

Underground Tank Technology Update

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Article summaries

- ☐ Oxygen-enhanced biodegradation 2**
This article describes a subsurface oxygen diffusion system that used gas-pressurized silicone tubing to deliver dissolved oxygen to a plume.

- ☐ Field testing of a permeable reactive zone 5**
Investigators created a permeable reactive zone using magnesium peroxide at a gasoline spill in North Carolina.

- ☐ Inspector's guide for impressed current CP systems: checklist, part 2 7**
This is a continuation of the checklist published in the July/August 1998 issue of *UTTU*.

- ☐ RBCA implementation case study: Idaho 9**
How the Idaho Division of Environmental Quality has implemented its RBCA program is the subject of this article.

- ☐ MTBE impacts on California's groundwater resources 10**
This article is an edited version of the Lawrence Livermore National Laboratory (LLNL) 1998 report, "An Evaluation of MTBE Impacts to California Groundwater Resources".
A map of MTBE Groundwater Cleanup Regulations: Current and Future appears on page 11.

- ☐ Information sources 13**
Listed in this article are phone numbers/addresses/e-mails of recent publications and other sources of information.

UTTU's home page, <http://epdwww.engr.wisc.edu/uttu/>, contains an alphabetical and topical list of every article that has appeared in *UTTU* since 1987.



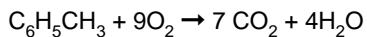
Oxygen-enhanced biodegradation

Investigators recently studied a BTEX plume in a sandy, iron-rich aquifer (*Gibson and others, 1998*). They installed an oxygen diffusion system, which delivered dissolved oxygen (DO) to part of the plume. The objectives of this study were twofold:

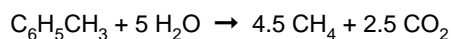
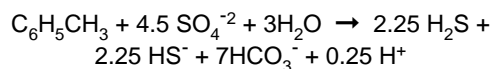
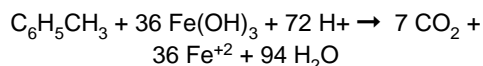
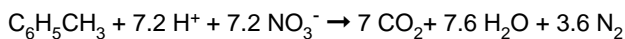
- to evaluate the use of oxygen diffusion through gas-pressurized silicone rubber tubing (so as to enhance aerobic biodegradation in groundwater)
- to assess some of the DO's effects on subsurface geochemistry, microbiology and permeability

Review of biodegradation basics and oxygen delivery systems

Dissolved hydrocarbons act as carbon sources for aerobic microbes at petroleum-contaminated sites. In the presence of oxygen, aerobic hydrocarbon metabolism using molecular oxygen is thermodynamically favored (see equation below); oxygen in excess of 0.5 mg/L, however, is toxic to obligate anaerobes.



"In contaminated aquifers, however, microbially mediated aerobic degradation is limited by the amount of oxygen in the groundwater. Aerobic processes rapidly use up the dissolved molecular oxygen (DO) in contaminated areas and can depress the DO to less than 0.5 mg/L. Under conditions of oxygen depletion several anaerobic biodegradation processes, including denitrification, iron reduction, sulfate reduction and methanogenesis (see equations below), can use other electron acceptors."



"The dominant process within a given region of the contaminant plume can switch between denitrification, iron (III) reduction, sulfate reduction and methanogenesis as a result of changes in the natural flux of dissolved hydrocarbons, oxygen, and other electron acceptors" (*Gibson and others, 1998*).

Investigators can inject air, oxygen, hydrogen peroxide or nitrate to change conditions by providing additional electron acceptors. In the past, remediators have used reactive barrier walls that contain magnesium peroxide and release DO into the groundwater. A problem here is the potential for iron to clog well screens. The method discussed in this article relies on release of solutes into groundwater by diffusion through permeable polymeric tubing.

Plume and study area description

Investigators studied a LUST site in southeastern Michigan. Leaks of unleaded gasoline had created a plume of dissolved BTEX 24 m long by 18 m wide. Investigators found no free NAPL (nonaqueous phase liquid) hydrocarbon. Geology consisted of medium to fine sand layers from the surface to about 3 m, then a thick layer of dense clay. Groundwater existed at a depth of about 2 to 3 m, where the sand met a clay layer. This was also the plume location. Average hydraulic gradient was 0.015 m/m, and average water temperature was 15.9°C. Using a bromide tracer study, investigators estimated groundwater flow velocity in the test zone to be 25.3 cm/day (0.83 ft/day). In the oxygen delivery zone, velocity ranged from 26.0 cm/day to 24.5 cm/day. Within the plume, intrinsic bioremediation processes

- depleted dissolved BTEX
- created elevated concentrations of metabolic byproducts, including
 - dissolved ferrous iron (iron-reducing bacteria produce this using ferric minerals as electron acceptors)
 - carbon dioxide
 - methane

Oxygen delivery system

Investigators set up the oxygen delivery system in the northeastern section of the plume. The system consisted of

- a 10.2-cm (4-inch) ID injection well, used for oxygen delivery
- several 5.1-cm (2-inch) PVC monitoring wells, screened at 2.4 to 2.6 m and used for groundwater sampling and hydraulic measurements
- two multi-level piezometers
- four closely spaced groundwater sampling points, installed directly downgradient of the oxygen delivery well; when packed with coarse silica sand, along with the injection well, these wells formed a continuous oxygen delivery zone of high permeability
- another 10.2-cm (4-inch) well perpendicular to groundwater flow, used as an untreated control well

The oxygen injection system

- delivered oxygen through the injection well, which was surrounded by a highly permeable zone of coarse sand
- contained coils of silicone polymer tubing 46 m x 1.6 mm (150 ft x 1/16 inch); silicone tubing is sturdy and allows a higher diffusion rate than other polymeric materials
 - the tubing extended from just below water level to about 3.0 m
 - the tubing was connected to an oxygen cylinder (99.99% oxygen)

This system "acts as a permeation membrane to deliver the oxygen molecules slowly over a large surface area to maximize oxygen dissolution in the water ('bubbleless' injection)" (*Gibson and others, 1998*).

Investigators also designed a water flushing system to slowly pump clean water into the injection well to facilitate

the spread of dissolved oxygen. "The flushing action increased oxygen dissolution and advective spreading and also retarded potential well screen fouling by minerals and biomass" (*Gibson and others, 1998*). Flushing ceased for 24 hours before sampling occurred.

Characterization of geochemistry and microbiology

Investigators characterized the geochemical and microbiological environment by measuring the following:

- dissolved oxygen (DO)
- oxidation-reduction potential (Eh)
- pH
- hydraulic conductivity (Ks) in the saturated zone
- ferrous iron
- total iron
- sulfate
- carbon dioxide
- phosphate
- ammonium
- benzene
- toluene
- ethylbenzene
- xylenes

The specific tests used are described in Gibson and others (*1998*).

