

# Underground Tank Technology Update

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## Pulsing in air sparging

This article describes three studies. The first study measured the effect of continuous vs. pulsed air sparging/soil vapor extraction (AS/SVE) in a low permeability clayey soil. The second study assessed pulsing with respect to grain size. The last considered diffusion's role in air sparging.

### Air sparging and soil vapor extraction

Air sparging relies on injecting air into an aquifer to promote vapor phase mass transfer of VOCs (volatile organic compounds) and mass transfer of oxygen to the aqueous phase. "The injected air forms channels through the contaminant plume as it flows upward through the saturated zone and into the vadose zone. The injected air volatilizes the contaminants in the flow channels and transports them to the vadose zone where they are either biodegraded or removed by SVE. SVE strips VOCs bound to soil particles and induces atmosphere-soil vapor exchange in the unsaturated zone" (*Kirtland and Aelion, 2000*).

Factors that control SVE performance include

- contaminant composition
- vapor flow rates through the vadose zone
- distribution of air flow channels through the contaminant zone

The injected air will not penetrate the entire plume; thus, contaminant diffusion into the flow channels is usually the rate limiting factor after several days of operation.

In general, low permeability sediments, such as clays and silts, are not appropriate for AS/SVE because such soils allow only limited air flow and consequently reduced mass exchange rates of VOCs to the vapor phase. "Low-permeability lenses can cause air to migrate laterally from the sparge points, leaving contaminants within and above the lens untouched by air flow" (*Kirtland and Aelion, 2000*). Factors that affect air flow patterns include

- hydraulic conductivity
- soil permeability
- soil structure

In low-permeability sediments, distinct air-flow channels will form, resulting in less-than-ideal air distribution. These sediments will require higher air injection pressures to achieve air flow in the saturated zone; however, excessive pressures can destroy the soil structure and promote soil fracturing, which may reduce AS/SVE effectiveness.

### Pulsed AS/SVE

One strategy to overcome low flow through soils is pulsed air sparging. Pulsing, on the order of minutes or hours, can

enhance mixing, which increases oxygenation and volatilization of dissolved-phase and NAPL contaminants. Studies have indicated that pulsed AS may induce groundwater mixing and increase mass removal rates in sandy aquifers.

During the first minutes/hours/days of operation, AS, depending on sediment grain size, causes groundwater mounding because injected air displaces the water. When AS stops, air channels collapse, causing a temporary depression of the aquifer. "Pulsed AS utilizes this mounding and depression of an aquifer to induce bulk groundwater mixing, which redistributes dissolved-phase contaminants relative to the air channels and may yield a larger radius of influence and reduce diffusion limitations" (*Kirtland and Aelion, 2000*).

Groundwater mixing, induced by continuous AS, occurs by the following processes:

- frictional drag from flowing air
- physical displacement of groundwater, forming channels
- capillary interaction of air and water
- thermal convection
- migration of fine materials, resulting in redirection of air flow
- evaporative loss of water in the air stream and resulting groundwater inflow to maintain water balance

The magnitude of mixing is likely greater during pulsed rather than continuous operation. Although this theory has been tested in sandy soil, *Kirtland and Aelion (2000)* sought to test it in low permeability saprolite. Saprolite is formed by weathering of igneous or metamorphic rocks and contains many clay-rich minerals.

### Study site description

The study site, in Columbia, South Carolina, is in a transition zone between the Appalachian Piedmont and the Upper Atlantic Coastal Plain. A UST released an undetermined volume of gasoline from 1989 to 1992. After performing Phase I, II and III site assessments, remediators installed monitoring wells and analyzed soil borings and groundwater samples. For the next two years, they assessed the site using groundwater data, soil property data, soil contaminant levels and geophysical testing.

Groundwater characteristics included the following:

- TPH, < 1 to 370 mg/L
- BTEX levels, 0.5 to 60 mg/L
- water table, 6.1 to 7.6 m below land surface
- pH, 3.8 to 6.3
- dissolved oxygen, 0.24 to 7.32 mg/L
- hydraulic conductivity ( $K_{sat}$ ),  $6.2 \times 10^{-7}$  to  $3.4 \times 10^{-4}$  cm/s
- average temperature, 24.3°C
- water flow, northeast at a rate of 1.0 to  $4.8 \times 10^{-6}$  cm/s

Soil characteristics included the following:

- TPH, < non detect to 7,400 mg/kg
- BTEX levels, 20,000 to 50,000 mg/m<sup>3</sup>
- air-phase permeability ( $K_{air}$ ),  $1.6 \times 10^{-7}$  to  $2.2 \times 10^{-7}$  cm<sup>2</sup>
- bulk density, 1.431 g/cm<sup>3</sup>
- particle density, 4.8 g/cm<sup>3</sup>
- porosity, 0.3
- soil moisture content, 0.1

### AS/SVE description

Remediators created an AS/SVE system consisting of two lines of six SVE wells, constructed of 10 cm-diameter PVC and spaced 1 m apart. Wells were screened over at 5.2 to 6.7 m below land surface. AS wells, also constructed of 10 cm-diameter PVC, were installed at 9.5 m below ground surface and screened from 7.9 to 9.5 m. Field workers installed six AS wells in the same soil bore hole as one row (set of six) of SVE wells. Workers connected the SVE wells to a 5.22-kW vacuum pump and the AS wells to a 2.24-kW air compressor.

A pilot study using soil vapor probes in the low permeability soil indicated an SVE radius of influence of 3 to 6 m. AS radius of influence, although not measured, was indicated by oxygenation in a soil vapor probe 5.2 m away.

### Contaminant levels

Remediators collected stack gas samples daily for 44 days from the AS/SVE system to determine contaminant removal levels. They analyzed for the following:

- O<sub>2</sub>
- CO<sub>2</sub>
- total combustible hydrocarbon (TCH)
- BTEX concentration

They determined mass removal rate (MRR) as follows:

$$\text{MRR} = Q \times C \times (\text{HC mol wt g/mol}) / (22.4 \times 10^{-3} \text{ m}^3/\text{mol}) \times 10^3 \text{ mg/g} \times 273/T \times P/1 \text{ atm} \times 0.0283 \text{ m}^3/\text{ft}^3 \times 1440 \text{ min/d} \times 1/10^6 \text{ mg/kg}$$

Q is measured flow rate in the exhaust stack (cfm)

C is hydrocarbon concentration (ppm)

HC mol wt is average molecular weight of gasoline's more volatile fraction (111 g/mol)

T is exhaust temperature (°K)

P is pressure in the exhaust (atm)

The above formula reduced to

$$\text{Mass removal rate} = Q \times C \times 1.6073 \times 10^{-4} \text{ kg min/d ft}^3$$

Remediators conducted 10 pulsing tests, two a week, after the 44 days of continuous operation. "Pulsed" is defined as 8 hours of operation per day, or 24 hours of operation followed by 24 hours of no operation. They took stack gas samples at system startup, 1-hour, and 8-hour intervals; during the 24 hours of no operation, samples were taken once.

Remediators also installed vadose zone soil vapor probes (38 mm PVC) at 4.9, 5.5, 6.1 and 6.7 m below land surface. They sampled for TCH, BTEX, O<sub>2</sub> and CO<sub>2</sub>.

### Results from continuous operation

During the 44 days of continuous operation, approximately 608 kg of hydrocarbon was removed, with highest rates at operation startup. Remediators shut down the operation on day 24 through 27 because of overheating and this caused a small contaminant rebound. Removal levels were lowest during the last 15 days. AS pressure was 1 to 8 psig. Water levels increased in all wells during the continuous operation. Figure 1 shows BTEX and TCH levels.

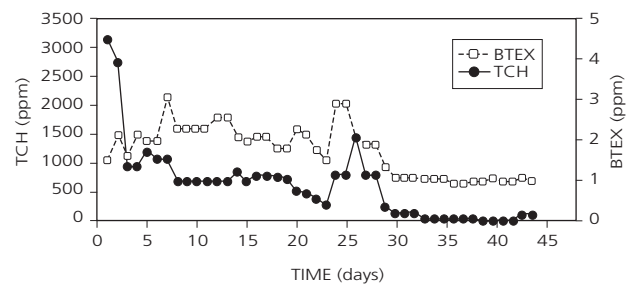


Figure 1. TCH and BTEX concentrations measured from stack exhaust during 44 days of continuous operation (Kirtland and Aelion, 2000).

