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UTTU is on the Web

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

U.S. EPA OUST has two excellent websites:

<http://www.epa.gov/swerust1/state/stateurl.htm>

Contains state home pages for UST, LUST and Fund agencies

<http://www.epa.gov/swerust1/mtbe/index.htm>

Contains advisories, publications, and links on MTBE



Four MTBE treatment technologies

This article summarizes four MTBE treatment technologies studied by Keller and others (1999a) at the University of California (Santa Barbara and Davis):

- air stripping
- granular activated carbon (GAC)
- hydrophobic hollow fiber membranes
- advanced oxidation processes (AOP) using ozone or ozone/hydrogen peroxide

For their evaluations, the researchers used design parameters from the published literature and/or conducted experimental studies to identify parameter values and validate published data. Researchers evaluated 10 different flow rates/concentrations (see Table 1). The goal of each simulation was to produce effluent water with 5 µg/L or less MTBE.

These concentrations and flow rates were designed to represent two conditions:

- low concentration (30 to 100 µg/L) levels and high flow rates (500 to 1,000 gpm) typical of contaminated drinking water supplies from surface waters or groundwater pumping wells
- high concentration (100 to 5,000 µg/L) and low flow rates (10 to 500 gpm) typical of groundwater wells near the contaminant source, usually a LUST

MTBE, an ether, is more difficult to remove from groundwater than hydrocarbons because of MTBE's physicochemical properties, which include

- high solubility, which gives MTBE its mobility and movement at essentially the same rate as groundwater flow
- weak partitioning to the organic fraction of soils/sediments/suspended particles and thus a penchant to remain in the aqueous phase
- slow to no biodegradability by virtue of
 - the strength and stability of the ether bond, which requires acidic conditions to cleave it
 - the bulky tert-butyl group, which does not allow easy access to the ether linkage
 - its recent introduction into the environment, which means indigenous microbes have not yet developed enzymatic systems to transform MTBE (Reviewer comment: This may be speculative.)

Cost considerations

Researchers amortized costs over a 20-year period with a 4 percent discount rate. Operation and maintenance (O & M) costs include

- operators for the units
- materials and electrical power
- fuel for the thermal treatment

Costs have an accuracy to -30 to +50 percent, although additional costs may be required for pretreatment and post-treatment polishing or storage.

Using the CapCost[®] software (in Turton and others, 1998, "Analysis, synthesis and design of chemical processes," Prentice Hall, New York, New York) to estimate total capital costs, researchers considered the following factors:

- (1) piping, electricity valves: 30 percent of equipment
- (2) site work: 10 percent of equipment
- (3) contractor fees: 15 percent of equipment plus 1 and 2
- (4) engineering costs: 5 percent on top of equipment plus items 1, 2 and 3
- (5) contingency: 20 percent on top of all previous costs

O & M costs were based on

- electrical power requirements at \$0.08/kW-h
- fuel at \$1.6 million BTU and 3 BTU/scfm
- labor at \$30/hr
- materials, about 3 percent/yr
- contingency plus administrative costs of 15 percent on top of all other O & M costs

The four technologies are described in detail below.

Air stripping

"Air stripping involves continuously contacting contaminated water with a large volume of air to transfer a significant fraction of the volatile organic compounds (VOCs) to the air phase" (Keller and others, 1999a). Contaminant removal efficiency is a function of

- the contaminant's Henry's law constant, H
- air stripping tower design
- water and air temperatures

MTBE's Henry's constant is so low at ambient temperatures that contaminant removal by air stripping is inefficient. Additional treatment of outlet vapors may be required by local regulations if more than 0.45 kg/day (1 lb/day) is emitted.

Case	1	2	3	4	5	6	7	8	9	10
Concentration (µg/L)	100	100	100	500	1,000	5,000	100	500	1,000	5,000
Flow rate (gpm)	1,000	500	100	100	100	100	10	10	10	10

Table 1. MTBE concentrations and flow rates (Keller and others, 1999a).

Complications include the presence of other VOCs. Of the 10 cases examined (see Table 1), outlet air cases 1, 5 and 6 exceeded the 0.45 kg/day limit. Thus remediators focused on creating more efficient air stripping tower designs.

Designs include

- packed towers
- spray towers
- bubble diffusion towers
- aspiration air strippers
- low-profile towers

The packed tower is the most cost-effective technology, followed by the low-profile tower. The low-profile tower is limited to a maximum flow rate of 100 gpm. Thus, researchers investigated packed towers. When available as off-the-shelf systems, these towers can be custom designed. To treat air emissions, the following technologies were considered:

- vapor-phase granulated activated carbon (GAC) adsorption.
- catalytic oxidation
- thermal treatment
- biofiltration
- vapor-phase oxidation using UV, ozone or UV/ozone

GAC. VOC vapors, passing over a bed of activated carbon, sorb onto active GAC sites. Once sites are filled, VOCs break through the exhaust end of the bed. "There are no well-documented studies of gas-phase sorption of MTBE onto GAC, in particular in the presence of other competing hydrocarbons, such as BTEX, typically present at MTBE sites. Given the relatively low sorption affinity of MTBE for GAC, it is possible that it will be displaced out of the GAC bed by other hydrocarbons, resulting in early breakthrough and increased carbon usage. Adsorption decreases with higher humidity and/or temperature in the gas stream entering the GAC bed" (*Keller and others, 1999a*).

Catalytic oxidation. A VOC-laden air stream passing over a catalyst bed, typically at temperatures above 200°C (392°F), oxidizes organic compounds to CO₂ and H₂O in catalytic oxidation. Some products of incomplete combustion form; however, ongoing studies will identify typical products of incomplete combustion and optimal operating conditions.

Thermal treatment. This technology uses either an internal combustion engine (ICE) or a furnace to oxidize MTBE. The ICE oxidizes hydrocarbons and MTBE to CO₂ and H₂O at efficiencies greater than 99.9 percent. Furnaces are usually used for higher air flow rates, but they are operated at higher temperatures and require greater amounts of fuel.

Biofiltration. Gas-phase biofiltration relies on MTBE-degrading bacterial species to mineralize MTBE. (See also *UTTU*, Vol. 13, No. 6, 1999, "MTBE biodegradation in biofilters".)

Vapor phase oxidation. At present, information is insufficient to determine if vapor phase oxidation of MTBE using AOP systems is feasible or cost-effective. Oxidation of by-products is expected to be an issue.

Design considerations and air stripping costs

Design of efficient air and membrane stripping systems relies on an accurate determination of Henry's law constant. "Since the oxygenates are quite soluble, precise experimental determination of Henry's constant presents some challenges" (*Keller and others, 1999a*). Researchers used two methods to evaluate Henry's law constant for MTBE: SPME/GC/MS and vapor-pressure data. Details are given in their text.

Using the following five scenarios, Researchers evaluated air stripping costs for the 10 cases listed in Table 1, with influent water at 15°C and an effluent of 5 µg/L:

- no vapor treatment
- vapor treatment using thermal oxidation with no heat recovery to preheat the influent water
- vapor treatment using thermal oxidation with heat recovery to bring the water temperature to 25°C
- vapor treatment using GAC
- vapor treatment using a gas-phase biofilter

Capital costs included stripping towers, pumping station, fired heater and heat exchanger, GAC bed and carbon replacement costs, accessories, contractor installation and engineering. Table 2 on the next page shows air stripping cost data (in dollars per 1,000 gallons) for the five treatment scenarios in the previous list.

Researchers (*1999a*) report that "treating MTBE-contaminated water to the 5 µg/L standard is 20 to 80 percent more expensive than treating the same influent to the 35 µg/L, with the largest impact on low flow rate units." Costs to treat ETBE (ethyl tertiary butyl ether) and TAME (tertiary amyl methyl ether) would be similar to MTBE costs because Henry's law constants of these compounds are similar.

