

Underground Tank Technology Update

Vol. 15, No. 4
July/August 2001

Department of Engineering Professional Development The College of Engineering University of Wisconsin–Madison

Underground Tank Technology Update is published bimonthly by the University of Wisconsin–Madison, Department of Engineering Professional Development. *UTTU* supplies useful information to federal, state, and local officials working with groundwater technology and to other interested technical specialists. For new subscriptions or address corrections, use the form on inside back page.

UTTU is funded by the U.S. EPA under Cooperative Agreement No. 826455010 to the University of Wisconsin–Madison, which is responsible for its preparation. Mention of trade names or commercial products does not constitute endorsement or recommendation for use.

Comments and suggestions are welcome and may be directed to John T. Quigley, Project Director, 432 N. Lake St., Madison, WI 53706. Tel 608/265-2083.

If you have a problem locating a reference cited in *UTTU*, please contact Pat Dutt: pmdutt@msn.com or 607/272-3212

Advisory Board

Gilberto Alvarez, Environmental Engineer
OUST, U.S. EPA, Region 5, Chicago, Illinois

Bruce Bauman, Research Coordinator
Soil/Groundwater, API, Washington D.C.

Shushona A. Clark, Project Officer, OUST
U.S. EPA, Washington, D.C.

James Davidson, President
Alpine Environmental, Inc.
Fort Collins, Colorado

Jeff Kuhn
DEQ, Petroleum Section
Helena, Montana

George Mickelson, Environmental Engineer
Wisconsin Department of Natural Resources
Madison, Wisconsin

Joseph Odencrantz, Principal
Tri-S Environmental, Inc.
Newport Beach, California

Phil O'Leary, Professor
Department of Engineering Professional
Development, UW–Madison

Gerald W. Phillips
U.S. EPA, Region 5, Chicago, Illinois

Hal White, Hydrogeologist
OUST, U.S. EPA, Washington D.C.

Staff

<i>John T. Quigley</i>	Project Director
<i>Pat Dutt</i>	Geologist/Writer
<i>Darrell Petska</i>	Copy Editor
<i>Debbie Benell</i>	Program Assistant
<i>Susan Kummer/Artifax</i>	Graphics

Article summaries

- Understanding redox zones2**
No standard or universally accepted procedures exist for determining redox conditions in pristine and contaminated groundwater. By understanding redox zones, researchers hope to identify a plume's reduced and oxidized conditions, assign redox zones, and determine predominant redox reactions.
- Ozonation of petroleum-contaminated groundwater8**
Engineers designed an in-situ ozone sparging system to clean up petroleum-contaminated groundwater in Wisconsin. The system consisted of an air compressor, a programmable logic controller, gauges and controls.
- Partitioning tracer tests12**
Partitioning tracer tests, developed by the petroleum industry, are techniques that detect and quantify NAPL (nonaqueous phase liquid). PTTs have the capability to measure a much larger portion of the aquifer than point sampling methods, such as coring.
- Innovative partition, interfacial and biogeochemical tracers14**
This article describes tracers used to estimate NAPL saturation, NAPL-water interfacial area, biogeochemical reactivity and transformation rate.
- VOCs from a parking lot..... 17**
Researchers investigated non-point sources of VOCs from a parking lot in Minnesota. Non-point sources of VOCs include spill residues trapped in the pore space of concrete and asphalt, nonaqueous phase (asphalt, oil and grease) particles that accumulate on impervious areas, and VOCs. VOCs come from the atmosphere, auto exhaust and leaking gas tanks and may partition into asphalt, oil, grease, vehicle soot, vegetation and other organic particles.
- Information sources18**
Information sources give phone numbers and web addresses of recently published material.

UTTU is on the Web <http://epd.engr.wisc.edu/uttu/>

UTTU is now available in an electronic version. See page 19.



Understanding redox zones

No standard or universally accepted procedures exist for determining redox conditions in pristine and contaminated groundwater (*Christensen and others, 2000*). By understanding redox zones, researchers can

- identify a plume's reduced and oxidized conditions in terms of redox zones
- determine likely redox reactions and contaminant fate

Redox reactions can involve

- gases: O₂, N₂, CH₄, CO₂
- dissolved components: NO₃⁻, NH₄⁺, Fe²⁺, Mn²⁺, SO₄²⁻, HS⁻, dissolved organic carbon
- solids: FeOOH, MnO₂, FeCO₃, MnCO₃, FeS, FeS₂
- components: Fe²⁺, Mn²⁺, NH₄⁺ associated with solids by ion exchange

Redox environments in plumes generally show the following:

- strongly reduced redox conditions develop close to the source
- a redox gradient occurs along, as well as transverse to, the main groundwater flow direction
- a large, reduced plume within an aerobic aquifer suggests that the plume has existed for some time
- remediation potential, with oxygen injection, depends on the plume's current redox condition as well as the aquifer's redox buffering capacity
- laboratory studies of microbial activity and contaminant degradation make field-correlation difficult unless studies incorporate in-situ redox conditions

Relative electron activity and Gibbs energy of reaction

According to Christensen and others (2000), "Aqueous systems contain no free electrons, but the relative electron activity, as an intensity parameter, can be defined as $p\epsilon = -\log \{e^{-}\}$; $p\epsilon$ gives the hypothetical electron activity $\{e^{-}\}$ and measures the tendency of a system to accept or transfer electrons. In a highly reducing system, the tendency to donate

electrons, that is the hypothetical 'electron pressure' or electron activity, is relatively large and $p\epsilon$ is low. In contrast, high $p\epsilon$ values indicate a relatively low electron activity and a relatively oxidized system."