### Results of pulsed operation

"The first 24-hour pulsed AS/SVE test removed the largest amount of contamination, 30 kg, and had the highest hydrocarbon removal rate with a value of 1.24 kg/h. . . . The average 8- and 24-hour hydrocarbon removal rate was compared to the average hydrocarbon removal rate during the entire continuous AS/SVE operation. A t-test showed there was not a significant difference ( $p$ -value = 0.39) between pulsed and continuous AS/SVE removal rates. But hydrocarbon removal rates from pulsed AS/SVE were significantly higher ( $p$ -value < 0.00001;  $\alpha$  = 0.05) than the last 15 days of continuous AS/SVE, when contaminant mass removal rates were the lowest and the system was at steady state" (Kirtland and Aelion, 2000).

### Conclusions

From the pattern of AS/SVE contaminant removal rates, Kirtland and Aelion (2000) concluded that after approximately 1 to 2 days of operation, AS/SVE became diffusion-limited " as high initial values of hydrocarbon, TCH, and BTEX removal quickly decreased to steady-state level. AS/SVE mass removal corresponded to TCH and BTEX concentration in the exhaust stack. Thus, mass removal was contaminant concentration dependent as opposed to flow rate or AS psi dependent."

Researchers also recognized that groundwater level may have impacted AS/SVE's effectiveness. Increased groundwater levels from increased precipitation/infiltration reduced the length of screen well in the vadose zone. Consequently, contaminant removal rates decreased. Lowering water table levels to expose the usually highly contaminated capillary fringe is known to benefit SVE operation. At this site, sand fractions increased at lower depths, and lowering groundwater levels effectively increased the system's radius of influence.

Researchers concluded the following:

- AS/SVE could remove hydrocarbons from low permeability sediments with hydraulic conductivities lower than those previously recommended
- pulsed AS/SVE of 8 or 24 hours per operational period produced significantly higher mass extraction rates than those during the last 15 days of continuous system operation
- system operation can be enhanced by manipulating groundwater level
- this data was consistent with other in-situ pulsed studies showing that pulsing is effective
- vacuum pump size and amount of suction applied, two major factors in contaminant removal rate, were not compared in this study because the data are rarely reported in other studies
- this study had mass extraction rates comparable to other studies conducted in more permeable sandy soils
- pulsed operation may optimize mass removal while reducing electrical costs

*Reviewer's note: Remediators use pump-and-treat systems to capture contaminated plumes, and pulsing may complicate demonstrations that the plume had been captured. Thus, operators of such systems should consider how they will demonstrate capture prior to pulsing. Contingency planning and/or additional groundwater modeling may be warranted in some situations where maintaining capture is critical.*

### Related study

Using one-dimensional columns and monitoring injected air flow rates, Reddy and Adams (1998) investigated the effect of sparging factors on contaminant removal. They looked at

- soil type (using gravel, coarse/medium/fine sand and well-graded sand)
- pulsed injection
- synergistic effects of co-contaminants

Their conclusions follow.

**Soil type.** In gravel, injected air traveled in bubble form and distributed uniformly throughout the soil. The fine sand required higher air entry pressures and had fewer channels, which meant that most of the contaminant, benzene in this study, "had no direct contact with the injected air and had to migrate to the air channels via diffusion, a process that requires much more time than volatilization." An extensive channel network did develop in the coarse, medium and well-

graded sands, reducing diffusion path length. "The channels appeared to be more numerous in the coarse sand than in the well-graded and medium sands, resulting in slightly quicker removal. These results also showed that the well-graded sand behaved similarly to the medium sand, which implies that the grain size may be a more critical factor than the grain size distribution when considering contaminant removal efficiencies" (Reddy and Adams, 1998). In all sands, a large portion of the benzene was removed quickly, indicating—with the exception of the gravel—a "tailing" effect associated with removal of residual benzene. Removing the last 10 percent of benzene generally took five times longer than removing the first 90 percent.

**Pulsed injection.** In the fine sand, higher entry pressures were required; thus the high-density channel network that characterized the coarser sands was not established here. "The benefits of a well-established channel network, including short diffusion paths and mixing, are not achieved in the fine sand. As a result, the 'resting' of the soil profile during shut-down allows diffusion to occur. In addition, when the air is reinjected into the fine sand, a very small number of channels are again formed, but these are located in different regions throughout the soil profile. Benzene that may not have been previously removed because of long diffusion paths may suddenly be in the vicinity of a channel, allowing faster removal. By allowing better coverage and increased mixing and diffusion, the use of pulsed air injection may offer greater efficiency than continuous air injection when dealing with residual contamination in fine sands" (Reddy and Adams, 1998). Pulsed air injected into the coarse sand, however, did not benefit contaminant removal.

**Synergistic effects of co-contaminants.** Researchers conducted sparging tests using toluene alone and a combination of toluene and benzene. Data indicated that toluene removal was slightly faster than the benzene, likely a factor of lower solubility and direct volatilization of free-phase toluene. The synergistic effects of toluene and benzene together led to slightly faster removal rates.

### Study concerning role of diffusion

In an effort to more clearly define the role of diffusion and predict VOC volatilization for AS, Braida and Ong (2000) developed a radial diffusion model with a defined air-water mass transfer boundary condition. "Incorporated in this model is the concept of mass transfer zone (MTZ), where VOC diffusion in this zone was impacted by VOC volatilization at the air-water interface but with negligible impact outside the zone. . . . The results suggested that air-sparged soil columns may be modeled as a composite of individual air channels surrounded by a MTZ. For a given air flow rate and air saturation, the VOC removal was found to be inversely proportional to the radius of the air channel."

VOC volatilization during air sparging occurs at the air-water interface of the air channels. "Several researchers have speculated that at the air channel level, VOC volatilization during air sparging is controlled by the aqueous diffusion of

the VOCs through a MTZ adjacent to the air channels. Using a single air channel apparatus, Braida showed experimentally the presence of the MTZ in porous media during air sparging" (Braida and Ong, 2000). MTZ size, estimated to be between 17 mm and 41 mm, was a function of VOC chemical properties and system characteristics such as mean particle size and uniformity coefficient.

Braida and Ong (2000) concluded that "air-sparged soil columns may be represented by a composite of individual air channels surrounded by a non-advective region of porous media or MTZ. In addition, model parameters, determined by using a single air channel setup (microscale) were able to predict the performance of sparged soil columns. The extent of the non-advective region present in a soil column depends on the air saturation and the physical-chemical properties of the air sparging system. Under these conditions, closer air channels produce better VOC removal. Also, the smaller the air channels for a given air saturation, the higher the removal of VOCs" (Braida and Ong, 2000).

## References

Braida, W. and S.K. Ong, "Modeling of Air Sparging of VOC-Contaminated Soil Columns," *Journal of Contaminant Hydrology*, Vol. 41, pgs. 385-402, 2000; <http://www.elsevier.com/locate/jconhyd>.

Kirtland, B.C. and C.M. Aelion, "Petroleum Mass Removal from Low Permeability Sediment Using Air Sparging/Soil Vapor Extraction: Impact of Continuous or Pulsed Operation," *Journal of Contaminant Hydrology*, Vol. 41, pgs. 367-383, 2000; <http://www.elsevier.com/locate/jconhyd>.

Reddy, K.R. and J.A. Adams, "System Effects on Benzene Removal from Saturated Soils and Ground Water Using Air Sparging," *Journal of Environmental Engineering*, March 1998; 1801 Alexander Bell Drive, Reston, Virginia 20191-4400.

For additional information, see

- "Special Feature on Advances in Air Sparging," *UTTU*, Vol. 8, No. 4, August 1994
- "Influence of Porous Media, Airflow Rate and Air Channel Sparging on Benzene NAPL Removal During Air Sparging," Rodgers, S.W. and S.K. Ong, *Environmental Science and Technology*, pgs. 764-770, Vol. 34, No. 5, 2000; <http://www.pubs.acs.org>

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## MTBE summary and cost comparison

Knowledge of MTBE, methyl tertiary butyl ether, an oxygenate and octane enhancer in gasoline, has increased greatly over the past few years. Only during the past few years, however, have states been monitoring for MTBE in groundwater.