Advantages of air stripping include the following:

- a proven, commercially applied technology
- suitability for treating MTBE and ETBE and TAME (all have similar Henry's law constants)
- ability to achieve very high removal efficiencies
- mechanical reliability and flexibility to handle variations in feed streams
- ability to design packed air stripping units to treat up to 1,000 gpm

Disadvantages include:

- either contaminated air is emitted or expensive air treatment is required because MTBE is transferred to air rather than destroyed
- a post-treatment polishing step may be required
- dissolved iron, calcium and magnesium may build up on the packing material and require cleaning or replacing of the packing material

Granular activated carbon

GAC is a substance made from materials with high carbon content, such as coconut shells, various coals, peat or wood. GAC has a high affinity for organic compounds and is useful in removing organic compounds from contaminated water or gas streams. "The most important property of an adsorbent/adsorbate pair is their affinity, usually measured in terms of mass of organic adsorbed per unit mass of adsorbent" (Keller and others, 1999a). The adsorbent can either be renewed, i.e., activated carbon can be regenerated using steam, or replaced with other new adsorbent material.

From laboratory and bench-scale tests, scientists have found that coconut-based activated carbon is most suitable for MTBE adsorption from contaminated water. MTBE-contaminated water may contain other organics, however, that compete for sorption sites. Keller and others (1999a) have observed that "in several field cases, as the composition of the contaminated water changes, other dissolved VOCs such as benzene can easily displace MTBE from the GAC, releasing a strong pulse of MTBE into the effluent."

Design considerations and costs

Researchers used commercial vessels to evaluate GAC operating conditions. Of concern is empty bed contact time, which assures sufficient contact time between the adsorbate and adsorbent and the mass transfer zone, MTZ. The MTZ, a region of rapidly changing concentration, moves wave-like through the sorption vessel.

Keller and others (1999a; Table 3) considered two criteria when estimating costs:

- low vs. high organic loading in influent water, as this has a significant effect on GAC usage rate
- new GAC replacement every time vs. on-site regeneration using steam

GAC costs \$1.25/pound while shipping spent GAC to an off-site regenerator would cost about \$0.25/pound. For flow rates of 100 gpm or higher, on-site regeneration using steam would be more cost-effective; at 10 gpm when the influent concentration is very high (5,000 µg/L), on-site regeneration would also be cost-effective. For smaller systems, such as those used at gas stations, on-site regeneration is not cost-effective because skilled personnel are required to perform the process.

Advantages of GAC include the following:

- the technology is proven
- with proper operation, very high removal efficiencies can be achieved
- the technology is simple, and because of its mechanical reliability, it can accommodate large variations in influent MTBE concentrations as well as variations in water flow rate
- expertise exists in system design and operation

Disadvantages include the following:

- natural organic matter and other dissolved organic chemicals in the influent have a stronger affinity for GAC than MTBE and thus displace MTBE from adsorption sites, decreasing removal efficiency

Case	1	2	3	4	5	6	7	8	9	10
Concentration (µg/L)	100	100	100	500	1000	5000	100	500	1000	5000
Flow rate	1000	500	100	100	100	100	10	10	10	10
Effluent at 5 µg/L										
No air treatment	0.23	0.25	0.40	0.59	0.68	0.88	1.54	2.30	2.65	3.55
Thermal oxidation w/o heat recovery	0.56	0.62	0.93	1.17	1.28	1.54	3.07	3.56	3.96	5.92
Thermal oxidation with heat recovery	0.50	0.53	0.76	0.84	0.88	0.97	2.35	2.68	2.84	3.22
GAC for air treatment	0.66	0.70	1.08	1.58	1.86	2.81	2.90	4.37	5.14	7.45
Gas phase biofilter for air	0.33	0.41	0.73	0.97	1.07	1.33	3.51	4.60	5.11	6.42
Effluent at 35 µg/L										
No air treatment	0.17	0.17	0.28	0.48	0.59	0.87	1.15	2.06	2.58	3.45
Thermal oxidation w/o heat recovery	0.48	0.51	0.73	0.92	1.04	1.31	2.17	3.08	3.60	4.97
Thermal oxidation with heat recovery	0.31	0.33	0.46	0.50	0.53	0.60	1.24	1.43	1.53	1.76
GAC for air treatment	0.58	0.59	0.87	1.33	1.62	2.59	2.00	3.29	4.08	5.95
Gas phase biofilter for air treatment	0.25	0.30	0.52	0.72	0.83	1.11	2.62	3.53	4.05	4.92
Benzene at 1 µg/L										
Benzene (no air treatment)	0.16	0.17	0.29	0.38	0.42	NA	1.08	1.36	1.47	NA

Table 2. Air stripping: amortized cost, dollars per 1,000 gallons treated (Keller and others, 1999a).

- an abrupt change in influent concentration of other organics can cause a sudden desorption of large amounts of MTBE into the effluent
- commercially available models may be less cost-effective than custom-made ones because design options are limited
- because the maximum GAC vessel size is typically 20,000 lbs, flow rates above 500 gpm cannot be accommodated (*Reviewer comment: They can be, but flow must be split into parallel lines of GAC vessels.*)

Ozone/hydrogen peroxide oxidation processes

“Ozonation involves a large number of reactions, which include molecular ozone, oxygen, and free radical reactions. The hydroxyl radical (OH⁻) is a product of ozone decomposition. It has been seen to react non-selectively with many organic and inorganic compounds and is hypothesized to be the most important reactive intermediate in aqueous systems. Hydroxyl radicals have an oxidizing power that ranks behind only that of fluorine and molecular oxygen; they are twice as strong as an oxidizing reagent as chlorine. Ozone, alone or in combination with hydrogen peroxide, has the potential to fully oxidize organic compounds such as MTBE to carbon dioxide and water” (*Keller and others, 1999a*).

Of great concern are byproducts formed from incomplete oxidation. TBF (tert-butyl formate) and TBA (tert-butyl alcohol), which are more toxic than MTBE, can be created from MTBE

ozonation if sufficient time is not allotted for complete oxidation. Full oxidation of MTBE requires five moles of ozone (O₃), which is generated from dehydrated air. MTBE degradation proceeds faster when the O₃/H₂O₂ combination is used.

Design considerations and experimental studies

The design for the ozone/hydrogen peroxide oxidation process was a continuously stirred flow reactor (CSFR) coupled to an ozone generator. Kinetic data helped determine reactor size. Keller and others (*1999a*) performed experimental studies to

- confirm kinetic rate constants and determine temperature dependency
- evaluate the combined effect of ozone and hydrogen peroxide reacting with MTBE
- carry out a mass balance of reactants and products of species involved

Details of the studies appear in the text of Keller and others (*1999a*). Researchers also found that TBF was produced during ozonation and ozone/hydrogen peroxide treatment, with a yield of 25 to 63 percent of initial MTBE. Longer residence times in the reactor would produce higher conversion of TBF to CO₂. TBA was detected, but only in residual amounts.

Table 4 shows design parameters for the ozone reactor. Assumptions include an influent water temperature of 15°C and mean ozone concentration of 5 µg/L. Table 5 shows amortized cost, in dollars per 1,000 gallons water treated using O₃.

Case	1	2	3	4	5	6	7	8	9	10
Concentration (µg/L)	100	100	100	500	1,000	5,000	100	500	1,000	5,000
Flow rate (gpm)	1,000	500	100	100	100	100	10	10	10	10
Low organics, replace GAC	0.65	0.66	0.93	1.43	1.77	3.07	1.20	1.81	2.24	3.85
High organics, replace GAC	0.74	0.76	1.03	1.65	2.08	3.77	1.32	2.09	2.62	4.71
Low organics, regenerate GAC	0.34	0.38	0.55	0.81	.098	1.67	1.98	2.25	2.50	3.29
High organics, regenerate GAC	0.39	0.44	0.61	0.93	1.15	2.05	2.18	2.60	2.92	4.02
Benzene, low organics, replace GAC	0.17	0.18	0.42	0.43	0.43	NA	0.57	0.58	0.59	NA

Table 3. GAC: amortized cost dollars per 1,000 gallons treated (*Keller and others, 1999a*).

