



# Underground Tank Technology Update

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Department of Engineering Professional Development

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## EDB contamination from leaded gasoline

By Ronald W. Falta, Nimeesha Bulsara, Richard A. Mayer and James K. Henderson

Ethylene dibromide (1,2-dibromoethane or EDB) is a synthetic halogenated organic chemical. EDB along with 1,2-dichloroethane (1,2-DCA) was an integral part of the tetraalkyl lead-based antiknock additive packages used in the United States and other countries from the mid 1920s through the phaseout of leaded gasoline in the 1980s. EDB was also used as a pesticide from the late 1940s until the U.S. EPA banned its use in 1984. Approximately 90 percent of the EDB consumption in the United States was as a leaded gasoline additive.

EDB is an unusually toxic chemical, and it is a potent carcinogen. In 1978, the National Cancer Institute found EDB to be the most potent carcinogen yet discovered in animal tests (Bulsara, 2004). On the basis of this carcinogenicity, the U.S. EPA has established a MCL (maximum contaminant level) of 0.05  $\mu\text{g}/\text{l}$ . EDB's MCL is lower than all other regulated chemicals except dioxin, and EDB's MCL is 100 times lower than benzene's MCL.

Falta (2004a) estimated the United States' annual average EDB concentrations in gasoline using historical lead and gasoline consumption data. This study concluded that the typical EDB level in gasoline prior to the mid 1970s was about 0.3 g/l.

Because EDB has a high aqueous solubility—4,300 mg/l—substantial partitioning into water from leaded gasoline occurs. Falta (2004a) calculated that gasoline containing 0.29 g/l of EDB would produce an equilibrium aqueous concentration of 1,900  $\mu\text{g}/\text{l}$ . This value, which could be expected in groundwater near

unweathered leaded gasoline, is 38,000 times above the MCL. Over time the EDB would be expected to dissolve out of the gasoline phase into the groundwater, where it would form a dissolved plume.

### The problem is not widely recognized

Despite the universal use of EDB in leaded gasoline and its extreme toxicity, its occurrence and fate at LUST sites has not been studied much (Falta, 2004a; Falta and Bulsara, 2004; Ellis, 2004). There are almost no scientific or engineering papers on occurrence, fate, or transport of EDB from leaded gasoline releases. Most LUST site investigators have not analyzed groundwater for EDB.

The Association for Environmental Health and Sciences (AEHS) conducts biannual surveys of state regulations related to sites contaminated by petroleum hydrocarbons. Falta (2004a) analyzed the AEHS survey results from 2003 and found that most states do not require testing for EDB at sites contaminated by gasoline (Figure 1). While it is important to remember that this map is based on survey responses and not on an exhaustive analysis of state regulations, it nonetheless illustrates the lack of attention given to EDB at LUST sites. In contrast, virtually every state in this survey required testing for benzene, toluene, ethylbenzene, and xylenes (BTEX). Most states required testing for MTBE.

Commonly used analytical methods such as US EPA Methods 8021 and 8260 are capable of detecting EDB in groundwater. It is not likely, however, that EDB concentration values would be reported unless a full VOC scan is requested, or unless EDB is specifically requested in the target analyte list. Even if EDB is included in the target analyte list, the typical analytical detection limit using these methods (without dilution) is about 5  $\mu\text{g}/\text{l}$ , or 100 times above the EDB MCL.

US EPA Method 8011, a microextraction technique that uses an electron capture detector, is specific to EDB

identification. Detection limits of 0.01  $\mu\text{g}/\text{l}$  can be obtained. The states in Figure 1 (see page 3) that require testing for EDB at gasoline sites generally specify this method, or the equivalent drinking water analytical method. We strongly recommend that this analysis be included at sites where leaded gasoline may have been released. We also recommend that the other lead scavenger, 1,2-DCA, (MCL of 5  $\mu\text{g}/\text{l}$ ), be included in the Method 8260 or 8021 target analyte list.

### More than 500 EDB sites identified to date in South Carolina

South Carolina, one of the few states that has routinely tested for EDB at gasoline sites, began doing so in the early 1990s. Many of the early EDB analyses were performed using Method 8260 or 8021 with detection limits of 5  $\mu\text{g}/\text{l}$ , while the more recent analyses use Method 8011 with a detection limit of 0.02  $\mu\text{g}/\text{l}$ . We have been working closely with the South Carolina Department of Health and Environmental Control (SCDHEC) over the past year to better characterize EDB occurrence and behavior at LUST sites. SCDHEC maintains a comprehensive database of the approximately 7,200 documented petroleum release sites. This database includes entries for the maximum groundwater concentration of various chemicals of concern (including EDB) at the most recent sampling event.

Falta and Bulsara (2004) and Bulsara (2004) described the occurrence of EDB at South Carolina sites based on queries of the database done in late 2003. They identified 316 sites where EDB in groundwater was above the MCL. As a quality assurance check, Bulsara (2004) hand-checked 169 of these site files to verify the database values. She found that most (> 80 percent) of the maximum EDB values in the database were consistent with values found in the site files. In addition to the 316 sites that were above the MCL, the database also contained EDB entries of 0.00  $\mu\text{g}/\text{l}$  for

### 2003 State requirements for EDB testing at sites contaminated by gasoline

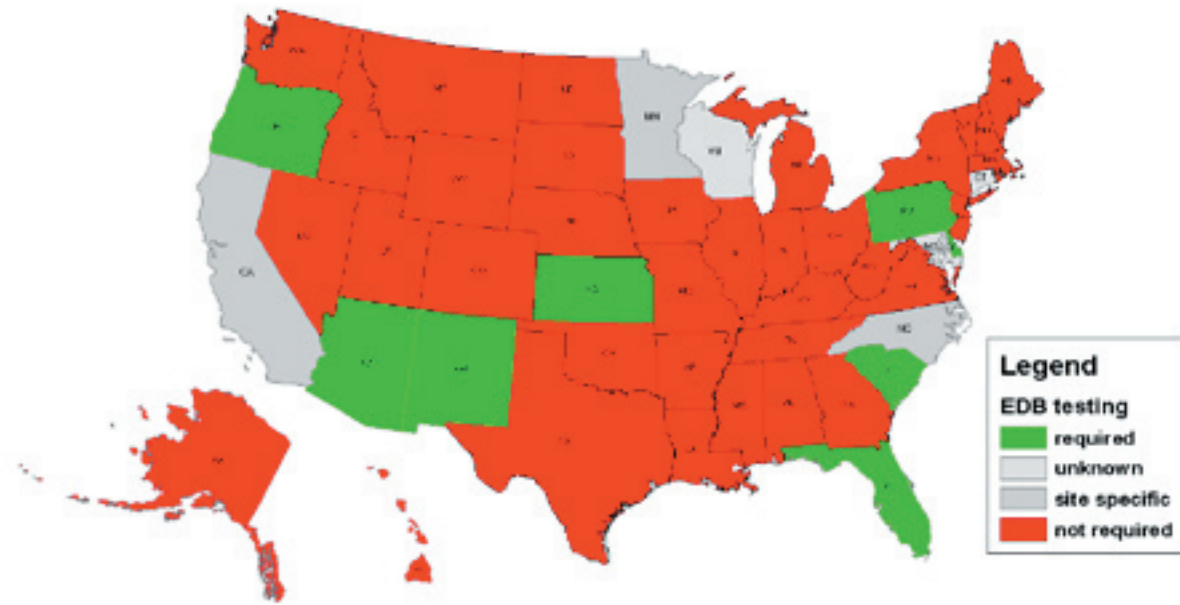


Figure 1. State regulations for EDB testing in groundwater at sites contaminated by gasoline. Data are from AEHS (2003) survey results, and have not been verified on a state-by-state basis.

an additional 864 sites. Since 0.00  $\mu\text{g}/\text{l}$  is not a valid analytical result, the meaning of these database entries was not clear.