Electron activity can be linked to redox potential, E_H by the Nernst equation:

$$p\epsilon = E_H / (2.3RT/F)$$
 or

$$E_H = E_H^0 + (2.3RT/nF) \log \{[Ox]/[Red]\}$$

T is absolute temperature in Kelvin

R is the gas constant

F is Faraday's number

At 25°C, $2.3 RT/F = 0.059 \text{ V/mol}$

Ox is an oxidized species

Red is a reduced species

Another important consideration is the Gibbs energy of reaction, a measure of a system's ability to do work:

$$G = H - TS$$

H is enthalpy of the system

S is entropy of the system

A reaction with the most negative $\Delta G^0(W)$ will occur before a reaction with a higher ΔG . If ΔG is negative, the reaction may proceed spontaneously to equilibrium. Table 1 shows Gibbs energy of reaction for oxidation of organic carbon by electron acceptors and methane fermentation. Table 2 shows Gibbs energy of reaction for oxidation of reduced species by oxygen.

If the activities of the species are known (for instance if goethite, FeOOH, is being reduced, the species produced could be H₂, H⁺ and Fe²⁺—depending on what is reducing the goethite), researchers can calculate the energy available ($-\Delta G_r$) for the reaction and "the feasibility of the reaction being microbiologically mediated can be evaluated if minimum energy requirements are known" (*Christensen and others, 2000*).

The redox process

Figure 1 shows the redox half reactions for contaminant plumes and electron activity at a pH of 7. "Combining half reactions to create a full redox reaction does not necessarily indicate that the reaction will occur, nor does it suggest how the reaction proceeds. The "redox ladder" only indicates that the reaction is possible from a thermodynamic point of

Process	Reactants	Products	$\Delta G^0(W)$ [kJeq ⁻¹]
Aerobic respiration	1/4 CH ₂ O + 1/4 O ₂	1/4 CO ₂ + 1/4 H ₂ O	-125
Denitrification	1/4 CH ₂ O + 1/5 NO ₃ ⁻ + 1/5 H ⁺	1/4 CO ₂ + 1/10 N ₂ + 1/2 H ₂ O	-119
Mn reduction	1/4 CH ₂ O + 1/2 MnO ₂ + 1/2 HCO ₃ ⁻ + 1/2 H ⁺	1/4 CO ₂ + 1/2 MnCO ₃ + 3/4 H ₂ O	-98
Fe reduction	1/4 CH ₂ O + FeOOH + HCO ₃ ⁻ + H ⁺	1/4 CO ₂ + FeCO ₃ + 7/4 H ₂ O	-42
SO ₄ reduction	1/4 CH ₂ O + 1/8 SO ₄ ²⁻ + 1/8 H ⁺	1/4 CO ₂ + 1/8 HS ⁻ + 1/4 H ₂ O	-25
CO ₂ reduction/methane fermentation	1/4 CH ₂ O	1/8 CO ₂ + 1/8 CH ₄	-23

Table 1. Gibbs energy of reaction for oxidation of organic carbon by electron acceptors and methane fermentation of organic carbon (*Christensen and others, 2000*).

Process	Reactants	Products	$\Delta G^0(W)$ [kJeq ⁻¹]
Aerobic respiration	1/4 O ₂ + 1/4 CH ₂ O	1/4 CO ₂ + 1/4 H ₂ O	-125
Sulfide oxidation	1/4 O ₂ + 1/8 HS ⁻	1/8 SO ₄ ²⁻ + 1/8 H ⁺	-100
Fe oxidation	1/4 O ₂ + FeCO ₃ + 3/2 H ₂ O	FeOOH + HCO ₃ ⁻ + H ⁺	-83
NH ₄ ⁺ oxidation	1/4 O ₂ + 1/8 NH ₄ ⁺	1/8 NO ₃ ⁻ + 1/4 H ⁺ + 1/4 H ₂ O	-43
Mn oxidation	1/4 O ₂ + 1/2 MnCO ₃ + 1/2 H ₂ O	1/2 MnO ₂ + 1/2 HCO ₃ ⁻ + 1/2 H ⁺	-28