Case	1	2	3	4	5	6	7	8	9	10
Concentration (µg/L)	100	100	100	500	1,000	5,000	100	500	1,000	5,000
Flow rate (gpm)	1,000	500	100	100	100	100	10	10	10	10
Reactor volume (gal)	1,000	500	300	500	500	1,000	100	100	100	200
Number of reactors	3	3	2	2	2	3	1	2	2	2
Ozone production (kg/hr)	0.25	0.12	0.025	0.12	0.25	1.24	0.003	0.012	0.025	0.12

Table 4. Design parameters of ozone reactor (*Keller and others, 1999a*).

Advantages of treating MTBE with ozone include:

- air treatment or hazardous waste disposal (e.g. spent GAC) is not required because MTBE is destroyed
- the process can be economically competitive at higher flow rates
- the process may reduce cost of water chlorination

Disadvantages of the process include:

- the process forms oxidation intermediates and other oxidized compounds, such as bromate
- there is limited experience with the process
- high organic loading and high levels of dissolved minerals in water reduce MTBE removal efficiency
- low flow rates and high capital costs limit technology application

Hollow fiber membranes

A membrane is a semi-permeable thin layer of material that, because of its physical and chemical properties, can separate two fluids. The hollow fiber membrane (HFM), just one type of membrane, is used to degas liquids. Membranes can

- be made of one material (asymmetric) or two different layers (composite)
- be made of different materials
- be porous or non-porous
- have different shapes

Researchers have used microporous HFM to strip VOCs. The process, pervaporation, "uses a vacuum sweep to remove gases and vapors from the membrane surface. The activity difference driving this process is maintained with a partial vacuum on the permeate side. A large concentration gradient is established between the aqueous phase concentration and the concentration in the gas phase" (Keller and others, 1999a).

With respect to HFM, "contaminated water is pumped through the lumen side of bundled microporous polypropylene hollow fibers while a vacuum is drawn counter-currently on the outside of the fibers. The hydrophobic membrane allows for efficient transfer of volatile compounds, from aqueous to gas phase. While the water is pumped through the hollow fibers, volatile components volatilize and diffuse through the gas-filled pores of the hollow fiber due to the large concentration gradient. Volatile compounds can then be pulled through by a

vacuum, swept away by a sweep gas or reacted with a second solution. Pollutants can be effectively transferred through the gas-filled pores to the gas phase while water does not permeate due to the polymer's hydrophobic nature. Compounds transfer from water to air in response to a concentration gradient maintained by the constant flow of contaminant-free air across the exterior of the fibers. Hollow fibers have a large surface area per unit volume, allowing greater contact between the phases" (Keller and others, 1999a).

Experimental results, module characteristics and cost estimates

Researchers investigated the efficiency of HFM, using air flow rates of 0.4 and 1.4 SCFM and water flow rates from 0.05 to 0.5 gpm at temperatures of 23°C, 30°C and 40°C. Researchers found that at low water flow rates (<0.3 L/min), temperature and air flow effects on removal efficiency were not significant. Removal was between 80 and 99 percent. At high flow rates, temperature significantly affected MTBE removal. The increase in water temperature increased MTBE's Henry's law constant, driving the equilibrium partitioning toward the gas phase. Increase in air flow rate did not significantly affect removal efficiency at the three temperatures investigated.

HFM properties include

- an interfacial area of 40 m²
- an effective length of 0.5 m
- the ability to accommodate water flow rates of up to 21 gpm
- the ability to use multiple modules in parallel to treat higher flow rates
- an air to water volumetric ratio of 30, compared to 150 for air stripping

Costs include the membrane module, influent water pump, vacuum pump and pressure instrumentation. Capital costs without vapor treatment are about \$10,000. The most effective air treatment for HFM is gas phase GAC. Table 6 shows amortized treatment costs, which accelerate at higher flow rates because multiple HFM units must be used in series or parallel.

HFM have distinct advantages over air-stripping, including:

- lower air-flow rates can be used, requiring smaller vapor-phase treatment units

Case	1	2	3	4	5	6	7	8	9	10
Concentration (µg/L)	100	100	100	500	1,000	5,000	100	500	1,000	5,000
Flow rate (gpm)	1,000	500	100	100	100	100	10	10	10	10
Only ozone	0.29	0.41	1.17	1.52	1.68	3.48	3.55	4.19	4.19	5.78
Ozone + GAC	0.67	0.75	1.44	1.95	2.14	3.45	5.99	6.02	6.05	7.25
UV/Hydrogen peroxide	0.62	0.65	1.30	1.35	1.40	1.83	3.15	3.20	4.01	4.06

Table 5. Ozone treatment: amortized cost dollars per 1,000 gallons (Keller and others, 1999a).

- water and air-flow rates can be controlled independently to maximize mass transfer rates because they are separated by the membrane
- the hollow flow configuration prevents aqueous flow channeling
- the air stream will contain little water due to the membrane's hydrophobic nature

General advantages of HFM include:

- the membrane module has a very small footprint
- high removal efficiencies can be obtained in modular steps
- the technology is mechanically reliable, with few moving parts
- all components are off-the-shelf items that can be easily assembled

Disadvantages include:

- field testing has been limited
- iron, calcium and manganese will precipitate on the fiber surface, plugging fiber pores
- useful unit life is unknown
- limited economies of scale because multiple modules must be used to treat higher air flows
- surge tank is required, if significant fluctuations in flow rate or MTBE concentrations are expected, to achieve desired removal efficiency

Conclusions

Researchers reached the following conclusions:

- if no air treatment is required, air stripping is the lowest-cost technology for high flow rates of 100 to 1,000 gpm, and hollow air treatment is the lowest-cost for flow rates of 10 to 100 gpm
- GAC is the most cost-effective at all flow rates, if air treatment is required and the influent water has low levels of other organic compounds
- when air stripping is required and high levels of organics exist in the influent, air stripping is more cost-effective than GAC at flow rates ≥100 gpm
- advanced oxidation is the most expensive alternative technology
- enough uncertainty exists concerning byproducts of advanced oxidation to warrant further study

- advanced oxidation could be potentially cost-competitive at high flow rates
- advanced oxidation and hollow fiber membranes are not proven technologies and should be compared on a case-by-case basis with air stripping and GAC
- the cost for treating MTBE-contaminated water is 40 to 80 percent higher than treating hydrocarbon-contaminated water

Field-scale HFM unit

Keller and others (1999b) recently conducted a field-scale HFM test at two California sites characterized by a high degree of water hardness as well as organic contamination. Free product and VOC-laden vapors also required treatment. Both sites had LUST contamination in shallow aquifers of fluvial-deltaic origin. Hydraulic conductivity ranged from 0.2 x 10⁻³ to 1.4 x 10⁻³ m/sec while average linear groundwater velocity was 70 to 440 m/yr, assuming a porosity of 0.3.

Researchers coupled an HFM module that could accommodate up to 38 L/min (10 gal/min) with a Spray Aeration Vapor Extraction (SAVE) system. The SAVE system's internal combustion engine extracted and combusted soil vapors while the spray aeration tank treated water. The SAVE technology, completely self-contained, can include an electrical generator of up to 40 kW and compressed air to power other pumps or actuator valves (Keller and others, 1999b).