Since the original database query in late 2003, the database has been substantially updated with respect to EDB values. A database query performed in December 2004 indicated that the number of LUST sites with EDB above the MCL was 537. The cumulative distribution of EDB concentrations at these 537 sites is shown in Figure 2. The median EDB concentration at these sites is about 5  $\mu\text{g}/\text{l}$ , but EDB concentrations of 50  $\mu\text{g}/\text{l}$  or more occur at more than 20 percent of these sites, and EDB

concentrations above 200  $\mu\text{g}/\text{l}$  occur at 10 percent of these sites.

An important statistic is the percentage of LUST sites where EDB occurs above the MCL (Figure 2, see page 4). To estimate this percentage for South Carolina, it is necessary to estimate the number of sites where EDB has actually been analyzed. The current (December 2004) database lists 537 sites with EDB above the MCL, 251 sites with non-zero EDB values that are below the MCL, and 894 sites with 0.00 EDB entries. We hand-checked 81 of these 0.00 entry site files and found that in many cases (42 percent) there was no

direct evidence of EDB testing. In several other cases (~10 percent) the 0.00 entry was actually a false negative, and EDB is present at the site. Extrapolating our findings to the entire database, we estimate that EDB is found above the MCL at about 50 percent of the sites that are tested in South Carolina.

This number is consistent with the findings of R. Miner (personal communication, 2005) of SCDHEC. After analyzing 149 UST sites in six counties, he found that EDB had been tested for at 125 of the sites. Of these 125 sites, EDB is present above the MCL at 67 sites, or 54 percent of the tested sites. Considering that there have been more than 400,000 confirmed releases of gasoline in the United States, the implications of this EDB occurrence rate are significant.

### EDB plume behavior is poorly understood

EDB has chemical properties that favor rapid movement in groundwater (Table 1, see page 4). It has a very low organic carbon partition coefficient, so it would not be expected to adsorb strongly to aquifer materials. While it has a moderately high vapor pressure, it has a very low Henry's constant, so it is not likely to volatilize once it is dissolved in water. Groundwater retardation coefficients for the chemicals in Table 1 can be calculated assuming different fractions of organic carbon ( $f_{oc}$ ) in the aquifer. It is apparent from these retardation factors that EDB is more mobile than benzene, but somewhat less mobile than MTBE in groundwater.

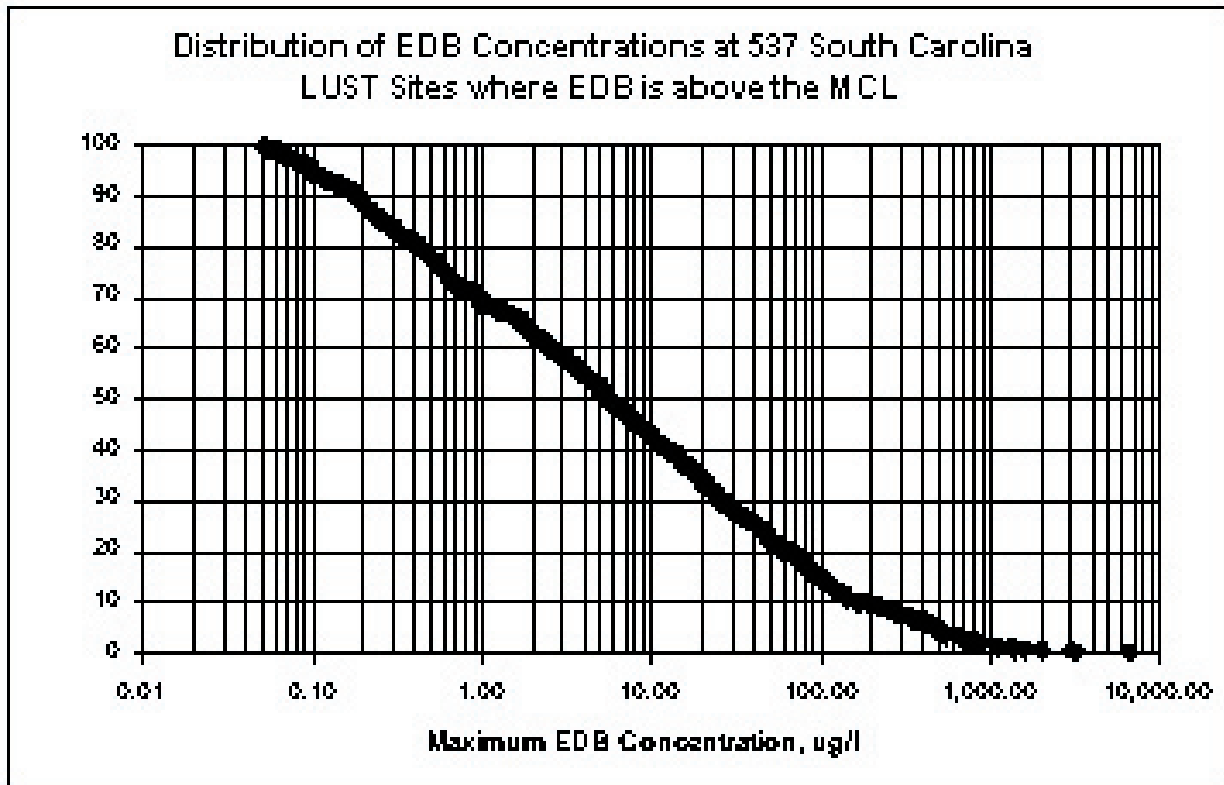


Figure 2. Cumulative distribution of maximum EDB groundwater concentrations at South Carolina sites where EDB is present above the MCL.

Property	Benzene	MTBE	EDB	1,2-DCA
Molecular weight	78.11 g/mol	88.15 g/mol	187.86 g/mol	98.96 g/mol
Aqueous solubility	1,750 mg/l	51,260 mg/l	4,321 mg/l	8,520 mg/l
Vapor pressure	8.00 kPa	32.62 kPa	1.47 kPa	8.10 kPa
Organic carbon partition coefficient, $K_{oc}$	83.0 l/kg	12.3 l/kg	44.0 l/kg	14.0 l/kg
Henry's constant (dimensionless)	0.220	0.023	0.029	0.050
Ground water retardation coefficient, $f_{oc}=0.001$	1.31	1.05	1.17	1.05
Ground water retardation coefficient, $f_{oc}=0.01$	4.11	1.46	2.65	1.53

Table 1. Transport properties of benzene, MTBE, EDB, and 1,2-DCA (from Falta, 2004b)

The mechanisms and rates of EDB degradation at sites where it was a component of gasoline have not been evaluated. EDB degradation has been studied, but only in the context of agricultural uses where the geochemical conditions are likely to be much different from LUST sites. It is reasonable to believe that the aerobic and anaerobic degradation of BTEX compounds at a UST site would have important effects on EDB degradation, perhaps enhancing the reductive dehalogenation process.

