



# Underground Tank Technology Update

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## Geochemical plume evolution

Cozzarelli and others (2001) have been studying the crude oil plume in Bemidji, Minnesota for more than 16 years. They sampled plume groundwater and aquifer solids on a scale of centimeters, trying to define "small-scale spatial variability of biogeochemical processes that would provide insight into how naturally occurring microbes degrade hydrocarbons in contaminated aquifers and thus improve estimates of hydrocarbon degradation rates." Researchers believe that "the continued evolution of the contaminant plume over time is related to changes in aquifer geochemistry and microbial populations."

### Site description

In 1979 a high-pressure oil pipeline burst, creating two subsurface oil bodies, one (the "north pool") with a layer approximately one meter thick floating on the water table. This plume evolved from aerobic to manganese-reducing to methanogenic conditions and is the focus of the research presented in this article. "The aquifer sediment is glacially deposited, moderately calcareous, silty sand with local lenses of silty material and lenses of coarser sand and pebbles. Sediment mineralogy is roughly 50 percent quartz, 30 percent feldspar, 5 to 6 percent calcite and dolomite and about 5 percent heavy minerals" (Cozzarelli and others, 2001). The water table is six to 10 m below land surface, and groundwater flow velocities near the water table range from 0.05 m/day in fine-grained sediment to 0.50 m/day in coarse-grained sediment.

### Sample collection

Researchers collected groundwater samples from water table wells and cores. The bottom 10 cm of the

core was frozen and plugged, and the core top was connected to  $N_2$  gas for preservation purposes. (For a more detailed description of sample care and analysis, see the original text.) Sediment and water samples were analyzed for the following:

- total iron, ferric iron and ferrous iron
- microbial population
- dissolved oxygen
- hydrocarbons including BTEX
- methane
- dissolved organic carbon

Bekins and others (2001) studied microbial physiological types and the processes that control microbial spatial distribution at the Bemidji site. Along with physiological type, researchers analyzed permeability, pore-water chemistry, nonaqueous oil content and extractable sediment iron.

Researchers used the most probable number (MPN) method to identify the four microbial physiological types:

- aerobes
- iron reducers
- heterotrophic fermenters
- methanogens

### Results

Analyses of groundwater and cores allowed researchers to determine the following concerning the evolution of the contaminated plume, the anoxic zone, Fe distribution and the methanogenic zone:

*The contaminated plume:*

- rate of BTEX transport over the past 11 years has been slower than predicted by conservative transport; plume movement was about 8 m/year from 1987 to 1992, then slower from 1992 to 1995

- examination of core water chemistry from the anoxic plume center and plume edge indicated that subtle changes with time occur in plume geometry
- hydrocarbon concentration at the plume center decreased from 1988 to 1992
- low concentrations of BTEX,  $CH_4$  and  $Fe^{2+}$  at the plume base in 1993 indicated a plume thickness of 1 to 1.5 m
- concentrations of  $Fe^{2+}$ ,  $CH_4$  and BTEX determined in core fluids indicated that the plume is increasing in vertical thickness over time

*The anoxic zone:*

- in 1992 an anoxic plume extended approximately 80 m downgradient from the crude oil; this was defined on the basis of DO analysis
- the zone containing anoxic groundwater and high  $Fe^{2+}$  and BTEX concentrations was spreading
- from 1992 to 1995, the zero DO contour line moved several meters farther downgradient
- within the anoxic plume, the zone with high dissolved-iron concentrations increased in vertical extent over time, and the maximum benzene, toluene, ethylbenzene and xylene (BTEX) concentrations have also spread in this zone
- at the anoxic plume center, maximum concentrations of methane and iron are approximately the same; however, depths over which these high concentrations exist have increased

*Iron distribution:*

- rate of movement of the high dissolved  $Fe^{2+}$  plume was approximately 3 m/yr
- the downgradient extent of the  $Fe^{2+}$  and BTEX plumes has not noticeably changed, indicating that supply of compounds from upgradient-contaminated water is balanced by processes that impede

movement of these compounds at the downgradient edge

- movement of the dissolved iron plume is controlled by the balance between microbial iron reduction and precipitation, sorption and/or oxidation of  $\text{Fe}^{2+}$ 
  - depth profiles of  $\text{Fe(III)}$  concentrations from several cores show that  $\text{Fe(III)}$  is depleted, relative to background, in the anoxic zone and underneath the oil due to microbial reduction of iron coupled to hydrocarbon degradation
  - at the edge of the anoxic zone, reduced iron that has been transported downgradient is oxidized and precipitates; in this oxic/anoxic transition zone, sediment  $\text{Fe(III)}$  accumulates and concentrations reach high levels, significantly greater than background
- prolonged iron reduction in the plume has caused measurable temporal changes in the sediment iron chemistry within the anoxic plume;  $\text{Fe(III)}$  is being depleted from the sediment while  $\text{Fe(II)}$  is being deposited; some reduced iron is being stored in the plume sediments as  $\text{Fe(II)}$ -bearing minerals (e.g. ferrous calcite), while some  $\text{Fe(II)}$  might be present as organically bound iron
- vertical differences in sediment iron chemistry are observed because of the reoxidation and precipitation of iron that occurs near the water table as the anoxic plume mixes with oxygenated recharge water, resulting in higher concentrations of  $\text{Fe(III)}$  near the top of core profiles
- availability of reducible  $\text{Fe(III)}$  in sediments is important for continued biodegradation in the contaminant plume

*Methanogenic zone:*

- areas of high contamination near the oil body contained the highest methane concentrations and

greatest numbers of culturable methanogens

- methanogenesis occurs concurrent with iron reduction in thin layers of sediment (as thin as 25 cm) beneath the oil body, indicating that redox zones evolve on a small spatial scale and that terminal electron-accepting processes are not exclusive
- downgradient, within the anoxic plume, the evolution of a methanogenic zone would likely take longer, since a greater amount of readily reducible  $\text{Fe(III)}$  is still available for iron reduction

Researchers have found that hydrocarbon concentrations vary over space and time and that redox zones can have a significant effect on hydrocarbon fate and transport. Transport is dependent on compound degradability. Spreading of dissolved methane and iron plumes between 1993 and 1997 indicates that iron reduction and methanogenesis continue to be important processes in the aquifer close to the oil body. Previously undetected hydrocarbons, such as ortho-xylene, are migrating in narrow zones in the aquifer as the microbial degradation reactions shift from iron reduction to methanogenesis. The availability of an electron acceptor, such as  $\text{Fe(III)}$  oxides, thus has a significant impact on hydrocarbon transport downgradient. Identification of the biogeochemical zones is essential to predict long-term impact of hydrocarbon spills on aquifer chemistry and to assess the potential for hydrocarbon transport through the aquifer.

### Evolution of microbial populations

Bekins and others (2001) found microbial type to be strongly controlled by aquifer properties and crude oil location. Data from three vertical profiles through the anaerobic portion of the contaminated aquifer showed a progression from iron-reducing to methanogenic microbial populations. "These locations contain lower numbers of iron reducers and increased numbers of fermenters with detectable methanogens. Methanogenic condi-

tions exist both in the area contaminated by nonaqueous oil and also below the oil where high hydrocarbon concentrations correspond to local increases in aquifer permeability" (Bekins and others, 2001). Whether or not an area becomes methanogenic depends primarily on contaminant flux either from local dissolution or by advective transport. Another factor besides flux that affects progression of microbial degradation process includes the sediment  $\text{Fe(II)}$  content. With a more detailed description of geochemical conditions and microbial physiologic zones, researchers hope to better predict the fate and transport of contaminant plumes.

### Results and implications

Researchers found that "high flux zones where methanogenic conditions develop are laterally continuous; they may be very thin vertically, making them difficult to locate" (Bekins and others, 2001). Cozzarelli and others (1999) noted that thin redox zones at a gasoline-contaminated site resulted in mixed geochemical indicators in well-water samples...this aspect of plume behavior complicates the use of aqueous geochemical indicators to infer terminal electron accepting processes. Assays of microbial populations attached to the sediments may provide a better indication of the microbial physiologic processes at a given location than do aqueous redox indicators.

Because microbial analyses are costly, Bekins and others (2001) suggest using other indicators such as dissolved  $\text{Fe(II)}$  to locate horizons where microbial populations change. At the Bemidji site methanogenic zones generally correspond to centers of peak concentrations in dissolved  $\text{Fe(II)}$ . "A strategy of analyzing dissolved iron in the field from pore waters drained from cores over 15-cm intervals proved useful in formulating our 1997 sediment sampling scheme for microbial analyses. Note that the activities of the microbial populations attached to the sediments as measured by the MPN meth-

ods were ultimately used to define the microbial zones. The field-dissolved Fe(II) concentrations were simply a successful field proxy for choosing sample locations. At each site, a different proxy would need to be identified. The key idea is that a search for correlations between microbial population changes and small-scale variations in either pore-water chemistry or sediment properties may be useful for formulating a strategy that limits the number of required microbial analyses."