Investigators enumerated groundwater bacteria using a total heterotrophic count (THC) method. They used biological activity reaction tests to determine degradative pathways of native bacteria. Groundwater samples were also tested in six types of reactors:

- total aerobic bacteria
- denitrifying bacteria
- iron-related bacteria
- sulfate-reducing bacteria
- fluorescing pseudomonads
- slime-forming bacteria

Results

Conclusions drawn from the presence of DO indicate:

- DO in the control well remained at a level of 0.25 mg/L
- DO was initially low (0.2 to 0.5 mg/L) in the contaminated area compared to background level (2.0mg/L)
- DO in the injection well area increased from 0.23 mg/L to 33.8 mg/L in 30 days and to 39.0 mg/L in 60 days
- DO also increased in monitoring points downgradient of the delivery zone

The study's Eh values

- in the oxygen delivery zone were strongly negative (-55 to -10 mV); after oxygen delivery, Eh increased to as high as 395 mV
- in the monitoring points also shifted from negative to positive, which indicates that added oxygen changed conditions from anaerobic to aerobic

BTEX concentration results were as follows:

- in the oxygen delivery zone, after 60 days, concentrations decreased 90 percent
- in the monitoring wells, after 60 days, concentrations decreased 98 percent
- in contrast, anaerobic bioremediation in an upgradient well caused an insignificant increase in total BTEX

Conclusions regarding iron included:

- dissolved iron results from the activity of iron-reducing bacteria that oxidize hydrocarbons and convert soluble ferric minerals from sediments to soluble ferrous species in groundwater; ferrous iron, which is a byproduct of hydrocarbon biodegradation by iron-related bacteria (IRB), has been used to estimate potential biodegradation rates by this pathway
- increased ferrous ions corresponded to lower groundwater Ehs
- concentrations of iron (II) decreased in the oxygen delivery zone
- ferric iron concentrations increased in groundwater after 30 days of oxygen treatment
- concentrations of oxidized iron (III) and reduced iron (II) are also related to groundwater Eh; the change from negative to positive Eh in the test zone coincides with the oxidation of iron (II) to iron (III)

With the onset of oxygen injection

- in the oxygen delivery zone, the microbiology changed from anaerobic to aerobic, causing changes in the subsurface microbial population; total aerobic bacteria increased from less than 100 to 100,000 CFU/mL
- iron-reducing bacteria increased
- anaerobic bacteria, i.e., the sulfate-reducing bacteria, decreased

Investigators found these other concentrations:

- carbon dioxide concentrations initially increased downgradient, suggesting an enhanced rate of aerobic biodegradation
- carbon dioxide levels remained constant, or fell slightly in the control well
- methane levels downgradient decreased, indicating a decreased rate of methanogenesis
- sulfate concentrations also decreased, but the reasons why are unclear
- low concentrations of nitrate indicated that denitrification was not a major biodegradation process
- ammonium and phosphate decreases near the oxygen delivery zone may have resulted from their usage for biomass growth to enhance the population of aerobic bacteria
- total heterotrophic counts and total aerobic bacteria increased most in the delivery zone, suggesting greater biomass formation

Biodegradation rate determination

Researchers estimated biodegradation rates before and after oxygen injection by conceptualizing the oxygen delivery zone as a reactive barrier zone. "This model assumes that the mass flux of BTEX into the oxygen delivery zone minus mass flux out of the zone equals the biodegradation rate." Researchers did not use the tracer TMB, trimethylbenzene, because they believed it could be reactive under strongly aerobic methods. Thus, they measured BTEX in the upgradient well and injection test well before and after oxygen injection. According to Gibson and others (1998), "The absolute values of the biodegradation rates estimated from field data may have been affected by dilution, flow convergence and uncertainties in the extent of the oxygen delivery zone and flow velocity. Thus, the estimated rates may be more useful as a means of comparing biodegradation rates before and after oxygen delivery than as measurements to establish the absolute rates. Convergence of groundwater flow when passing through a zone of higher permeability is a serious likelihood. This could increase the flow rate and solute flux entering a groundwater barrier zone like ours. In our study, the groundwater velocity was measured by movement of an inert tracer in the oxygen delivery zone from the injection well to the downgradient sampling points. The tracer experiment did not show a major increase in flow rate within the zone, which could be attributed to convergence or caused by the extra 10 L/day of deionized water injected with the oxygen."

"The biodegradation rates determined from the decrease in BTEX do not distinguish between the various aerobic and anaerobic processes" (Gibson and others, 1998). Investigators examined the changes in mass fluxes of electron acceptors and reaction products to evaluate the contribution to biodegradation by the various pathways. Biodegradation rate estimates were computed for

- aerobic respiration
- denitrification
- iron reduction
- sulfate reduction
- methanogenesis

Table 1 shows, for instance, that under initial anoxic conditions 949 mg/day of BTEX could be potentially degraded. After oxygen injection, potential biodegradation rates could have been as high as 2,124 mg/day.

Conclusions

Injection of oxygen through diffusion tubing into groundwater created a zone "of sustained high DO (39 mg/L) in groundwater around the injection well and changed the dominant groundwater conditions from anaerobic to aerobic. Rate estimates based on the decrease in the flux of BTEX indicate that oxygen delivery resulted in a three-fold increase in BTEX biodegradation. Increased aerobic conditions and aerobic bacterial activity were observed in the oxygen delivery zone and at downgradient sampling monitors for 2.3 m (7.5 feet), but not in the control wells located in contaminated areas upgradient or lateral to the test zone.

"The oxygen-enhanced zone was able to biodegrade benzene and ethylbenzene, which had been relatively resistant to natural attenuation in the plume under the initial anaerobic conditions. Thus, the oxygen delivery zone was effective as an in-situ bioremediation method or reactive barrier for dissolved BTEX under the study conditions. Iron precipitation was observed at the oxygen injection well but did not clog the well screen or seriously reduce the permeability of the well and surrounding zone" (Gibson and others, 1998).

Reference

Gibson, T.L., Abdul, S.A. and P.D. Chalmer, "Enhancement of In Situ Bioremediation of BTEX-Contaminated Ground Water by Oxygen Diffusion from Silicone Tubing," *Ground Water Monitoring and Remediation*, Winter 1998; 614-898-7791; GWPC@ngwa.org

UTTU thanks Thomas L. Gibson, GM R & D, Warren, Michigan, for his help on this article.

Aerobic respiration	Reactant-product	Mass ratio	Conc. (June) mg/L	Conc. (August) mg/L	Initial rate mg/L	Enhanced rate mg/day
Aerobic respiration	DO	0.32	0.20	39	9.4	1,835
Denitrification	NO ₃ ⁻	0.21	<0.40	<0.40	<12	<12
Iron reduction	Fe (II)	0.046	17.4	6.3	118	42.6
Sulfate reduction	SO ₄ ⁻²	0.21	4.0	0.44	123	13.6
Methanogenesis	CH ₄	1.32	3.6	1.2	699	233
Total					949	2,124

Table 1. Estimated biodegradation rates in the oxygen delivery zone: intrinsic rate (June) and enhanced rate after oxygen injection (August) based on groundwater concentrations at the injection well and stoichiometry of individual degradation processes (Gibson and others, 1998).