Laboratory and field studies at agricultural sites have demonstrated EDB degradation in soils and groundwater (see, for example, Pignatello and Cohen, 1990). Some of these studies have found fairly rapid aerobic and anaerobic degradation of EDB; however, low levels of EDB (above the MCL) have also been found to persist for decades after EDB releases (Pignatello and Cohen, 1990). Falta (2004a) describes several large (longer than one mile) EDB groundwater plumes from aviation gasoline releases at the Massachusetts Military Reservation where EDB does not appear to be degrading significantly. One of these plumes has an estimated EDB half-life of 18 years.

We are not aware of any comprehensive analysis of EDB plume geometry or longevity at LUST sites. The lack of such studies, along with the lack of laboratory and field studies of EDB degradation at LUST sites, severely restricts our understanding of EDB plume behavior.

### Conclusions

It has been demonstrated that past releases of leaded gasoline have resulted in groundwater contamination by EDB. EDB is 100 times more toxic than benzene, yet this contaminant has received little attention at LUST sites. Very little is known about the geometry and stability of EDB plumes at LUST sites, or about EDB attenuation at these sites.

Responsible risk management at sites where leaded gasoline was released will require an improved understanding of the occurrence, transport, degradation, and remediation of EDB in these settings.

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**UTTU thanks Dr. Ron Falta, Departments of Geological Sciences and Environmental Engineering, Clemson University, Clemson, SC 29634-0919, [faltar@clemson.edu](mailto:faltar@clemson.edu), for contributing this article.**



## Natural attenuation models and protocols

Mulligan and Yong (2004) describe the common models and protocols used for natural attenuation of pollutants at contaminated sites. The success of natural attenuation depends on the site geology, hydrology and microbiology.

Factors that will determine the efficiency of ongoing abiotic processes (such as adsorption) include

- soil fraction surface properties
- porewater chemistry
- chemical and physical-chemical properties of pollutants and soils
- interaction mechanisms, which are influenced by soil fractions, type and size of organic molecule, presence of water
- intermolecular-level interactions, which include London-van der Waals forces, hydrophobic reactions, hydrogen bonding and charge transfer, ligand and ion exchange and chemisorption
- volatilization
- partitioning
- hydrolysis
- oxidation/reduction
- retention and retardation

In terms of biotic processes, factors of concern include

- type and amount of microorganisms present
- availability of oxygen and other electron acceptors
- presence of water and mineral nutrients

## Bioattenuation and bioavailability processes

Sorption and sequestration, processes of bioattenuation, are influenced by

- pH
- organic matter content
- temperature
- pollutant characteristics

Solid Fe(III) also plays a role; it "must be available and in direct contact for the microorganisms. Otherwise, these electron acceptors can be obtained from humic acids that can chelate iron bioavailability. The presence of humic acids can significantly increase iron bioavailability. Nutrients such as nitrogen and phosphorus can also be limiting" (Mulligan and Yong, 2004). Also important in determining a soil's biodegradation potential are changes in porosity, especially with respect to calcareous sediments. Other factors include soil pH, any bacterial products that can influence hydrocarbon desorption, and organic acids produced by fungi that can chelate and remove metals from soils.

## Fate and transport models

Mulligan and Yong (2004) give descriptions of 20 fate and transport models in their paper. Factors described include applicability, assumptions, inputs and outputs, calibration and verification parameters. "Decisions concerning what model to use should be based on available data, site complexity and accuracy of the information required." The models examined are

- BIO1D
- BIOF and T 3-D

- BIOREDOX
- BIOPLUME II
- BIOPLUME III
- BIOSLURP
- BIOTRACKER
- CHEMFLO
- 3DFATMIC
- MODFLOW
- MT3D, MT3DMS
- PESTAN
- RITZ
- RT3D
- SEAM3D
- SESOIL
- SWIFT, SWIFT/486
- SWMSM\_2D
- UTCHEM
- VLEACH

Some generalizations about the models are as follows:

- they require 19 to 40 input parameters
- some are used for evaluation of natural attenuation
- some can predict plume length without calibration
- some are analytical: they provide exact solutions, are useful to simulate advection, biodegradation, dispersion and sorption, and can be used with limited data
- some are numerical: they provide approximate solutions and are applicable to heterogeneous aquifers
- quality input data is key to successful model and calibration; verification and prediction are essential to model accuracy
- depending on the attenuation processes modeled,

- source degradation and reduction can have a significant influence on contaminant concentration
- the most appropriate model must be chosen for each site and data from that site used in the model
- models should not be forced if the data don't fit
- model results should not be extrapolated beyond what is reasonable

### Natural attenuation protocols

Several protocols can help to determine if natural attenuation is occurring. The Air Force Center for Environmental Excellence has determined three lines of evidence commonly accepted for occurrence of natural attenuation, which include

- primary: a decrease in contaminant amounts at the site
- secondary: data from contaminant or geochemical analysis
- tertiary: microbial data

Remediators usually emphasize the first two lines of data.

The ASTM (<http://www.techstreet.com/info/astm.tmpl>) protocol, which applies specifically to petroleum UST releases, includes characterizing the site and potential risks. "The plume should be stable or shrinking. The time frame for achieving goals is determined by the regulatory agency. Source control should be integrated into the remedial decisions, but whether or not to remove the source is determined by the regulatory agency. Monitoring is based on site-specific conditions until objectives are met. Contingency plans are to be implemented if the objectives cannot be met by natural attenuation" (Mulligan and Yong, 2004).

The NRC (National Research Council) suggests three lines of evidence to determine if natural attenuation is working:

- decreases in contaminant concentration and/or plume size over time
- chemical indicators of microbiological activity as evidenced by oxygen, nitrate and sulphate consumption and production of Fe(II), Mn(II) and methane
- laboratory microcosm studies to identify bacterial activity

The U.S. EPA's guidance document recommends characterization of the site for nature and concentration of contaminants and potential impacts to receptors. "Contributions of sorption, dilution and dispersion of contaminants should be evaluated in groundwater in addition to the hydraulic regime. This includes recharge, discharge areas and volumes. For biodegradation, scientists should evaluate the presences of nutrients, electron donors and acceptors, metabolites and by-products and available microbial populations. This information can be incorporated into a site-specific fate and transport model" (Mulligan and Yong, 2004).

The OSWER policy states that a natural attenuation remedy must demonstrate that natural attenuation is occurring as expected, and that toxic byproducts are identified along with plume expansion and other environmental releases. For instance, during petroleum remediation, arsenic and manganese can be released into an aquifer, and they should be identified. Environmental conditions that could affect the process of natural attenuation should also be identified.

Other policies and procedures reviewed by the NRC indicate that acceptable final contaminant concentrations can vary substantially among the protocols.