To reduce water hardness and minimize calcium, manganese and iron deposits, researchers passed extracted water through a coarse filter and then to an ion exchange unit; the ion exchange unit also sorbed MTBE and BTEX. Next, they passed the softened water through a heat exchanger that served as the radiator for the internal combustion engine. This water was sprayed into a counter-current air flow in a fine mist within the SAVE. Workers subsequently passed the effluent through the HFM unit, then through the two tanks filled with GAC, and collected water samples from before and after all major units and between the two GAC units. VOC-laden vapors from SVE (soil vapor extraction), spray aeration and HFM were routed toward the internal combustion engine. "The latest version of the SAVE system includes an oxygen sensor in the engine's exhaust to adjust the air-fuel mixture automatically and thus achieve extremely low emissions of

Case	1	2	3	4	5	6	7	8	9	10
Concentration (µg/L)	100	100	100	500	1,000	5,000	100	500	1,000	5,000
Flow rate (gpm)	1,000	500	100	100	100	100	10	10	10	10
MTBE (no air treatment)	0.69	0.72	0.78	0.78	1.16	1.16	1.05	1.05	1.46	1.46
MTBE (air treatment)	1.05	1.12	1.35	1.66	2.25	3.05	1.91	2.29	2.96	3.96
Benzene (no air treatment)	0.69	0.72	0.78	0.78	1.16	NA	1.05	1.05	1.46	NA

Table 6. HFM: amortized cost in dollars/1,000 gallons treated (Keller and others, 1999a).

NO_x, CO₂ and uncombusted hydrocarbons . . . the unit also has telemetry capabilities to transmit operating conditions to an off-site computer, as well as receive changes in operating parameters via a cellular phone modem connection" (*Keller and others, 1999b*).

Test results

The system successfully decreased calcium, manganese and iron ions, thereby decreasing water hardness. The unit achieved an overall MTBE removal efficiency of 97 percent when the water temperature was above 40°C and flowrate was 19 L/min (5 gal/min). With flowrates above 26.5 L/min (7 gal/min), overall efficiency decreased 85 to 89 percent while water temperature was at 33 to 36°C. BTEX components were not detected in water treated by SAVE or HFM modules.

Estimated costs included the following:

- \$4,800 to \$5,500/month for SAVE and HFM rental
- \$500 to \$1,000/month for propane
- \$143/month rental for the ion exchange unit
- \$248 exchange fee for resin—which would occur every two or three months
- \$250/month for GAC unit rentals
- \$1,485 for GAC replacement, which would occur every 6 to 8 months

In addition, there would be mobilization and demobilization costs. Overall costs using this system to treat MTBE- and VOC-contaminated water would be about \$3.80/1,000 gallons.

"The current tests were run for five days each. Although the SAVE system has significant long-term experience, the HFM has not been tested under long-term conditions. Additional work is needed to determine the frequency with which the HFM module must be serviced or repaired. The treatment train is most applicable for sites where a significant amount of free product exists to operate the internal combustion engine. The system provides treatment of soil, water and gas phases at a very cost-effective rate. If the site requires only water treatment, then a better option is to use a stand-alone HFM unit with GAC for polishing, and electrical heating elements" (*Keller and others, 1999b*).

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UTTU thanks Arturo Keller, Bren School of Environmental Science and Management, University of California, for his help on this article. He can be reached at keller@bren.ucsb.edu.



Effects of ORC^R on MTBE degradation

This article summarizes experiences some investigators have had with oxygen release compounds (ORC^R) as applied to MTBE-contaminated sites.

Southern California site

While replacing a UST at a service station along the coast of southern California, site assessors found soil contaminated with 9,000 mg TPH/kg. Groundwater at about 18 feet was contaminated with up to 25,000 µg/L benzene and 13,000 µg/L MTBE. Both plumes appeared to be stable. Although remediators operated a soil vapor extraction system for 13 months, fine-grained sediments still retained a significant mass of fuel hydrocarbons (*Defibaugh and Fischman, 1999*).

Site characteristics

The site is characterized by:

- a groundwater flow gradient of 0.0037 ft/ft
- silt and clay from ground surface to about 20 feet
- silty, fine-grained sands to medium-grained sands in the saturated zone
- high concentration of chloride, 950 µg/L, and total dissolved solids, 4,700 µg/L
- a Darcy flow velocity of 0.067 to 0.24 ft/day

Oxygen release compound

ORC, Oxygen Release Compound^R, is a proprietary formulation of phosphate magnesium peroxide that releases dissolved oxygen, which stimulates aerobic biodegradation and theoretically helps metabolize dissolved hydrocarbons. ORC^R, whose release rate is dependent on contaminant flux and groundwater temperature, generally produces oxygen for about 6 months; however, in this brackish (salty) environment, release time was expected to be halved. A 10-degree temperature change (from 20°C) can also halve (10°C) or double (30°C) release rate. Other factors that affect ORC^R include groundwater velocity, biological oxygen demand, soil texture, porosity, pH, temperature and concentrations of other electron acceptors. For instance, saline and highly acidic environments (pH below 5) will reduce ORC^R lifetime. Although metals will take up oxygen, this oxygen can be returned to the system. The presence of electron acceptors, therefore, enhances ORC^R effectiveness (*Koenigsberg, personal communication, 1999*).

Remediators estimated that the mass of both BTEX and MTBE plumes (i.e., dissolved phase) at this site was 3.1 pounds. Using a stoichiometric relationship of 3:1 and assuming an additional oxygen demand by competing organic material (such as organic carbon in the soil), remediators determined that the site required 75 pounds of oxygen, or 750 pounds of

ORC^R. Remediators injected an additional 150 pounds of ORC^R at the property line and in the source area.

Remediators injected the ORC^R slurry through 18 direct-push boreholes, some as deep as 28 feet. Remediators wanted not only to degrade BTEX and MTBE but also to create a barrier.

Sampling

Field workers collected baseline groundwater samples prior to ORC^R injection, and then monthly for five months. Samples were analyzed for TPHg, BTEX, and MTBE using standard procedures. Baseline conditions were established by measuring in the field, prior to sample analyses, the depth to water, dissolved oxygen, temperature, pH, oxidation/reduction potential and conductivity.

Results

Figure 1 shows dissolved MTBE and BTEX concentrations and oxidation/reduction potential vs. time. Dissolved MTBE and BTEX concentrations dropped by 82 and 77 percent, respectively, after the first month, then an additional 1 and 20 percent, respectively, after the second month. By the third month, however, both BTEX and MTBE concentrations rebounded to or above pre-treatment level. Typically, rebound levels will decrease with time. Regensis, the company that produces ORC^R, estimates that of the 5,000 applications of its compound over the past five years, about 1/3 of the sites required one or more additional applications of ORC^R; in terms of life-cycle cost, the technology is less expensive than other technologies such as pump-and-treat. At sites with predominantly MTBE, rebound should not be as significant because of MTBE's low retardation factor (Koenigsberg, 1999).

Dissolved oxygen readings never varied more than 1 µg/L, ranging from 0 to 1 µg/L. The lowest potential was measured at the well located in the source area.

Defibaugh and Fischman (1999) believe that rebound may have been caused by

- fuel hydrocarbons adsorbed to the soil particles in the capillary fringe, which may have provided a source to reintroduce hydrocarbons in the dissolved phase

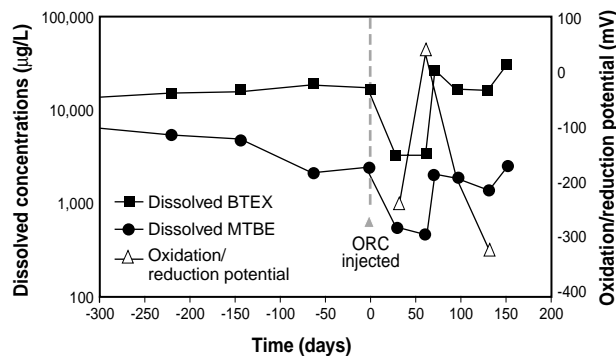


Figure 1. Dissolved MTBE, BTEX and oxidation/reduction potential before and after ORC injection (at time 0) in a monitoring well (Defibaugh and Fischman, 1999).