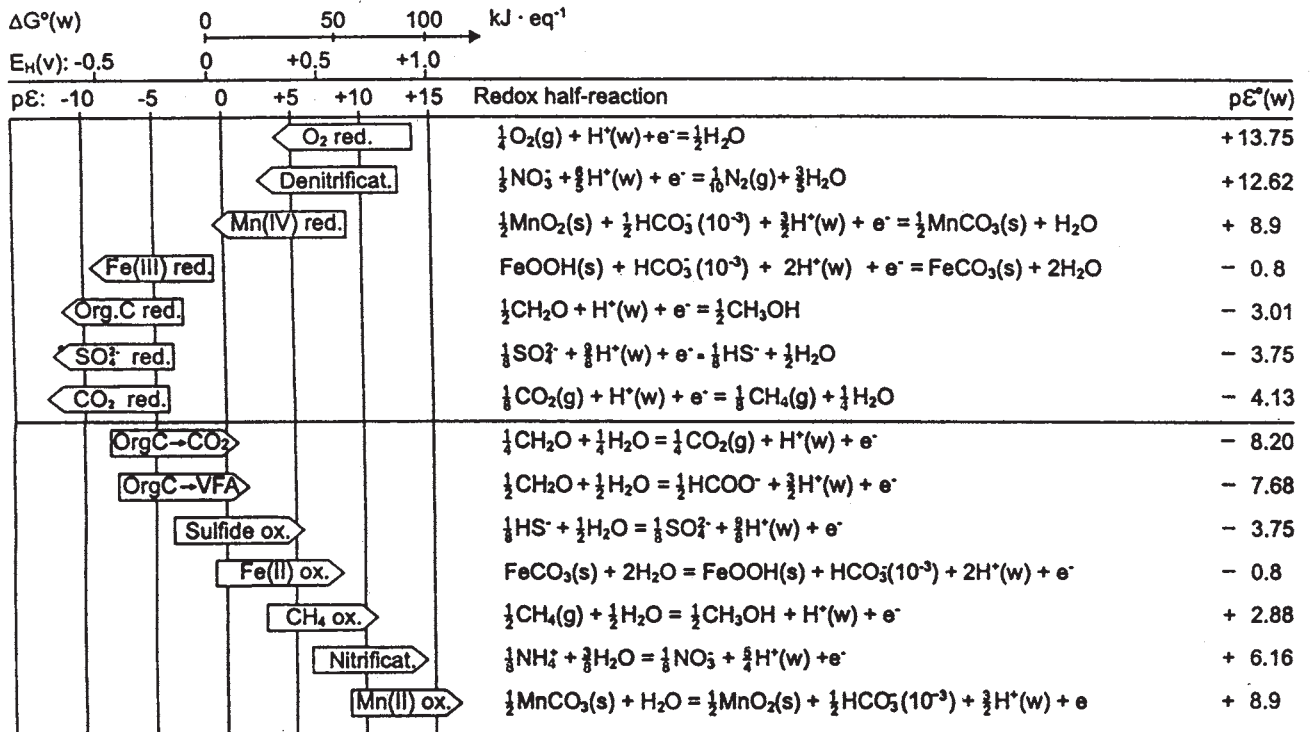
Table 2. Gibb's energy of reaction for oxidation of reduced species by oxygen (Christensen and others, 2000).

view... the reactions involving organic compounds and iron and manganese solids are only sample reactions, since the actual organic matter and the composition of the iron and manganese minerals may vary substantially and hence shift the $pE^0(W)$ of the reaction" (Christensen and others, 2000).

The pathways are likely more complex than those indicated by the half reactions. "A redox process is sometimes referred to as a terminal electron-accepting process, TEAP, a chemical reaction picturing the overall process of electrons from a reduced electron-donor, terminally being accepted by an oxidized species without paying attention to the actual electron-transfer chain and the role of intermediates."

"The kinetics of redox reactions often depend strongly on the number of electrons that must be transferred to form stable

reaction products... multiple electron transfers are generally associated with complex changes in molecular configuration, while single electron transfers often involve much less change in molecular structure." Consider, for instance, the oxidation of Fe²⁺ to Fe³⁺, which requires little activation energy and therefore can take place rapidly at groundwater temperature and pressure. "... reductive dissolution of ferric oxyhydroxide minerals, in contrast, requires greater changes in the coordination environment for iron. Structural Fe (III) at the mineral surface must form chemical bonds with adsorbed reductants, organic compounds, reduced metal complexes or extracellular iron reductase" (Christensen and others, 2000). Chemical, mineralogical and microbiological factors will also influence electron-transfer kinetics, and hence redox processes.



a. $pE^0(w)$ is the standard electron activity of the half-reaction at pH = 7.

Figure 1. Common redox half-reactions and electron activity in plumes (Christensen and others, 2000).

Difficulties in applying redox concept

Researchers have defined the conditions that make difficult the application of redox theory to contaminant plumes:

- contaminant plumes are not likely to be in internal equilibrium; "Lindberg and Runnels (*in Christensen and others, 2000*) investigated 30 groundwater systems and found none in equilibrium with respect to measurable redox couples; only when the pE is identical for all redox couples is the system at internal or thermodynamic equilibrium, and only in this case can a system pE be defined and applied to estimate reduced and oxidized species of all redox couples"
- redox processes generally have very slow kinetics, thus, finding a groundwater system in thermodynamic or internal equilibrium is unlikely

Researchers assert that plumes, because they have strong redox gradients, can have identifiable redox conditions. "We suggest that the term redox condition be used to characterize the dominating redox potential to the system. Ideally, the evaluated redox condition should be accompanied by an evaluation of associated capacities, depending on the purpose of the investigation" (*Christensen and others, 2000*). For instance, when researchers constructed a hypothetical contaminant plume with redox zones, they found plume length and time scale depended on

- size and strength of the point source
- groundwater flow velocity
- aquifer geochemistry

Measurements that can be acquired to define a plume's redox condition include

- electrochemical measurement
- groundwater composition
- groundwater sediment composition

Redox condition based on electrochemical measurement

Authors state that an electrical potential, hence an estimate of a sample's redox condition, may be acquired by "immersing two electrical leads in a groundwater sample and connecting them to the input of a voltmeter." Such a procedure has been successfully applied in analytical chemistry to aquatic solutions of pure chemicals, yet in a system where complex biological and geochemical processes are being assessed, questions to be addressed include:

- to what solutes and processes do such measurements respond?
- do measured potentials correspond to rigorously defined electrochemical potentials, and thus, free energies of relevant reactions?
- what information would be useful for assessing groundwater redox conditions?