A U.S. EPA recommendation for MTBE includes:

- evaluating MTBE biodegradability and other oxygenates under field conditions
- determining with more certainty MTBE and fuel component dissolution rates

- establishing a database for MTBE natural attenuation

For protocols presently in existence, The NRC recommends

- there should be agreement on protocol use and how they are used to obtain regulatory approval
- independent experts should peer-review all protocols
- conceptual models rather than scoring systems for decision guidelines should be used
- easy-to-use documents should support the protocols
- training on proper protocol use should be provided

Mulligan and Yong (2004) also point out that "most protocols are designed for groundwater natural attenuation and not for soil natural attenuation or sediments." In their article, they do describe studies of soil natural attenuation involving contamination by trichloroethylene, polychlorinated biphenyls, chlorinated ethenes and diesel-oil. They present summaries of case studies of natural attenuation in clay soils involving diesel fuel and other hydrocarbons. Soil vapor is often not considered, and to integrate the soil and groundwater models can often be complicated.

## Conclusions

Mulligan and Yong (2004) conclude that there are advantages and disadvantages to natural attenuation. Advantages include

- possibility of completely destroying the contaminant
- technology that is generally acceptable to the public
- ability to be used with other methods as a pre- or post-treatment
- possibility of significantly reducing remediation costs

Disadvantages may include

- longer remediation times as compared to other technologies
- lack of knowledge of some remedial mechanisms
- substantial requirements for monitoring
- possibility of producing by-products that are more hazardous than the original contaminant
- possibility of desorption and resolubilization of contaminants
- possible slow public acceptance
- uncertainty of modeling efforts

## Reference

Mulligan, C.N and R.N. Yong, "Natural Attenuation of Contaminated Soils," *Environment International*, Vol. 30, p. 587-601, 2004; <http://www.elsevier.com/locate/envint>.

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## MTBE and TBA degradation

TBA, or tert-butyl alcohol, is a key intermediary in the degradation of several dialky ethers such as MTBE and ETBE. Scientists know that MTBE and TBA "may be biodegradable under oxic and nearly all anoxic conditions, although results of various studies are often contradictory, which suggests that site-specific conditions are important parameters." Under methanogenic conditions, "TBA is a recalcitrant dead-end product of MTBE." Degradation pathways under anoxic conditions have not yet been identified, but to date, all pure cultures capable of MTBE or TBA degradation use oxygen as terminal electron acceptor.

Schmidt and others (2004) reviewed current MTBE and

TBA data with a threefold intent:

- to highlight the role of TBA as co-contaminant and intermediary in MTBE degradation
- to discuss the degradation of MTBE and TBA under anoxic conditions
- to present the potential of using stable isotope techniques for assessing the fate of slowly degrading compounds such as MTBE and TBA

## Physico-chemical and thermodynamic data

An analysis of relevant physico-chemical and thermodynamic data yields the following:

- at equilibrium, TBA and MTBE degradation will occur "under all environmentally relevant standard redox conditions"
- "there is no thermodynamic rationale for an accumulation of TBA since TBA degradation yields nearly as much energy as MTBE degradation"
- "these calculations account for the thermodynamic feasibility of a reaction, not for kinetic limitations that may lead to imperceptibly slow reaction rates"
- an examination of free energy values for the reactions in question indicates that "the concentrations of oxidants and reductants have only a minor influence on the free energies of reaction"; an exception is MTBE or TBA oxidation under iron-reducing conditions because ferrihydrite is "rather sensitive to both pH and concentration of dissolved  $Fe^{2+}$ "
- in a microaerophilic environment, oxygen concentration has little impact on the free energy of reaction; however, "the actual concentrations of all species in bacteria microenvironments are highly variable and generally not known at the field scale"

## Microcosm studies of MTBE and TBA degradation

Schmidt and others (2004) list almost 40 microcosm studies undertaken to evaluate MTBE and TBA degradation. The scientists caution one "to keep in mind that site-specific conditions may substantially influence the capability of MTBE or TBA degradation in microcosms. For instance, Bradley and others (2001a in Schmidt and others, 2004) point out that the effect of redox conditions on contaminant degradation in surface-water and aquifer sediments is similar, but degradation rates are usually substantially lower in aquifer sediments."

To quantify degradation rates, scientists measure MTBE or TBA loss or mineralization over time. Because TBA was used as a substrate in only a few studies, TBA degradation studies are usually obtained from TBA removal during MTBE mineralization. At low TBA concentrations, analytical methods become an issue; in particular the headspace-GC-FID method becomes less suitable because of the TBA's low Henry's constant.

Other considerations concerning these studies include the following:

- if a study occurs under anoxic conditions, it is important that no oxygen traces should be present
- if a study does not use a <sup>14</sup>C-labelled compound, then it is difficult to report mass balances or electron balances, and the total amount of available electron donors cannot be accurately estimated

From analyses of reports, researchers found that "MTBE and TBA degradation has been reported in the presence of all environmentally relevant terminal electron acceptors; however, except for oxic conditions, results are controversial in literature, or only very limited studies have been carried out to date. Under methanogenic conditions, TBA degradation has not been observed, and it is currently widely accepted that TBA is an accumulating dead-end product of MTBE degradation under

such conditions" (Schmidt and others, 2004).

## Results from laboratory microcosm studies

Following are the results from laboratory microcosm studies:

- most studies performed under oxic conditions indicate MTBE and TBA degradation
- in surface-water sediments under oxic conditions, MTBE degradation rate was highly variable, ranging from 5 to 66 percent
- TBA was never reported to be recalcitrant under oxic conditions
- under anoxic conditions, TBA was degraded after an acclimation period; furthermore, easily degradable substrate impeded TBA degradation; this was also true for MTBE and ETBE
- one study reported MTBE and TBA degradation under denitrifying conditions using [<sup>14</sup>C]MTBE and [<sup>14</sup>C]TBA; another reported only TBA degradation
- under sulfidogenic conditions, MTBE degradation was found in one study, but not in another
- TBA degradation has not been unambiguously demonstrated
- under Fe(III) conditions, studies show MTBE degradation; yet a recent study indicated no MTBE degradation
- under Fe(III) conditions, TBA mineralization was observed, but this may have been attributable to sulfidogenic activity
- under Mn(IV) conditions, mineralization of MTBE has occurred
- under methanogenic conditions, MTBE biodegradability is controversial: several studies showed no degradation, whereas others have indicated biodegradation

- the general consensus for TBA under methanogenic conditions is that it is recalcitrant

## Field studies

Schmidt and others (2004) summarized the very few field studies completed, and concluded: "At this point, it should be emphasized that there is not enough known about the crucial biogeochemical factors that limit degradation of MTBE and TBA on the field scale to infer general conclusions. For example, although it is generally accepted that degradation of MTBE under anoxic conditions is much slower than under oxic conditions, or that MTBE is even recalcitrant, the only available degradation rates derived from field studies indicate the opposite: for methanogenic conditions, a 5-10 times higher rate than for oxic conditions has been found."

## Aerobic MTBE and TBA degradation

Schmidt and others (2004) list 18 studies of MTBE and TBA degradation using pure and mixed microbial cultures in an aerobic environment. Degradation rates for these studies showed a high variability and "no apparent difference between rates for cometabolic degradation and for microorganisms that utilize MTBE as sole substrate. In general, such rates should be used and interpreted with care since they often differ substantially in repetitive experiments with the same organism."