Researchers conclude that "Combined studies of microbial populations together with physical and chemical conditions in the Bemidji aquifer have provided insights into the long-term behavior of petroleum hydrocarbon plumes. The dominant physiological type of the microbial population changes from iron-reducing to methanogenic over vertical scales as small as 25 cm. Near the oil body, methanogenic zones have evolved in two high-flux areas. One zone is found within the nonaqueous oil where high fluxes are due to local dissolution and diffusion of contaminants from the oil. A second zone exists along high permeability horizons in the laterally migrating contaminant plume. Methanogenic conditions are less advanced than below the oil at a distance of 65 m downgradient from the oil, where there are lower numbers of methanogens. The spatial correspondence between methanogenic zones and peaks in hydrocarbon flux suggests that the methanogenic zone in the plume is growing laterally along a narrow, connected, high-permeability pathway.

Results presented by Cozzarelli and others (2001) show that the growth of the methanogenic zone results in a slow expansion of the hydrocarbon plume. A computer simulation of the plume predicted an initial decrease in concentrations between 5 and 10 years after the spill at an observation well 36 m downgradient of the oil body, followed by an increase in simulated concentrations between 10 and 15 years as iron oxides are depleted and iron-reducing bacteria decrease

in number. At sites with large petroleum hydrocarbon plumes from persistent nonaqueous sources, risk analyses should account for expansion of methanogenic conditions along narrow, connected high-permeability pathways" (Bekins and others, 2001).

## References

Bekins, B.A., Cozzarelli, I.M., Godsy, E.M., Warren, E., Essaid, H.I. and M.E. Tuccillo, "Progression of Natural Attenuation Processes at a Crude Oil Spill Site: II. Controls on Spatial Distribution of Microbial Populations," *Journal of Contaminant Hydrology*, Vol. 53, 2001; <http://www.elsevier.com/locate/jconhyd>.

Cozzarelli, I.M., Bekins, B.A., Baedecker, M.J., Aiken, G.R., Eganhouse, R.P. and M.E. Tuccillo, "Progression of Natural Attenuation Processes at a Crude Oil Spill Site: I. Geochemical Evolution of the Plume," *Journal of Contaminant Hydrology*, Vol. 53, 2001; <http://www.elsevier.com/locate/jconhyd>.

Cozzarelli, I.M., Herman, J.S., Baedecker, M.J. and J.M. Fischer, "Geochemical Heterogeneity of a Gasoline-Contaminated Aquifer," *Journal of Contaminant Hydrology*, Vol. 40, 1999; <http://www.elsevier.com/locate/jconhyd>.

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## Borden plume revisited

In 1988 researchers injected "a slug of groundwater spiked with dissolved oxygenate-containing gasoline below the water table." Researchers monitored for 16 months the migration of the BTEX, MTBE and Cl<sup>-</sup> (tracer) as it moved through a three-dimensional sampling network. "The mass of BTEX compounds in the plume diminished significantly with time due to intrinsic biodegra-

tion, whereas MTBE showed only a small decrease in mass. In 1995-1996, a comprehensive groundwater sampling program was undertaken to define the mass of MTBE still present in the aquifer. The plume had migrated into an unmonitored section of the aquifer by this time, thus numerical modeling and geostatistical methods were applied to define an optimal sampling grid. Field workers used a drive-point profiling system to obtain more than 500 groundwater samples for plume delineation. Numerical modeling, with no consideration of degradation, predicted maximum concentrations in excess of 3,000 µg/l; yet, field sampling found maximum concentrations of less than 200 µg/l. A mass balance for the remaining MTBE mass in the aquifer eight years after injection showed that only 3 percent of the original mass remained" (Schirmer and others, 2003). Characteristics of the Borden aquifer include the following:

- a relatively homogeneous, unconfined aquifer composed of clean, well-sorted, fine- to medium-grain sand
- bulk density of 1.81 g/cm<sup>3</sup>
- porosity of 0.33
- average organic carbon content of 0.02 percent
- hydraulic conductivity ranging from 4.5 x 10<sup>-5</sup> to 1.49 x 10<sup>-4</sup>
- groundwater flow of 9 cm/day
- average groundwater temperature of 10°C
- aerobic, with DO (dissolved oxygen) ranging from < 0.1 to 8.5 mg/l

As to the fate of the MTBE, researchers hypothesize the following:

- because the contaminant slug was introduced 1.5 m below the water table, sorption, volatilization and abiotic degradation were likely not significant attenuation processes

- the Borden aquifer is underlain by an 8-meter-thick clayey till aquitard that has a calculated Darcy flux of about 3.3 mm/year; little of the missing MTBE would have been lost to/through the aquitard
- again, because the slug was introduced 1.5 m below the water table, researchers did not expect plant uptake to be a potential contributor to MTBE attenuation; 90 percent of a tree root's mass is typically within 0.6 m of the soil surface, and root growth may cease when air-filled pore space falls below 2 percent

Using microcosm studies, researchers initiated a step-wise elimination of most other attenuation processes.

### Microcosm studies

Microcosms consisted of aquifer material cored from two sites at the Borden field site: one uncontaminated, and the other contaminated. Other features of the microcosms included the following:

- amendments were added as necessary
- aquifer materials normally contained ambient levels of oxygen
- air inside the headspace also provided oxygen to the system

Researchers carried out three experiments using these microcosms:

- experiment one investigated the potential for MTBE biodegradation under various environmental conditions
- experiment two tested the capacity for MTBE cometabolism
- experiment three compared biodegradation of MTBE with its potential daughter product, tert-butanol (TBA)

*Experiment 1: MTBE degradation potential.* Microcosms contained 150 g of aquifer solids and 200 ml of

MTBE-amended groundwater. Solids were either from the shallow or deep aquifer. Microcosm types created included the following:

- sterile control (using shallow and deep solids)
- unaltered (using shallow and deep solids)
- NH<sub>4</sub>-amended (using deep solids only)
- low DO (using deep solids only)
- low pH (using deep solids only)
- biomass-augmented (using shallow and deep solids only)

Researchers examined the microcosms at various times, generally around days 267, 363 and 666.

*Experiment 2: MTBE cometabolism potential.* These microcosms were composed of shallow aquifer material (25 g) and groundwater (70 ml) that had never been exposed to MTBE. Microcosms were consequently amended with an aqueous stock solution of MTBE (to about 3.8 mg/l) and 19-28 mg/l of primary substrate injected as neat compound. The primary substrates tested were

- n-pentane
- isopentane
- hexane
- cyclohexane
- 3-methylpentane
- toluene
- methane
- methanol

After seven days, a mineral medium was added to each microcosm, and after 17 days, with the exception of the cyclohexane-spiked microcosm, microcosms were opened to the atmosphere. Microcosms containing pentanes or hexanes were re-amended a second time. After day 53, researchers sampled microcosms.

*Experiment 3: MTBE vs. TBA biotransformation.* These microcosms consisted of 20 g of deep core and 50 ml of groundwater. Researchers amended groundwater with MTBE or TBA, created sterile controls and analyzed samples soon after their creation.

### Analytical methods

Researchers analyzed MTBE, TBA and tert-butyl formate (TBF) from experiment 1, using direct aqueous injection-gas chromatography-mass spectroscopy. For experiment 3, MTBE and TBA were measured using a solid-phase microextraction (SPME) technique coupled to gas chromatography.

### Summary of results

The microcosms were intended to test for the following conditions:

- low DO conditions that might typify microaerophilic conditions and zones through which the plume may have passed
- biomass-augmented microcosms, to offset the possibility that MTBE-degrading microorganisms were rare in the aquifer
- moderately acidic conditions, because elsewhere such conditions reportedly enhanced MTBE degradation
- methane- and ammonium-oxidizing conditions, "as the oxygenases involved in these two activities are renowned for a broad substrate range"

Some of these conditions could typify deeper situations in the aquifer. In addition an anaerobic leachate plume existed near the aquitard, which is a potential source of ammonium, methane or acidic water.