A review of basic electrochemical principles related to direct measurement of redox potentials can be found at www.shef.ac.uk/~gprg. Christensen and others (*2000*) state that "the main problem in applying these principles to measuring redox potentials in polluted groundwater is the very slow chemical kinetics of redox reactions involving C, S and N species. Actually, the only redox couple that may respond kinetically fast and have sufficient ion activity is the Fe^{3+}/Fe^{2+} redox couple."

Redox condition based on groundwater composition

The species of concern for redox reactions in groundwater include

- dissolved gases: O_2 , N_2O , CH_4
- dissolved ions: NO_3^- , NH_4^+ , Fe^{2+} , Mn^{2+} , SO_4^{2-} , HS^- , NO_2^-
- components such as DOC and organic N

Redox potentials **cannot** usually be calculated for each redox couple for the following reasons:

- analytical methods may have detection limits too high to quantify both species of a redox couple due to a very low concentration of one of them
- analytical methods may not exist for both redox species, and lack of analytical detection of one species of a redox couple may be circumvented by measuring total concentration
- several redox-sensitive species are also precipitates, and the dissolution/precipitation reactions are not necessarily at equilibrium, or the actual precipitate is not known

Other conditions that can affect sampling and behavior of groundwater species include species transport within the plume, cation exchange, volatility and instability. Researchers also mention that ammonium and arsenic species have been used as redox indicators: ammonium is oxidized at high redox potentials while arsenic is reduced and becomes mobile at low redox potentials.

Researchers assert that "Using redox-sensitive compounds for redox characterization requires proper sampling of redox-sensitive species from representative screens. **Screen length is critical, because long screens may cause mixing of groundwater having significantly different composition with respect to groundwater chemistry.** This may be specifically critical in layered geological media or shallow contaminant plumes" (*Christensen and others, 2000*).

Regarding sampling and analysis:

- when sampling at the ground surface, electrode measurements (e.g., oxygen) should be performed in-line (tubing connected directly to a flow cell) to avoid contact with the atmosphere
- samples used for analysis of compounds where solid species may interfere (Fe^{2+} , Fe, Mn) should be properly filtered

- analysis of Fe^{2+} and H_2S should be performed in the field
- dissolved gases should not be filtered
- preservation of samples should ensure that
 - Fe^{2+} and Mn do not precipitate
 - H_2S , Fe^{2+} , Mn, NH_4^+ do not oxidize
 - there is no conversion of NO_3^- or CH_4

By analyzing studies of redox-sensitive species at the Bemidji site in Minnesota, scientists could use significant methane and Fe(II) increases as an indication of redox condition change from aerobic to anaerobic.

At a landfill plume site (the Vejen Landfill), researchers found that differences in methane, iron and manganese between two plumes was attributable to flow velocities, sediment characteristics and dilution. At this site, for assignment of redox zones, **“a high spatial resolution in the sampling network, short screens, and small sample volumes are crucial to avoid mixing of groundwater from different redox zones** and to identify the steep redox gradients often observed. This is especially critical in the outskirts of the plume, where horizontal and vertical variations will be significant, and in geological settings with local heterogeneity containing deviating redox environments by nature” (Christensen and others, 2000).

Christensen and others also assert that “quantifying redox-sensitive species in groundwater samples is a simple and useful tool for identifying the redox conditions of a groundwater contaminant plume. The basic principles are thermodynamically sound, but the actual criteria for assigning the redox status depend, to some extent, on local conditions, such as

- natural groundwater geochemistry
- compounds leaching from the source
- quality of sampling and analytical equipment”

Application of redox condition concepts is limited because redox-sensitive species migrate away from active zones, geochemical processes cause precipitation of compounds, and overlap exists between different redox zones. “The transport of reduced redox-sensitive species, e.g., methane and ferrous ion, will smear out the redox zones identified by groundwater sample composition. Presumably the strongly reduced zones will be slightly overestimated. Precipitation and ion exchange of iron and manganese and precipitation of sulfur species will also affect redox state identification at a given point.”

Significance of hydrogen in redox zones

H_2 concentrations are not necessarily indicative of a given redox process; two different redox processes may occur depending on substrate and product activities leading to the same H_2 concentration. “Still, the measurement of H_2 is an extremely valuable tool in analyzing the **energies of microbiological processes** as it (H_2) appears to enable the integration of redox processes in a thermodynamically based description of a given system.”

When anaerobic matter is degraded, H_2 is produced. In groundwater, the pool of H_2 is extremely small compared to the rate of production and consumption. “The residence time is thus on the order of seconds at high TEAP rates (> 30 mM/year) to minutes in systems with low TEAP rates (<0.5 mM/year). Therefore H_2 concentrations must reflect ongoing processes, as transport is extremely limited within this time frame. Even in a groundwater system with a high flow rate of 1 m/day, which is a 1-minute residence time for H_2 , the advective transport distance for H_2 is < 1 mm” (Christensen and others, 2000).