Cometabolic studies indicated the following:

- a study of fuel oxygenates grown on propane showed that several organisms could degrade MTBE, ETBE, TAME and TBA; TBA was the most recalcitrant of the four co-substrates
- microbes grown on aromatic compounds were able to cometabolically degrade MTBE and TBA
- the microbe, *Arthrobacter*, grown on butane, could degrade MTBE and TBA, but not when grown on other substrates such as glucose, 1-butanol, tryptone phosphate broth; TBA degradation rates were lower

than MTBE rates; increasing TBA concentrations inhibited MTBE degradation

Schmidt and others (2004) also report on organisms that can grow on MTBE or TBA as the sole carbon and energy source. This discussion centered around mixed cultures, the  $\beta$ -proteobacterium strain PM1, an autochthonous bacteria similar to PM1, *Hydrogenophaga flava*, *Mycobacterium astroafricanum*, and *Burkholderia cepacia*. The authors also describe MTBE and TBA degradation pathways, key intermediates formed, and degradation mechanisms under oxic conditions.

### Isotope studies

Isotope studies rely on the fact that "The rate-determining step in compound biodegradation is often accompanied by a kinetic isotope effect that leads to a relative depletion of the compound fraction containing lower mass isotopes because they are preferentially degraded." Using this theory, a ratio of the heavy to the light isotope in the substrate and product, respectively, can be calculated. The stable isotope technique has become an "invaluable tool for the investigation of degradation processes, in particular regarding the ratio of  $^{13}\text{C}/^{12}\text{C}$ ." Hydrogen isotope analysis can also help quantify degradation. In addition, the isotopic composition of MTBE in gasolines falls into a narrow range.

Schmidt and others (2004) list some enrichment factors for macrocosms containing MTBE and TBA. From these studies, researchers concluded that "carbon isotope analysis is best suited for quantification of biodegradation at a contaminant site, whereas the large hydrogen isotopic fractionation enables a more sensitive identification of in-situ biodegradation."

"The few studies published so far have shown the potential of compound-specific isotope analysis for the identification and quantification of degradation pro-

cesses of MTBE and related compounds. In addition to the measured  $\delta^2\text{H}$  and  $\delta^{13}\text{C}$  (enrichment factors), the compound-specific determination of  $\delta^{18}\text{O}$  values is now possible with commercial instruments. Analysis of  $\delta^{18}\text{O}$  might be useful for a further elucidation of degradation mechanisms for ethers and alcohols because a substantial fractionation should only be obtained in cases where the carbon-oxygen bond is affected in the rate-determining step" (Schmidt and others, 2004).

### Conclusions

Schmidt and others (2004) conclude the following:

- MTBE and TBA do not degrade as readily in the field as gasoline-derived hydrocarbons
- under oxic conditions, TBA was not found in substantial amounts after MTBE depletion
- under anoxic conditions where MTBE is being degraded, studies show TBA accumulation
- many field studies lack TBA data because of the difficulty of TBA analyses at trace levels
- studies indicate that TBA is as recalcitrant as MTBE but can be a chemical of greater concern because of its greater toxicity; "depending on biogeochemical conditions, TBA instead of MTBE might therefore be an appropriate parameter to evaluate the success of natural attenuation approaches and remediation efforts"
- carbon and/or hydrogen isotope signatures on MTBE and TBA can foster understanding of degradation of recalcitrant compounds
- inhibitory effects (e.g., presence of BTEX) on TBA degradation need to be studied; however, such studies can occur only if analytical methods have been established to determine MTBE and TBA content and TBA degradation products

### Reference

Schmidt, T.C., Schirmer, M., Weib, H. and S.B. Haderlein, "Microbial Degradation of Methyl Tert-Butyl Ether and Tert-Butyl Alcohol in the Subsurface," *Journal of Contaminant Hydrology*, Vol. 70, 2004; <http://www.elsevier.com>.



### MTBE hydrolysis to form TBA

Groundwater contaminated with MTBE often contains TBA, tertiary butyl alcohol. TBA can occur in MTBE releases via degradation of MTBE or as an impurity. It is important to know the concentration of TBA in a release as TBA is thought to be more toxic than MTBE. Yet a recent study indicated that analytical procedures to determine TBA amounts may be flawed; in particular, it appears that MTBE hydrolysis could occur during TBA analysis, and concentrations of TBA and MTBE identified using the analytical procedure EPA Method 8260B (gas chromatography/mass spectrometry) may be giving inaccurate MTBE and TBA concentrations. Rong and Kerfoot (2003) raise several questions:

- is ether hydrolysis a pervasive problem?
- could groundwater TBA concentrations reported in the past be artifacts of hydrolysis of MTBE?
- under what conditions is hydrolysis an issue, or is it always a potential problem?

### Sampling and analysis of MTBE and TBA

Sampling and analysis for contaminants in groundwater occurs in three steps:

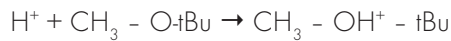
- sampling and preservation
- transporting the sample to a laboratory and storing it

- analysis, as well as pre-analysis

Hydrolysis of samples can occur during any one of these steps.

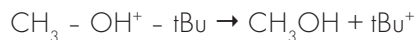
## Hydrolysis

This section is taken verbatim from Rong and Kerfoot (2003). Hydrolysis of ethers can occur by one of two mechanisms—unimolecular or bimolecular substitution—depending on the ether's molecular structure. For either mechanism, the first step is protonation of the ether to produce a cation, the carbonium ion:



tBu represents the tertiary butyl group  $[CH_3]_3C$ .

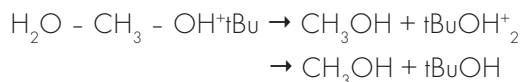
The resultant carbonium ion then undergoes nucleophilic substitution by either a unimolecular or bimolecular mechanism. For the unimolecular substitution reaction mechanism, the protonated alcohol decomposes to form an alcohol and a carbonium ion. For MTBE, this would be



The carbonium ion (tBu<sup>+</sup>) can then combine with a water molecule to form a protonated alcohol that can expel a proton and become an alcohol. Continuing from the equation above,



The bimolecular reaction mechanism involves the essentially simultaneous breaking of one of the ether C-O bonds and formation of a bond between that carbon and the oxygen atom of a water molecule. For MTBE this could be:



The water molecule is the nucleophile that reacts with the tBu<sup>+</sup> carbonium ion in both the unimolecular and bimolecular processes. Because of this, evaluation of the rate of MTBE hydrolysis does not provide data that can

be used to distinguish between the two mechanisms; to accomplish that requires data from experiments using isotopically labeled MTBE."

By understanding the hydrolysis kinetics, scientists could then ascertain if ether hydrolysis could alter MTBE or TBA concentrations in samples. Scientists found that a decrease of 1 in pH would increase hydrolysis rate by a factor of 10. Temperature also affects MTBE hydrolysis rate.

Because of the low reactivity of the ether bond, ether hydrolysis should not occur at a significant rate under normal environmental conditions. However, when conditions are not normal, such as when laboratory samples are preheated prior to analysis, MTBE can undergo hydrolysis. For instance, heating MTBE to a temperature of 80°C for 60 minutes at a pH of 1 can increase TBA concentrations and decrease MTBE concentrations. Results from studies suggest that "the extent of hydrolysis may not be significant except under the simultaneous conditions of both low pH (approximately 1) and a temperature of 80°C." When during the course of MTBE and/or TBA analysis would these two conditions occur? If they occur at all, it would most likely be during headspace analysis.