### MTBE facts

We know the following about MTBE: (*U.S. EPA Fact Sheets, Squillance and others, 1998; and Zogorski and others, 1996, and Reiser and O'Brien, 1998, in UTTU, Vol. 13, No. 4, 1999*):

- MTBE moves in groundwater at the same velocity as groundwater
- it has a retardation factor of 1
- MTBE is 30 times more soluble than benzene in water
- its effective water solubility is higher when gasoline is present
- pure MTBE can reach an equilibrium concentration in water of approximately 5 percent, i.e., 48,000 mg/L
- at 25°C, the water solubility of MTBE is about 5,000 mg/L for a gasoline that is 10 percent MTBE by weight
- MTBE's relatively high solubility allows it to dissolve into the groundwater in "pulses" that result in rapid order-of-magnitude changes in groundwater concentrations
- MTBE is much more resistant to biodegradation than benzene
- MTBE can biodegrade under limited conditions, but it is generally regarded as recalcitrant
- even in states where MTBE is not used, MTBE has been detected
- MTBE is classified as a probable/possible carcinogen; the U.S. EPA won't have a definite ruling on MTBE until 2006

### Remediation techniques

Remedial techniques (*Creek and Davidson, 1998 in UTTU, Vol. 13, No. 4, 1999*) used to treat MTBE-contaminated water include:

- groundwater extraction (pump-and-treat) with treatment consisting of granular activated carbon (GAC)
- groundwater extraction with soil vapor extraction
- soil vapor extraction with air sparging
- biosparging
- use of oxygen release compound (*Koenigsberg and others, 1999 in UTTU, Vol. 14, No. 2, 2000*)

Technologies with potential to treat MTBE (*Keller and others, 1999a, and Keller and others 1999b in UTTU, Vol. 14, No. 2, 2000*) include the following:



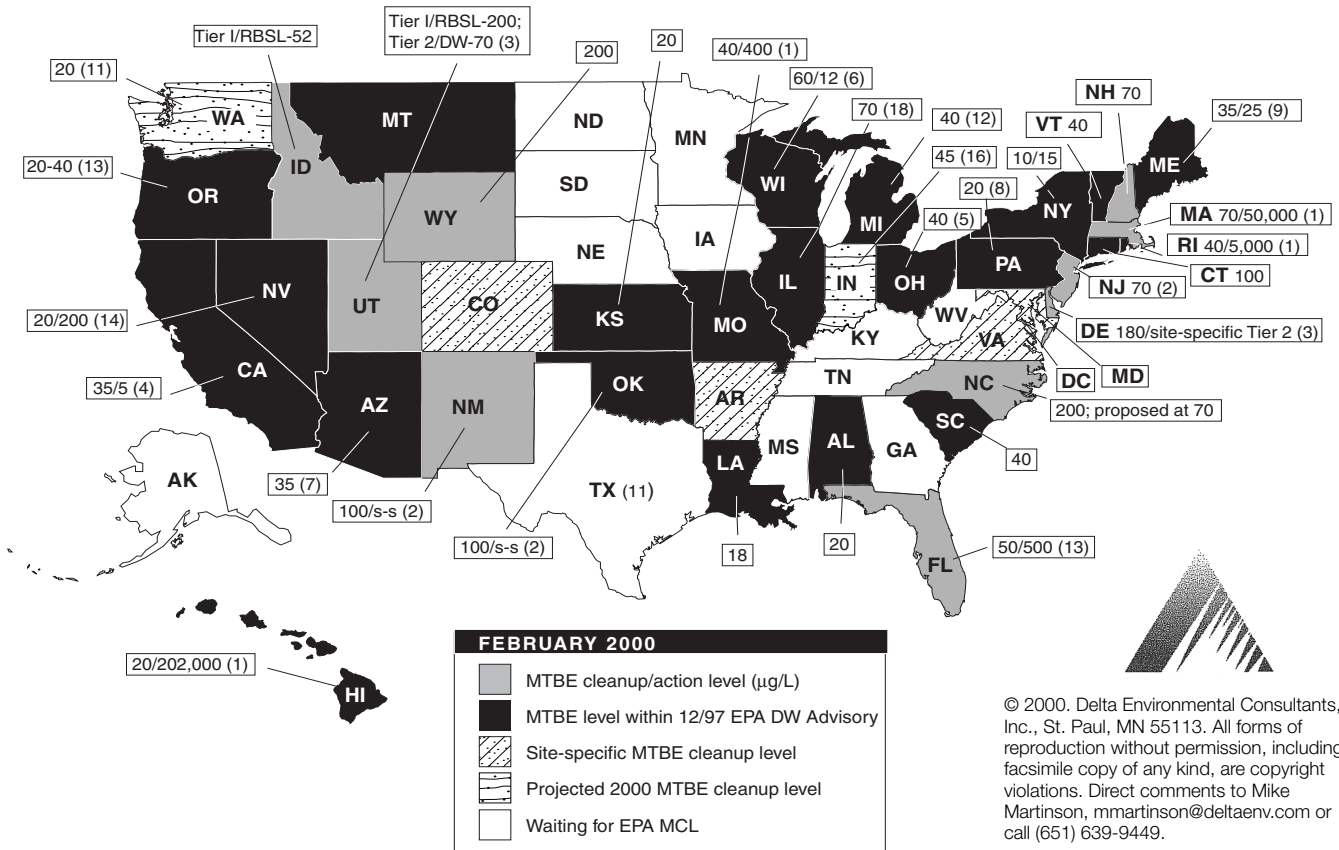
levels for groundwater enforcement and cleanup. In January 2000, EPA-OUST strongly recommended monitoring and reporting of MTBE and other oxygenates at UST release sites. EPA is expected to propose an unenforceable secondary standard for MTBE sometime in 2000 to codify EPA's *Drinking Water Advisory: Consumer Acceptability Advice and Health Effects Analysis on MTBE, December 1997* (see <http://www.epa.gov/ostwater/drinking/index.html>). EPA expects that some states will adopt this framework and initiate enforcement and cleanup of MTBE on a state-specific basis; however, the earliest that EPA could promulgate a federal MCL is 2006, and more likely no earlier than 2010 (*EPA Office of Water, July 1999*; see <http://www.epa.gov/ostwater/drinking/index.html>).

**California guidelines on investigation and cleanup**

California, with an estimated 10,000 MTBE-contaminated leaking underground fuel tank (LUFT) sites, recently published "Guidelines for Investigation and Cleanup of MTBE and Other Ether-Based Oxygenates" (*SWRCB, 2000*). The guidance does not address site-specific closure; however, it does recommend a quick response to a release and a need for vertical definition of the release. It also addresses the following:

- identifying vulnerable areas to groundwater resources
- creating a site conceptual model (SCM)
- classifying MTBE sites as A, B, C or D

**MTBE Groundwater Cleanup Levels for LUST Sites: Current and Proposed**



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**FOOTNOTES FOR MTBE MAP**

- |  |   |   |
|--|---|---|
| (1) Cleanup goal dependent on GW use as potable/non-potable                      | (5) Action level  | (11) Method A MTBE groundwater cleanup level proposed at 20 µg/L                |
| (2) Cleanup level/enforceable site-specific standard possible for drinking water | (6) WDNR NR 140 Enforcement Standard/ Preventative Action Limit goals         | (12) Tier 1 RBSL level based on aesthetics, effective March 2000                |
| (3) Tier 1/RBSL cleanup/action level/Tier 2 drinking water cleanup level         | (7) Health-risk guidance level; not enforced for LUST cleanup                 | (13) Revised Guidance (OR) or Rule (FL) expected to be effective in August 1999 |
| (4) Proposed Public Health Goal (PHG)/ enforceable secondary standard            | (8) Groundwater resource used as drinking water                               | (14) Interim action MTBE levels (i.e., NV 20/200)                               |
|  | (9) Cleanup level/action (i.e., ME 35/25)                                     | (15) Enforceable guidance criteria  |
|  | (10) No PST (LUST) cleanup level/non-PST aesthetic guideline level at 15 µg/L | (16) Proposed closure/cleanup level   |

Figure 3. MTBE groundwater cleanup levels for LUST sites: current and proposed (Martinson, 2000).