Field testing of a permeable reactive zone

Permeable reactive zones in aquifers allow contaminated groundwater movement so that contaminants can be scavenged or degraded. Ideally, downgradient of the reactive zone, uncontaminated groundwater emerges (*Borden and others, 1996*).

Field- and bench-scale studies of permeable reactive zones have, in the past, involved

- the funnel-and-gate concept, whereby contaminated water is forced to flow through a small permeable reactive zone
- MgO₂ pencils in treatment lines
- peat and nutrient briquets in the treatment zone
- hydraulic fracturing

The Borden study involved a full-scale permeable barrier system. Investigators used concrete with magnesium peroxide (MgO₂) briquets to deliver oxygen at a controlled rate to petroleum-contaminated water.

Site description

The site was located near Leland, North Carolina. Soil and groundwater contamination resulted from the release of gasoline from a former UST nearby. Contamination was discovered when dissolved hydrocarbons were found in nearby domestic water supply wells. At this site the water table existed at less than 3 m below grade; it occurred shallower downgradient. Groundwater flow had transported the gasoline components at least 150 m downgradient. Before barrier installation, workers removed some of the contaminated soil; some soil remained because of a shallow water table and interference caused by a nearby building. The site consisted of

- silty sand to a depth of 0.6 to 1.2 m
- clayey silty-sand for the next 0.6 m
- medium to coarse sand beneath the clayey, silty-sand that extended for 15 m, to the unconfined aquifer

Average hydraulic conductivity of the aquifer was 23 m/d. Vertical extent of the contamination was limited to about 7.6 m below grade.

Batch experiments

Investigators performed batch reactor experiments which indicated that nitrate addition would enhance the aerobic BTEX biodegradation at the site. Investigators did incorporate sodium nitrate (NaNO₃) into the concrete briquets at 0.5 to 0.7 percent by weight; nitrate levels did not exceed regulatory levels.

Barrier design

Investigators constructed the barrier 27 m downgradient from the former UST location. The barrier consisted of 15-cm-diameter PVC wells installed approximately 1.5 m on center. Each well would

- release a DO (dissolved oxygen) plume
- mix over a 6- to 15-m distance, as suggested by modeling efforts

Site characterization data indicated the barrier would need to be 40 m wide and extend 3 m beneath the water table.

Investigators installed 20 remediation wells in a line perpendicular to the plume. Nine of these wells contained no oxygen-releasing substance; they were designated as control wells. After the project had been ongoing for about one year, 10 wells were installed 1.5 m upgradient to further increase the oxygen supply. Investigators loaded the concrete briquets "into permeable filter socks and placed them into the fully screened polyvinyl chloride (PVC) wells When groundwater passed through a line of remediation wells, the MgO₂ in the concrete reacted with water, producing oxygen. Indigenous microorganisms then used the released oxygen to aerobically biodegrade the petroleum hydrocarbons present in the groundwater" (*Borden and others, 1996, p. 1-2*).

Groundwater sampling

Before wells were sampled, workers purged the well headspace with pre-purified argon gas to prevent introducing atmospheric oxygen. Workers purged the wells, pumping a minimum of five well volumes, then took water samples. Workers sampled water for the following:

- DO
- temperature
- pH

In addition, samples were examined for

- BTEX compounds
- Cl⁻
- Br⁻
- SO₄⁻
- soluble Na
- soluble K
- soluble Ca
- soluble Mg
- soluble Fe
- soluble Al
- soluble Cu
- soluble Mn
- nitrogen compounds
- alkalinity
- phosphate

Workers also collected soil samples to determine if iron was precipitating next to remediation wells. Investigators performed tracer tests to evaluate the effect of the oxygen-releasing concrete as related to a well's specific discharge.

Well clogging

Investigators found that well clogging severely affected oxygen delivery to the aquifer. "Tracer tests conducted at the end of the project indicated that the average specific discharge through the control remediation wells (no concrete) was over four times higher than in the original remediation wells that received concrete . . . Soil iron concentrations were significantly higher around the active remediation wells than in upgradient site soils, indicating that the clogging was at least partially due to precipitation of insoluble iron oxides" (*Borden and others, 1996*).

Results

Monitoring of an upgradient well and a sideline control well indicated that "BTEX concentration started out very low and increased steadily over the first 100 days of barrier operation. Prior to startup of the barrier, the site experienced a period of very heavy precipitation. The high precipitation is believed to have diluted the contaminants, resulting in lower BTEX concentrations in the aquifer immediately before startup. Over time, the effects of the high recharge diminished, and the BTEX concentrations in both wells returned to the 15 to 40 mg/L range. The low BTEX concentrations observed around days 180 and 390 were also associated with periods of high groundwater recharge and high water table elevation. Dissolved iron concentration in the [two wells] averaged 19 and 22 mg/L. The pH values in both wells were approximately 6. The higher pH in the contaminated wells is believed to be due to $\text{Fe}(\text{OH})_3$ reduction in the upgradient aquifer. The reduction of the $\text{Fe}(\text{OH})_3$ releases OH^- ion and this release increases the groundwater pH" (*Borden and others, 1996*).

After 18 months of monitoring, investigators sampled the barrier wells and found the following:

- BTEX concentrations decreased and DO concentrations increased during passage through the barrier
- BTEX reductions were statistically significant, but not sufficient to contain the plume
- only toluene was reduced below regulatory standards downgradient
- BTEX reductions on the control side of the barrier were much greater than on the active side

Investigators did not understand the cause of the apparent BTEX reductions. "Consequently it is not possible to determine whether the decline in BTEX was due to the

barrier system or due to natural variations in BTEX concentration throughout the site. The modifications made to the barrier during the course of the project did not dramatically improve BTEX removal efficiency" (*Borden and others, 1996*).

In addition, investigators hypothesized that "the continued presence of high concentrations of both DO and BTEX in several monitoring wells may be due to inadequate mixing between layers in the aquifer. If high oxygen concentrations were present in one layer and high BTEX concentrations were present in an adjoining layer, there would be little opportunity for biodegradation, yet monitoring wells screened over the two layers would show high concentrations of both oxygen and BTEX" (*Borden and others, 1996, p. 5-8*).

Investigators concluded that the permeable barrier system failed to adequately clean up BTEX because of

- high total BTEX concentrations entering the barrier, which created a high demand for oxygen that was difficult to meet with a reasonable number of remediation wells
- high dissolved iron concentration entering the barrier, which caused clogging of remediation wells and reduced oxygen delivery to the aquifer

Recommendations

Borden and others (*1996*) believe future work should consider the following:

- sites with lower concentrations of biodegradable organics and dissolved iron; it is difficult to deliver sufficient oxygen to the aquifer where dissolved iron concentration or oxygen demand is high
- before constructing the full-scale barrier, "field measurements of specific discharge should be combined with laboratory measurements of oxygen and nitrate release to predict more precisely the amount of oxygen and nitrate that will be introduced into the aquifer"
- increasing the concrete's nitrate content for further enhancement of aerobic biodegradation and for use as an electron acceptor
- aquifer stratification: stratification may prevent mixing of oxygenated- and BTEX-contaminated groundwater

Reference

Borden, R.C., Goin, R.T., Kao, C. and C.G. Rosal, *Enhanced Bioremediation of BTEX Using Immobilized Nutrients: Field Demonstration and Monitoring*, 1996, EPA/600/R-96/145, U.S. EPA, Center for Environmental Research Information, G-72, Cincinnati, OH 45268.