Results and conclusions are as follows:

- for three of the four microcosms, a MTBE loss of greater than 50 percent was noted by day 68; no further loss ensued after day 267

- on day 363 additional MTBE was added to active microcosms, but no re-initiation of activity occurred
- neither TBA nor TBF were detected in microcosms
- on day 666, MTBE persisted at levels similar to the sterile controls in most microcosms; in three microcosms (two originally low DO, the third, biomass-augmented prepared with deep material), MTBE was depleted
- in the cometabolic tests, MTBE loss was detected in the microcosm containing C<sub>5</sub> and C<sub>6</sub> alkanes; toluene, methanol, methane and MTBE alone did not support MTBE loss
- some conversion of MTBE to TBA and a decrease in measured dissolved oxygen suggests that MTBE biodegradation is favored by aerobic conditions
- TBA degradation would have been indicated by its degradation products of acetone and isopropanol, neither of which were found; further experimentation indicated that TBA degraded at high rates but did not accumulate to detectable levels
- TBA degradation rates can be two orders of magnitude higher than MTBE, which may explain why TBA was never measured in the field
- lack of measurable TBA in the field may reflect the fact that researchers looked at only a remnant of the plume; most degradation had occurred upgradient, and if TBA accumulated, it subsequently degraded
- TBA was detected in column experiments
- no particular environmental manipulation led to initiation of MTBE degradation in the microcosms
- results imply no enrichment of MTBE-degrading community in the tested deep aquifer materials, although material was cored from an area through which the MTBE plume passed; researchers suggest
  - field workers did not sample soil within the exact plume path

- exposure to the slug of MTBE-containing water may have been short-term; if so, significant development of MTBE-degrading cells did not occur
- MTBE levels may have been insufficient at the sampled point in the aquifer to allow significant population development, as most MTBE had been degraded upgradient
- observed lag periods (related to MTBE degradation) may reflect the slow growth of a population originating from a very small number of cells, or a fortuitous genetic change plus selective pressure had led to an MTBE-degrading capacity
- readily initiated cometabolism of MTBE in the field suggests MTBE removal could be enhanced with C<sub>5</sub> and C<sub>6</sub> alkanes

### Reference

Schirmer, S., Butler, B.J., Church, C.D., Barker, J.F. and N. Nadarajah, "Laboratory Evidence of MTBE Biodegradation in Borden Aquifer Material," *Journal of Contaminant Hydrology*, Vol. 60, p. 229-249, 2003; <http://www.elsevier.com/locate/jconhyd>



### Identifying MTBE biodegradation in groundwater with carbon isotopes

Researchers studied the carbon isotopic (<sup>13</sup>C/<sup>12</sup>C) changes of MTBE in groundwater along a flow path at a site in New Jersey. Their primary objective was to determine the extent to which isotope ratios increase with a reduction in MTBE. Their second objective was to compare the <sup>13</sup>C/<sup>12</sup>C enrichment of MTBE found at the field scale to that found in laboratory microcosms. This article summarizes the work by Kolhatkar and others (2002), the first researchers to use MTBE <sup>13</sup>C/<sup>12</sup>C

data in groundwater and laboratory microcosm studies to demonstrate anaerobic MTBE biodegradation.

A plume of dissolved MTBE that is temporally or spatially stable or shrinking is generally not sufficient evidence to invoke MNA (monitored natural attenuation) as a remedial alternative. Other traditional indicators of biodegradation, such as electron acceptor depletion (dissolved oxygen, nitrate, sulfate) or elevated concentrations of biodegradation products (ferrous iron, dissolved methane and total alkalinity) can result from degradation of other carbon sources. Researchers recently used compound-specific carbon isotope analyses (<sup>13</sup>C/<sup>12</sup>C expressed in δ<sup>13</sup>C ‰ notation) to demonstrate the existence of aerobic MTBE biodegradation.

### Previous studies of MTBE biodegradation

Previous studies of MTBE biodegradation include the following:

- natural biodegradation of MTBE under iron-reducing conditions in the bed sediments of a stream that received groundwater impacted by a gasoline spill; first-order biodegradation rate was very slow, 0.06/year; when biologically available iron was added to aquifer sediments, MTBE biodegradation rate increased
- slow, natural MTBE biodegradation in bed sediments of freshwater streams that were impacted by gasoline releases; under sulfate-reducing conditions, 9 to 20 percent of MTBE was degraded to carbon dioxide after 166 days of incubation; under methanogenic conditions, approximately 8 percent of MTBE was degraded to TBA (tertiary butyl alcohol)
- rapid, extensive MTBE biodegradation in methanogenic groundwater at a JP-4 jet fuel spill; anaerobic MTBE biodegradation was confirmed in laboratory microcosm studies using soil and groundwater

## Carbon isotopes as an indicator parameter

Carbon 13 ( $^{13}\text{C}$ ) is a stable isotope of carbon that is naturally present in the atmosphere at about one part in 111. "The extra neutron in the C 13 nucleus makes the bonds to  $^{13}\text{C}$  atoms slightly stronger than analogous bonds to the more abundant carbon 12 ( $^{12}\text{C}$ ). Microbial enzymes will discriminate (statistically) between the  $^{12}\text{C}$  and  $^{13}\text{C}$  compounds because of the slight differences in bond strength and preferentially degrade the lighter  $^{12}\text{C}$ , enriching the contaminant in  $^{13}\text{C}$ . Thus,  $^{12}\text{C}$  would be expected to be greater near the source area; along the flow path, where more opportunity for biodegradation exists,  $^{13}\text{C}$  should be enriched (Day and others, 2002).

According to Kolhatkar and others (2002), "Compound-specific stable carbon isotopic ratios ( $^{13}\text{C}/^{12}\text{C}$ ) have a potential to demonstrate in-situ biodegradation of organic contaminants. Depending upon the source and release history, contaminant molecules have a particular  $^{13}\text{C}/^{12}\text{C}$  ratio. This ratio is reported in  $\delta^{13}\text{C}$  (‰) notation as follows:

$$\delta^{13}\text{C} = (R_{\text{sample}}/R_{\text{standard}} - 1) \times 1000$$

where  $R_{\text{sample}}$  and  $R_{\text{standard}}$  represent the  $^{13}\text{C}/^{12}\text{C}$  ratios of the sample and the international standard, respectively. Physical, chemical and biological reactions normally proceed faster and/or have lower bond activation energies for the lighter isotope,  $^{12}\text{C}$ , compared to the heavier isotope,  $^{13}\text{C}$ . This results in the reaction products becoming enriched in  $^{12}\text{C}$  while the residual substrate is enriched in  $^{13}\text{C}$ . The observed difference between the  $\delta^{13}\text{C}$  is that the  $\delta^{13}\text{C}$  values of the original and the residual substrate are referred to as isotopic fractionation...Increase in  $\delta^{13}\text{C}$  of a substrate associated with decreased substrate concentrations is indicative of substrate biotransformation" (Day and others, 2002). Physical processes such as dissolution, advective-disper-

sive transport or sorption will not significantly change isotope ratios.

Other studies involving  $^{13}\text{C}/^{12}\text{C}$  have indicated the following:

- extent of fractionation due to microbial biodegradation in a study of BTEX biodegradation and higher alkylbenzenes showed significantly greater fractionations than that due to abiotic processes, such as dissolution, sorption and volatilization
- analysis of aerobic MTBE biodegradation of 95 to 97 percent indicated  $\delta^{13}\text{C}$  enrichments from 5.1 ‰ to 6.9 ‰
- laboratory experiments of aerobic MTBE biodegradation reported  $^{13}\text{C}$  enrichments of up to 8.1 ‰ with 99.7 percent MTBE biodegradation

(Kolhatkar and others, 2002)

## Site and plume description

The researchers' carbon isotope study site is a gasoline station in New Jersey. Site characteristics include the following:

- alternating layers of medium to coarse sand
- groundwater depth varying 0.3 to 1.0 m
- hydraulic conductivity ranging from 0.37 to 0.91 m/d
- hydraulic gradient varying from 0.004 to 0.015 m/m
- groundwater velocity ranging from 3 to 26 m/year

A gasoline release was detected in 1990, but field workers did not collect samples until 1999, 2000 and 2001. Researchers used mass spectrometry to analyze samples and found that the data suggested "a stable or possibly shrinking MTBE plume where MTBE concentrations attenuate by a factor of 40 within 18 m of groundwater travel" (Kolhatkar and others, 2002).

## Microcosms

Researchers constructed microcosms using aquifer material collected near a monitoring well. Sediment in the microcosms contained measurable concentrations of MTBE, TBA and BTEX; to some microcosms, researchers added additional MTBE and BTEX. Ethanol was added to other microcosms. Researchers also set up abiotic controls. Data from the microcosms and monitoring wells were compared.

## Data analysis

Researchers used a simplified form of the Rayleigh equation to describe carbon isotopic fractionation due to MTBE biodegradation:

$$\delta^{13}\text{C} = \delta^{13}\text{C}_0 + \epsilon \times \ln ([\text{MTBE}]/[\text{MTBE}]_0)$$

where

$\delta^{13}\text{C}$  and  $\delta^{13}\text{C}_0$  represent the isotopic composition of MTBE at  $t$  and  $t = 0$

$\epsilon$  is the isotopic enrichment factor for carbon in MTBE (Kolhatkar and others, 2002)

[ $\delta^{13}\text{C}$  is read "delta per mil" or " $\delta$  ‰". Fossil hydrocarbons are depleted in  $^{13}\text{C}$  relative to the present atmosphere ( $\delta^{13}\text{C} = -7$  ‰). A  $^{13}\text{C}$  enrichment would correspond to a trend toward less negative  $\delta^{13}\text{C}$  values (Day and others, 2002).]

Kolhatkar and others (2002) assert that long-term monitoring data from monitoring wells show that the concentrations of dissolved MTBE in the plume have stabilized and started to decline. "The plume is receding back toward the source area. These reductions in concentration with distance from the source could be attributed to dilution and dispersion or to natural biodegradation. If natural biodegradation of MTBE is an important process in groundwater, then  $\delta^{13}\text{C}$  of MTBE in groundwater should increase with distance from the presumed source."

Researchers did find that MTBE in groundwater became increasingly enriched in  $\delta^{13}\text{C}$  as the concentration decreased along the groundwater flow line, a pattern observed during all sampling events.