**Vulnerable groundwater areas.** These areas have one or more of the following characteristics:

- a high degree of hydrogeologic susceptibility to contamination as shown on various maps
- near-surface fractured bedrock geology that is a water supply source for a community
- above an aquifer that is a water supply source
- located within a 1,000-foot radius of a drinking water well or surface water body used as a drinking water source

**Site conceptual model.** The site conceptual model (SCM) describes “the release scenario, surrounding land use, geology, well locations and the likely distribution of chemicals at a site, existing and projected water use patterns and other factors considered when making decisions at a site. It functions as the framework for the investigation, remediation and ultimately site closure and serves as the basis for communication between responsible parties, regulators, and other interested parties” (SWRCB, 2000). The model evolves as new data become available. The seven steps of the SCM development are:

- investigate the site, which includes sampling and locating existing wells
- develop initial conceptual model; assign investigation priority class, which uses a model to estimate travel time and classifies water wells as A, B, C, or D (Figure 4, SWRCB, 2000; note D falls off the figure; D represents the least vulnerable site)
- perform an interim remedial action that may include use of interdiction wells to contain a highly concentrated plume
- perform a site characterization/investigation, which includes collecting more data and updating the SCM
- update conceptual model and assign cleanup priority class based on estimated travel time to the nearest down-gradient receptor; determine cleanup class (A,B,C or D) and response time to cleanup by using criteria given
- apply corrective action/remediation that may include soil excavation and/or dewatering of source areas, soil vapor extraction, groundwater extraction and above-ground treatment, flow-through remediation cells/in-situ bioremediation, free-product removal, in-situ air sparging, soil vapor extraction/dual phase extraction
- perform verification monitoring

**MTBE classification.** Sites are categorized based on a function of theoretical travel time to the nearest receptor. The computer model incorporates a statistical simulation of a three-dimension transport equation and separates sites as shown in Figure 4. For instance, a Class A site represents the most vulnerable site while class D (not shown on this figure) represents the least vulnerable. At about 5 ppb and 500 feet to the nearest receptor, a class A site becomes a class B, whereas at about 5 ppb and 1,000 feet, a class B site becomes class C. The class D site is not located in an area vulnerable to MTBE because its groundwater concentrations will always be under 5 ppb. Regulatory response time is quicker for a class A vs. a C site.

## Cost implications

Using California’s initial draft “Guidelines for Investigation and Cleanup of MTBE and Other Ether-Based Oxygenates” (SWRCB, January 2000), Martinson (2000) identified various costs across the three MTBE site classifications A, B and C. He compared these MTBE sites to the more conventionally understood BTEX-only/on-site LUFT scenario. For instance, Figure 5 shows the estimated percentage cost increases for all California work phases at a UST site detecting MTBE vs. a similar site that detects on-site BTEX. Class A sites (those most vulnerable to contamination) have the highest percentage increase. The remedial action plan (RAP) is the work component in each scenario that shows the greatest percentage increase. Although the percentages appear to be great, actual costs do not vary significantly, as Figure 6 indicates. For instance, the remedial action plan for a Class C site is about \$10,000, a class A site is \$15,000, and a BTEX-only site (BTEX onsite) is about \$7,500. The work phases of interim response, site assessment and closure/NFA show increases of \$20,000 to \$30,000 for Class A, B, or C MTBE sites compared to the on-site BTEX-only scenario (Figure 7). Figure 8 shows significant cost increases for MTBE/BTEX sites vs. BTEX-alone; the greatest increase was for remedial action plan implementation, and the least for two years of operation and maintenance. Figure 9 shows that actual costs of remedial action plan implementation, two years of operation and maintenance and four years of monitoring were large, \$30,000 to \$50,000. Figure 10 shows that the total cost of remediating an MTBE/BTEX site (class A) could be twice that of a BTEX-only site, \$450,000 vs. \$220,000.

While the two-fold total cost estimate appears substantial for a Class A MTBE site compared to an on-site BTEX-only site, Martinson (2000) conservatively estimated only two years of remedial system operation and maintenance and only four years of groundwater monitoring. It’s very likely that the typical MTBE groundwater cleanup site may experience 2-3 times higher durations for operation and maintenance and/or groundwater monitoring beyond the conventional on-site BTEX-only site. Thus, total costs for a Class A MTBE site in California could easily be 3-4 times higher compared to the on-site BTEX-only site, resulting in Class A total site costs exceeding \$1,000,000.

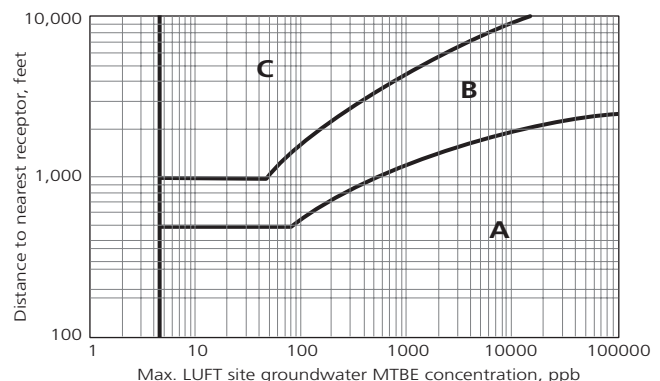


Figure 4. Classification of water wells using distance to nearest receptor and MTBE concentration (SWRCB, 2000).

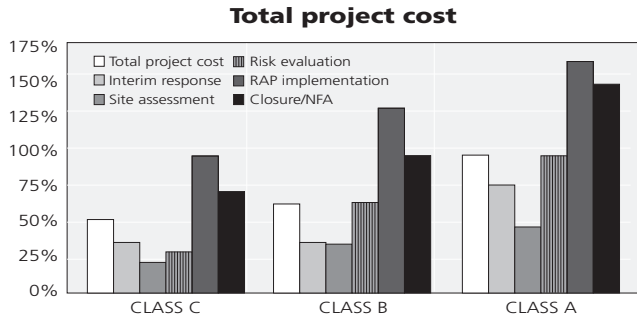


Figure 5. Percentage cost increases of remedial cost (from risk evaluation to closure) for MTBE sites A, B, and C vs. BTEX-only sites (Figures 5-10 are from Martinson, 2000).

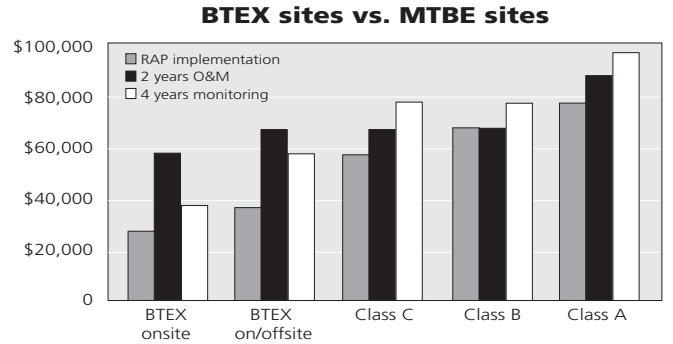


Figure 9. Cost differences of remedial action plan implementation, two years of operation and maintenance and four years of monitoring for MTBE sites A, B, and C vs. BTEX-only sites.

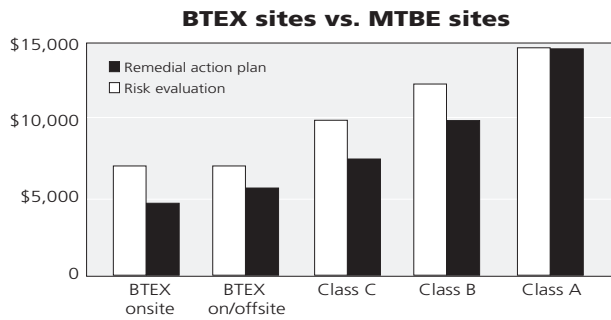


Figure 6. Cost differences of risk evaluation and remedial action plan for BTEX-only sites vs. MTBE sites A, B and C.

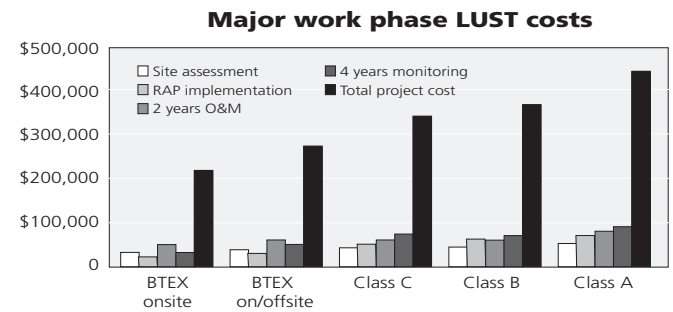


Figure 10. Cost differences of site assessment, remedial action plan implementation, two years of operation and maintenance and four years of monitoring and total project cost for MTBE sites A, B, and C vs. BTEX-only sites.