Inspector's guide for impressed current CP systems: checklist, part 2

This article is a continuation of the checklist that appeared in the July/August issue of *UTTU*.

Materials delivered to the job site

The inspector should record answers for the following questions with respect to materials delivered to the job site.

1. Were a sufficient number of the specified anodes delivered?

Yes No

Number of anodes _____
 Anode type(s) _____

2. Were the anodes prepackaged in a special backfill (i.e., canistered) or bare (i.e., without a special backfill surrounding each anode)?

Prepackaged Bare

3. Weight of the anode(s) packages: _____

4. Dimensions of anode(s) packages: _____

5. Were the weights and/or dimensions of the anode(s) packages within +/- 10 percent of those identified in the specifications and/or engineering drawings?

Yes No

For example, a Type TA2, tubular, high-silicon chromium-bearing, cast iron anode should have an outside diameter of 2.2 +/- 0.2 inches, a length of 84 +/- 8.4 inches, a wall thickness of 0.41 inch and a weight of 46 +/- pounds.

6. Based upon the certified chemical analysis reports furnished by the anode manufacturer/supplier, did the anodes satisfy the chemical composition required of the specifications and/or engineering drawings?

Yes No

7. Was there reason to believe (e.g., the submittal of a certified report from the anode provider) that the backfill surrounding each canistered anode was the type and weight required by the specifications?

Yes No

8. Did any canisters show signs of damage?

Yes No

9. If graphite anodes were to be used and these had been specified to be 100 percent impregnated with, for example, polymerized linseed oil (e.g., see MIL-A-182790), was at least one randomly selected anode sectioned at the job site to ensure that the required impregnation had been achieved?

Yes No

10. Did the sectioned graphite anode satisfy the impregnation specification requirements?

Yes No

11. If all anodes were to have the same insulated-conductor length (i.e., the length of the cable attached to each anode), what is this length? _____

12. If the anodes were to have different cable lengths (e.g., such as that required for the installation of a deep anode bed), what were these lengths on the anodes, and was each anode identified numerically or alphabetically with regard to cable length?

Cable identity _____
 Cable length _____

13. Were the anode-cable lengths at least as long as those required by the specifications?

Yes No

14. Did any anode cables contain splices?

Yes No

15. Did the copper conductors on the anode cables have the specified number of strands?

Yes No

Number of strands _____

16. Diameter of conductor on anode cables _____
 Diameter of each strand on anode cable _____
 Conductor size _____

17. Did the copper conductors on the anode cables have the size required by the specifications and/or engineering drawings?

Yes No

18. If dual (i.e. two layers) insulation did not exist, give the following for the copper conductors on the anode cables:

Insulation type _____
 Insulation thickness _____

19. If dual insulation existed on the anode cables, give the following:

Outer layer type _____
 Outer layer thickness _____
 Inner layer type _____
 Inner layer thickness _____

20. Did the anode cables have the specified type(s) and thickness(es) of insulation?
 Yes No
21. Did the insulation on the anode cables have any defects/nicks that extended below the outer surface more than 20 percent of the insulation thickness?
 Yes No
22. What was the copper-conductor size, insulation thickness(es), and insulation type(s) for the header cable (i.e., the primary/main conductor to which each of the anode conductors was to be attached) on the cathodic protection system?
 Conductor size _____
 Insulation type _____
 Insulation thickness _____
23. Did the header cable satisfy the requirements of the specifications?
 Yes No
24. Did the insulation on the header cable have any defects/nicks that extended below the outer surface more than 20 percent of the insulation thickness?
 Yes No
25. Was the external sealing concept(s) at the anode ends, from which the connecting cable existed, in accordance with specifications?
 Yes No
26. How were the electrical connections between the anode cables and head to the cable made?
 Split-bolt Crimp connector Exothermic weld
 Other _____
27. If the copper conductors on the anode cables were to be exothermically welded to the copper conductor on the header cable, what was the weld-metal-part number and the mold-part number to be used?
 Weld-metal-part number _____
 Mold-part number _____
28. Were the weld-metal-part number and mold-part number to be used in making the anode-header cable electrical connections in accordance with the manufacturer's recommendations?
 Yes No
29. If the copper conductors on the anode cables were to be attached to the copper conductor on the header cable using crimp-type connectors, list the manufacturer and the catalog number for the crimp-type connectors.
 Manufacturer _____
 Catalog number _____
30. Were the crimp-type connectors to be used in accordance with the manufacturer's recommendations for the conductor sizes involved?
 Yes No
31. Were the manufacturer's recommended devices/tools available at the job site for making electrical connections using crimp-type connectors?
 Yes No
32. Were the required number and type(s) of splice kits delivered to the job site for waterproofing the electrical connections between the anode cables and the header cable?
 Yes No
 Manufacturer of splice kit _____
 Catalog number of splice kit _____

(Note that the split-bolt-type connectors are not permitted according to the U.S. Army Corps of Engineers Guide Specification CEGS-16642.)

UTTU thanks Dr. James Myers for sending us this article.



RBCA implementation case study: Idaho

To date, staff in 49 states and territorial UST/LUST programs are either receiving risk-based corrective action (RBCA) training, or actively developing a RBCA process. State UST/LUST and fund program managers have been considering a risk-based approach to corrective action because it offers a responsible way to make decisions, given states' growing workloads and decreasing resources. By focusing on the risk posed by each site rather than striving for an often unachievable cleanup level at all sites (regardless of risk), state managers can target their limited cleanup resources. This article describes Idaho's RBCA implementation experience, which has focused, since the initiation of its RBCA effort, on involving and interacting with a broad array of stakeholders.

Like most state UST programs, the Idaho Division of Environmental Quality (IDEQ) Underground Storage Tank program participates in EPA's OUST RBCA training initiative. This training initiative is conducted through a cooperative agreement with ASTM (Association for Standards and Testing of Materials). Idaho recognized that this training initiative would provide a mechanism to secure a better understanding of the ASTM RBCA standard. IDEQ also acknowledged that the resulting Partnership in RBCA Implementation, or PIRI, would provide a means to facilitate private sector involvement in its RBCA design and development.