"The values of isotopic enrichment factors observed in the field (-8.10 ‰) and in the laboratory (-9.16 ‰) at this site are comparable. The enrichment factor observed in the laboratory microcosms ( $\epsilon_{\text{lab}}$ ) is determined entirely by MTBE biodegradation. On the other hand, the 'apparent' isotopic enrichment factor estimated from the groundwater data ( $\epsilon_{\text{field}}$ ) represents the combined effect of the variability in  $\delta^{13}\text{C}$  of MTBE in the release(s), and the net effect of biodegradation and other abiotic attenuation processes (dilution, dispersion and volatilization) in the plume. If it is assumed that isotopic enrichment associated with abiotic processes is negligible compared to that occurring during biodegradation, then the ratio of  $\epsilon_{\text{field}}$  to  $\epsilon_{\text{lab}}$  can be used to define the relative importance of biodegradation and the other abiotic processes in the plume. Theoretically, the maximum value of  $\beta$  is 1. Natural attenuation in a plume where  $\beta \sim 1$  will likely be dominated by biodegradation, whereas a plume with  $\beta \ll 1$  would indicate that abiotic processes are more important than biodegradation" (Kolhatkar and others, 2002).

At this site, where the groundwater plume is anaerobic,  $\beta = 0.88$ . Authors believe "this is the first site to demonstrate rapid natural biodegradation of MTBE under anaerobic conditions at a gasoline spill site. These are also the first set of data correlating decrease in MTBE concentrations in the groundwater and laboratory microcosms to an increase in  $\delta^{13}\text{C}$  of MTBE."

### Measuring small isotopic differences

Day and others (2002) point out that "The differences in biodegradation rates between molecules with different isotopes are relatively small; therefore, specialized analytical equipment is required to measure shifts in iso-

tope ratios...The instrument [normally used] consists of a gas chromatograph coupled via a combustion interface to an isotope-ratio mass spectrometer. With this system, isotope ratios of individual contaminants in complex mixtures can be analyzed since the compounds are first separated before they are combusted to  $\text{CO}_2$ , the form in which carbon isotope ratios are usually measured by isotope-ratio mass spectrometry."

### Future applications

If a plume is stable or shrinking, then "compound-specific stable carbon isotopic analyses could be used to test the hypothesis that concentration reduction is due to biodegradation in a cost-effective and expeditious manner. It is noteworthy that changes in  $\delta^{13}\text{C}$  of MTBE indicate MTBE transformation and not complete mineralization. The simplified Rayleigh model could be applied to a number of  $\delta^{13}\text{C}$  and concentration measurements of MTBE. A plot of  $\delta^{13}\text{C}$  vs. natural logarithm of MTBE concentration on these data could be used to evaluate the effectiveness of in-situ or ex-situ bioremediation technologies for MTBE. As the data indicate, the changes in  $\delta^{13}\text{C}$  of MTBE due to biodegradation at this site are considerably greater than the variability in  $\delta^{13}\text{C}$  of MTBE based on the differences in gasoline source (-28.3 ‰ to -31.6 ‰)" (Kolhatkar and others, 2002).

The authors conclude that

- extensive MTBE biodegradation would exceed the "noise" resulting from source variation or multiple releases, yet quantifying  $\delta^{13}\text{C}$  where MTBE is highly biodegraded and in low concentrations may be difficult
- higher or lower enrichment factors may result from differences in pathways of anaerobic vs. aerobic MTBE biodegradation and may be a function of bacteria type present
- the possibility of acid-hydrolysis of MTBE on clay

surfaces—a potential abiotic MTBE transformation—would be important to understand

- TBA data analysis indicated negligible changes in  $\delta^{13}\text{C}$ ; TBA, however, can be either a daughter product of MTBE biotransformation or part of the original release

### References

- Day, M., Arvena, R., Hunkeler, D. and T. Gulliver, "Application of Carbon Isotopes to Document Biodegradation of tert-Butyl Alcohol Under Field Conditions," *Contaminated Soil, Sediment and Water*, July/August 2002; <http://www.aehsmag.com>.
- Kolhatkar, R., Kuder, T., Philip, P., Allen, J. and J.T. Wilson, "Use of Compound-Specific Stable Carbon Isotope Analyses to Demonstrate Anaerobic Biodegradation of MTBE in Groundwater at a Gasoline Release Site," *Environmental Science & Technology*, Vol. 36, No. 23, 2002; <http://www.pubs.acs.org>.



### First-order rate constants for monitored natural attenuation studies

By Charles J. Newell, Hanadi S. Rifai, John T. Wilson, John A. Connor, Julia A. Aziz and Monica P. Suarez

This article is a summary of a recent U.S. EPA groundwater issue paper. The issue paper describes the three attenuation rate constants commonly used in monitored natural attenuation (MNA) studies, and how and when to apply them. These rate constants are

- concentration vs. time
- concentration vs. distance
- biodegradation rate constant

## Why are attenuation rate constants important?

Monitored natural attenuation (MNA) refers to the reliance on natural attenuation processes to achieve site-specific remediation objectives within a reasonable time frame. Natural attenuation processes include a variety of physical, chemical and/or biological processes that act without human intervention to reduce the mass or concentration of contaminants in soil and groundwater. These in-situ processes include biodegradation, dispersion, dilution, sorption, volatilization, radioactive decay and chemical or biological stabilization, transformation, or destruction of contaminants.

Remediators can assess the impact of natural attenuation processes by evaluating the rate that contaminant concentrations decrease either spatially or temporally at a site. Recent guidelines issued by the U.S. EPA and the American Society for Testing and Materials have endorsed the use of site-specific attenuation rate constants for evaluating natural attenuation processes in groundwater.

The technical literature contains numerous guidelines regarding methods for deriving site-specific attenuation rate constants based on observed plume concentration trends. Other sources, such as the BIOSCREEN and BIOCHLOR natural attenuation models, include use of first-order rate constants for simulating attenuation of dissolved contaminants once they leave the source, and the attenuation of the source itself. Many references, however, do not distinguish between the different types of rate constants and their appropriate application in evaluating natural attenuation processes. The objective of this article is to address this gap by describing the derivation, significance and appropriate use of the three key types of attenuation rate constants listed above.

## First-order attenuation rate constants

The three types of first-order rate constants, all given in units of inverse time (e.g., per day), are described below.

*The concentration vs. time attenuation rate constant* is derived as the slope of the natural log concentration vs. time curve measured at a selected monitoring location.

*The concentration vs. distance attenuation rate constant* is derived by plotting the natural log of the concentration vs. distance and, if determined to match a first-order pattern, calculating the rate as the product of the slope of the transformed data plot and the groundwater seepage velocity.

*The biodegradation rate constant, ( $\lambda$ )*, can be derived by a variety of methods, such as comparison of contaminant transport vs. transport of a tracer, or more commonly, calibration of solute transport model to field data.

## Distinctions between rate constants

To interpret the past behavior of plumes and to forecast their future behavior, we need to describe plume behavior in both space and time. Long-term monitoring data from wells that are distributed throughout the plume must be collected, then we can possibly identify the three constants. Briefly:

- the concentration vs. time rate constant describes plume behavior at one point in space
- the concentration vs. distance rate constant describes the behavior of the entire plume at a point in time
- the biodegradation rate constant is usually applied over both time and space but applies to one attenuation mechanism

Under appropriate conditions each of the three constants can assist in site-specific evaluation and quantification of natural attenuation processes. Each term

is identified as an "attenuation rate," but because the terms differ in significance and application, data users need to understand the potential for misapplication of each rate, as summarized below.

*Concentration vs. time rate constants* (Figure 1). A rate constant derived from a concentration vs. time (C vs. T) plot at a single monitoring location provides information regarding the potential plume lifetime at that location but cannot be used to evaluate contaminant mass distribution within the groundwater system. The C vs. T rate constant at a location within the source zone represents the persistence in source strength over time and can be used to estimate the time required to reach a remediation goal at that particular location. To adequately assess an entire plume, monitoring wells must be available that adequately delineate the entire plume, and an adequate record of monitoring data must be available to calculate a C vs. T plot for each well. At most sites, attenuation rate at the source (due to weathering of residual source materials such as NAPLs) is slower than attenuation rate of materials in groundwater; thus, concentration profiles in plumes tend to retreat back toward the source over time. In this circumstance, plume lifecycle is controlled by source attenuation rate and can be predicted by the C vs. T plots in the most contaminated wells. At some sites, source attenuation rate is rapid compared to attenuation rate in groundwater. This pattern is most common when contaminants are readily soluble but not biodegradable in groundwater. In this case, source attenuation rate, as predicted by a C vs. T plot, will underestimate plume lifetime.

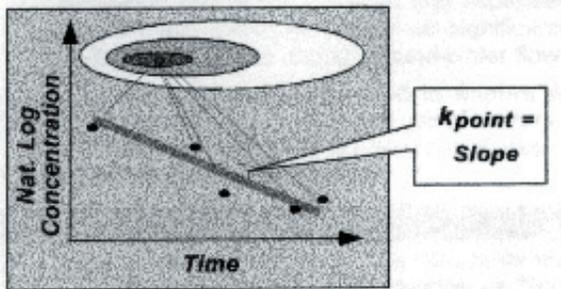


Figure 1. Determining concentration vs. time rate constant ( $k_{point}$ ).