- apparent vs. actual dissolved fuel hydrocarbon concentrations; samples from monitoring wells may not have accurately sampled actual contaminant concentrations, and oxygen may have been exhausted before all hydrocarbons were metabolized (Reviewer comment: Not substantiated.)
- groundwater salinity that may have caused oxygen to be released at a greater rate than could be used by the in-situ microbes

Although researchers collected no data to confirm an increase in microbial activity, Defibaugh and Fischman believe that the greater oxygen availability and reduction of dissolved hydrocarbon concentrations support the idea that some biodegradation occurred. Because MTBE and BTEX concentrations decreased at the same time, it is likely both compounds were affected by the same processes. (Reviewer comment: There is no evidence to substantiate this claim.)

Evidence from other studies

From laboratory and field studies, Koenigsberg and others (1999) determined that with respect to biodegradation, MTBE

- follows Michaelis-Menten kinetics (zero order to first order with a hyperbolic change between) which is related to the uptake rate of one compound and diminishing concentrations of another
- is subject to interference by background hydrocarbons such as benzene and xylene; this interference may be described in terms of classical competitive inhibition (that is, MTBE destruction is inhibited)
- degraded at a majority of sites, only after BTEX levels decreased

MTBE bioremediation in Wisconsin

At a service station in Lake Geneva, Wisconsin, BTEX concentrations in groundwater were up to 800 ppb, and MTBE up to 14,000 ppb. Groundwater velocity here was about 0.2 ft/day. Geologists injected 1,700 pounds of ORC^R as a slurry to enhance aerobic degradation. Measurements from two downgradient monitoring wells initially at 750 ppb and 1,700 ppb showed that MTBE concentrations degraded to less than 2 ppb after about nine months (Koenigsberg and others, 1999; Regensis website, technical bulletin 3.1.11).

MTBE laboratory study

Researchers at the University of California (Koenigsberg and others, 1999) investigated MTBE biodegradation with a mixed culture. Their study concluded:

- MTBE biodegradation rate was proportional to the concentration of dissolved oxygen in water
- MTBE uptake followed a Michaelis-Menten kinetics with respect to the dissolved oxygen
- competitive inhibition can be significant; in a mixed plume, the microorganisms will prefer benzene to MTBE

Competitive inhibition

Competitive inhibition describes enzymatic activity in which two or more different substrates compete for the same enzyme. The degradation of one substrate, MTBE for instance, is repressed in the presence of another, i.e. BTEX. At the majority of MTBE sites using ORC^R, MTBE degradation occurs after BTEX concentrations decrease (see Figure 2).

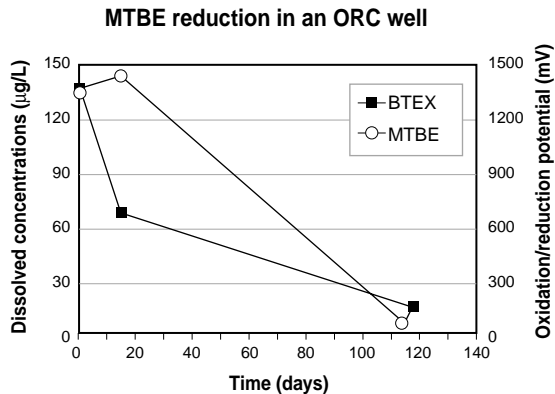


Figure 2. MTBE reduction following BTEX decrease (Koenigsberg and others, 1999).

Mahaffey, Sandefur and Deshusses (Koenigsberg and others, 1999) set up an in-vitro experiment using an aerobic bacteria capable of degrading MTBE and BTEX. Laboratory workers measured MTBE degradation during a 7-day period

- in the presence of MTBE only
- in the presence of MTBE and xylene

Researchers found a 52 percent reduction of MTBE in the absence of xylene, and 9 percent when xylene was present.

Another laboratory experiment sought to test whether

- MTBE biodegradation is aerobic and co-oxidative
- competitive inhibition could exist between a primary substrate and MTBE

Researchers surmised that substrates involved with co-oxidation and competitive inhibition would most likely be found at the hydrocarbon plume's aerobic fringe. "Initial studies, using resting cell transformation tests, demonstrated that substantial removal of MTBE was achieved with cultures that were acclimated to benzene, camphor, o-xylene and cyclohexanone. In those tests, a specific benzene-acclimated mixed culture, designated PEL-B201 [grown in basal salts media on benzene vapors], was most efficient in degrading MTBE (58 percent removal). This established the possibility that a single organism could metabolize both MTBE and alternate substrates and therefore be under the influence of competitive inhibition dynamics. This competitive inhibition hypothesis was bolstered by demonstrating both MTBE inhibition of benzene metabolism and the inhibition of MTBE with increasing benzene concentrations" (Koenigsberg and others, 1999).

Figure 3 shows the results of the biotransformation experiments using PEL-B201. "Benzene-induced cell suspensions degrade more than 99 percent of the added MTBE. Increasing benzene concentration to 1.9 µM (micromolar) and 3.8 result in a significant reduction in MTBE degradation rate." (1 µM of benzene C₆H₆ is equivalent to 78 g/L). MTBE degradation was not observed with cells grown on the non-inducing substrate succinate. "The lack of MTBE degradation on the succinate-grown cells indicates that MTBE metabolism occurs with an enzyme system associated with benzene metabolism and reaffirms the hypothesis that MTBE is metabolized by co-oxidation" (Koenigsberg and others, 1999). Co-oxidative processes are a function of Gibbs free energy; a measure of a system's ability to do work, Gibbs free energy depends on the energy liberated or absorbed in a reversible process at a constant pressure and temperature. According to Mahaffey (1999) "Co-oxidative processes are most influenced by the K_m (a constant) of the enzyme for the substrate. If the K_m (a constant) for MTBE was substantially lower than that for the enzyme's natural substrate, i.e. benzene, then low levels of MTBE could significantly inhibit benzene degradation. The consequence would be the inability of those organisms containing this co-oxidative enzyme to maintain their survival on benzene as a food source."

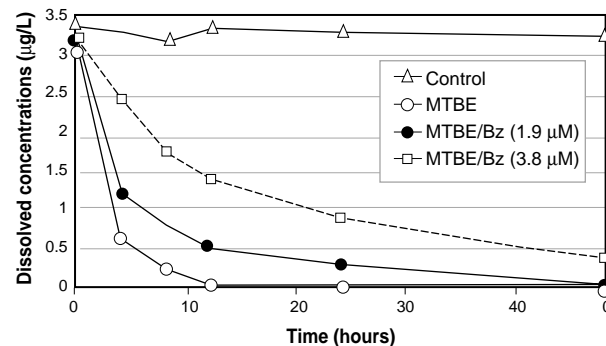


Figure 3. Illustration of competitive inhibition of MTBE co-oxidation. Controls were inoculated with non-acclimated PEL-B201 cells grown on succinate. Addition of benzene inhibits MTBE degradation (Koenigsberg and others, 1999).

Other perspectives on ORC^R

When planning to inject or add a terminal electron acceptor to a site to expedite natural biodegradation, remediators should consider all reactions likely to occur. Petroleum-contaminated sites usually include BTEX and/or polycyclic aromatic hydrocarbons (PAHs) in dissolved and residual (smeared zone) phases. Sites may have a small contaminant mass in the vapor phase, and in addition, non-regulated hydrocarbons in dissolved, residual and vapor phases. Each contaminant in each phase will exert a demand for oxygen. Geochemical reactions involving natural organic carbon and dissolved iron, for instance, may also consume oxygen. If the remediation strategy calls for addition of one or more terminal electron

acceptors to the site, a calculation of the total oxygen demand is warranted.