## Evaluation of field data

Rong and Kerfoot (2003) analyzed groundwater data from three field data case studies. Some samples were preserved with an acid, some with an alkaline. Differences in MTBE concentrations ranged from 0 to 22 percent, but below 40°C, pH did not greatly affect analytical results. "The deciding factor may be the fact that the analysis temperature was below 80°C, that samples were not heated for 60 minutes before analysis, or a combination of the two. Furthermore, four samples... show no evidence of TBA in the presence of MTBE with acid preservation, which indicates that no detectable ether hydrolysis has occurred. Even for wells #1 and

#2, where TBA was detected, TBA concentrations are higher for alkaline preservative than acid preservative in one case and lower in the other case, which does not show a consistent effect. Although these data are not sufficient to prove or disprove causality, they may suggest that the concern over MTBE hydrolysis may be overstated."

Results from the second case study indicate small differences among results from the three options of preservation: acid, alkaline and none. Researchers found that "alkaline sample preservation resulted in both higher and lower MTBE concentration than acid sample preservation, results that are not consistent with hydrolysis induced by acid preservation."

Data from the last case study were somewhat inconsistent: one sampling quarter showed lower MTBE with acid preservative than with no preservative, while the data from the other three quarters showed the opposite relationship. "These data, although limited, are not consistent with a significant hydrolysis effect from HCL preservation."

## Conclusion

Rong and Kerfoot (2003) ascertain that MTBE hydrolysis due to acid preservation of groundwater samples is likely not a pervasive problem. "Therefore, concerns about the validity of historical TBA data may not be warranted. The reason for this result may be simple: there are two necessary factors that promote hydrolysis: low pH and high (above 40°C) analysis temperature." Temperatures below 40°C do not seem to cause measurable hydrolysis effects. "The data considered in this study are limited in number and location, and further evaluation of more data would be required to make broad-reaching judgments, but these data suggest that the concern over MTBE hydrolysis from acid preservation may only be justified in the case of analysis at high temperatures."

## Reference

Rong, Y. and H.B. Kerfoot, "Much Ado: How Big is the Problem of Hydrolysis of Methyl Tertiary Butyl Ether (MTBE) to Form Tertiary Butyl Alcohol (TBA)?" *Environmental Forensics*, Vol. 4, 2003; <http://www.sciencedirect.com>

UTTU thanks Dr. Yue Rong, [YRONG@rb4.swrcb.ca.gov](mailto:YRONG@rb4.swrcb.ca.gov), for his help on this article.



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

Part III of this series describes considerations in addressing abandoned sites, tax delinquent properties, private lien holders, bankruptcy and liability of current and former owners.

Issues related to former gas station sites can complicate redevelopment but may also present opportunities. This section describes how to evaluate barriers and opportunities while supporting site redevelopment.

### Abandoned sites

Many vacant former gas station sites appear to be abandoned. The term "abandoned" may be applied to sites that no one is managing, where the owner cannot be identified or located, or where the owner has stopped paying the mortgage and/or taxes. In this guide, "abandoned" means that the owner has stopped paying taxes and has stopped maintaining the site.

In some cases, the owner may think that nonpayment of taxes will result in reversion of the property to government ownership. In California, this is not so: ownership changes only when property is actively transferred to another owner. When an owner stops maintaining a property, it often becomes a site for illegal waste

disposal, graffiti, or other activities that create blight and community problems. To control such activities, the City will fence the site and place a lien on the property to obtain repayment for the fence cost. Such a lien has the potential to speed the site sale and may facilitate an agency in acquiring the site as described below under "Tax delinquent properties."

### Opportunity

Cleaning up an abandoned property may be easier than for a property whose current owner occupies or leases the property and whose income will be interrupted by tank removal activities. In addition, in California abandoned properties that have LUST contamination are eligible for cleanup costs to be covered by the EAR Account. Chapter 4, Paying for Site Assessment, describes this program in more detail (see <http://www.lacity.org/ead/labf/>).

### Tax delinquent properties

Distressed properties are often tax delinquent. Below is a summary of some relevant sections of California law governing disposal of tax delinquent properties. Readers outside of Los Angeles County should verify procedures in their counties.

### State law

California law governing disposition of tax delinquent property is found largely in the Revenue and Taxation Code Section 3591-3731.1, 3841, 7063 and 15640-15646. Procedures for auction of tax-defaulted property are published by the California State Controller in a three-volume document, "Guide to the Sale of Tax-Defaulted Property." This document can be downloaded from the State Controller's Web site (see <http://ttax.co.la.ca.us/main.htm>).

When a property becomes tax delinquent, the tax collector must notify the owner about the delinquency

for five years, after which the property is considered to be in tax default and may be offered for sale. The tax collector must offer tax defaulted properties for sale within four years of being in tax default. One exception to this rule is Revenue and Taxation Code Section 3691 (b)(1)(A), which states "three years or more after the property has become tax-defaulted and subject to a nuisance abatement lien, the tax collector shall have the power to see and may sell all or any portion of tax-defaulted property..." However, the LA County tax collector does not have the ability to track liens by local government entities and is not currently implementing this provision. If other counties in California have implemented this provision, properties that have nuisance abatement liens (such as to cover the cost of fencing) can be offered for sale after three years.

### Opportunity

Taxing agencies, revenue districts, and redevelopment agencies are eligible to acquire tax-defaulted property outside of the public bid/auction process if the property is needed for a "public use." Certain non-profit agencies are also eligible to purchase residential or vacant tax delinquent property to expand availability of low-income housing. This may be done after three years of tax delinquency if the property is subject to a nuisance abatement lien. (See Revenue and Taxation Code Section 3791.4). The guide mentioned above explains the criteria and procedures for such purchases. One strategy could be for a city to inform local non-profit housing developers about the property they could obtain from the tax collector. The city could then work with a developer to apply for U.S EPA grants to assess and remediate the property.

### Auction of tax delinquent properties

In Los Angeles County, tax delinquent properties are managed by the treasurer and tax collector—a county

agency that is separated from the tax assessor. Approximately every six months, the Los Angeles tax collector holds an auction of tax delinquent properties. A book listing the properties to be auctioned is published several weeks beforehand and can be purchased through the mail. Bidders must pre-register and make a cash deposit of \$1,000, which is applied to a purchase or refunded if no property is purchased. Persons attending only to observe are not charged or required to register in advance. The minimum bid on each property is given in the book and represents taxes owed plus fees charged by the tax collector's office. When a property is purchased at an auction, the fee portion goes to the tax collector, the taxes owed go to the state, and any remainder goes to the previous property owner. The new owner is liable for liens owed to other agencies, but private liens are extinguished.

Several factors can contribute to properties not being sold in the minimum time provided by law: the tax collector may choose to wait; owners can delay the auctioning of properties by agreeing to a payment schedule, and an ownership or bankruptcy can delay the process.

The tax collector may auction contaminated properties as long as they are not federal Superfund sites. If someone buys a site and then discovers contamination, the Los Angeles County tax collector may take it back but other counties may not do so. The City of Los Angeles Brownfields Program informs the tax collector of properties with identified environmental problems. The tax collector then places a note on the property listing to inform potential purchasers of its condition. The Los Angeles County tax collector has no procedure in place to notify local agencies about properties that cannot be auctioned because of environmental contamination or uncertainty, since the tax collector does not gather that information.