Concentration vs. distance rate constants (Figure 2). Attenuation rate constants derived from concentration vs. distance (C vs. D) plots serve to characterize contaminant mass distribution within space at a given point in time. A single C vs. D plot provides no information with regard to the variation of dissolved contaminant mass over time; it therefore cannot be employed to estimate the time required for the dissolved plume concentrations to be reduced to a specified remediation goal. This rate constant incorporates all attenuation parameters (sorption, dispersion, biodegradation) for dissolved constituents after they leave the source. Use of the rate constant derived from a C vs. D plot (characterization of contaminant mass over space) for this purpose (to characterize contaminant mass over time) will provide erroneous results. The C vs. D-based rate constant indicates how quickly dissolved contaminants are attenuated once they leave the source but provides no information on how quickly a residual source zone is being attenuated. Most sites with organic contamination will have some type of continuing residual source zone, even after active remediation, making the C vs. D rate constant inappropriate for estimating plume lifetimes here.

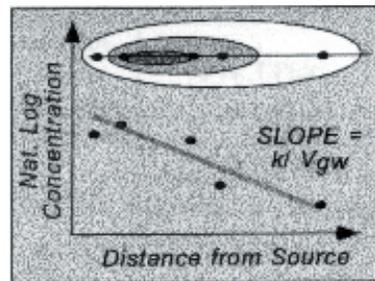


Figure 2. Determining concentration vs. distance rate constant ( $k$ ).

Biodegradation rate constant (Figure 3). Another type of error occurs if a C vs. D constant is used as the biodegradation rate term ( $\lambda$ ) in a solute transport model. The attenuation rate constant derived from the C vs. D plot already reflects the combined effects of contaminant sorption, dispersion, and biodegradation. Consequently, use of a C vs. D rate constant as the biodegradation rate within a model that separately accounts for sorption and dispersion effects will significantly overestimate attenuation effects during groundwater flow.

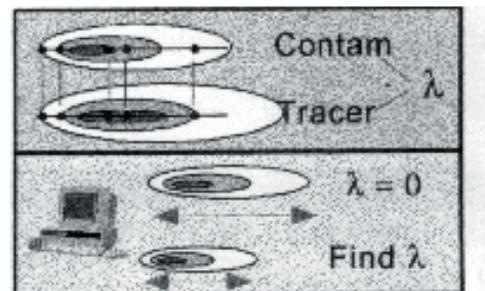


Figure 3. Determining biodegradation rate constant ( $\lambda$ ).

## Rate constants and half-lives

Both first-order rate constants and attenuation half-lives represent the same process, first-order decay. Some environmental professionals prefer to use rate constants (in unit of per time) to describe the first-order decay process, while others prefer half-lives. These two terms are linearly related by:

$$\text{Rate constant} = 0.693 / [\text{half-life}]$$

$$\text{Half-life} = 0.693 / [\text{rate constant}]$$

For example, a 2-year half-life is equivalent to a first-order rate constant of 0.35/year.

## Use of attenuation rate constants in natural attenuation studies

Attenuation rate constants may be used for the following three purposes:

- to demonstrate plume attenuation and ascertain that contaminants are being attenuated within the groundwater system
- to define plume trends and determine if the affected groundwater plume is expanding, showing relatively little change, or shrinking
- to define plume duration and estimate the time required to reach groundwater remediation goals by natural attenuation alone

Site characterization and monitoring data are typically used for estimating attenuation rates. These calculated rates may be expressed with respect to either time or distance from the source. Time-based estimates are used to predict the time required for MNA to achieve remediation objectives, and distance-based estimates provide an evaluation of whether a plume will expand, remain stable or shrink.

Appropriate use of the various attenuation rate constants for evaluation of plume attenuation, trends and duration is shown in Table 1.

Use of rate constant

Rate constant	Analysis method	Significance	Plume attenuation	Plume trends	Plume duration
Point attenuation	C vs. T plot	Reduction in contaminant concentration over time at a single point	No	No*	Yes
Bulk attenuation rate	C vs. D plot	Reduction in dissolved contaminant concentration with distance from source	Yes	No*	No
Biodegradation rate	Model calibration, tracer studies, calculations	Biodegradation rate for dissolved contaminants after leaving source, exclusive of advection, dispersion, etc.	Yes	No	No

\*Although assessment of an attenuation rate constant at a single location does not yield plume attenuation or plume trend information, an assessment of general trends of multiple wells over the entire plume is useful to assess overall plume attenuation and plume trends.

Table 1. Summary of first-order rate constants for natural attenuation studies.

In general, any of the three rate constants can indicate ongoing attenuation. Concentration vs. time rate constants can be used to estimate contaminant duration at a particular location. Concentration vs. time rate constants for wells encompassing the entire plume can be used to identify overall trends and predict plume duration. Concentration vs. distance rate constants and biodegradation rate constants can be used to project contaminant attenuation rate along the flow path in groundwater and predict spatial plume extent.

### Other types of rate constants

*Mass-based rate constants.* The previous discussion focused on concentration-based rates. It is also possible to calculate mass vs. time constants and mass vs. distance rate constants. In practice, these rates would be very similar to the concentration-based rates.

*Mass vs. time rate constant.* This constant compares changes in the total mass of contaminants in the plume over time. A Thiessen polygon network can be used to weigh the concentration data from the site's wells to derive a comprehensive estimate of the contaminant mass in the plume at any sampling round. Mass vs. time decay rates (in units of inverse time) are estimated

by plotting the natural log of total dissolved mass as a function of time, then estimating the line's slope. This rate is similar to the concentration vs. time rate, and because it accounts for the entire plume, it is a good indicator of how long a plume will persist. Many plumes change flow direction over time, making it difficult to identify a stable centerline. Estimates based on the entire plume are less subject to errors caused by changes in flow direction.

*Mass flux vs. distance rate constant.* A mass vs. distance decay rate (in units of inverse time) can be calculated by plotting the natural log of mass flux through different transects perpendicular to the flow as a function of distance from the source. The slope of the best-fit line is then multiplied by the seepage velocity. Comparable to the bulk attenuation rate, this rate can indicate if a plume is expanding, showing relatively little change, or shrinking.

*Mass flux-based biodegradation rate constant.* Mass fluxes across plume transects can be further analyzed to determine whether the observed mass loss spatially and temporally can be attributed to biodegradation and/or source decay. For this purpose, the mass flux across the source area is compared to the mass flux through the

next downgradient section. Theoretically, mass fluxes at the downgradient transect should mimic trends observed in the source transect if source decay, sorption, and dispersion were the only mass reduction attenuation mechanisms. If there is additional mass loss, it can only be attributed to biodegradation since the other processes are already accounted for in the mass flux calculation. Once the actual mass loss attributable to biodegradation has been determined, it is plotted as a function of time, and a biodegradation rate is estimated using linear regression or a first-order decay model fit to the data.

Mass-based rate constants are not often used because of data requirements that include a dense well network, localized gradients, conductivity measurements and aquifer thickness at monitoring points.

*Average-plume concentration rate constants.* Some researchers have calculated rate constants for the change in average plume concentration. This rate constant reflects primarily the change in source strength over time.

### Effect of residual NAPL on point decay rate constant

When a monitoring well is screened across an interval that contains a residual NAPL, and when the NAPL weathering rate is slow, the water well may sustain high concentrations of contaminants over long periods of time.

### Effect of NA processes on rate constants

Natural attenuation processes include a variety of physical, chemical or biological processes that act without human intervention to reduce contaminant mass or concentration in soil and groundwater. These in-situ processes include biodegradation, dispersion, dilution, sorption, volatilization, radioactive decay and chemical or biological stabilization, transformation, or destruction of contaminants.

Each of these processes influences contaminant concentrations in soil and groundwater spatially and temporally. Contaminant concentrations in groundwater are reduced as contaminants travel downgradient from the source. Subject to source degradation, contaminant concentrations will also be reduced with time at any given distance downgradient from the source. Newell and others (2003) give more detail in their text.

### Uncertainty in rate calculations

Rate calculations can be affected by uncertainty from a number of sources, such as the design of the monitoring network, seasonal variations, uncertainty in sampling methods and lab analyses and the heterogeneity in most groundwater plumes.

ORD (Office of Research and Development) has developed software (RaCES) to extract rate constants from field data. This software is intended to facilitate an evaluation of the uncertainty associated with computer-modeled projections of the future behavior of contaminant plumes in groundwater. The software is available from The Ecosystem Research Division of the National Exposure Research Laboratory in Athens, Georgia.

### Reference

Newell, C.J., Rifai, H.S., Wilson, J.T., Connor, J.A., Aziz, J.A. and M.P. Suarez, "Calculation and Use of First-Order Rate Constants for Monitored Natural Attenuation Studies," Issue Paper, EPA/540/S-02-500, 2003; the complete issue paper can be found at <http://www.epa.gov/ada/pubs/issue.html>.