Some conclusions about H_2 :

- the representation of measured H_2 concentrations may depend on the system generating the H_2
- several redox processes may be occurring concomitantly, at comparable rates, along several paths in a system
- the H_2 measured from groundwater often reflects bulk water concentration—and the TEAP bacteria’s intracellular concentration of H_2
- if organic matter being fermented is dissolved (as in most pollution plumes), and the fermenting and TEAP bacteria are not closely associated, there will be a gradient in the H_2 concentration from the fermenting to the TEAP bacteria, and sampling of bulk water might give an intermediate H_2 concentration
- H_2 concentration, controlled by the TEAP-mediating bacteria, is related to the minimum energy requirements; the H_2 concentration in a system, therefore, is closely tied to the system’s thermodynamics (energy available to a microorganism for a given TEAP is part of the Gibb’s energy of reaction: the more negative the ΔG , the higher the energy available)
- theoretically, variations in temperature, Fe-oxide stability and Fe^{2+} activities would affect H_2 concentrations for Fe-oxide reduction
- the use of a specific H_2 range to separate sulfate and Fe reduction seems difficult, since they may take place concurrently
- the TEAP allowing the lowest H_2 concentration at given in-situ conditions is preferred because possible competitors not able to use this TEAP are excluded
- the tendency of bacteria to always minimize the energy of ongoing TEAPs to a fixed value close to equilibrium suggests that the system can be viewed as being in a state of partial equilibrium, but an assumption of steady state is not valid
- H_2 concentrations in pollution plumes might vary, depending on the plume’s ionic strength
- where Fe-oxide reduction is indicated, measured H_2 concentrations should give an estimate of which Fe oxide apparently controls H_2 concentration

Researchers conclude that

- the significance of a given H_2 concentration is uncertain
- bulk and stagnant water may be represented differently, and H_2 concentrations in the two might be different
- research requires a larger database on minimum energies necessary for processes to occur, and under what conditions; evidence suggests that minimum energies may be related to temperature and Na^+ concentration
- more information on TEAP threshold concentrations would be helpful, especially with respect to reduction of solid phases, such as Fe and Mn oxides
- steady-state H_2 levels are not applicable to pollution plumes due to variability in iron oxides being reduced, aquifer temperature, and the overlapping redox processes that are not exclusive

Still, researchers believe that regardless of the chosen approach, H_2 concentration will indicate a relative redox level: high H_2 concentrations are more indicative of reduced systems than low H_2 concentrations, and repeated monitoring of H_2 concentrations may help investigators evaluate a plume's redox condition.

Volatile fatty acids in redox zones

Volatile fatty acids (VFAs), such as acetate, formate, propionate and butyrate, are produced from the degradation of organic matter under anaerobic conditions. Although the concentration of VFAs increases as electron acceptors become depleted, VFAs do not function well as redox indicators because of the difficulty in relating VFA concentration to TEAP concentration. Furthermore, VFAs are mobile and can move downstream (they are three orders of magnitude larger than the H_2 pool). VFAs, however, might be useful in monitoring plume stability.

Aquifer sediments in redox zones

Pools of redox-sensitive species in aquifer sediments include the solid oxidized species

- iron oxides and manganese oxides
- sulfate in minerals or on anion exchange sites
- solid reduced species: organic matter, sulfides, iron and manganese carbonates
- reduced species, such as Fe^{2+} , Mn^{2+} and NH_4^+ , on cation exchange sites

Solid organic carbon may have significant capacities, both as electron donors and acceptors, but reactivity is limited.

"To learn about plume development with respect to redox and to assess the pools of redox species that have reacted or may react, sediment pools must be addressed. This may be done by quantifying solid pools of primarily organic carbon, iron, sulfur and manganese species or as capacities in terms of OXC and RDC" (*Christensen and others, 2000*).

Researchers have concluded from aquifer sediments:

- iron, sulfur, and manganese species associated with the solid phase (on the basis of aquifer volume) are the most important redox species in a contaminant plume
- iron oxides seem to be the dominant electron acceptor; iron oxides contribute more to the overall OXC than dissolved species such as oxygen, nitrate and sulphate; this is based on data from a few aquifers and contaminant plumes
- reduced iron and sulphur species associated with aquifer sediments seem to constitute the main RDC of contaminant plumes
- reactivity of mineral species is a factor; reactivity depends on crystallinity, size and surface area of minerals

Microbial activity

Because most redox processes in plumes are microbially mediated, it is important to characterize the microorganisms involved. "Instead of focusing on the number of the individual microorganisms or groups of microorganisms, specific types of processes (e.g., sulphate reduction, denitrification, etc.) can be investigated by TEAP bioassays, where each of the processes can be detected and quantified. The TEAP bioassays, although tedious and laborious, provide the most valuable information, such as identification of on-going processes, physical location of on-going processes in a redox sequence, identification of spatial variation of redox processes (which cannot be observed from dissolved redox-sensitive parameters) and verification of the occurrence of simultaneous redox processes" (*Christensen and others, 2000*).