Like most state regulators, IDEQ expressed concerns regarding the nature and extent of the private sector's role in the RBCA process. In addition, OUST never defined those roles and responsibilities in the PIRI Memorandum of Understanding (MOU). In part, the decision to proceed with any type of modification/enhancement to a risk-based decision-making process (e.g., as a result of obtaining the ASTM RBCA training) was left to each state. The PIRI MOU only defined roles and responsibilities for participants on the national level. It was incumbent, therefore, for each state to decide how state-specific partnerships would operate, e.g., who would participate, what would change, how would the participation process operate, when would changes occur, and to which regulatory programs would the changes apply.

From the outset, IDEQ understood that their role in the partnership was to provide

- information exchanges with selected stakeholders regarding ongoing activities/needs
- support to peer states encountering comparable implementation challenges
- guidance on RBCA development and operation to stakeholders and the regulated community

As a state regulatory program, IDEQ also fully understood the confusion typically associated with perceived or actual change. To clarify those concerns, the IDEQ program manager submitted a written workplan to OUST and to his designated key stakeholder at Mobil.

This workplan identified all of the tasks that the state, to the best of their knowledge (based on input obtained regarding activities occurring in other states), determined to be necessary components of their customized RBCA process. This workplan provided a framework that each partner (federal, state and private) could review, evaluate (identify available resources/funding mechanisms) and discuss as they assessed options for supporting needs. Working collectively, the "stakeholders" were able to coordinate with IDEQ and determine the most cost-effective and timely options available.

Tasks

The program manager's initial list of implementation tasks included the following:

- revise Tier 1 lookup tables
- revise Tier 1 and 2 summary worksheets
- review and revise final overall plan
- develop Idaho software for consultants and DEQ staff
- brief DEQ senior management and other program staff
- distribute final Idaho RBCA guidance document
- conduct Idaho RBCA implementation workshops for consultants
- conduct two-phased RBCA "how to use" training workshops for DEQ staff
- conduct one-year review and revision of Idaho guidance document

Idaho guidance document and benefits of stakeholder participation

Each task was prioritized according to a general structure of the RBCA process. By providing the above referenced task list, associated cost projections, and implementation time-frames, "stakeholders" were able to facilitate the timely delivery of necessary support. Stakeholders supporting IDEQ's initiative were able to ascertain how their contributions were assisting the state's RBCA development effort.

In addition to developing a comprehensive workplan, IDEQ also designated a lead RBCA contact who coordinated interactions with the respective stakeholders.

In August 1996, IDEQ published its RBCA guidance document for petroleum releases. In July 1997, with help from PIRI and other stakeholders, IDEQ distributed RBCA Tier 2 software and documentation.

The state's ability to sponsor consultant workshops is another direct result of Idaho's willingness to work cooperatively with industry. Completion of these RBCA tools marks the full implementation of the RBCA process for petroleum releases in Idaho.



MTBE impacts on California's groundwater resources

The following article is an edited version of the Lawrence Livermore National Laboratory (LLNL) 1998 report, "An Evaluation of MTBE Impacts to California Groundwater Resources". A copy of this report can be found at <http://www-erd.llnl.gov/mtbe/new-mtbe.html>.

Methyl tertiary-butyl ether (MTBE) is a fuel oxygenate added to gasoline to reduce air pollution and increase octane ratings. Widespread use of this chemical has resulted in frequent detections of MTBE in samples of shallow groundwater from urban areas throughout the United States. The U.S. EPA considers MTBE a possible human carcinogen; in addition, MTBE has a disagreeable taste and odor at extremely low concentrations.

This study focused specifically on MTBE releases from LUSTs in California. (In the LLNL report, LUSTs are referred to as LUFTs: leaking underground fuel tanks.) Because the study is ongoing, results presented are preliminary. **MTBE monitoring has been required only since July 1996;** thus, sufficient data for even the simplest statistical and time-series analyses are just now becoming available.

Initially the study sought to answer the following questions:

- how applicable are U.S. EPA and ASTM methods for the analysis of MTBE and similar fuel oxygenates in groundwater samples?
- how frequently is MTBE detected in groundwater at LUST sites?
- what is the overall frequency of monitoring and occurrence of MTBE in California's public drinking water wells?
- how do the spatial extents of MTBE and benzene plumes at LUST sites compare?
- how do MTBE groundwater plumes behave over time?

How applicable are U.S. EPA and ASTM methods for the analysis of MTBE and similar fuel oxygenates in groundwater samples? LLNL examined analytical methods to determine the precision and accuracy of oxygenate analysis in groundwater containing dissolved gasoline compounds. EPA Method 8020A/21B is most commonly used for analysis of MTBE in groundwater from LUST sites. LLNL identified the following limitations. First, analysis of tertiary-butyl alcohol (TBA) suffered from poor sensitivity and yielded unreliable results even when only small amounts of gasoline were present in the sample (<500 µg/L). Second, in the presence of high concentrations of non-oxygenated gasoline (50,000 µg/L), EPA Method 8020A/21B yielded false-positive results for all oxygenates tested including MTBE, TBA, diisopropyl ether (DIPE), ethyl tertiary-butyl ether (ETBE), and tertiary-amyl methyl ether (TAME). These misidentifications resulted from using method detection

limits (MDLs) determined in clean water, rather than up to two orders of magnitude higher values, appropriate for oxygenate analysis in groundwater samples with high total petroleum hydrocarbon-gasoline (TPH-g) content. EPA Method 8020A/21B should be revised to account for this phenomenon of variable analyte sensitivity due to matrix effects, thereby minimizing the occurrence of false-positive misidentification of oxygenates. In contrast, EPA Method 8260A and a modified version of ASTM Method D4815 produced excellent results for all analytes regardless of the amount of gasoline interference present in the sample.

LLNL identified EPA Method 8020A/21B as a very conservative monitoring tool due to the lack of false-negative results, and its tendency for over-estimating analyte concentrations and false-positive misidentifications. In the absence of required method modifications, however, more definitive tests such as EPA Method 8260A and the modified ASTM Method D4815 are recommended when monitoring low concentrations of oxygenates in samples that may be significant in regulatory actions.

How frequently is MTBE detected in groundwater at LUST sites? LLNL examined groundwater data from 1,858 monitoring wells at 236 LUFT sites located in 24 counties. In 1995/96, MTBE was detected at 78 percent of these sites, indicating that MTBE is a likely contaminant at most LUST sites in California where fuel hydrocarbons have impacted groundwater. Concentrations ranged from several µg/L to approximately 100,000 µg/L.

What is the overall frequency of monitoring and occurrence of MTBE in California's public drinking water wells? As of March 1998, 32 percent of the 6,593 active drinking water wells within large public water supply systems, and up to 7 percent of wells in small water systems, have been monitored for MTBE. Among the 2,297 active public water supply wells monitored, the frequencies of impact by MTBE (0.35 percent) and benzene (0.42 percent) were similar, given current action levels of 20 µg/L and 1 µg/L, respectively. For MTBE, this frequency of impact to public drinking wells may not be a reliable indicator of future trends because it reflects a history of releases, including releases involving gasoline formulations containing no or only low volumes of MTBE. Even infrequent occurrences of MTBE, however, may have significant effects on regional water supplies as illustrated by the closure of the City of Santa Monica's groundwater wells.