**UTTU thanks John T. Wilson, 580-436-8534, for his help on this article.**



## UST testing, part 1

By John Hartmann

Industry standards, model codes, fire and environmental regulations all require underground storage system components to be tested for tightness before, during and after installation. The tank installation contractor is responsible for conducting inspections and tightness tests on tanks, piping and containment components, as well as making tank deflection measurements and testing line pressure leak detectors and monitoring systems. This article explains the tests required for tank system components before installation and summarizes procedures for conducting them.

### Why test?

For most of the 20th century, tank systems were simply installed, paved over and placed into operation. Many conscientious installers inspected and tested their work as it was performed, but most specification and trade practices failed to include comprehensive requirements. In fact, little effort was made to ensure that connections were tight or that industry recommended practices were followed. Small leaks, if they occurred, were not considered a serious problem. Corrosion of metal components was deemed to be inevitable. The manufacturers' installation instructions were brief and designed to avoid the implication that installing their products was not more demanding than installing their competitors' products.

Meticulous testing is a relatively new requirement in underground storage tank (UST) installation. Current environmental regulations insist that systems not leak at the time of installation and remain testable and secure throughout their operational lives. Tank owners and other industry experts recognize that the best time to identify and correct problems of a UST system is before the system has been completely backfilled and paved

over. A leaking pipe joint is far cheaper to find and fix while the joint is still exposed than after it is buried under a deep layer of backfill and a paving slab.

These changing attitudes toward the integrity of USTs have spawned new requirements for rigorous tests and inspections at various stages of the installation process. Most of these tests and inspections are required by industry codes that have also been adopted by reference in both state and federal regulations. Test methods and hardware systems for performing them have been refined and are currently routinely employed.

### Tests by tank manufacturers

Some of the most rigid tank-system tests imposed by codes are required of tank manufacturers. In a section on testing and maintenance, Code 30 of the National Fire Protection Association (NFPA) requires all tanks to be tested under the applicable paragraph of the code (that is, the paragraph that covers the type of tank system being installed) before being placed into service. Examples of applicable codes include the following from Underwriters Laboratories (UL):

- UL 58, Steel Underground Tanks for Flammable and Combustible Liquids
- UL 1316, Glass-Fiber-Reinforced Plastic Underground Storage Tanks for Petroleum Products
- UL 1746, Standard for External Corrosion Protection Systems for Steel Underground Tanks

Tanks bearing a UL label or similar designation must meet the standards and test requirements set forth by the code of the organization issuing the label, including requirements for testing after fabrication and approval of installation instructions.

Underwriters Laboratories of Canada publishes standards for USTs that are similar to those published in the United States. USTs manufactured in the United States and Canada are constructed to exacting code speci-

fications and leave the manufacturing plant only after passing prescribed tests for strength and operational characteristics.

### Pre-installation tightness tests for tanks

NFPA 30 and other industry codes require underground storage tanks to pass a tightness test at the job site before they are lowered into the excavation. The test involves introducing 3-5 psig of air into a single-wall tank. While the tank is under pressure, coat the entire exterior surface with soapy water. Bubbles formed in the soap and water solution indicate a leak. While more sophisticated test methods have been developed, the carefully performed air/soap test remains a very sensitive and accurate test.

Pre-installation tightness tests for double-wall tanks are somewhat different. Introduce 3-5 psig of compressed air into the inner tank. Disconnect the air source, hold pressure for one hour and observe for pressure change. Bleed air from the inner tank into the interstice between the inner and outer tanks. Again, coat the exterior tank wall with soapy water and check for bubbles (Petroleum Equipment Institute, PEI/RP100)].

Consult the tank manufacturer's instructions before introducing pressure into a tank, because test procedures vary. Some manufacturers, for example, do not tighten the fittings on their tanks at the time of shipment to allow tanks to accommodate temperature changes during transit. Thread protectors and loose plugs must be replaced or made liquid-tight before testing.

When conducting tightness tests, use two pressure gauges in case one fails; always check to ensure a vacuum gauge is not used. While some recommend that tightness tests last for about an hour, the test must be long enough to allow the soaping and inspection of the entire tank surface regardless of the length of time required. Safety procedures include keeping personnel away from tank end caps while the test is underway,

never leaving tanks being tested unattended, and never allowing the internal pressure to exceed the test requirements.

Double-wall tanks may be delivered from the manufacturer with either liquid or vacuum in the interstice. In these cases, confirmation that the level in the interstice is unchanged and a careful inspection of observable components should satisfy pre-installation testing requirements.

### Holiday test

Both steel and fiberglass-coated steel tanks leave the factory protected against corrosion by a thick layer of fiberglass applied by the manufacturer at the factory and tested there for holidays. Factory-applied coatings may incur abrasions during the trip from the manufacturing plant to the job site. These abrasions tend to be tiny holes, called holidays, and are the most likely spots for corrosion. To keep these holes from causing future problems, industry codes call for a holiday test to be conducted at the job site before the steel or composite tank is installed. NACE/RP02-85 (National Association of Corrosion Engineers) recommends that tank coatings be tested immediately before installation by both visual inspection and use of appropriate holiday detectors. All detected coating damage must be repaired.

The holiday detector referred to by NACE is also called a sparking instrument. It is a hand-held, battery-operated, wand-like device that can develop up to 35,000 volts. The instrument is moved over the entire surface of the tank. If the coating or fiberglass skin of the tank is entirely intact, no reaction will occur. If a holiday is present, however, a spark will leap from the instrument to the metal exposed by the holiday: the spark reveals the location of the holiday so it can be repaired.

### Piping testing

Piping is inspected before being used. Fractured or dis-

colored fiberglass pipe should not be used. After piping has been installed in an UST, industry codes require that it pass a tightness test before backfilling and connecting it to the tanks or dispensers. The conventional test for new piping uses compressed air, but testing piping that has previously held product is performed with an inert gas, usually nitrogen, or hydrostatically.

Before beginning a test, carefully inspect all piping. Isolate piping from tanks and dispensers before either conducting air or hydrostatic tests. To ensure isolation, the piping must be disconnected at the endpoints and plugged. Air test the piping for one hour at a pressure of 150 percent of the maximum operating pressure, or at least 50 psig, then coat all joints in the piping system with a mixture of soap and water. Check for bubbles. The presence of bubbles, of course, indicates that the joint is not completely tight. Make the necessary repairs, then retest before covering the system.

Do not run air tests on piping that has contained gasoline, diesel fuel or other flammable or combustible products. Instead, use nitrogen to apply pressure or perform a hydrostatic test with the pressure at 100 percent of normal operating pressure.

### Testing cathodic protection systems

Sacrificial-anode-type cathodic protection systems are destined to protect steel tanks, steel piping or other steel components from corrosion. Cathodic protection systems do not use electronic or mechanical devices that ring bells or turn on lights when a problem develops.

A lack of bells or lights does not mean the system is operating properly. The connecting wire between an anode and the structure it is supposed to protect might break, as might the Thermite connection. In some cases, the electrolytic potential in the soil may exceed the potency of the cathodic protection system installed due to a change in soil conditions or dissipation of the anodes over time.

At locations with cathodically protected steel tanks or piping, test to determine whether the system is working and the protection is adequate for the tank and/or piping. If the test indicates the protection is inadequate, the location may still be put into service, but a second test should be performed 90 days later. If protection is still inadequate, the system should be repaired. The location can continue to operate while these repairs are being performed (PEI/RP100).

Because cathodic protection systems are essentially inert, even when working properly, the operator has no obvious way of knowing when something goes wrong. That's why several tests and inspections of cathodic protection systems have been devised. The principal tests are listed below.

**Anode integrity.** After placing a STI-p3 tank in the excavation, check the lead wire connecting the anode to the tank to make sure it is still intact. Sometimes this wire is jerked loose during installation.

**Electrical isolation.** In a STI-p3 system, contact between the steel tank and ancillary components (piping, pumps, gauges, grounding devices, etc.) can nullify the cathodic protection design of the system. Thus, it is important to verify that each of these components is dielectrically isolated from the tank. To accomplish this, STI recommends use of a simple continuity test between the PP2 lead wire and each connected system. There will be a 3mV difference if isolation exists. Another test checks isolation flanges for bushings to ensure that the tank is indeed isolated.

**Tank-to-soil potential readings.** To take these readings, place a high impedance voltmeter and a copper/copper-sulfate reference electrode in the soil directly above the tank. A reading more negative than minus 850 millivolts indicates the tank is adequately protected (PEI/RP100; see also NACE RP 0285-85 for more specific details on this test). Tank-to-soil potential read-

ings should be made within one year after the system is installed and then at five-year intervals during the life of the installation.

*Other criteria for cathodic protection.* NACE has developed other criteria for evaluating the adequacy of cathodic protection systems. These criteria involve measurements of cathodic voltage, voltage shifts, negative polarization voltage and structure-to-electrolyte voltage.

Part 2 of this article will describe the importance of witnessing and documenting testing, tank deflection, line-leak detectors and indicators, in-tank electronic monitors and more.