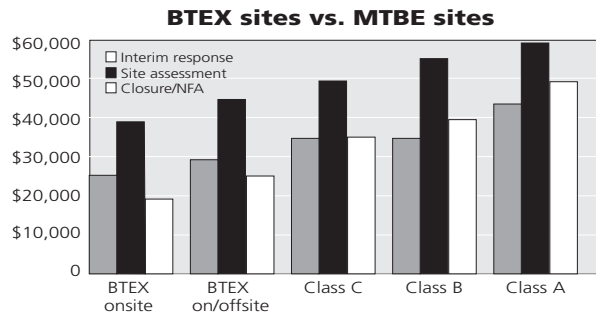


Figure 7. Cost differences of interim response, site assessment and closure/NFA for BTEX-only sites vs. MTBE sites A, B and C.

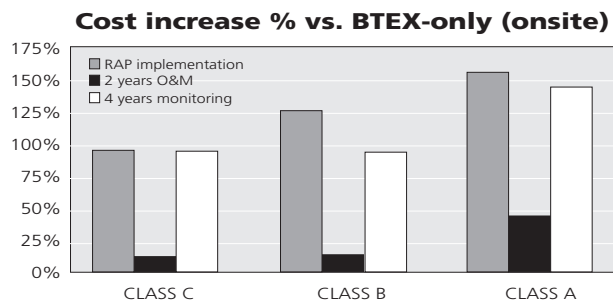


Figure 8. Percentage cost increase to implement remedial action plan, two years of operation and maintenance and four years of monitoring for MTBE sites A, B, and C vs. BTEX-only sites.

Martinson developed these projected costs using the initial draft California guidelines (SWRCB, January 2000). Historical cost data for the various phases of work at California LUFT sites, derived from responsible parties and industry associations, were extrapolated to create the cost projections. As experience is gained in utilizing the California Guidelines for MTBE LUFT sites, it is possible that these estimates may increase (Martinson, 2000).

**MTBE references**

The most recent and comprehensive sources of MTBE information can be found on the following websites:

- American Petroleum Institute, <http://www.api.org/mtbe>
- American Society of Testing and Materials <http://www.astm.org>
- Association of California Water Agencies <http://www.acwanet.com>
- Association of State and Territorial Solid Waste Management Officials (ASTSWMO), and in particular, the MTBE newsletters at <http://www.astswmo.org/Publications/summaries.htm#MTBE>
- California Department of Health Services <http://www.dhs.ca.gov>
- California Environmental Protection Agency <http://www.calepa.ca.gov>

- Lawrence Livermore National Laboratory  
<http://www.llnl.gov>
- National Water Research Institute  
<http://www.ocwd.com/nwri>
- State Water Resources Control Board  
<http://www.swrcb.ca.gov>
- U.S. Geological Survey, MTBE bibliography, sorted by entry date, keywords, free text or author  
<http://wwwsd.cr.usgs.gov/navqa/vocns/mtbe/bib/>
- U.S. EPA OUST, <http://www.epa.gov/OUST/mtbe>
- Western States Petroleum Association  
<http://www.wspa.org>

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Martinson, M., personal communications, May, August 2000.

Martinson, M., "MTBE Regulatory Overview: Cost Implications for MTBE Cleanup," talk given at the 12<sup>th</sup> Annual UST/LUST National Conference, Portland, Oregon, March 20-22, 2000.

SWRCB, State Water Resources Control Board, "Guidelines for Investigation and Cleanup of MTBE and Other Ether-Based Oxygenates", March 2000 (previously January 2000); <http://www.swrcb.ca.gov/~cwphome/ust/usthmpg.htm>.

UTTU, Vol. 13, No. 4, 1999.

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UTTU thanks Mike Martinson, Delta Environmental, Minnesota ([mmartinson@deltaenv.com](mailto:mmartinson@deltaenv.com)), for his help on this article.



## MTBE sorbents

Davis and Powers (2000) recently screened several substances in an effort to identify sorbents other than activated carbon that could effectively remove MTBE from groundwater.

### Hydrophilic nature

MTBE,  $\text{CH}_3\text{-O-C}(\text{CH}_3)_3$ , is hydrophilic by virtue of its polar oxygen atom. In addition, it has a high aqueous solubility, a high vapor pressure, a low Henry's constant, and a low organic partition coefficient. "Thus, treatment technologies that are dependent on the hydrophobic properties of contaminants are generally ineffective for the removal of MTBE from drinking water. . . . The air/water ratio required for treatment of water containing MTBE by air stripping is over six times higher than for other petroleum hydrocarbons" (Davis and Powers, 2000). MTBE adsorption efficiency on activated carbon is less than 10 percent the adsorption efficiency of gasoline contaminants.

### Potential sorbents

Sorbents that Davis and Powers (2000) investigated included activated carbon, carbonaceous resins, acrylic resins, C18 bonded silica, and graphic carbon (Table 1).

Sorbent type	Brand name	Grain size ( $\mu\text{m}$ )	Previous uses
Activated carbon	Filtrisorb 400	10-50	BTEX, TCE, phenol
Carbonaceous resins	Ambersorb 563, 572	85-300	TCE, chloroform
C18 bonded silica	Hypersil ODS	10	Phenols, BTEX
Acrylic resins	Polysorb MP-1	25-60	Phenols, nitramines
Graphic carbon	Hypercarb	7-40	Phenols, pesticides

Table 1. Sorbents, brand name, size and uses (Davis and Powers, 2000).

**Activated carbon** is commonly used for treating VOC-contaminated water. Activated carbon is manufactured from coal, wood and coconut shells, which in the process creates a pore structure within the carbon particle. Pore structure is related to adsorption. For instance, MTBE requires "high-energy" pores typically present in coconut-based carbons. Because its raw materials are variable, however, coconut-based activated carbon produces activated carbon that varies significantly from one sample to another. Performance varies too. One type of activated carbon produced from select grades of bituminous coal can effectively treat MTBE-contaminated waters at trace levels (Carter and others, 2000).

**Carbonaceous resins** are similar to ion exchange resins but lack the ionic functional groups; they have been used for treatment of VOC-contaminated water. At low concentrations of MTBE, synthetic carbonaceous resins have greater capacity for adsorption than activated carbon. "The nature of the internal pore structure of the carbonaceous resins affects the mechanisms of sorption. Adsorption occurs in the micropores through physical adsorption, including van der Waals forces, dipole-dipole interactions and hydrogen bonding. Due to the limited volume of micropores, the capacity of the resins levels off at high aqueous concentrations as the micropores are actually filled with solute molecules. Since the adsorption fields from the pore walls overlap, the micropore filling process enhances adsorption" (Davis and Powers, 2000).

**Acrylic (styrene divinyl-benzene copolymer) resins, C18 bonded silica and graphic carbon** have been previously used to concentrate polar compounds in solid-phase extraction applications. "The octadecyl group on C18 silicas allows for concentration of moderately polar organic compounds. . . . sorption of small, polar organic compounds on bonded silica sorbents is largely due to nonpolar interactions. . . . Aromatic rings present in the styrene/divinylbenzene matrix of acrylic resins allow for electron-donor interaction. The presence of

polar species on the surface of porous graphitic carbons allows for adsorption of highly polar compounds" (Davis and Powers, 2000).

Some of these synthetic sorbents require a prewetting and/or conditioning step. Wetting agents include acetone, methanol and ethanol. Wetting allows the very hydrophobic sorbents to be suspended in water and activates the surface functional groups of the sorbent, thereby increasing sorption capacity.

### Experimental study

Batch equilibrium adsorption experiments with MTBE alone were performed for the sorbents considered. Bi-solute solutions of MTBE and m-xylene were also tested for selected sorbents. Experimental details are given in the Davis and Powers text.

"To best compare sorption capacities among the adsorbents, isotherm models were applied to experimental data." Researchers used the Freundlich isotherm to fit log-transformed experimental data. For the curvilinear data obtained from the two carbonaceous resins, researchers used the Dubinin-Astakov isotherm for data analyses. Again, see the text for details.