### Opportunity

A former gas station with USTs in place and no testing to determine whether contamination exists is unlikely to sell at auction. Someone might purchase the property, however, if the auction cost of the property and cost to remove the USTs and any contamination is substantially less than the property's resale value.

In some cases it may be possible for a city to test the property, then work with the tax collector to provide the testing results to prospective purchasers and thereby facilitate the property sale. Another option would be for a city to remediate the property so that it can be sold, or purchase the property from the tax collector, remove the tanks, remediate the property and then resell it.

### Private lien holders

Owners also abandon sites by defaulting on the mortgage. By not paying the mortgage, the owner may think he or she is giving the property to the bank. Although the bank has the option to repossess property that provided collateral on a loan, if the property is contaminated, and the cost to remediate the property exceeds its value, the bank may not foreclose.

The right of a prior lien holder, such as a bank, however, must be considered in deciding how to approach redevelopment of such a property. The bank can exercise its lien at any time. For example, if a city were to purchase a tax delinquent property from the owner and remediate it, the bank could reclaim the property as payment on their lien. In such a case, it could be advisable for the city to work out a settlement with the bank before taking ownership of the property. If the city, however, obtains the property from the tax collector, private liens are extinguished.

### Bankruptcy

Many properties that are in tax default also have bankruptcy filings against them. Filing for bankruptcy is

a way for property owners to obtain relief from debts. Bankruptcy, however, does not discharge taxes owed. Bankruptcy may not discharge a lien held by a bank on property pledged as collateral for a loan.

### Opportunities

The LA County tax collector will not auction a property that has an active bankruptcy against it. Interested parties may, however, be able to determine that the bankruptcy has been dismissed by the court or withdrawn by the petitioner. If so, they can inform the tax collector about this and thereby free the property to be auctioned by the tax collector.

### Liability of current and former owners

This is too large and complex an issue to be dealt with here in any detail. For former gas station sites in the City of Los Angeles, if the current owner appears to have the ability to pay for removal of USTs, the city takes an enforcement approach. The Los Angeles Fire Department issues an order to the owner to remove the tank. If the owner fails to do so, the case is referred to the city attorney who can file a civil or criminal complaint against the owner. If the site owner has substantial assets, consult with your regulating agency and/or your city attorney regarding the proper action to take.

### 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

### Biodegradation of petroleum hydrocarbon vapors: laboratory studies on rates and kinetics in unsaturated alluvial sand

Hohener, P., Duwig, C., Pasteris, G., Kaufmann, K., Dakhel, N. and H. Harms, *Journal of Contaminant Hydrology*, Vol. 66, 2003; <http://www.elsevier.com/locate/jconhyd>

Scientists endeavored to determine kinetic rate laws for the aerobic biodegradation of a mixture of 12 volatile petroleum hydrocarbons and MTBE in an unsaturated alluvial sand, a mixture that would be typical for gasoline or kerosene. Using two recalcitrant fluorinated tracers, they performed tests in both laboratory and batch settings. From a column experiment they determined that acclimatization took 23 days before steady-state diffusive vapor transport was achieved. For toluene, m-xylene, n-octane and n-hexane, monod kinetic parameters were derived using concentration profiles. "The removal of cyclic alkanes, isooctane, and 1,2,3-trimethylbenzene followed first-order kinetics over the whole concentration range applied. MTBE, n-pentane and chlorofluorocarbons (CFCs) were not visibly degraded... For many compounds including MTBE, disappearance rates in abiotic batch experiments were as high as in live batches, indicating sorption."

Researchers report that they were able to define kinetic rate laws of VOC biodegradation in unsaturated alluvial sands. "First-order kinetics was a good approximation for most of the compounds in both experimental systems, with n-octane as the only exception out of 10 VOCs that were biodegraded. Only the column approach allowed us to measure Monod kinetic parameters. The correct interpretation of kinetic biodegradation

parameters in unsaturated batch experiments remains a difficult task" (Hohener and others, 2003).

### Degradation of MTBE in dilute aqueous solution by gamma radiolysis

Hsieh, L.L., Lin, Y.L. and C.H. Wu, *Water Research*, Vol. 38, 2004; <http://www.elsevier.com/locate/watres>

Hsieh and others (2004), while investigating the potential of the  $\gamma$ -irradiation (gamma ray) process to remediate MTBE-contaminated waters, formulated four objectives:

- to measure the intermediates of MTBE destruction as a function of dose
- to determine the dose constant to evaluate degradation efficiency for various MTBE concentrations
- to study the effect of benzene at various concentrations
- to investigate the effect of cupric ion concentration on MTBE degradation

Scientists first irradiated samples for 5 minutes with a dose ranging from 2.3 to 90.2 Gy/min. The G value is used in radiolysis studies to describe destruction efficiency; in this article, scientists will use the term dose constant rather than G.

Gas chromatography, used to analyze degradation products, indicated that the MTBE peak was reduced with increasing  $\gamma$ -ray dose. Four major intermediate products formed:

- TBF, tert butyl formate
- TBA, tert butyl alcohol
- acetone
- MA, methyl acetate

"MTBE oxidative degradation in water follows two major pathways, both of which are initiated with hydrogen atom abstraction by hydroxyl radicals, followed by

the addition of oxygen to form peroxy radicals. These peroxy radicals undergo self-recombination to produce a tetraoxide intermediate that decomposes to give a variety of products. According to the characteristics of these adducts, it is concluded that hydrogen abstraction by the  $\text{OCH}_3$  group and t-butyl group occurs in yields of 71 percent and 29 percent respectively."

When benzene is present, treatment of MTBE-contaminated water can be complicated because benzene is highly reactive toward the hydroxyl radical, and "benzene, acting as a hydroxyl radical scavenger, might reduce the removal efficiency of MTBE."

"Product species competition for hydroxyl radicals is another important consideration. For benzene, the initial reaction products include substituted phenols, which are more electron rich than the starting substrates and therefore more reactive toward the electrophilic hydroxyl radical. Reaction by-products that are not specified in the system act as radical scavengers and thus compete with MTBE for OH radicals. If problems of by-product formation can also be overcome, a better agreement to the experimental measurements even at a higher initial concentration of benzene could be obtained" (Hsieh and others, 2004).

Scientists also found that the presence of cupric ions did not significantly affect MTBE removal.

### Laboratory-scale bioremediation experiments on hydrocarbon-contaminated soils

Sabate, J., Vinas, M., and A.M. Solanas, *International Biodeterioration & Biodegradation Journal*, Vol. 54, 2004; <http://www.elsevier.com/locate/ibiod>

Scientists developed a simple protocol for treating hydrocarbon-contaminated soils, which included a first phase of examining the "type and metabolic activity of the indigenous microorganisms at the site and the

presence of possible inhibitors." In this phase, which takes about a month, scientists characterize heterotrophic and degrader microbes using the most-probable-number (MPN) technique. Respirometry experiments are conducted using nitrogen, phosphorus and glucose to "assess the real and potential metabolic activity of indigenous microorganisms." Toxicity tests were conducted and soils were examined for organic carbon and nitrogen. Scientists created soils slurries and from them measured TPH using column chromatography.