Reviewer comment: If calculations are based solely on oxygen demand of the dissolved phase BTEX, those calculations may severely underestimate the mass of oxygen necessary for remediation.

Second reviewer's comment: While most evidence has shown that ORC^R works for BTEX-contaminated sites, there is not yet enough validated scientific data to establish that ORC^R enhances the biodegradation of MTBE in the field. Data obtained, to date, shows mixed results, is mostly short-term (i.e., three to six months) and may reflect seasonal variations in contaminant concentrations rather than enhanced MTBE biodegradation attributable to ORC^R application.

BioGroup discussion on the effectiveness of ORC^R can be reviewed by going to <http://biogroup.gzea.com>, then to message archive; click on 1999 and scroll down the list to find message subject "MTBE half-life/remediation."

Researchers have also found that native organic matter or reduced minerals in aquifers may exert a considerable oxygen demand and decrease effectiveness of ORC^R (Wilson, 1998).

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Mahaffey, W., personal communication, December 15, 1999.

Regenesis website, <http://www.regenesis.com>; for technical bulletins, double click on ORC; publications from various conferences around the country are also available from the website.

Wilson, J.T., "The Efficacy of ORC for Containment of BTEX Plumes in Groundwater Contaminated by Fuel Spills," March/April 1999, presented at The U.S.EPA OUST National Conference; wilson.johnt@epamail.epa.gov.

See also Technology Status Review: In-Situ Oxidation, http://www.estcp.org/technical_documents.htm.

UTTU thanks Dr. Stephen Koenigsberg, Regenesis, San Clemente, California, and Bill Mahaffey, Pelorus EnBiotech, Evergreen, Colorado, for their help on this article.



MTBE mineralization and biodegradation

Bradley and others (1999) studied MTBE (methyl tert-butyl ether) and TBA (tert-butyl alcohol) biodegradation using sediments from a stream-bed environment. The sediments from two sites in South Carolina were analyzed in the lab for CO₂ production, which would indicate MTBE biodegradation.

Study site descriptions

Researchers obtained sediments from LUST sites in Laurens and Charleston (Oasis), South Carolina. Contaminants at both sites included BTEX, MTBE and TBA.

The Laurens site had the following dissolved contaminants observed in groundwater monitoring wells 20 m upgradient of the stream:

- BTEX, 105 mg/L
- MTBE, 64 mg/L
- TBA, 14 mg/L

Sediments here were poorly sorted, coarse-grained sand with angular grains, about 26 percent water content (by dry weight). Geochemical analysis indicated that stream bed sediment samples were predominantly aerobic at time of sample collection, with the bed sediment O₂ ≥ 2 mg/L and the water column O₂ ≥ 7 mg/L. Trace CH₄ was also present.

At the Charleston site, dissolved concentrations of contaminants observed in groundwater monitoring wells 7 m upgradient were as follows:

- BTEX, 476 µg/L (0.476 mg/L)
- MTBE, 138 µg/L (0.138 mg/L)
- TBA, 2,094 µg/L (2.094 mg/L)

Sediments consisted of fine-grained, organic-rich silt and clay, with about 66 percent water content and about 17 percent organic content. At collection time, the streamwater column was aerobic O₂ ≥ 5 mg/L; however, analysis of gases released by bed sediments indicated highly methanogenic sediments, overlain by a 1- to 2-cm thickness of reduced material.

Sediments collected at both sites had concentrations of BTEX, MTBE and TBA below detection limits, less than 5 ppb (5 µg/L or .005 mg/L).

Microcosm studies and results

Scientists prepared microcosms within 2 days of sediment collection. Microcosms consisted of 15 g of saturated bed sediment (from either the Laurens or Charleston site). For each microcosm, the scientists prepared 5 replicate samples. They also prepared triplicate, killed control microcosms for each substrate and sediment and autoclaved them twice for 1 hour at 15 psi and 121°C. Then they added to the microcosms either 0.1 µCi of [U-¹⁴C]-MTBE, or 0.2 µCi of

[U-¹⁴C]-TBA, which yielded dissolved concentrations, respectively, of 150 and 400 µg/L MTBE and TBA. (Ci is a Curie, a measurement of radioactivity; a µCi is 3 X 10⁶ dpm, decays per minute.)

Scientists analyzed headspace using GC/GRD with thermal conductivity detection for the following gases:

- CH₄
- ¹⁴CH₄
- CO₂
- ¹⁴CO₂

Figure 4 shows MTBE and TBA mineralization as percentage of ¹⁴CO₂. For the aerobic sediments, after 105 days, recoveries for ¹⁴CO₂ were 73 ± 14 percent and 30 ± 8 percent for the Laurens and Charleston (Oasis) bed sediments, respectively.

CH₄ production was not observed. Production of ¹⁴CO₂ is entirely attributable to biological activity because no mineralization was observed in the autoclaved control microcosm. Bradley and others (1999) assert that: "Microbial mineralization of MTBE under aerobic conditions has been demonstrated previously for pure cultures, bench-top bioreactors and sludge. To our knowledge, however, this is the first demonstration of extensive, aerobic MTBE mineralization by indigenous microbial assemblages" (consortia).

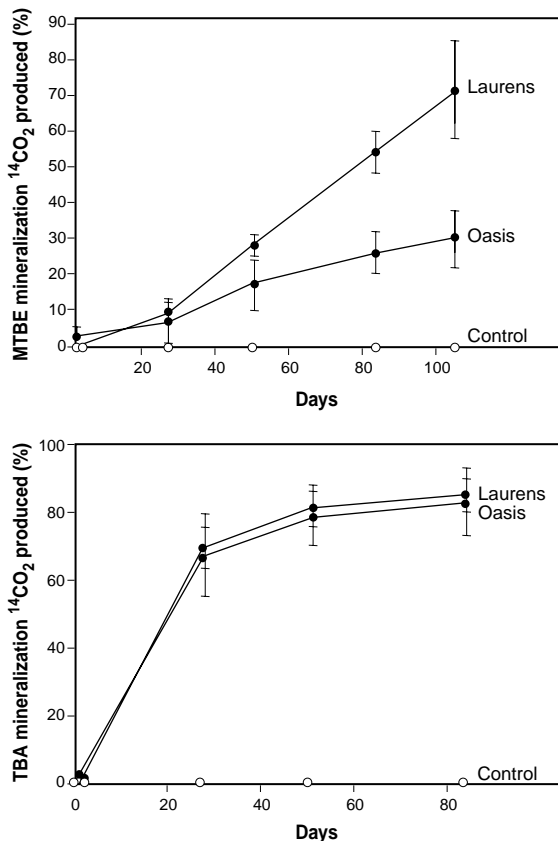


Figure 4. MTBE (top graph) and TBA mineralization (bottom) as percentage of ¹⁴CO₂ (Bradley and others, 1999).

The microcosms under anaerobic conditions showed no significant mineralization. A previous study under Fe(III)-reducing conditions, however, did indicate low (2.7 ± 0.3 percent) MTBE mineralization (Landmeyer and others, 1998). Researchers did analyze for MTBE vapors; however, there was little evidence of volatilization because the microcosms of sediment and water slurries reduced the chances that MTBE would volatilize. "In any case," Landmeyer states (1999), "MTBE losses by volatilization would not have affected our results because

- any volatilized MTBE would have stayed in the microcosm, re-equilibrated with the slurry and later degraded
- our lab study measured the production of radiolabeled CO₂ from radiolabeled MTBE, not the disappearance of MTBE mass"

Scientists attribute the difference in mineralization rate between the Laurens and Charleston sediments to the sediments' organic content; high organic content promotes significant methanogenic activity, which inhibits MTBE mineralization. Scientists also hypothesize that MTBE mineralization activity is likely limited to a thin aerobic zone at the sediment/water column surface.