## References

John Hartmann, "Testing," section 5 in *Underground and Aboveground Storage Tank Inspection*, April 21 - 23, 2003, Ft. Gordon, Georgia, given by the University of Wisconsin-Madison, <http://epdweb.engr.wisc.edu>

NACE, 281-228-6200; <http://nace.org>

NFPA, 617-770-3000; <http://www.nfpa.org>

PEI, 918-494-9696; <http://www.pei.org>

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## Research notes

### Dissolved Organic Matter Effects on the Performance of a Barrier to Polycyclic Aromatic Hydrocarbon Transport by Groundwater

Moon, J.W., Goltz, M.A., Ahn, K.H. and J.W. Park, *Journal of Contaminant Hydrology*, Vol. 60, 2003; <http://www.elsevier.com/locate/jconhyd>

Researchers performed batch experiments that investigated the movement of organic contaminants such as naphthalene and phenanthrene in groundwater. They wanted to quantify the effect of a subsurface sorption barrier of sand or clay (such as bentonite) coated with a cationic surfactant in the presence of dissolved organic matter, DOM.

"DOM, which is ubiquitous in aquatic systems, is largely composed of humic substances. Due to its high organic content, DOM serves as a sorbent to hydrophobic organic compounds such as PAHs (polycyclic aromatic hydrocarbons). Owing to the prevalence and relative stability of DOM in natural water, it is likely that it can significantly affect PAH sorption. Many sites have demonstrated that DOM enhances the apparent water solubility and mobility of highly hydrophobic contaminants...Conversely, due to its hydrophobicity, DOM can also be sorbed onto soil organic material, thus increasing the sorption and reducing the mobility of contaminants that may be associated with the DOM. Therefore, as a mobile phase, DOM can enhance the mobility of hydrophobic organic compounds such as PAHs, or as a sorbed phase, it can increase PAH sorption and decrease mobility."

Researchers used an overall mechanistic sorption (OMS) model and a competitive multiphase sorption

(CMS) model to describe the distribution of PAHs. They found that PAH sorption coefficients were unaffected if hexadecyltrimethylammonium bromide coated the bentonite of a barrier; sands coated with cetylpridinium chloride in a sand barrier showed a decrease in sorption coefficient.

### Distribution and Reactivity of O<sub>2</sub>-Reducing Components in Sediments from a Layered Aquifer

Hartog, N., Griffioen, J. and C.H. Van Der Weijden, *Environmental Science & Technology*, Vol. 36, No. 11, 2002; <http://www.pubs.acs.org>

The reactivity of reductants in aquifer sediments becomes important for issues of in-situ bioremediation in contaminated aquifers, especially where injected oxidants are used. Reductants in aquifer sediments can include

- SOM, sedimentary organic matter
- pyrite, FeS<sub>2</sub>
- iron silicates
- siderite, FeCO<sub>3</sub>
- vivanite

"Pyrite and siderite are commonly found in close association with organic matter due to redox processes occurring during or after deposition. Therefore, a relationship between the reduction capacity and the diagenetic history of sediment can be expected. Furthermore, fine-grained sediments are generally richer in organic material and associated reduced mineral phases, and higher total reduction capacities for aquifer sediments with a larger fine fraction have been suggested."

"The TRC (total reduction capacity) of sediments can be calculated if all relevant reduced components are recognized and their quantification is sufficiently accurate. This approach, however, yields a maximum potential,

since it does not account for the reactivities of these components." Hartog and others (2002) took samples of aquifer material, incubated it and measured oxygen consumed. Researchers then sought to

- determine the relative contribution of identified reductants to reduction activity
- assess the difference in reduction capacity of different grain-size fractions
- evaluate the impact of geological stratification on the reduction activity with a layered single aquifer unit that consists of three geological units

Researchers found that "organic matter, pyrite, and siderite are the main potentially reactive reductants present in the aquifer sediments studied. Predicting which reductant is most prone to oxidation, however, is difficult because these species have comparable energy yields for oxidation, while their oxidation mechanisms are distinctly different." Subsurface reductant activity depends on "physicochemical conditions (oxidant type, temperature, pH) as well as on the intrinsic characteristics of the reductants that make up the TRC. For instance, SOM degradability is determined by its chemical composition and strength of the degrading oxidant, while the occurrence of iron sulfide oxidation depends strongly on oxidant types and pH...Our oxidation experiments with O<sub>2</sub> showed the simultaneous oxidation of reductants." Their contribution depends both on concentrations and reactivity toward O<sub>2</sub>. Limited knowledge exists concerning controls on reactivity of characteristics, which may include

- specific surface area involved
- coatings on, for instance, pyrite
- association and composition of SOM
- SOM reactivity of aquifer sediments
- other conditions of the system

### Hybrid Fuzzy-Stochastic Modeling Approach for Assessing Environmental Risks at Contaminated Groundwater Systems

Chen, Z., Huang, G.H. and A. Chakma, *Journal of Environmental Engineering*, January 2003; <http://ojs.aip.org/eeo>

Researchers developed a hybrid fuzzy-stochastic risk assessment (FUSRA) approach for examining uncertainties associated with both source/media conditions and evaluation criteria of a petroleum-contaminated groundwater quality management system.

"In the majority of the existing risk assessment research, local environmental guidelines have been used as the evaluation criteria. In practical site management, however, these guidelines are mostly impractical and cannot be implemented. Additional and complex factors need to be considered when in-depth risk assessment is undertaken, such as dose-response effects, contaminant physical, chemical and toxic characteristics, media conditions, land-use pattern and receptor sensitivities. Most of these uncertain factors, however, cannot be expressed as probability distributions, and thus methods of stochastic risk assessment are inapplicable. Fuzzy set theory has been used widely for handling uncertainties with discrete and/or imprecise characteristics. For the problem under consideration, fuzzy membership functions can be employed to quantify uncertainties associated with evaluation criteria."

The hybrid FUSRA for quantifying uncertainties associated with source/media consists of

- a Monte Carlo simulation of contaminant fate and consideration of source/media uncertainties
- examination of contaminant levels based on simulation results, expressed as probability density functions

- quantification of evaluation criteria for fuzzy membership functions
- risk assessment based on fuzzy/stochastic inputs

Researchers developed the FUSRA and applied it to a petroleum-contaminated groundwater system. According to Chen and others (2003), "This study is the first attempt to characterize uncertainties related to environmental standards based on human exposure mechanisms, within an integrated risk modeling framework. A triangle fuzzy membership function is formulated, which could be used for estimating the suitability of a standard for risk assessment and therefore addressing uncertainty of the standard. In fact, uncertainties in human exposure mechanisms, such as the daily ingestion rate, body weight, and exposure time, may also affect the standard suitability."

This proposed FUSRA reflects not only uncertainties of pollutant and media conditions but also those of evaluation criteria. Using the FUSRA can help remediators "effectively elucidate the relevant health risks."

### In-Situ Transformation of Deuterated Toluene and Xylene to Benzylsuccinic Acid Analogues in BTEX-Contaminated Aquifers

Reusser, D.E., Istok, J.D., Beller, H.R. and J.A. Field, *Environmental Science & Technology*, Vol. 36, No. 19, 2002; <http://www.pubs.acs.org>

Using single-well push-pull tests, researchers injected deuterated toluene and xylene (toluene-d<sub>8</sub> and o-xylene-d<sub>10</sub>) and bromide (a tracer) into a BTEX-contaminated groundwater aquifer. (A deuterated compound is one in which some or all of the hydrogen-1 atoms have been replaced by deuterium atoms.) Researchers then monitored degradation products benzylsuccinic acid (BSA-d<sub>8</sub>) and o-methyl-BSA-d<sub>10</sub>; benzylsuccinic acid (BSA) and methyl-BSA are products of anaerobic metabolism

of toluene and xylenes. The observance of BSA-d<sub>8</sub> and o-methyl-BSA-d<sub>10</sub> would "unequivocally demonstrate anaerobic in-situ toluene-d<sub>8</sub> and o-xylene-d<sub>10</sub> transformation with calculated zero-order formation rates ranging from 1.0 to 7.4 nM/day. Concurrent utilization of co-injected nitrate was rapid in all tests at both sites, with zero-order rates ranging from 13 to 39 μM/h."

Researchers chose this approach because the usual approach of "monitoring temporal and spatial changes in concentration of BTEX, electron acceptors and reduction products (e.g. methane) is problematic for several reasons:

- small changes in BTEX concentrations are difficult to quantify in the presence of high background concentrations
- concentrations of reduction products are typically low
- BTEX concentration changes due to metabolism are often obscured by non-biological processes such as advection, dispersion, sorption/desorption and dissolution of non-aqueous-phase liquids"

Researchers found that sorption to aquifer sediments was likely responsible for the retardation of toluene-d<sub>8</sub> and o-xylene-d<sub>10</sub>. Volatilization was considered negligible while "dilution due to advection and dispersion was accounted for by normalization to bromide."

### Modeling Biodegradation of Hydrocarbons in Aquifers: When Is the Use of the Instantaneous Reaction Approximation Justified?