### Results of single solute experiments

Results from the single solute (MTBE) experiments follow:

- activated carbon, Filtrasorb 400: ineffective for MTBE removal at low concentrations
- carbonaceous resin, Ambersorb 563, 572: higher adsorption than activated carbon; at MTBE concentration of 1 mg/L, Ambersorb 563 can adsorb five times the mass of MTBE that activated carbon can, while Ambersorb 572 can adsorb three times this mass; above 600 mg/L, Filtrasorb 400 is a more effective sorbent
- C18 bonded silica, Hypersil ODS: no statistically significant decrease in MTBE concentration
- acrylic resins, Polysorb MP-1: much lower adsorption capacity than the activated carbon
- graphitic carbon, Hypercarb: higher adsorption than activated carbon; in fact, capacity is more than double activated carbon's; Hypercarb requires prewetting, however, and the prewetting agent (alcohol) is an undesirable addition to groundwater

### Bi-solute experiment results

In the field, MTBE will usually be accompanied by BTEX compounds that will interfere with adsorption of MTBE. Researchers modeled the bi-solute effect in the laboratory, using m-xylene to represent the BTEX compounds in bisolute experiments. They found the following:

- m-xylene was removed to below-detection limits (0.1 mg/L) in all competitive adsorption experiments
- resins (Ambersorb) preferentially sorb m-xylene over MTBE; Ambersorb is more hydrophobic than activated carbon and thus would readily adsorb m-xylene, which is hydrophobic

- carbonaceous resins had a greater affinity for m-xylene than MTBE
- the sorption capacities at aqueous concentrations of 1mg/L MTBE drop significantly when m-xylene is present
- activated carbon is most affected (35 percent reduction) while the Ambersorb 572 is least affected

### Sorbent capabilities, costs and conclusion

Davis and Powers (2000) suggest that before results of this study are applied to groundwater treatment scenarios, researchers must extend the isotherms (Freundlich and Dubinin-Astakov) to lower concentration ranges to quantify sorption capacities at drinking-water-quality guidelines. In addition, reduced MTBE sorption in the presence of xylene suggests that carbonaceous resins might be most valuable as a polishing step.

Sorbent cost is a consideration:

- Filtrasorb 400 is \$1.25/lb
- Ambersorb 563 is \$35.00/lb
- Ambersorb 572 is \$50.00/lb

Carbonaceous adsorbents have an advantage in being amenable to on-site regeneration. If on-site regeneration processes were developed for the Ambersorb resins, they would be more cost-effective than activated carbon.

Activated carbon is expensive to regenerate and is often disposed in landfills.

Davis and Powers (2000) conclude that the most promising agents for MTBE removal from groundwater are the carbonaceous resins, Ambersorb 563 and 572. (Reviewer's note: Lawrence Livermore Lab reported that coconut also worked well in this capacity.)

### Related study: zeolites for MTBE adsorption

A zeolite is a "natural or synthetic hydrated aluminosilicate with an open three-dimensional crystal structure in which water molecules are held in cavities in the lattice. The water can be driven off by heating and the zeolite can then absorb other molecules of suitable size. Zeolites are used for separating mixtures by selective adsorption—for this reason they are often called molecular sieves" (Daintith, pg. 312, 1990).

Anderson (2000) tested the ability of zeolites with high SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> ratios to remove MTBE, chloroform and trichloroethylene (TCE) from water. According to Anderson, "It is well-established that the sorption characteristics of zeolite-type minerals are defined by pore size and charge properties. Most naturally occurring zeolites bear a relatively high framework charge arising from Al<sup>3+</sup> substitution for Si<sup>4+</sup> in the crystal lattice, resulting in a structure with a high cation-exchange capacity. Such zeolites have been used as ion exchangers to treat water. . . Zeolites with high SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> ratios have a low capacity for retaining cations but are more hydrophobic and can therefore sorb uncharged molecules. Selectivity for molecules arises from constraints imposed by the pore size and shape; molecules larger than the pore diameter are effectively excluded from the internal spaces. Molecules

sufficiently small to enter the pore spaces interact with the zeolite to varying extents based upon the van der Waals and other electrostatic interactions that will be a function of the size, shape and molecule's chemical properties."

In addition, Anderson (2000) reports that zeolites

- maintain stability over a wide range of conditions including elevated temperature and acidic conditions
- may be regenerated with removal/destruction of organic contaminants by heating
- would be able to sorb MTBE from water even in the presence of other organic compounds
- are currently being studied in laboratory column experiments to more fully characterize the sorption properties of high silicon zeolites

## Reference

Anderson, M.A., "Removal of MTBE and Other Organic Contaminants from Water by Sorption to High Silica Zeolites," *Environmental Science and Technology*, Vol. 34, No. 4, 2000; <http://www.pubs.acs.org>.

Carter, S.R., Dussert, B.W. and N. Megonnell, "Reducing the Threat of MTBE-Contaminated Groundwater," *Pollution Engineering*, May 2000; <http://www.pollutionengineering.com>.

Daintith, J.D., *A Concise Dictionary of Chemistry*, 1990, Oxford University Press; <http://www.oup.com/>.

Davis, S.W. and S.E. Powers, "Alternative Sorbents for Removing MTBE from Gasoline-Contaminated Ground Water," *Journal of Environmental Engineering*, April 2000; 1801 Alexander Bell Drive, Reston, Virginia 20191-4400.



## Research notes

### *Seasonally Induced Fluctuations in Microbial Production and Consumption of Methane During Bioremediation of Aged Subsurface Refinery Contamination*

Conrad, M.E., Templeton, A.S., Daley, P.F. and L. Alvarez-Cohen, *Environmental Science and Technology*, Vol. 33, No. 22, 1999; <http://www.pubs.acs.org>.

Researchers examined carbon isotopic data ( $^{14}\text{C}$ ,  $\delta^{13}\text{C}$  and  $\delta\text{D}$ ) of  $\text{CO}_2$  and  $\text{CH}_4$  from 90- to 130-year-old refinery wastes in shallow saturated soils at three sites in Alameda Point, California, to determine the extent of intrinsic bioremediation.

At one site carbon isotopic compositions of  $\text{CO}_2$  and  $\text{CH}_4$  indicated processes of acetate fermentation rather than  $\text{CO}_2$  reduction or thermogenic processes. "The combination of stable and radio isotope data from all three sample sets indicate that the soil gas  $\text{CH}_4$  was produced by microbial fermentation of acetate that was primarily derived from the petroleum hydrocarbon contaminants in the soil." Thus, refinery wastes (hydrocarbons and asphaltene residues) were undergoing bioremediation.

Researchers also determined that  $\delta^{13}\text{C}$  values of  $\text{CO}_2$  varied greatly with depth. At another sampling location, the higher than expected  $^{14}\text{C}$  content found at depth (to 100 cm) could be derived from several factors such as

- degradation of natural organic matter
- root respiration
- dissolution of shells
- atmospheric  $\text{CO}_2$

Researchers noted that "In addition to the depth-dependent variations, strong seasonal variations in the content and isotopic composition of the soil gas were observed."

### *Complete Compositional Monitoring of the Weathering of Transportation Fuels Based on Elemental Compositions from Fourier Transform Ion Cyclotron Resonance Mass Spectrometry*

Rodgers, R., Blumer, E.N., Freitas, M.A. and A.G. Marshall, *Environmental Science and Technology*, Vol. 34, No. 9, 2000; <http://www.pubs.acs.org>.

Researchers developed a system to identify "elemental compositions for hundreds of components of diesel fuel, jet fuel (JP-8) and gasoline and characterized each of their chemical compositions before and after artificial "weathering." The system consists of a glass heated inlet system (AGHIS) coupled to a home-built 6.0 T Fourier transform ion cyclotron resonance (FT-ICR) mass spectrometer. According to researchers, "Elemental composition assignment of every peak in the mass spectrum of each fuel and its weathered analogues provides a unique chemical "fingerprint" that serves to identify positively the contaminant and quantitate extent of weathering. . . Fourier transform ion cyclotron resonance mass spectrometry offers ultrahigh mass resolving power ( $>1 \times 10^6$ ), sub ppm mass accuracy and simultaneous broadband analysis in a few seconds, making it an attractive option for complex volatile mixture analysis with little or no sample preparation."

### *Connecting Ecological Monitoring and Ecological Indicators: A Review of the Literature*

J.A. Griffith, *Journal of Environmental Systems*, 1998, Baywood Publishing Co., 26 Austin Avenue, P.O. Box 337, Amityville, New York 11701, <http://www.baywood.com>.