Conclusions

Currently, documentation and experience with measuring redox conditions in pollution plumes is limited. Christensen and others (2000) conclude the following:

- the number of actual plumes, where assessment of redox has been addressed in any elaborate way (e.g., in more than 20 sampling points and by more than one method), is less than 10
- most current investigations have involved relatively shallow, sandy, and originally aerobic plumes
- most plumes studied are fairly old (10 years or more) and in pseudo-steady-state
- most, if not all, current plumes assessed with respect to redox have been addressed within the framework of reduced, dissolved organic carbon being oxidized by inorganic electron acceptors (including carbon dioxide) present naturally in the aquifer; however, oxidation of methane, sulphides, ferrous iron, and ammonium have been dealt with only rudimentarily in the context of plumes, in spite of recent modeling suggesting the importance of secondary oxidation reactions
- most cases address natural gradient and non-engineered plumes; little experience is available on engineered and redox-managed plumes

Christensen and others (2000) recommend that investigators "measure as many different plumes as possible in many spatially distributed sampling points, repeat the measurements over time to learn about the temporal variations and trends, and always use several different methods . . . However, redox is usually not the main purpose of a scientific project or plume investigation but only a supportive framework for addressing the main issues, e.g., degradation of organic pollutants. In addition the resources may not allow for addressing redox conditions on an elaborate level."

The researchers make several key points with respect to redox zone interpretation:

- plumes usually contain several redox environments that are physically distributed, with the most reduced environments close to the source; the more oxidized environments are at the plume front and perimeters
- the overall distribution of redox environments agrees with basic thermodynamic theory; however, many redox processes may take place in a single redox zone
- redox changes at various depths may be dramatic: changes can occur within a few centimeters
- identifying a full sequence of redox zones requires many high-resolution samples from short screens
- a simple calculation based on the groundwater composition alone will often be erroneous because solid phases are neglected, especially with respect to iron
- ferric oxyhydroxides, very common in shallow aquifers, are the major chemical redox buffer in many plumes
- microbial processes may be the most important redox processes in pollution plumes, although four processes are important: mass transfer, availability of electron donors or acceptors, thermodynamic energetics and microbial kinetics

Remediators curious about redox conditions in contaminated plumes need to answer the following questions:

- has the plume existed for a long time?
- is the plume stationary or receding?
- is the apparent attenuation of a chemical in the plume consistent with current knowledge on degradability at the actual redox conditions?
- are the redox conditions in the laboratory or field experiments comparable to redox conditions in the plume? Do these conditions change over time?
- how easily can redox conditions be altered to enhance pollutant degradation?

- how detailed should the redox characterization be?
- is it sufficient to determine dominating redox environments, e.g., in terms of redox zones defined by the dominating redox process, or is redox diversity also important?
- are current redox conditions or processes required to be identified, e.g., do they simply happen, or are estimates of the reaction rates needed?
- are redox capacities important?

Finally, the researchers describe the promising and less promising approaches for measuring redox conditions:

- electrochemical redox potentials are easy to measure with a combination electrode and potentiometer, but any elaborate interpretation is not defensible
- dominant redox conditions can be assessed from the relative distribution of groundwater compounds, although mobility of some compounds increases uncertainty of the analysis
- hydrogen concentrations in groundwater samples can be fairly easily determined, but special precautions in well design, sampling and analysis are needed
- VFA concentrations might theoretically reflect ongoing redox processes, but the few attempts to apply this to real plumes have thus far provided no useful insight on plume redox conditions
- aquifer sediment characterization has a far larger redox buffer capacity than groundwater, and any evaluation of capacities must include sediment analysis
- microbial measurements indicate a diversity of microbial populations in plumes and confirm that microbial bioassays for various major redox processes are a very powerful approach for identifying multiple redox processes and obtaining estimates of actual rates

Reference

Christensen, T.H., Bjerg, P.L., Banwart, S.A., Jakobsen, R., Heron, G. and H.J. Albrechtsen, "Characterization of Redox Conditions in Groundwater Contaminant Plumes," *Journal of Contaminant Hydrology*, Vol. 45, pg. 165-241, 2000; <http://www.elsevier.com/locate/jconhyd>

UTTU thanks Dr. Thomas H. Christensen (thc@imt.dtu.dk), Department of Environmental Science and Engineering, Technical University of Denmark, for his help on this article.



Ozonation of petroleum-contaminated groundwater

Engineers designed an in-situ ozone sparging system to clean up petroleum-contaminated groundwater in Wisconsin. The system consisted of an air compressor, a programmable logic controller (PLC), gauges and controls.

Ozone

The ozone sparging system chemically oxidizes petroleum-contaminated water in-situ. Ozone, O_3 , is produced typically by "passing dry air (1-4 percent) or oxygen (6-14 percent) through an electric field of high potential sufficient to generate a corona discharge between the electrodes" (Nimmer and others, 2000). Properties of ozone include the following:

- stable in air, half life ≥ 12 hours
- unstable in water, half life $\leq 1-40$ minutes; 10-20 minutes is typical for most groundwater conditions
- strong oxidizing potential, 2.07 volts
- about 12 times more soluble in water than oxygen
- solubility in water increases with increased ozone concentration
- decomposition to oxygen increases at $> 95^\circ\text{F}$ (35°C)
- longer half life at lower pH; decomposes to hydroxyl radical at pH ~ 8.0
- hydroxyl radical oxidizing potential, 2.80 volts

Ozone reactions

Dissolved ozone reacts with aromatic compounds by

- direct oxidation with ozone
- generation of free radical intermediates, such as hydroxyl radicals

Alkaline conditions, exposure to ultraviolet light, and reaction with hydrogen peroxide favor production of hydroxyl radicals. Table 3 shows that reaction rates of a compound or species with the hydroxyl radical exceed that of ozone. Ozone, which is unstable and a powerful oxidant, will react faster with aromatic compounds that contain electron-donating groups.