How do the spatial extents of MTBE and benzene plumes at LUST sites compare? LLNL used 1995/96 data from 63 California LUST sites to define concentration contours of dissolved MTBE and benzene plumes using action levels of 20 and 1 µg/L, respectively. Among these sites, data from existing monitoring well networks were sufficient to estimate the length of 50 MTBE and benzene plumes. Cumulative distributions of plume lengths revealed that, on a population-wide basis, MTBE plumes were typically equivalent in length, or shorter than benzene plumes. On a site-by-site basis, this was also true in approximately 81 percent of the cases. At individual LUST sites, furthermore, **benzene**

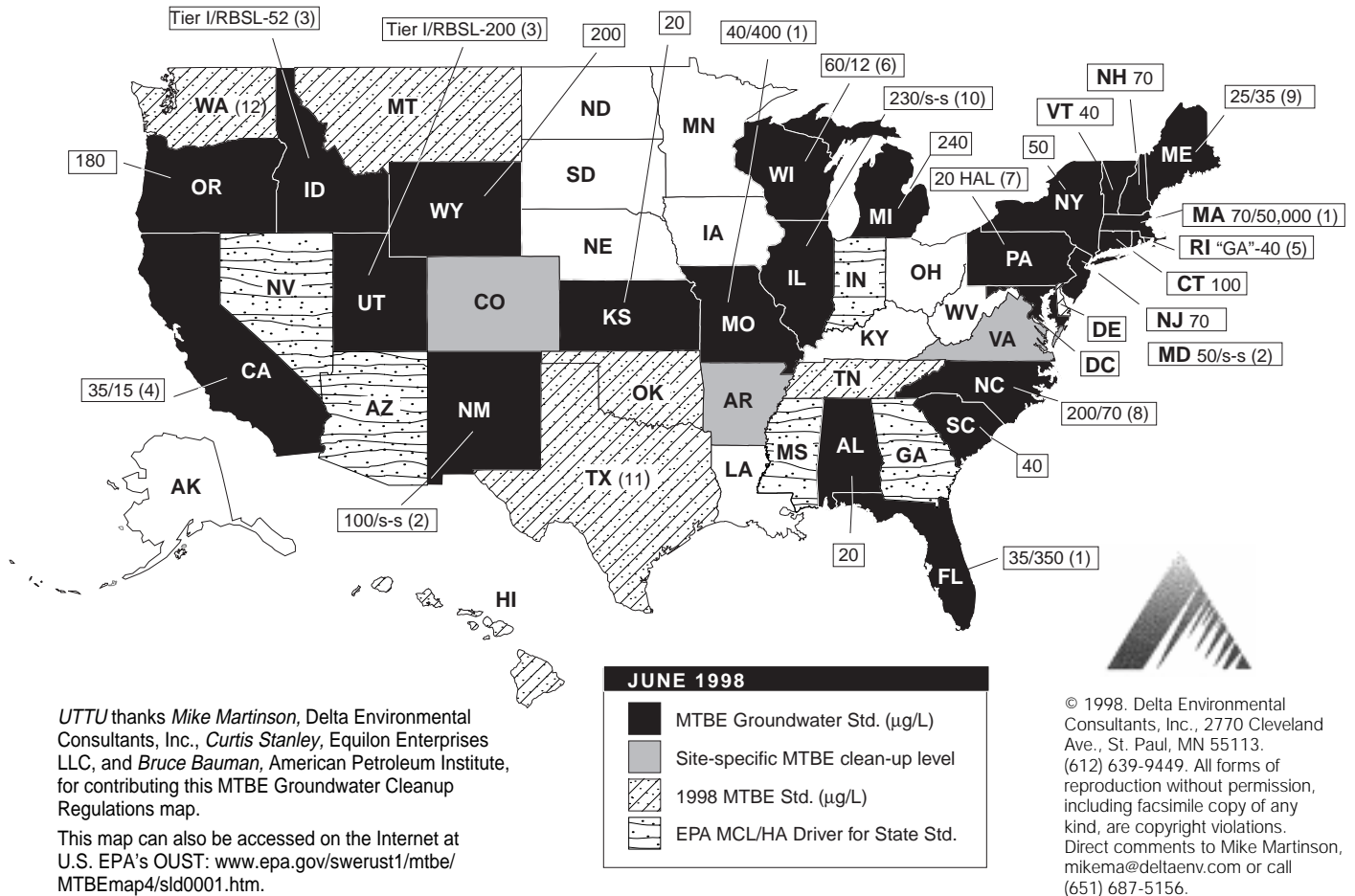
plume length only moderately correlated with the corresponding MTBE plume length; thus, the benzene plume length cannot be used to predict the extent of MTBE impact.

For most LUST sites analyzed, results suggest that dissolved benzene plumes were of larger regulatory concern during 1995/96 than the respective MTBE plumes.

Given both the anticipated high mobility and high recalcitrance of MTBE, these results appear to contradict expected behavior. For most LUST sites, however, release histories for MTBE and benzene likely differed significantly;

recent releases of gasoline containing significant quantities of MTBE may have occurred at sites where previous contaminants included little or no oxygenated fuels. Whereas several previous studies show that most benzene plumes are apparently stable, the present limited analysis of time-series data suggests that MTBE may behave differently, resulting in a gradual spatial dissociation of MTBE and BTEX plumes over time. Thus, plume lengths measured at a single point in time, e.g., 1995/96, may not be indicative of future MTBE plume behavior with respect to benzene.

MTBE Groundwater Clean-up Regulations: Current and Future



UTTU thanks Mike Martinson, Delta Environmental Consultants, Inc., Curtis Stanley, Equilon Enterprises LLC, and Bruce Bauman, American Petroleum Institute, for contributing this MTBE Groundwater Cleanup Regulations map.

This map can also be accessed on the Internet at U.S. EPA's OUST: www.epa.gov/swrust1/mtbe/MTBemap4/sld0001.htm.

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Footnotes for MTBE map

- (1) Clean-up goal dependent on GW potable/non-potable use (e.g., 35/350)
- (2) Clean-up goal stated, but can also be site-specific (e.g., 100/s-s)
- (3) RBCA program Tier I/RBSL clean-up goal
- (4) State Board clean-up goal/Santa Clara Water District clean-up goal
- (5) "GA" refers to potable groundwater
- (6) WDNR NR 140 Enforcement Standard/Preventative Action Limit goals
- (7) HAL refers to health advisory limit
- (8) Remedial action goal/value used primarily for toxicology purposes
- (9) Action level/drinking water standard (i.e., Maine's 25/35)
- (10) IEPA provisional enforcement level/site-specific clean-up goal possible
- (11) Evaluating Tier I MTBE values, currently not specified, for Revised Risk Reduction (RBCA) rule (11/98)
- (12) Method A clean-up level for MTBE (20 µg/L) proposed in rule amendments for implementation in 1999

How do MTBE groundwater plumes behave over time?

