Figure 2). Assuming benzene biodegrades at rates greater than 0.05 d (14 d half-life) consistent with aerobic biodegradation, the distance over which there is a potential for exposure to vapor intrusion ranges from approximately 20 ft. (Scenario 2) to 30 ft. (Scenario 1). The latter distance is consistent with off-set distances predicted by Abreu and Johnson (2005) for shallow hydrocarbon sources in sandy soils. Assuming a conservative biodegradation rate of 0.005 d (140 d half-life), consistent with anaerobic biodegradation, the distance increases to approximately 55 ft. (Scenario 2) to 100 ft. (Scenario 1). By comparison, if the benzene biodegradation rate is linked to oxygen (O_2) availability (e.g., dual-Monod kinetics), the lateral distance reduces to less than 10 ft. (see Figure 2) (Lahvis, 2003). Further, this result implies that anaerobic conditions are only likely to occur within 10 ft. of a small release source. Given that residences would typically be located well beyond this distance at UST sites, small releases of oxygenated gasoline (specifically) are not expected to pose a risk for vapor intrusion.

What key parameters affect benzene transport in the vadose zone?

Benzene will tend to migrate in the vadose zone in the gaseous phase rather than the aqueous phase, unless vapor diffusion is severely limited, as can occur in fine-grained soils. Consequently, benzene transport is typically more sensitive to factors that affect vapor diffusion (e.g., soil type), than to factors that affect aqueous-phase transport (e.g., groundwater infiltration). Benzene transport can also be affected by biodegradation and, in turn, O_2 availability. Under conditions where O_2 is readily available, the vapor intrusion pathway will be limited. The potential for vapor transport to indoor air would increase, however, if O_2 becomes depleted by the presence of sinks unrelated to the small release. In summary, the key factors to consider in evaluating the potential risk to vapor

intrusion are distance between the source and receptor, and O_2 availability.

Conclusions

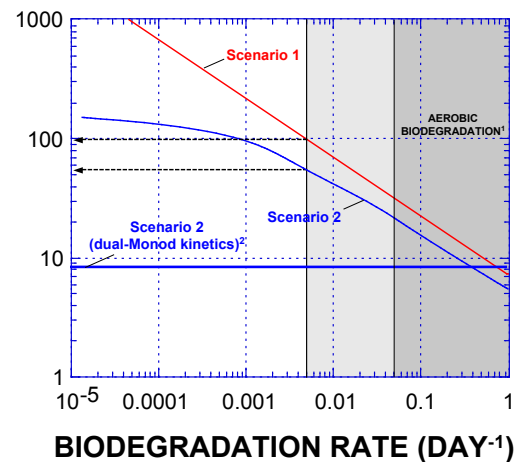
Under anaerobic conditions, benzene is predicted to exceed the risk-based screening level in the vadose zone at distances ranging from approximately 55 ft. to 100 ft. from the source, depending primarily on model geometry. If benzene biodegradation is linked to oxygen availability, the distance over which there is a potential for risk reduces to less than 10 ft. Considering that the distances to nearest receptor will likely exceed model predicted estimates at most UST sites and that anaerobic conditions will be limited in extent in soils conducive to vapor transport, small releases of oxygenated gasoline are not expected to pose a significant risk for vapor intrusion at UST sites

Reference

Lahvis, M.A., "Evaluation of Potential Vapor Transport to Indoor Air Associated with Small-Volume Releases of Oxygenated Gasoline in the Vadose Zone," American Petroleum Institute, No. 21, January 2005; <http://www.api.org/bulletins>

Other references cited in the UTTU article are found in this paper.

UTTU thanks Harley Hopkins, Hopkins@api.org and Matthew Lahvis, matthew.lahvis@shell.com, for their help on this article.



¹ from DeVaul et al. [1997]

² based on results from Lahvis [2003]

Figure 2. Lateral distances needed to meet a soil screening level for benzene in shallow soil gas of $3.1 \mu\text{g}/\text{m}^3$.



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

Part VI, the final chapter of this series, deals with gaining site access to certain UST/LUST sites. One of the most difficult challenges when redeveloping abandoned and contaminated properties can be gaining legal access to the property. Without the owner's permission, a government agency cannot legally enter the site, conduct testing, or remove USTs.

For instance, a city identifies a former gas station site that appears to have USTs in place. The site is vacant or occupied by someone who does not have permission to be there. The owner has not paid taxes in years, but the county has not been able to sell the property. The owner of record has not been located. If the site is contaminated, it may be eligible for California's EAR Account Funding. To test for contamination, however, the city would need to get on site. How does this occur?

Owner's permission

If the owner can be found, he or she may choose to grant access rights. An attorney should draw up an agreement between the owner and the agency to grant the agency the right to enter the property and take specific actions. Owners should be encouraged to seek their own legal counsel if they are able to do so. If the owner is not able to obtain legal representation, the agencies should attempt to design an access agreement that protects the owner's rights as well as the agency's.