Ferrous iron and hydrogen sulfide, common in aquifers, will react with ozone at a faster rate than petroleum constituents. Their ozone demand must be satisfied before an ozone residual can be established. In addition, radical scavengers such as carbonate and bicarbonate ions will remove the radicals from the chain reaction mechanism. Direct reaction of ozone with BTEX compounds can produce byproducts such as oxalic acid, acetic acids, ketones, aldehydes or carbon dioxide and water, all of which are readily biodegradable by microorganisms in aquifers. With sufficient ozone concentration and contact time, complete mineralization of hydrocarbons to carbon dioxide and water is expected.

	Rate coefficient with O_3 (L/mol-s)	Rate coefficient With OH^\cdot (L/mol-s)
Benzene	2.0	$7.9e^9$
Ethylbenzene	14	$7.5e^9$
Toluene	14	$5.1e^9$
o-Xylene	90	$6.7e^9$
m-Xylene	94	$7.5e^9$
Naphthalene	3000	$9.4e^9$
Fe^{2+}	$>5e^5$	$3.2e^8$
H_2S	$3e^9$	$1.5e^{10}$
Bicarbonate		$8.5e^6$
Carbonate		$3.9e^8$

Table 3. Reaction rate coefficients for hydrocarbons and other species with ozone and the hydroxyl radical (Nimmer and others, 2000).

Ozone sparging system

Using the concept of ozone and hydroxyl as strong oxidizing agents, Nimmer and others (2000) devised an in-situ ozone sparging system. Components included

- an air compressor: 3 or 5 hp (2.24 or 3.73 kW) oilless rotary scroll with 30- or 60-gallon tank and air-cooled aftercooler
- heatless regenerative air dryer: -71°F (-57°C) dew point at 100 psig (7 bar) and 4-minute cycle between desiccant beds with 0.085 – 0.11 m^3/min purge air required
- ozone generator: air-cooled, corona discharge, 32 grams/day production, 1-2 percent concentration by weight, -0.5 cfm (0.014 m^3/min) ozone produced
- programmable logic controller with alphanumeric display and NEMA 4 enclosure
- stainless steel flow meter and temperature gauge
- pressure regulators on ozone generator and main lines
- Teflon solenoids with needle valves to control flow to individual wells
- stainless steel solenoids with check valves to prevent ozone backflow
- system cut-outs: low and high pressure, ozone generator fault

"The ozone generator produces a maximum of 32 grams of ozone/hr at 1-2 percent by weight concentration. The ozone is then introduced to the main stream of dry air to be sent to the sparge wells. The PLC controls the grouping of the individual sparge wells, the duration of operation of each well, and the cycling between well groups; it also detects system faults."

"After the ozone combines with the main air stream, the mixture is sent to the sparge wells through Teflon tubing. The vertical sparge wells consist of schedule 40 polyvinyl chloride (PVC) piping. The Teflon tubing enters the well through a stainless steel quick-disconnect fitting at the well cap. The tubing continues to the bottom of the well where it connects

to a microporous stainless steel sparge point. The sparge points used are 12 inches (30.48 cm) long and one inch (2.54 cm) in diameter, with a pore size of 10 micrometers. The high surface area of the gas/water interface created by the sparge points increases the mass-transfer efficiency of ozone into the groundwater aquifer. The more volatile petroleum compounds are likely stripped out of the groundwater into the fine bubbles where the ozone then reacts with the contaminant vapor" (Nimmer and others, 2000).

Two well configurations are common:

- conventional air sparging wells
- density-driven convection system

Conventional air sparging wells. These wells have a single screened interval below the water table. Field workers inject an air/ozone mixture into the aquifer at a low flow rate that encourages a chemical reaction rather than volatilization. These flow rates range from ¼ to 2 cfm/sparge point. Because flow rates are low, the air/ozone follows the path of least resistance, which is usually the contaminant path. Ideally, soils will be reasonably permeable (hydraulic conductivity of 10⁻⁵ cm/s) and somewhat homogenous.

Density-driven convection system. This is a well with an "upper screen just below the water table and a lower screen separated by a solid casing. The air/ozone is introduced at the bottom of the well, creating a hydrostatic head gradient within the well due to the reduction in water density. This gradient drives aerated/ozonated water out of the upper well screen while simultaneously drawing groundwater from within the surrounding formation into the lower screen. A groundwater circulation cell is created around the well, allowing water to pass through the treatment well multiple times. Typical groundwater recirculation rates have been shown to range from 0.5 to 50 gpm (1.89 –1.89 L/min). They are dependent on aquifer thickness, the ratio of vertical to horizontal hydraulic conductivity and injection flow rate."

Nimmer and others (2000) tested their ozone sparge systems on three sites in Wisconsin.

Site 1

Site one, a former gas station, had gasoline contamination in tight clay and silt. The groundwater table was at 6 feet. Contamination extended approximately 80 feet from the former tank area and to a depth of 13 feet.

Remediators tested electrokinetic enhanced ozone sparging at this site. In the plume center, they excavated a remediation trench, approximately 13 feet deep and 2 feet wide, which ran the entire plume length. They installed six microporous sparge points and backfilled the area with pea gravel and clear stone.