Using this procedure, they tested two soils and found that one soil was not suitable for bioremediation because of its fraction of oil petroleum products; respiratory activity was not seen and little biodegradation occurred during the slurry test.

Scientists did attempt to treat both soils with nutrients, glucose, the surfactant Tween 80. For soil 1 (which was mostly contaminated with mineral oils), TPH concentration decreased with nutrient addition, while addition of nutrients and glucose was most efficient. For soil 2, TPH concentration decreased slightly following the first basic treatment (without nutrients). The other treatments were not effective until 270 days of incubation. An inoculation of consortium F1AA, which was specially engineered to biodegrade heavy fractions of petroleum products, had no effect.

### Phytoremediation of soil contaminated with used motor oil. I: enhanced microbial activities from laboratory and growth chamber studies

Dominguez-Rosado, E., Pichtel, J. and M. Coughlin, *Environmental Engineering Science*, Vol. 21, No. 2, 2004; <http://www.liebertpub.com/index.aspx>

Scientists investigated the use of plants for bioremediating used oil that contains lead, cadmium, barium and other potentially toxic metals. "Green plants, in

combination with indigenous soil microorganisms, hold promise for treating hydrocarbon-contaminated soils... Exudates from plant roots serve as a carbon source for heterotrophic microorganisms in the rhizosphere (i.e. active root zone); therefore, rhizosphere microbial populations are typically higher than those in bulk soil. Rhizosphere microbes have been found to degrade certain pollutants more rapidly in the presence of vegetation compared to those in bulk (i.e., nonvegetated) soil. The plant itself, in limited cases, takes up hydrocarbon contaminants; however, most compounds tend to be degraded by soil microbes into harmless products such as CO<sub>2</sub> and H<sub>2</sub>O."

Scientists have found that some plant species can even flourish in petroleum-contaminated soils. One study, however, found that concentrations of 3.5-5.0 TPH (total petroleum hydrocarbons) in soil were detrimental to the growth of perennial ryegrass.

This study evaluated the effects of used motor oil on the plant rhizosphere. Researchers found

- a decreasing trend in germination for all plant species tested as used oil concentration increased
- "leguminous plants appeared to be more resistant to motor oil contamination than non-leguminous species (perhaps because the root system provides for a more self-sufficient soil ecosystem by fixing atmospheric N)"
- soil bacteria, actinomycetes and fungal populations had exponential growth until 50 days, associated with a "readily utilizable C source from the used motor oil"
- microbial numbers returned to precontamination levels as soil microbes depleted the oil
- "greater diversity of bacteria was found at 100 days than at 50 days"
- "gram-positive species predominated in contami-

nated soils where clover, grasses and alfalfa were analyzed"

- "soil respiration increased significantly with the addition of used oil"

### Other papers of interest include:

"Application of GC-MS and GC-AED to the Evaluation of By-Products Formed by Solar Photo-Fenton Degradation of Methyl Tert-Butyl Ether in Water," Aguera, A., Milagros, M., Hernando, D., Malato, S., Caveres, J. and A. Fernandez-Alba, *International Journal of Environmental & Analytical Chemistry*, Vol. 84, No. 1-3, January-March 2004; <http://www.tandf.co.uk/journals/titles/03067319.asp>

"Bioslurping Model for Assessing Light Hydrocarbon Recovery in Contaminated Unconfined Aquifer. I. Simulation Analysis," Yen, H.K., Chang, N.B. and T.F. Lin, *Practice Periodical of Hazardous, Toxic, and Radioactive Waste Management*, April 2003; <http://www.pubs.asce.org/>

"Bioslurping Model for Assessing Light Hydrocarbon Recovery in Contaminated Unconfined Aquifer. II. Optimization Analysis," Yen, H.K., Chang, N.B. and T.F. Lin, *Practice Periodical of Hazardous, Toxic, and Radioactive Waste Management*, April 2003; <http://www.pubs.asce.org/>

"Comparison of BTX Measurement Using a Differential Optical Absorption Spectroscopy and an On-Line Gas Chromatograph System," K.H. Kim, *Environmental Science Engineering*, Vol. 21, No. 2, 2004; <http://www.esemag.com/>

"Development of an Expert System for the Remediation of Petroleum-Contaminated Sites," Chen, Z., Huang, G.H., Chan, C.W., Geng, L.Q. and J. Xia, *Environmental Modeling & Assessment*, Vol. 8, No. 4, December 2003; <http://www.environmental-center.com/magazine/kluwer/enmo/>

"Modeling of Diffusion-Limited Retardation of Contaminants in Hydraulically and Lithologically Nonuniform Media," R. Liedl and T. Ptak, *Journal of Contaminant Hydrology*, Vol. 66, 2003; <http://www.elsevier.com/locate/jconhyd>

"Numerical Simulation of Dual-Phase Vacuum Extraction to Remove Nonaqueous Phase Liquids in Subsurface," Li, J.B., Huang, G.H., Chakma, A. and G.M. Zeng, *Practice Periodical of Hazardous, Toxic, and Radioactive Waste Management*, April 2003; <http://www.pubs.asce.org/>

"Remediation of Contaminated Soils by Surfactant-Aided Soil Washing," W. Chu, *Practice Periodical of Hazardous, Toxic, and Radioactive Waste Management*, January 2003; <http://www.pubs.asce.org/>



## Information sources

### U.S. EPA publications and information

Reports that can be viewed or downloaded at <http://clu-in.org/techpubs.htm> include:

- Cleaning the Nation's Waste Sites: Markets and Technology Trends, 2004 Edition (EPA 542-R-04-015)
- Demonstration of Two Long-Term Groundwater Monitoring Optimization Approaches (EPA 542-R-04-001a)
- Facilitating Brownfields Transactions Using Triad and Environmental Insurance (from the *Journal of Remediation*)
- Pilot Project to Optimize Pump-and-Treat Systems at State-Funded Leaking Underground Storage Tank Sites: Summary Report and Lessons Learned (EPA 542-R-04-019)

- Pilot Project to Optimize Ground Water Remediation Systems at RCRA Corrective Action Facilities: Summary Report and Lessons Learned (EPA 542-R-04-018)
- Technology News and Trends

EPA documents available at <http://www.epa.gov/oust/> include:

- Brownfields Web site
- Corrective Action Performance Measures Data
- Evaluation of Releases from New and Upgraded Underground Storage Tank Systems
- Frequency and Extent of Dispenser Releases at Underground Storage Tank Facilities in South Carolina (EPA-510-R-04-004)

Other EPA documents include:

- Ground Water Use, Value and Vulnerability as Factors in Setting Cleanup Goals, draft, [http://gwtf.clu-in.org/docs/options/gw\\_use\\_paper.pdf](http://gwtf.clu-in.org/docs/options/gw_use_paper.pdf)
- National Institute for Environmental Health Studies (NIEHS) Biosensors for Environmental Monitoring, an Internet seminar, available at <http://clu-in.org/studio>
- Proceedings of the 2004 EPA/NGWA Fractured Rock Conference, State of the Science and Measuring Success in Remediation; papers can be downloaded at <http://clu-in.org/products/siteprof/2004fracrockconf/start.pdf>

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