"MTBE loss due to "mixing" is not a legitimate removal process in microcosm experiments, because there is no mixing at the microcosm scale. At the field scale, there can be MTBE-concentration decreases due to mixture with cleaner water (say, either uncontaminated ground or surface waters), particularly where both interface in a stream bed. The streams we studied, however, were mostly small creeks (i.e., slow flow rates, no rapids) and hence, very little vertical mixing of surface water with discharging ground water occurred" (Landmeyer, 1999).

TBA was also mineralized to CO₂ at a rate of 70 ± 6 percent for the Laurens and Charleston sediments. "Mineralization subsequently tapered off with a final mean ¹⁴CO₂ recovery for both sediments of 84 ± 8 percent. No significant mineralization of [U-¹⁴C]-TBA was observed in autoclaved control microcosms or in experimental microcosms incubated under anaerobic (methanogenic) conditions. ¹⁴CH₄ production was not observed in this study. The results of the current study are consistent with previous reports that TBA biodegradation in subsurface soils is significant under aerobic conditions but proceeds slowly under anaerobic conditions."

Conclusions

Bradley and others (1999) concluded the following:

- because "MTBE and TBA are highly soluble and recalcitrant under anaerobic conditions, there is a greater probability that these compounds will be transported to local surface water receptors in relatively high concentrations"
- microorganisms indigenous to the bed sediments of these systems can rapidly degrade MTBE and TBA and may provide protection against contamination of surface drinking water supplies

- no effort has yet been made to clarify the mechanism or intermediates involved in the observed biodegradation; but these processes merit further investigation
- degradation by microorganisms was the only mechanism to explain the production of CO₂ from MTBE

Another microcosm study in North Carolina

Zenker and others (1999) performed a similar microcosm study on soil previously exposed to alkyl ether oxygenates, such as MTBE. Their microcosms consisted of

- contaminated soil, 150 grams/microcosm
- sterile groundwater, 140 ml/microcosm, sparged for 12 hours with sterile water to oxygenate the water and remove any background volatile organic compounds
- various concentrations of alkyl ether oxygenates
 - MTBE added at concentrations of 300, 3,000 and 30,000 µg/L (0.3, 3 and 30 mg/L)
 - ETBE (ethyl tert-butyl ether), DIPE (diisopropyl ether) and TAME (tert-amyl methyl ether) added at 3,000 µg/L (3 mg/L) each

Researchers examined all microcosms for target contaminants and dissolved organic carbon (DOC) every 30 days. "Each treatment was constructed in triplicate with matching abiotic controls. The soils used for the controls were autoclaved for one hour on each of three consecutive days. Further, 250 mg/L of mercuric chloride was added to ensure no biological activity" (Zenker and others, 1999). Scientists used purge-and-trap gas chromatography to determine ether concentrations.

After 200 days, the TBA was completely biodegraded, but a year later, there was still no biodegradation of MTBE, ETBE, DIPE or TAME. Zenker and others (1999) concluded: "No detectable biodegradation of MTBE, ETBE, DIPE or TAME occurred after a year of incubation. Thus, natural attenuation of these chemicals in this specific aquifer was not demonstrated. Tert-butyl alcohol, however, was completely biodegraded to below detection limits within about 200 days of incubation. The initial drop in TBA concentration was due to an abiotic loss, as shown by comparison to the control bottles. MTBE was present in these bottles, but TBA degradation did not stimulate MTBE removal" (Zenker and others, 1999).

Study of MTBE/petroleum-contaminated aquifer

Cho and Wilson (1999) studied removal rates of hydrocarbons and MTBE at an aquifer in Elizabeth City, North Carolina. They estimated that benzene and MTBE depletion from its NAPL source would take 85 and 11 years, respectively, assessing depletion by natural attenuation.

Workers first removed floating product from recovery wells. Analysis of groundwater and soil sampling data and predictions from conceptual models allowed researchers "to estimate hydrocarbon loading and transport from the hydrocarbon source to sensitive receptors. Mass loading rates from the NAPL source to groundwater were verified by comparing the outflux along groundwater flow at the source zone boundary for mass balance analysis. A prediction based upon loading rate and initial assessment of hydrocarbon mass in the

source zone allowed the estimation of the time scale of plume management with natural attenuation" (Cho and Wilson, 1999).

Researchers found that most of the residual hydrocarbon was located in a narrow interval of about 1.5 to 3.5 meters below ground surface, which they suspected was the long-term contamination source to groundwater. "Steep concentration gradients of benzene and MTBE between the bottom of the residual NAPL and the top of the highly conductive zone suggest that vertical diffusion/dispersion along the concentration gradient is the major transport process of these contaminants from their source to the deeper, conductive part of the aquifer." NAPL dissolved into the water pores and moved downward by diffusion/dispersion along concentration gradients. NAPL then moved by convective transport with the major groundwater flow. "The flux of a dissolved component, and diffusion from the concentration maximum (at the NAPL layer contacting groundwater) down to the area with higher hydraulic conductivity, could be estimated with vertical dispersion and convective transport equations" (Cho and Wilson, 1999).

Researchers estimated that the average flux of benzene over the NAPL source zone was 1.9 g/m²/yr. MTBE dissolved into groundwater at 1.3 mg/m²/yr. The estimate for total loading of benzene into groundwater was 6.7 kg benzene/yr and 4.6 kg/yr for MTBE. With the mass of benzene estimated to be about 570 kg and MTBE mass about 50 kg, complete depletion from the NAPL source would take 85 years for benzene and 11 years for MTBE. This assumes constant removal rates through the period of natural attenuation (Cho and Wilson, 1999).

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UTTU thanks Dr. Jim Landmeyer, jlandmey@usgs.gov, U.S.G.S., for his help on this article.



Research notes

Comparing Two Methods for Addressing Uncertainty in Risk Assessments

Guyonnet, D., Come, B., Perrochet, P. and A. Parriaux, *Journal of Environmental Engineering*, Vol. 125, No. 7, 1999; 1801 Alexander Bell Drive, Reston, Virginia 20191-4400.

In this article, researchers in France and Switzerland compared the Monte Carlo method to the fuzzy number approach. "The Monte Carlo method assumes that the model parameters are random variables that can be represented by probability density functions (PDFs). Such functions are best derived from the statistical analysis of significant populations. But. . . in a risk assessment context, information is often sparse and imprecise; therefore it is questionable whether statistically meaningful probabilities can be assigned to parameter estimates, or whether these estimates should be considered as simply possible. . . In an environmental context, risk is often defined as the probability that damage may occur."

The probabilistic, or fuzzy approach, was developed to accommodate vague or imprecise data. "Instead of representing parameter uncertainty by a PDF, the theory of possibility uses fuzzy numbers. A fuzzy number describes the relationship between an uncertain quantity X and a membership function, μ . This function, which is contained between zero and one, describes the possibility that the quantity X may take on a certain value of x ." This function might, for instance, be associated with an aquifer's hydraulic conductivity.

Any fuzzy number shape is possible, but the selected shape should be justified by the data. ". . . unlike a fuzzy number, the area below a PDF equals unity: the probability that a random variable X should take on a value x lower than infinity is equal to one." In addition, ". . . compared to a PDF, the information conveyed by a fuzzy number is often more consistent with the nature of the information that is typically available in field situations. A rigorous definition of PDFs would require a large number of measurements, but in field situations information is often sparse."