LLNL analyzed data from 29 sites located in San Diego County where MTBE monitoring data existed from 1992 through 1996. This dataset consisted of 2,320 samples collected at 327 monitoring wells; groundwater had been analyzed for MTBE, TPH, and BTEX. Data analysis suggests the following:

- The **probability of co-occurrence** of MTBE and BTEX compounds detected in individual monitoring wells decreased significantly over time (from approximately 80 percent to 60 percent over a period of 3 years), whereas the **overall frequency of detection** of these compounds remained consistent. Assuming that most hydrocarbon plumes are stable, the observed gradual dissociation of BTEX and MTBE plumes indicates that MTBE plumes are mobile.
- MTBE concentrations in the downgradient wells of the San Diego County sites were often equivalent to, or significantly higher than corresponding concentrations of BTEX compounds, implying that at many sites MTBE was leaving established monitoring networks at significantly higher concentrations than BTEX compounds. In approximately 30 percent of the downgradient wells, the regulatory levels of 20 µg/L and 1 µg/L (for MTBE and benzene, respectively) were exceeded. Even so, benzene plumes would be likely to attenuate before MTBE plumes because of benzene's higher potential for in-situ biodegradation and retardation.
- Variability in hydrologic parameters, such as high precipitation events, resulted in brief increases in MTBE concentrations in monitoring wells with low TPH-g impacts (< 1,000 µg/L). Spikes in MTBE concentrations were observed after the particularly wet winters of 1992/93 and 1994/95. These concentration surges suggest that **periodic monitoring over limited time intervals may fail to detect the departure of significant amounts of MTBE from the monitoring network**. This may be especially important when evaluating the stability of an individual plume or when estimating mass migrating beyond downgradient monitoring wells.
- Reduction of benzene concentrations by as much as **several orders of magnitude** in the downgradient direction were observed within existing monitoring networks, indicating significant benzene attenuation at most sites. Attenuation of MTBE, however, appeared to be much more limited because concentration reductions generally did not exceed **one order of magnitude**. These results are consistent with the hypothesis that MTBE is generally recalcitrant and not likely to attenuate rapidly as do the BTEX compounds.

The authors of the LLNL report conclude the following:

1. MTBE is a frequent and widespread contaminant in shallow groundwater throughout California. There are presently 32,409 LUST sites identified in the state, 13,278 of which have hydrocarbon-impacted groundwater; at a minimum, 10,000 MTBE-impacted sites exist.
2. MTBE plumes are more mobile than BTEX plumes. LLNL's results using 1995/96 data indicate that, at most sites, individual MTBE plumes were nearly equivalent or shorter than their corresponding benzene plumes, defined by action levels of 20 and 1 µg/L respectively. Results suggest that at a portion of these sites this relationship will change over time as contaminant plumes gradually dissociate.
3. Comparison of BTEX and MTBE attenuation at downgradient monitor wells showed MTBE concentrations leaving these networks were greater than BTEX compounds, at a significant portion of LUST sites. MTBE's primary attenuation mechanism is dispersion; MTBE does not significantly degrade and is, in fact, recalcitrant. Thus, MTBE mass would not be depleted; it would instead travel significantly longer distances and require a longer time than a BTEX plume to attenuate.
4. MTBE has the potential to impact regional groundwater resources and may present a cumulative contamination hazard because MTBE is recalcitrant and mobile. To date, impacts of MTBE to public water systems have been limited and similar in frequency to benzene impacts. Based on historical data, and by virtue of retardation and biodegradation, future impacts of BTEX to water supplies are not expected to be common. Because MTBE is recalcitrant and mobile, however, MTBE contamination may be a progressive problem. Water resource management on the regional scale will become increasingly relevant with a compound that appears both ubiquitous and recalcitrant. For example, the potential long-term accumulation of mass resulting from dispersion of MTBE plumes may be a key consideration for management of specific regional groundwater basins. To ensure future protection of drinking water resources, therefore, leak prevention is a critical requirement for the continued use of MTBE.
5. LLNL has identified two major areas of uncertainty in the study's results:
 - available MTBE data are limited
 - the issue of MTBE recalcitrance has not been resolved

Ideally, time-series data from hundreds of LUFT sites representing all hydrogeologic regions of California should be utilized to characterize the behavior and impact of MTBE plumes. Analyses of an expanded dataset are important to confirm the study's initial findings regarding the mobility and recalcitrance of MTBE. Further time-series analyses are necessary for predicting future MTBE impacts to groundwater resources and assessing the vulnerability of drinking water resources.

A number of laboratory-cultured microorganisms isolated from various environments can degrade MTBE, yet no convincing evidence presently exists suggesting that this destructive process occurs quickly and/or commonly in the field. While future research is warranted to address these issues, it is appropriate to manage groundwater resources with the assumption that MTBE is both mobile and recalcitrant relative to benzene, until proven otherwise.

Reference

Happel, A.M., Beckenbach, E.H., and R.U. Halden, "An Evaluation of MTBE Impacts to California Groundwater Resources," June 1998, Lawrence Livermore National Laboratory, University of California, Livermore, California 94551; UCRL-AR-130897, <http://www-erd.llnl.gov/mtbe/new-mtbe.html>; send any e-mail comments to mtbe-comments@popout.llnl.gov.

UTTU thanks Mike Martinson, Curtis Stanley and Bruce Bauman for contributing the MTBE map on page 11.



Information sources

Publications from Lewis publishers (800-272-7737, <http://www.crcpress.com>, orders@crcpress.com, fax 800-374-3401) include the following:

- *Subsurface Restoration*
- *Groundwater and Soil Remediation: Practical Methods and Strategies*
- *Watershed Hydrology*
- *EPA Environmental Assessment Sourcebook*
- *EPA Environmental Engineering Sourcebook*
- *Physical Nonequilibrium in Soils: Modeling and Application*
- *Practical Environmental Bioremediation: The Field Guide*
- *Karst Water Resources*
- *The Design, Performance and Analysis of Slug Tests*

Innovative Site Remediation Technologies Design and Application: Liquid Extraction Technologies is available from the American Academy of Environmental Engineers; call 410-266-3390, fax 410-266-7653 or e-mail aees@ea.net.

The following U.S. Geological Survey reports are available:

- *Interdisciplinary Investigation of Subsurface Contaminant Transport and Fate at Point-Source Releases of Gasoline Containing MTBE*; call 609-771-3944, e-mail hbxton@usgs.gov
- *Method for Determination of MTBE and its Degradation Products in Water*; 503-690-1651; e-mail church@ese.ogi.edu
- *Occurrence of Nitrate, Pesticides and Volatile Organic Compounds in the Kirkwood-Cohansey Aquifer System, Southern New Jersey*; call 609-771-3951, e-mail pestack@usgs.gov
- *Occurrence of Volatile Organic Compounds in Streams on Long Island, New York, and New Jersey*; call 516-736-0783, e-mail saterrac@usgs.gov
- *Selected Bibliography of the Fuel Oxygenate Methyl Tert-Butyl Ether with Emphasis on Water Quality*; call 605-355-4560, ext. 262, e-mail evbracht@usgs.gov, visit website <http://www.sdr/cr/usgs.gov/nawqa/pubs/>
- *Summary of Published Aquatic Toxicity Information and Water-Quality Criteria for Selected VOCs*; call 605-355-4560, ext. 236 or e-mail blrowe@usgs.gov
- *The Urban Atmosphere as a Non-point Source for the Transport of MTBE and Other VOCs to Shallow Groundwater*; call 503-690-1080 or email pankow@ese.ogi.edu

- *USGS Compiled Data Set for National Assessment of VOCs in Ground Water*, call 703-648-5805, e-mail wlapham@usgs.gov.