This article focuses on important aspects of national ecological monitoring, such as

- the philosophy and objectives upon which monitoring programs are based
- the use of ecological indicators for assessing the status of the environment
- criteria upon which to base choice indicators

For instance, objectives/characteristics/attributes of environmental monitoring programs would ideally include:

- secured long-term funding and commitment
- flexible goals
- refined objectives
- adequate attention to information management
- experimental approach to sampling design

- peer and statistical review
- no bias in selection of long-term plot locations
- ensured adequate temporal replication
- blended theoretical and empirical models with means to validate both
- synthesized retrospective, experimental and related studies
- integration with larger- and smaller-scale programs to develop extensive outreach programs
- determination of the presence or absence of change/impact in an area
- ability to monitor or predict the response of organisms and ecosystems to change
- quality preparation, storage and analysis of samples, including lab quality control
- interpretation of results and provision to advise policy makers

Griffith states that the preplanning goal and objective formulation and rationale for choosing indicators are more important than the physical collection of data, data analysis, logistics or technical equipment.

Griffith (1998) says that "Regardless of the actual indicator choices, an adequate monitoring system designed to assess ecological condition on a regional scale will consist of a multivariate suite of indicators integrating biological, chemical and physical measures and integrating hierarchical levels rather than placing inordinate emphasis on any one or two indicators. The use of only one or two forest health indicators in Europe was a basic error in forest health monitoring in the late 1980s. After reviewing much of the literature, one can expect monitoring programs to be dynamic and not static" because

- concern over the types of impacts will change as restoration activities succeed in their goals and new forms of impact are identified and quantified
- results of basic research and surveillance programs will undoubtedly modify the suite of parameters deemed most useful for evaluating ecosystem health
- ecosystem goals and objectives will continue to be developed and refined to meet the broad and changing demands of various shareholders

In conclusion, Griffith believes that "Ecologists need to work toward defining what is 'good' ecological condition and to determine usefulness of the 'ecological health' analogy. Although scientists and environmental managers promoting the ecological or ecosystem health concept do not regard ecosystems as organisms, there still exists the notion among some professionals that this abstraction connotes an ecosystem/human medicine analogy which may prove misleading when communicating environmental information to the public. The debate over the issue of whether ecological monitoring and assessment should be a purely scientific endeavor or whether it should incorporate social values also needs to be resolved."

#### *Estimation of Hydrocarbon Biodegradation Rates in Gasoline-contaminated Sediments from Measured Respiration Rates*

Baker, R.J., Baehr, A.L. and M.A. Lahvis, *Journal of Contaminant Hydrology*, Vol. 41, 2000; <http://www.elsevier.com/locate/jconhyd>

Researchers created an "open-microcosm" method for determining respiration rates and hydrocarbon biodegradation rates in gasoline-contaminated unsaturated soils and sediments. The open microcosm allows for continuous/intermittent addition/removal of substrates, nutrients, electron acceptors or other constituents and sampling of one or two more phases. Experiments tested the hypothesis that hydrocarbon biodegradation rates can be calculated from O<sub>2</sub> and CO<sub>2</sub> reaction rates, assuming complete hydrocarbon mineralization is the predominant biochemical pathway for hydrocarbon utilization.

Cumulative hydrocarbon utilization is determined as follows:

- from direct monitoring of the hydrocarbon mass balance
- by calculating hydrocarbon utilization from O<sub>2</sub> consumption data
- by calculating hydrocarbon utilization from CO<sub>2</sub> production data

The latter two assume a certain stoichiometric relationship and complete hydrocarbon mineralization. "A close match of the three lines (elements) would support the use of CO<sub>2</sub> and O<sub>2</sub> data to estimate hydrocarbon utilization . . . showing an error of about ±50 percent in estimating hydrocarbon consumption from O<sub>2</sub> and CO<sub>2</sub> data. This error is a measure of the inherent limitations in applying the mineralization assumption in this method. Several measurement and reaction characteristics contribute to this error" (Baker and others, 2000):

- sampling and analysis accuracy of the vapor phase
- pH of the pore water (which may change over time) and effects of CO<sub>2</sub> + H<sub>2</sub>CO<sub>3</sub> and HCO<sub>3</sub><sup>-</sup> + CO<sub>2</sub><sup>2-</sup>
- net production or endogenous degradation of biomass
- microbial production of refractory organic compounds

The stoichiometric hypothesis and O<sub>2</sub> and CO<sub>2</sub> reaction rates overpredicted hydrocarbon degradation rates of toluene and p-xylene in sediment from the unsaturated zone. The reverse was true for water table aquifers and saturated-zone sediments, which may be attributable to microbiologic activity. Viable microbes in the saturated zone sediments increased by about three orders of magnitude. "The anticipated net increase in biomass necessitates a greater consumption of substrate (toluene or p-xylene) than would be evidenced by CO<sub>2</sub> or O<sub>2</sub> reaction rates. This is consistent with the data . . . where hydrocarbon is utilized at a higher rate than would be predicted by respiration rates. There was no change in total viable microbial count in the bioreactor filled with unsaturated-zone sediment with p-xylene as the substrate, and both O<sub>2</sub> and CO<sub>2</sub> data closely predicted hydrocarbon utilization . . . If significant biochemical or abiotic CO<sub>2</sub> production or O<sub>2</sub> consumption **unrelated** to hydrocarbon degradation are present, using O<sub>2</sub> and CO<sub>2</sub> data may not be valid for estimating hydrocarbon biodegradation rates." Thus, control experiments using uncontaminated sediment samples to define background conditions are essential. Respiration rates

from biodegradation of background organic substances can be subtracted from the total respiration observed in contaminated samples, giving a respiration value for contaminants.

Researchers also noted the following:

- all experiments to date “have used highly permeable sandy sediments, and rapid mixing of the vapor phase was observed; mixing may be problematic with silty or clayey sediments”
- using O<sub>2</sub> consumption data is preferable to using CO<sub>2</sub> production data because O<sub>2</sub> mass-balance calculations do not significantly depend on aqueous-phase partitioning; in addition, abiotic CO<sub>2</sub> production could be significant in carbonate-rich sediments
- reaction rates vary with depth-dependent factors such as hydrocarbon concentration, O<sub>2</sub> availability, moisture content and microbial populations
- values of in-situ measurement of respiration rates and hydrocarbon biodegradation rates were similar when researchers used an open microcosm containing gasoline-contaminated sandy sediments, suggesting that the bioreactor method can be used to produce meaningful and cost-effective estimates of in-situ hydrocarbon biodegradation

***A Controlled Field Evaluation of Continuous vs. Pulsed Pump-and-Treat Remediation of a VOC-contaminated Aquifer: Site Characterization, Experimental Setup and Overview of Results***

Mackay, D.M., Wilson, R.D., Brown, M.J., Ball, W.P., Xia, G. and D.P. Durfee, *Journal of Contaminant Hydrology*, Vol. 41, 2000, pgs. 81-131; <http://www.elsevier.com/locate/jconhyd>.

Researchers isolated two cells of a VOC plume to determine the effect of continuous vs. pulsed pump-and-treat on contaminant removal. A problem of continuous pump-and-treat is that contaminant removal rates decrease due to “slow mass transfer of contaminants into the flowing aqueous phase because of some combination of slow dissolution of non-aqueous-phase liquids (NAPLs), slow diffusion from less permeable strata of media and slow desorption of sorbed contaminants from aquifer solids. . . Although continuous pumping at a high rate can maximize rates of diffusion from mobile regions, periodically ceasing or slowing groundwater extraction should offer improved efficiency in terms of the mass removed per unit volume of extracted water.” Advantages of pulsed operation include

- decreased operation and maintenance costs
- decreased treatment costs
- less total groundwater extracted

During the periods of ceased pumping, contaminants would ostensibly diffuse out from contaminated sediments.

At present, no field data exist to confirm these advantages, thus researchers created two isolated cells far enough downgradient from the VOC source so that NAPLs were unlikely to be present. NAPLs, however, were near enough so that the aquifer media had probably been exposed to VOCs

for a decade or more. Researchers sought to “identify the most significant sources of mass transfer rate limitation at the site and develop appropriate computational models to describe and predict the resulting effects on aquifer decontamination.” They also sought to identify site conditions and objectives that would benefit from a pulsed application.

The three major mass transfer limitations for saturated zones contaminated with VOCs are

- slow dissolution of NAPL into the groundwater
- diffusive transfer of contaminant mass from low-permeability zones (originally contaminated by diffusion of contaminants in the more permeable strata)
- desorption of contaminant mass from aquifer media

At contaminated sites where aquifer solids have been in contact with contaminants for years, “this long exposure time allows contaminants initially in more permeable strata to diffuse or be slowly convected into lower permeability zones, which become sufficiently contaminated to serve as long-term contamination sources during remediation.” In addition, “the slow mass transfer from less conductive, i.e., relatively impermeable zones can be greatly exacerbated if these zones have relatively higher sorptive partitioning (higher K<sub>d</sub>) compared to the permeable zones.”