Comparing the Monte Carlo and fuzzy calculation approach (from the paper), authors concluded: "The fuzzy calculation may appear over-conservative because it considers all possible combinations of parameter values, while in the Monte Carlo calculation, scenarios that combine low probability parameter values have very little chance of being randomly selected."

Predicted Retardations of Concentration Fronts Using a Mass-Balance Approach

R.K. Stoessell, *Ground Water*, Vol. 37, No. 5, September-October 1999; 800-332-2104; <http://www.ngwa.org>.

According to Stoessell (1999), "a simple mass balance can be used to predict the retardation of the groundwater pollutant front moving downstream from a source of constant composition. The retardation is the ratio of the total molar difference of pollutant across the front to the molar difference in

groundwater." This approach is based on conservation of mass. Stoessell compared the retardation fronts derived from modeling and column experiments (using toluene) with those predicted by the mass-balance approach. Comparisons of results were good to excellent. Retardation, however, will not give the shape and width of the front; these characteristics are controlled by sorption, dispersion and diffusion.

This is the scenario for a moving contamination front:

- the concentration front moves downstream
- the front replaces the downstream groundwater with the source groundwater
- moles of pollutant in equilibrium with the source fluid replace moles of a pollutant on sediment sites
- if sediment composition is homogeneous, a constant difference in pollutant concentrations exists between the area upstream and downstream of a front
- if groundwater velocity is constant and the aquifer is isotropic, the front's rate of movement will be constant



The view from U.S. EPA: UST system performance evaluation

Evaluation of UST system performance is a priority of the UST program. Anecdotal evidence suggests that UST system performance has improved many times over relative to a decade ago. A more comprehensive effort, however, is needed to measure this evidence against reality and to identify areas that need clarification vs. those that may require fewer of the public/private sectors' scarce resources.

We need to find out what is working, what is not working, and why not. The information needed is real-world, in-the-field, and time-tested performance data — not simply data based on lab tests of factory-fresh systems. Because EPA does not have the relevant data, cooperation with industry and among agencies is essential; thus, several organizations are involved in evaluating UST system performance.

If you represent an organization interested in pursuing these evaluations or partnering with EPA, please contact Sammy Ng at ng.sammy@epa.gov or 703-603-9900. The following ongoing or completed UST system evaluation projects appear with more detailed information on the OUST website at <http://www.epa.gov/swerust1/ustsystem/usteval.htm>.

- *Leaking Underground Storage Tanks (USTs) as Point Sources of MTBE to Groundwater and Related MTBE-UST Compatibility Issues*, <http://tsrtp.ucdavis.edu/mtberpt/homepage.html>
- *Advisory Panel on the Leak History of New and Upgraded Systems: Leak Source and Leak Detection Data Collection and Analysis*, http://www.swrcb.ca.gov/~cwphome/ust/advisory_panel/advisory_panel.htm

- *Investigation of MTBE Occurrence Associated with Operating UST Systems*, contact Chris Tulloch at ChrisTul@scvwd.dst.ca.us
- *Field Verification of UST System Leak Detection Performance*, <http://cee.engr.ucdavis.edu/faculty/young/ldstudy/ld-study.htm>
- *Analysis of UST System Environmental Performance*, contact David Wiley (Wiley.David@epamail.epa.gov) at U.S. EPA OUST
- *UST System Performance Information Search*, executive summary at <http://www.epa.gov/swerust1/ustsystem/es.htm>
- *Survey of Current Management and Operation Practices, and Leak Prevention and Detection*, <http://www.ocwd.com/nwri/mtbe.htm>
- *Proposal for the Study of MTBE and BTEX Plumes at California LUFT Sites*, <http://www.api.org>

- *Remediation and Management of Degraded Lands*
- *Reuse of Surfactants and Cosolvents for NAPL Remediation*
- *Soils and Groundwater Pollution and Remediation: Asia, Africa and Oceania*
- *Soil Vapor Extraction*
- *Surfactants and Cosolvents for NAPL Remediation: A Technologies Practices Manual*

Books available from the National Ground Water Association (see website <http://www.ngwa.org>) include:

- *Aqueous Environmental Geochemistry*
- *Environmental Isotopes in Hydrogeology*
- *Ground Water Geochemistry: Fundamentals and Applications to Contamination*
- *Practical Manual of Groundwater Microbiology*

Analytical Solutions of Geohydrological Problems, G.A. Bruggeman, Elsevier Science Inc.; <http://www.elsevier.com>, or 212-633-3730.

Encyclopedia of Environmental Pollution and Cleanup, Vol. 1, Robert A. Meyers (ed.), John Wiley & Sons; <http://www.wiley.com>, or 800-225-5945.

Engineering and Design-Multiphase Extraction (EM 1110-1-401); detailed guidance on all phases of remediation projects using Multi-Phase Extraction; <http://www.usace.army.mil/usace-docs/eng-manuals/em1110-1-4010/>; or Publications Depot at 301-394-0081.

Hydrogeologic Models of Sedimentary Aquifers, Gordon Fraser and Mathew Davis (eds.), SEPM Publications; fax request to 918-493-2093.

Isotope Tracers in Catchment Hydrology, C. Kendall and J.J. McDonnell (eds.), Elsevier Science; <http://www.elsevier.com>, or 212-633-3730.

UTTU thanks David Wiley, U.S. EPA OUST, for help on this article.



Information sources

Recent publications

Books available from Lewis Publishers (call 800-272-7737, or see website, <http://www.crcpress.com>) include

- *Applied Mathematics in Hydrogeology*
- *Design of Thermal Oxidation Systems for Volatile Organic Compounds*
- *Environmental Chemistry*
- *Fate and Transport in the Vadose Zone*

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Modeling Density-Driven Flow in Porous Media, Ekkehard Holzbecher, Springer-Verlag New York; <http://www.springer-ny.com>, or call 800-springer.

U.S. and International Markets for Phytoremediation, 1999-2000, D.Glass Associates, Inc; call 617-726-5474, fax 781-449-8045 or e-mail DGlassAssc@aol.com. Executive summary available at <http://www.channel1.com/dglassassoc/INFO/phy99exc.htm>.

EPA publications and information

Ecological Risk Assessment and Risk Management Principles for Superfund Sites, <http://www.epa.gov/superfund/programs/risk/ecorisk/final99.pdf>; for hard copies call 800-424-9346 or 703-412-9810.

Microbial Processes Affecting Monitored Natural Attenuation of Contaminants in the Subsurface (EPA/540/S-99/001), <http://www.epa.gov/ada/issue.html>; for hard copies e-mail cooper.kay@epa.gov, or call 580-436-8651.

EPA OUST MTBE website

EPA OUST has an excellent collection of advisories, studies and links related to MTBE at <http://www.epa.gov/swerust1/mtbe/index.htm>. The following appear on the website:

- MTBE contacts
- Blue Ribbon Panel on oxygenates in gasoline
- *Panel Findings, Executive Summary and Recommendations*
- *Achieving Clean Air and Clean Water: The Report of the Blue Ribbon Panel on Oxygenates in Gasoline, 9/15/99*
- Drinking water advisory

- MTBE legislative issues
- Map of MTBE groundwater cleanup levels
- Characteristics of MTBE
- EPA publications on MTBE
- Non-EPA publications on MTBE
- MTBE policy documents
- State investigation reports on MTBE
- MTBE presentations and briefings
- ASTSWMO MTBE newsletters
- Models for MTBE simulation
- MTBE remediation/cleanup
- Other MTBE sites

Essential report on ethanol

Lawrence Livermore National Laboratory, Environmental Restoration Division, has posted a comprehensive report, "Health and Environmental Assessment of the Use of Ethanol as a Fuel Oxygenate" at the web address <http://www-erd.llnl.gov/ethanol>.

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. UTTU also obtained information from Ground Water (<http://www.ngwa.org>) and Environmental Progress (<http://www/aiche.org/>)

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