Koussis, A.D., Pasmajoglou, S. and D. Syriopoulou, *Journal of Contaminant Hydrology*, Vol. 50, 2003; <http://www.elsevier.com/locate/jconhyd>

Using theoretical analysis, non-dimensional variable and numerical modeling, researchers "established a quanti-

tative criterion demarcating the range of validity of the instantaneous reaction approximation against biodegradation kinetics. Oxygen was the limiting species and sorption was ignored." At issue are the BIOPLUME and BIOPLUME II models that assume an "instantaneous reaction between the contaminant and oxygen, thus ignoring microbial dynamics." Researchers assert that the "BIOPLUME II procedure should be valid when hydrocarbons are degraded readily and velocities are low. In active bioremediation, however, velocities can be high...[up] to two orders of magnitude higher than the natural ones. If the biodegradation rate is also low, the assumption of instantaneous reaction may not hold."

From their analyses, researchers concluded the following concerning instantaneous reaction with respect to hydrocarbon modeling:

- the relative availability of oxygen and hydrocarbons exerts a small influence on the results
- the validity of the instantaneous reaction is related to the Dahmkohler number, which reflects intrinsic physical transport characteristics and the biochemical reaction
- "a significant difference between kinetics and instantaneous reactions is expected in the 'initial period' and 'near source' region" and has been verified by numerical simulations
- "BIOPLUME is appropriate for most applications; kinetic modeling is likely to be required only in active, i.e., engineered bioremediation cases with high velocities (near pumped wells), and for short distances from the source"

## Used Motor Oil as a Source of MTBE, TAME and BTEX to Ground Water

Baker, R.J., Best, E.W. and A.L. Baehr, *Ground Water Monitoring & Remediation*, Vol. 22, No. 4, Fall 2002; <http://www.ngwa.org>

A survey of 956 domestic wells in Maine detected MTBE in 15.8 percent of wells, mostly at concentrations of < 0.1 µg/l. Baker and others (2002) believe these small and widely distributed MTBE spills did not necessarily result from LUSTs. Other potential sources of MTBE include

- the atmosphere; in urban areas, concentrations can reach 0.1 µg/l
- small spills from lawnmowers or boat-engine refueling
- home-heating oil
- used motor oil

Authors set out to assess the likelihood that "motor oil that is improperly disposed of or spilled is a source of MTBE to groundwater." They measured the MTBE content of new and used motor oil and found that new motor oil had no MTBE and used motor oil had mean concentrations averaging around 135 mg/l. Most likely, MTBE compounds accumulated in motor oil as a result of engine operation.

Researchers estimate that of the 1.3 billion gallons of used oil generated yearly in the United States, about 0.4 billion gallons are disposed in landfills, and perhaps 0.26 billion gallons are improperly disposed of. "If, for instance, a value of 100 mg/l of MTBE is assumed for oil disposed of in New Jersey, 1 liter of used motor oil that is improperly disposed of could render a maximum of 5,000 liters of nonpotable water...Because of its higher aqueous solubility, MTBE dissolves from used oil in higher concentrations than do BTEX compounds and other hydrocarbons. It has been shown

to attenuate much more slowly...Therefore, the use of MTBE in gasoline increases the risk of water-supply contamination from used motor oil that is improperly disposed of."

In addition, "shallow wells near sites where motor oil is spilled or improperly disposed of could intercept water contaminated with BTEX compounds in concentrations that are greater than federal drinking-water standards."

## Using a Passive Multilayer Sampler for Measuring Detailed Profiles of Gas-Phase VOCs in the Unsaturated Zone

Yaor, Y., Ronen, D. and E.R. Graber, *Environmental Science and Technology*, Vol. 27, No. 2, 2003; <http://www.pubs.acs.org>

Researchers recently created and tested a passive multilayer sampler (MLS). "The MLS is essentially a chain of isolated, cylindrical stainless steel dialysis cells filled with distilled water and closed with membranes at both ends. The sampling principle is based on passive equilibration of the unsaturated zone gas phase with water in the cells." The sampler has a vertical resolution of less than 3 cm and is capable of providing detailed vapor phase profiles that can give information about spatial and temporal changes of vapor phase plumes in the unsaturated zone and "unprecedented detail about VOC fluxes at the saturated/unsaturated interface region (SUIR)."

Use of the MLS "requires the existence of a borehole and a well screen along the saturated and unsaturated zones, which may limit the accessibility of this method. Using the MLS, each dialysis cell is a continuous passive sampling system where the concentration will change according to the concentration in both the gas and liquid phases in the cell vicinity...This unique feature makes the MLS an especially useful tool for exploring vapor transport behavior during water table fluctuations

and under the extremely variable conditions of water content prevailing in the SUIR."

Yaor and others tested their MLS at an extensively contaminated site near Tel Aviv, in the sandy phreatic Coastal Plain, and were able to define "sharp gas-phase TCE gradients." In addition, they assert that "detailed MLS profiles can also be useful for detecting VOCs below relatively impermeable barriers (such as clay or perched water), which could easily be missed in more traditional gas surveys."

## Other papers of interest include the following:

"Electron-Beam Treatment of Aromatic Hydrocarbons That Can Be Air-Stripped from Contaminated Groundwater: 1. Model Studies in Aqueous Solution," Mark, G., Schuchmann, H.P., Schuchmann, M.N., Prager, L. and C. Von Sonntag, *Environmental Science and Technology*, Vol. 37, No. 2, 2003; <http://www.pubs.acs.org>

"Performance Assessment of NAPL Remediation in Heterogeneous Alluvium," Meinardus, H.W., Dwarakanath, V., Ewing, J., Hirasaki, G.J., Jackson, R.E., Jin, M., Ginn, J.S., Londergan, J.T., Miller, C.A. and G.A. Pope, *Journal of Contaminant Hydrology*, Vol. 54, p. 173-193, 2002; <http://www.elsevier.com/locate/jconhyd>



## Information sources

### U.S. EPA publications and information

Publications that can be downloaded from <http://clu-in.org/techpubs.htm> include

- A Discussion of the Effects of Thermal Remediation Treatments on Microbial Degradation Processes
- In Search of Representativeness: Evolving the Environmental Data Quality Model
- NATO/CCMS Pilot Study Evaluation of Demonstrated and Emerging Technologies for the Treatment of Contaminated Land and Groundwater (Phase III) Reports

### Other EPA publications

Calculation and Use of First-Order Rate Constants for Monitored Natural Attenuation Studies (EPA 600-S-02-500), <http://www.epa.gov/ada/download/issue/540S02500.pdf>

Dynamic Field Activity Case Study: Soil and Groundwater Characterization, Marine Corps Air Station Tustin (EPA/540/R-2/005), <http://www.epa.gov/superfund/programs/dfa/casestudies/>

Environmental Technology Verification (ETV) Program, <http://www.epa.gov/etv>

EPA's Land Revitalization Agenda, [http://www.epa.gov/swerrims/landrevitalization/agenda\\_full.htm](http://www.epa.gov/swerrims/landrevitalization/agenda_full.htm)

New Contaminant Focus Area on CLU-IN, <http://clu-in.org/contaminantfocus>

Proceedings for the International Applied Phytotechnologies Conference, <http://clu-in.org/studio/2003phyto>

Using Dynamic Field Activities for On-Site Decision Making: A Guide for Project Managers (EPA/540/R-03/002), <http://www.epa.gov/superfund/programs/dfa/guidoc.htm>

### Other documents and Web sites

Answers to Frequently Asked Questions About Managing Risk at LNAPL Sites, API Soil and Groundwater Research Bulletin No. 18, May 2003, <http://api.ep.api.org>

Field Analytic Technologies Encyclopedia (FATE) Web site, <http://fate.clu-in.org>

Federal Remediation Technologies Roundtable Web site, <http://www.frtr.gov>

Guidance on the Use of Passive Diffusion Samplers to Detect Volatile Organic Compounds in Ground Water Discharge Areas and Example Application in New England, <http://water.usgs.gov/pubs/wri/wri024186/pdf/wri024186.pdf>

ITRC Advanced Techniques on Installation of Iron-Based Permeable Reactive Barriers and Non-Iron Based Barrier Treatment Material Documents and Web Resources, <http://www.itrcweb.org>

Models for Design of Free-Product Recovery Systems for Petroleum Hydrocarbon Liquids, API publication 4729, August 2003, <http://groundwater.api.org/lnapl>

NYSERDA (New York State Energy Research and Development Authority) Web site, <http://www.nyserda.org/upcoming.html>

Study of Five Discrete Interval-Type Groundwater Sampling Devices (TR-02-12), [http://www.crrel.usace.army.mil/techpub/CRREL\\_Reports/reports/TR02-12.pdf](http://www.crrel.usace.army.mil/techpub/CRREL_Reports/reports/TR02-12.pdf)

Technical and Regulatory Guidance for Surfactant/Cosolvent Flushing of DNAPL Source Zones (DNAPLs-3), <http://www.itrcweb.org/DNAPL-3.pdf>

Western Hazardous Substance Research Center, <http://www.wrsrc.orst.edu/database/index.htm>; to receive research briefs, sign up at <http://wrsrc.orst.edu/news/listserv.htm>

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