For information on the national monitoring of VOCs in groundwater and surface water, call John Zogorski at 605-355-4560 or email jszogors@usgs.gov.

The following government documents are available:

- *Accelerating Cleanup: Paths to Closure* (DOE/EM-1342); <http://www.em.doe.gov/closure/np98.html>, call 800-736-3282 or 202-863-5084, fax 202-554-3267
- *Activity Factors* (EPA-600-P-95-992Fc), which gives data to assess exposure factors; <http://www.epa.gov/cincl>
- *A Dynamic Site Investigation: Adaptive Sampling and Analysis Program for Operable Unit 1 at Hanscom Air Force Base, Bedford, Massachusetts*; <http://clu-in.com/techpubs.htm>.
- *Bibliography for Innovative Site Cleanup Technologies* (EPA542-B-98-001); <http://clu-in.com/techpubs.htm>, call 800-490-9198, or 513-489-8190, fax 513-891-6685
- *Bioremediation of Soils Using Windrow Composting* (CEGS 02191); <http://www.hnd.usace.army.mil/techinfo/cegs/cegstoc.htm>
- *Compendium of Federal Facilities Cleanup Management Information* (EPA 540/R-98/004); <http://clu-in.com/techpubs.htm>
- *Catalog of EPA Materials on Underground Storage Tanks* (EPA 510-B-98-001); <http://www.epa.gov/swerust1/pubs/index.htm>, call 800-490-9198 or 513-489-8190, fax 513-891-6685
- *Design Guidance for Application of Permeable Barriers to Remediate Dissolved Chlorinated Solvents*; call National Technical Information Service (NTIS), 800-553-6847 or 703-605-6000
- *EPA Oil Spill Program Update*; <http://www.epa.gov/superfund/oerr/er/oilspill/publications/pubs.htm>
- *Expediting Cleanup and Redevelopment of Brownfields: Addressing the Major Barriers to Private Sector Involvement—Real or Perceived*; <http://www.epa.gov/swerosps/bf/liab.htm>
- *Field Sampling and Analysis Technologies Matrix and Reference Guide* (EPA 542-B-98-002); <http://Solaris.frtr.gov/site>, call 800-490-9198 or 513-489-8190, fax 513-891-6685
- *Ground Water Currents* (EPA 542-R-98-004); <http://clu-in.com/techpubs.htm>, call 800-490-9196 or 513-489-8190, fax 513-891-6685
- *Natural Attenuation of Chlorinated Volatile Organic Compounds in a Freshwater Tidal Wetlands, Aberdeen Proving Ground, Maryland*; call 303-202-4700, write U.S. G.S. Branch of Information Services, P.O. Box 25286, Denver, Colorado 80225-0286
- *Recommended Guidelines for Applying Field Screening Methods in Conducting Expedited Site Investigations at Underground Storage Tank Sites in Connecticut*; <http://www.sp.uconn.edu/~hydrogeo/deprept.htm>, or call 860-424-3555; \$5.00 per hard copy
- *Recommended Guidelines for Multilevel Sampling of Soil and Ground Water in Conducting Expedited Site Investigations at Underground Storage Tank Sites in Connecticut*; same as preceding source
- *Rapid Commercialization Initiative (RCI) Final Report for an Integrated In-Situ Remediation Technology (Lasagna™)* (DOE/OR/22459-1); <http://www.rtdf.org/lastechp.htm>
- *Site Characterization and Monitoring Technologies: Bibliography of EPA Information Resources* (EPA 542-B-98-003); <http://clu-in.com/CSCT/Bib0498.htm>, call 800-490-9198 or 513-489-8190; fax 513-891-6685
- *Tech Trends* (EPA 542-N-98-005); <http://clu-in.com/techpubs.htm>, call 800-490-9198 or 513-489-8190, fax 513-891-6685

SW-846 Version 2.0 on CD-ROM is available from NTIS, phone 800-533-6847, e-mail orders@ntis.fedworld.gov; price ranges from \$129 for a single user to \$1,254 for unlimited users.

Websites

Airforce's draft of "Test Plan and Technical Protocol for a Field Treatability Test for POL-free Product Recovery": <http://www.afcee.brooks.af.mil/er/toolbox.htm>

Association for Testing and Materials: <http://www.astm.org>

Association for the Environmental Health of Soils: <http://www.aehs.com>

EPA's VISITT database: <http://www.prcmi.com:80/visitt/>

The Bioenvironmental Hazards Research Program: http://www.mcl.tulane.edu/cbr/DoD_Home.html

Biotechnology Industry Organization: <http://www.bio.org>

Compost information: <http://www.maine.com/tse/pals/compost.html>

Geochemist Workbench: <http://www.rockwater.com>

Ground Water Remediation Technologies Analysis Center which contains the paper, "Technology Evaluation Report: Phytoremediation" (TE-98-01): http://www.gwrtac.org/html/tech_eval.html

Ground Water On-Line: <http://www.ngwa.org/gwonline/index.html>

Key brownfields, contacts, addresses and phone numbers: http://www.epa.gov:6706/brwncd/owa/pkg_cntcts.cntct_form

Links to hydrogeological organizations, software, etc.:
<http://www.ems.psu.edu/Hydrogeologist>

Phytonet—Phytoremediation Electronic Newsgroup
 and links: <http://www.dsa.unipr.it/phytonet/>

Soil and Groundwater Cleanup: <http://www.sgcleanup.com/bioremediation.html>

TechDirect archives, information on subscribing to this free
 EPA electronic newsletter: <http://clu-in.com/techdrct.htm>

United States Army Environmental Center (remediation
 web site): <http://aec-www.apgea.army>

Water Science and Technology Board: <http://www2.nas.edu/wstb>

US EPA, Ada, Oklahoma Research Laboratory, <http://earth1.epa.gov/ada/tsc.html>, has recently published papers that can be downloaded including

- *Steam Injection for Soil and Aquifer Remediation*
- *How Heat Can Enhance In-situ Soil and Aquifer Remediation*

Also at the site:

List of Kerr Lab research projects

List of groundwater models, such as BIOPLUME IIII

UTTU obtained many of these sites and other information from the Groundwater Mailing List (<http://groundwater.com>), Bioremediation Discussion Group (<http://biogroup.gzea.com>) and TechDirect (<http://clu-in.com/techdrct.htm>).

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