Researchers concluded the following from their study:

- larger differences in efficiency between pulsed and continuous pumping would be expected at sites with more strongly sorbing aquifer media and with greater heterogeneity in hydraulic conductivity (i.e. presence of silt or clay layers)
- the pulsed approach would be slightly more efficient at mass removal than continuous pumping for contaminants with large reservoirs of mass in the aquitard (vs. aquifer)
- greater benefits would be expected if duration of pump-off periods could be extended beyond those studied here; during the 9-month study period, there were five major pump-on/pump-off cycles of 28 and 21 days respectively
- contaminant transport and remediation may be influenced by spatial variability
  - of the transport medium (aquifer)
  - in the pre-remediation contaminant distribution
  - of aquitard sorption properties

***Stochastic Analysis of Oxygen-Limited Biodegradation in Heterogeneous Aquifers with Transient Microbial Dynamics***

Miralles-Wilhelm, F. and L.W. Gelhar, *Journal of Contaminant Hydrology*, Vol. 42, 2000; <http://www.elsevier.com/locate/jconhyd>

Researchers developed a stochastic (random input variables assigned a range of variability) model to address the problem of oxygen-limited biodegradation of contaminants in aquifers in relation to transient microbial growth dynamics. This theory is applicable only after significant displacement of the plume has occurred. The model researchers developed is appropriate for a system (heterogeneous and anisotropic aquifer) characterized by the following:

- a contaminant (an electron donor)
- an oxidizer (i.e., dissolved oxygen—an electron acceptor)
- an active biomass

The theory considers effects of the following:

- physical, chemical and microbiological heterogeneities
- coupled transport/transformation equations

To evaluate the assumption of a steady-state biomass, researchers sought to quantify the effects of mean concentrations on the field scale coefficients of decay, retardation, and macrodispersion.

Their analyses (more than 60 equations are included in their paper) indicated that “the effects of transient microbial growth on the effective retardation factor and macrodispersivities are minor, while the effects are modest for the effective decay rate. Transient microbial growth dynamics occur over most contaminant and dissolved oxygen mean concentration ranges, and therefore a transient mean balance equation for biomass should be included in modeling efforts directed at quantifying oxygen-limited biodegradation at field scales. As in previous research, the effective decay rate is found to be less than the mean, which results in a larger field-scale contaminant half-life in a heterogeneous aquifer, compared to that in a homogeneous aquifer.”

Researchers also concluded that microbial growth can be sustained in a heterogeneous system under conditions that would preclude growth in a homogeneous system. Contaminant loss rate (effective half-life), however, “is lower in a heterogeneous system than in a homogeneous one with the same mean conditions.” (*Reviewer’s note: It is important to look at the macroscopic behavior of plumes and estimate the impact of all processes working together.*)

“Overall, the results suggest that the effects of heterogeneous biodegradation rate parameters can be significant and point

to the need to measure the heterogeneity of these biochemical properties along with physical heterogeneity. These measurements constitute an onerous task since they require significant temporal and spatial resolution. The design of the space-time network for such measurements can be aided with calculations made using the theoretical approach presented in this work.”



## Information sources

*Encyclopedia of Geochemistry*, 1999, edited by Marshall and Fairbridge, Kluwer, Academic Publishers, see <http://www.wkap.nl/kaphtml.htm/EOGC> for sample pages.

*Environmental Forensics: Principles and Applications*, 2000, by R. Morrison, CRC Press, call 800-272-7737 or see the website <http://www.crcpress.com>.

### U.S. EPA documents

For hard copies of these U.S. EPA documents, call 800-490-9198 or 513-489-8190 or fax 513-489-8695:

- *Abstracts of Remediation Case Studies*, Vol. 4 (EPA 542-R-00-006); abstracts of 78 cost and performance case studies, <http://www.frtr.gov/publications/abstractsvol4.pdf>
- *An Analysis of Barriers to Innovative Treatment Technologies: Summary of Existing Studies and Current Initiatives* (EPA 542-B-00-003), <http://clu-in.org/techpubs.htm>
- *FRTR Cost and Remediation Case Studies and Related Information* (EPA 542-C-00-001), a CD ROM of 218 cost performance reports, <http://www.frtr.gov/cost>
- *Ground Water Currents* (EPA 542-N-00-002), available at <http://clu-in.org/techpubs.htm>

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TITLE \_\_\_\_\_ PHONE \_\_\_\_\_

COMPANY/ STATE GOV. AGENCY \_\_\_\_\_

ADDRESS \_\_\_\_\_

E-MAIL \_\_\_\_\_

CITY \_\_\_\_\_ STATE \_\_\_\_\_ ZIP \_\_\_\_\_

**Website: <http://epd.engr.wisc.edu/uttu/>**

- *Innovative Remediation Technologies: Field Scale Demonstration Projects in North America*, 2<sup>nd</sup> Ed. (EPA 542-F-00-001), <http://clu-in.org/techpubs.htm>
- *Tech Trends* (EPA 542-N-00-0013) <http://clu-in.org/techpubs.htm>

*Guide to Optimal Ground Water Monitoring*; information on designing new monitoring programs that will achieve results cost effectively; <http://www.frtr.gov/optimization/>

*In-Situ Flushing with Surfactants and Cosolvents* <http://clu-in.org/techpubs.htm>

*In-Situ Thermal Technologies Netcast*; different methods of using heat in the subsurface for vadose and groundwater source zone remediation; <http://clu-in.org/thermal>

*Oil Spill Program Update* (EPA 540-R-00-001); view or download at <http://www.epa.gov/oilspill/docs/index.htm> or contact Beatriz Oliveira at [oliveira.beatriz@epa.gov](mailto:oliveira.beatriz@epa.gov)

*Remedial Systems Optimization*, on the Federal Remediation Technologies Roundtable home page: guidance documents, research projects, optimization tools for remedial systems, <http://www.frtr.gov/optimization/index.html>.

## Websites

Chemical Health and Safety Data: data on over 2,000 chemicals, [http://ntp-server.niehs.gov/Main\\_Pages/Chem-HS.html](http://ntp-server.niehs.gov/Main_Pages/Chem-HS.html)

Chemical Registry System, search for EPA chemical information by CAS number, chemical name, molecular formula, chemical type, definition, <http://www.epa.gov/crs/index.htm>

Federal Register and Code of Federal Regulations [http://www.access.gpo.gov/su\\_docs/](http://www.access.gpo.gov/su_docs/)

GPO access and federal government databases, including Federal Register and Code of Federal Regulations <http://www.access.gpo.gov>

National Library for the Environment, an environmental research exchange for educators, researchers, and foundation representatives, contains links to funding resources, <http://www.cnle.org/nle/crsnew.html>

The Toxicology and Environmental Health Information Program, which is an access point to Toxicology Data Network (TOXNET), <http://sis.nlm.nih.gov/tehip.htm>

U.S. EPA OnLine Library system databases, <http://cave.epa.gov>:

- National Service Center for Environmental Publications
- Environmental Financing Network
- National Enforcement Training Institute
- Subsurface Remediation Center
- Region I, V, and IX databases

Wisconsin libraries:

- Wiscat, combined catalog of the holdings of most Wisconsin libraries, <http://wiscat.brodart.com>
- Madcat, combined catalog of the holdings of the UW-Madison libraries, <http://madcat.library.wisc.edu/>

## New listservs

Subscribe to *EnvirotechNews* for business opportunities and recent EPA New England enforcement actions. Send e-mail to [listserv@unixmail.rtpnc.epa.gov](mailto:listserv@unixmail.rtpnc.epa.gov). Leave subject line blank and in the body of the message write: "Subscribe envirotechnews [your first name] [your last name]. Questions can be directed to Maggie Theroux at 800-575-CEIT or 617-918-1783.

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*UTTU obtained many of these sites and other information from the Groundwater Mailing List (<http://groundwater.com>), the Bioremediation Discussion Group (<http://biogroup.gzea.com>) and TechDirect (<http://clu-in.com/techdrct.htm>). UTTU thanks the moderators/editors from these groups—Ken Bannister of Groundwater, Richard Schaffner of Biogroup and Jeff Heimerman from U.S. EPA's TechDirect.*

## Underground Tank Technology Update

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