Polanco Act

Through a state law, the Polanco Act (California Health and Safety Code 33459-33459.8), a redevelopment agency can get access to a property (in a designated redevelopment area) for which it has a redevelopment

plan. This law provides a procedure by which a redevelopment agency can order responsible parties to perform needed actions such as testing and cleaning up contamination. If the owner, or other responsible party, does not cooperate, the redevelopment agency can test and remediate the property itself or through a contractor, then seek cost recovery and attorney fees through a civil action. The redevelopment agency can also require the responsible parties to provide environmental information that they may possess. These actions can be taken on the property owned by the redevelopment agency or on property owned by others. The cleanup plan must be approved by the applicable state agency, such as the Regional Water Quality Control Board or the Department of Toxic Substances Control. For properties on which the Polanco Act is used, the redevelopment agency and future owners (but not persons responsible for the contamination) receive immunity for liability imposed by the contamination.

The Polanco Act process requires the assistance of an attorney knowledgeable about using this mechanism. The process can require substantial legal assistance; however, the law is a powerful mechanism to bring about remediation and redevelopment of contaminated properties.

California Land Environmental Restoration and Reuse Act of 2001 (CLERRA)

In 2001, the California Legislature passed SB 32, also known as the California Land Environmental Restoration and Reuse Act of 2001. This act established a procedure through which municipal governments can access the same powers granted by the Polanco Act, but for use in geographic areas that are not designated as redevelopment areas. The powers, however, can

only be used on very small vacant sites. Each city or county must pass an ordinance implementing the legislation, then designate an implementing agency, and next define the geographic areas under consideration. The notice and public participation aspects require extensive effort, but in certain circumstances, this law may be an effective way to gain access to some abandoned properties.

Bankruptcy judgment

In an active bankruptcy, creditors try to gain access to the debtor's assets. It may be possible for the bankruptcy judge to grant the city site access to conduct investigations and remediation that would enhance property value so that the property could be sold or transferred to pay off the debtor's debts. An attorney could help sort out bankruptcy issues.

Court order

A governmental agency could, under certain circumstances, get a court order to enter a site to correct a danger to public health, but most abandoned gas station sites do not present a hazard that would warrant obtaining such an order.

Eminent domain

If the agency plans to purchase the property ownership through an eminent domain process, the agency may ask the court to approve property access to assess contaminant level and determine property value. Determining property value is a normal part of such a procedure. Redevelopment agencies, cities or other agencies that acquire property for public use are familiar with this process. In the City of Los Angeles, this is the General Services Department.

Reference

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

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



Research notes

Steranes and triterpanes as a tool for identification of petroleum-type pollutants in alluvial ground waters, Danube alluvial sediments, Yugoslavia

Jovancicevic, B., Polic, P., Mikasinovic, B., Scheeder, G., Teschner, M. and H. Wehner, *Fresenius Environmental Bulletin*, Vol. 10, No. 6, 2001; http://www.psp-parlar.de/feb_auswahl.asp

Scientists evaluated n-alkane fractions in groundwater from the Danube River's alluvial formation. They quantified extracts and determined bulk compositions. "...GC was applied for the analysis of n-alkanes and the isoprenoids pristane and phytane. Since the obtained results, as a whole, do not represent a sound basis for a clear solution for the organic substance's origin and type identification, an attempt was made to solve this problem by applying GC-MS analysis of biological markers of polycyclic alkanes of the sterane and triterpane type" (Jovancicevic and others, 2001).

"The obtained results have shown that in the case of n-alkanes, pristane and phytane cannot be used (e.g., if their biodegradation has occurred in groundwaters), but steranes and triterpanes may serve as most useful tools in identifying oil-type pollution" (Jovancicevic and others, 2001).

Transformations of n-alkanes from petroleum pollutants in alluvial groundwaters

Jovancicevic, B., Polic, P., Vric, M., Scheeder, G., Teschner, M. and H. Wehner, *Environmental Chemistry Letters*, No. 1, 2003; <http://www.springeronline.com/sgw/cda/frontpage>

Scientists sought to define n-alkane alterations in oil-polluted alluvial sediments. They took samples at five different time intervals over a period of two years, from two boreholes, then analyzed the groundwater by

- group composition
- GC analysis of n-alkanes and isoprenoid aliphatic alkanes
- GC-MS analysis of polycyclic alkanes

"In both boreholes significant alterations with characteristic degradation of 'oil' n-alkanes with no odd- or even-member predominance were observed, as well as subsequent synthesis of new ones with pronounced even-member predominance and with maxima at C₁₆ and C₁₈. Since no additional contamination of boreholes was observed by analyses of steranes and triterpanes, the observed changes can only be attributed to microbial activity. It is assumed that for the degradation of oil n-alkanes, as well as for the synthesis of 'new' n-alkanes, algae such as dinoflagellates are responsible" (Jovancicevic and others, 2003).

Jovancicevic and others (2003) report that "... homologues of n-alkanes in the range C₁₂-C₂₂ may have originated from metabolic products of some microorganisms such as *Desulfovibrio desulfuricans*, *Corynebacterium* sp., *Escherichia coli*, *Rhizopus stolonifer* and *Penicillium* sp... Also, it is well known that in oil-polluted groundwater, nonphotosynthetic-nutritional, unicellular, sporulating algae, *Pyrrophyta*, sometimes called 'fire algae', and many other types

of dinoflagellates possess the ability of n-alkane biosynthesis (with an even number of C-atoms), especially in the range C₁₄-C₂₈... The algae accumulate the n-alkanes in the form of lipid endogenic inclusions, often called 'oil drops'... These algae have the ability to use oil hydrocarbons as carbon sources, and degrade them in the process of B-oxidation" (Jovancicevic and others, 2003).