Groundwater moved through the soil by electroosmosis. "Electroosmosis occurs in a subsurface environment due to an electrical 'double' layer of positive and negative ions that exist

at the soil/water interface. Soil particles typically contain a negative charge while groundwater is typically positively charged. When a direct-current electric field is applied to the moist soil, the positive ions (e.g. contaminants) dissolved in the groundwater are transported across the electric field. Contaminants that do not carry a charge will also be transported by electroosmosis provided they are soluble in water."

Remediators drilled six boreholes on both sides of the trench and filled them with a graphite material. These electrodes were connected to a direct current power source (electrodes) "with the positive electrodes (anodes) on one side of the trench and the negative electrodes (cathodes) on the opposite side of the trench. When subjected to an electrical field, the pore water within the soil formation was driven from the anodes to the cathodes, carrying with it any dissolved constituents or charged particles. The petroleum contamination dissolved in the groundwater was then passed through the treatment trench. After a period of time, the polarity to the electrodes was reversed, and the groundwater was moved back across the trench for additional treatment" (Nimmer and others, 2000).

The sparge points that were connected to the ozone sparging system operated under 5 to 10 pounds/in². The system operated for eight hours a day, but operation time was reduced when an ozone odor was detected. Operation of the system began in 1997; results to date indicate that benzene, ethylbenzene, toluene, xylenes and naphthalene concentrations decreased over a 15-month period (Table 4). Due to regulatory conditions at the site, the system was shut off permanently in early 1999. Contaminant concentrations did not change significantly from what is shown in Table 4.

	9/22/97	12/3/98
Benzene	120	74
Ethylbenzene	600	140
Toluene	30	22
Total xylenes	207	63
Naphthalene	86	ND

Table 4. Data in ppb (mg/L) from monitoring well 2 (Nimmer and others, 2000).

Site 2

Remediators discovered petroleum contamination, up to ½" in one monitoring well, at a former UST site with a fine sand/silt soil. Remediators designed an ozone sparging system for the groundwater; for the unsaturated soil, they installed a hydrogen peroxide system. Located near the former tank bed and pump island, the system consisted of five injection wells that periodically injected a dilute hydrogen peroxide solution to oxidize soil contaminants.

Characteristics of the ozone sparging system are as follows:

- wells in the source area—a total of 10—were spaced 6 to 12 feet apart
- wells contained a 2-foot screened interval between 23 to 25 feet
- a microporous sparge point was placed at the screened interval in each sparge well
- a shed nearby housed ozone sparging equipment
- two or three sparge wells were operating at one time and continuously cycling between groupings in 1-hour increments
- flow rate to each sparge well was set at 0.25-0.5 cfm
- sparging pressure was regulated at 20 psi
- two months after start-up, flow rate to each sparge well was increased to 0.75-1.0 cfm

Table 5 shows comparison concentrations of benzene, ethylbenzene, toluene and xylenes at pre-startup (2/25/98) and after one month of sparging (MW1 at 5/28/98) or after four months of sparging (MW2 and MW3, 8/27/98).

Researchers explain in the text that differences between the May and August concentrations (MW2 and MW3) likely resulted from a change in system operations.

Three sparge wells operating closest to MW2 were operated almost 24 hours a day with a flow rate of 0.75 to 1.0 cfm. "It is apparent that the larger radius of influence due to the increased flow rate and increased ozone volume dramatically improved the groundwater quality in the area of MW2." BTEX concentrations in MW3 did not decrease substantially because it was located beyond the radius of the sparge wells.

In the summer of 1999 (after about 15 months of total operation) the remediation system was shut off and received site closure seven months later. Within the seven months, concentrations at MW2 showed some rebound, but total contaminant removal percentages still ranged from 80 to 90 percent for all compounds (*Nimmer, personal communication, March 19, 2001*).

Site 3

The third site had both gasoline and diesel contaminants in soil and groundwater. Below-grade soil contamination extended from about 7 feet down to the water table at about 18 feet. Contamination extended for 300 feet in the coarse sand, making excavation impractical. Because contamination was not extensive, remediators chose a hydrogen peroxide system rather than soil vapor or bioventing.

The hydrogen peroxide system consisted of four injection wells, screened from 8 to 12 feet. These were installed directly over the source area. Field workers also screened two injection wells into the water table to promote groundwater and smear zone remediation.

The ozone sparging system consisted of five sparge wells located immediately downgradient of the source area. "The four-inch (10.16 cm) diameter wells were designated as density-driven wells, screened between 17 and 21 feet (5.18-6.40 m) and between 24 and 27 feet (7.31 to 8.23 m) below grade, separated by a solid casing. A microporous sparge point was installed near the bottom of the lower screen." A small trailer housed ozone sparging equipment. "The system was designed so it could easily be moved to the downgradient area for off-site groundwater treatment if needed. The ozone sparging system on-site was started in early July of 1998. The PLC was initially set to have either one or two sparge wells operating at a time and to continuously cycle between groupings in one-hour increments. The flow rate to each sparge well was set at 0.5 to 1.0 cfm (0.014 to 0.028 m³/min) upon startup, and the sparging pressure was regulated at 20 psi (1.4 bar). Approximately one month after startup, the flow rate to each sparge well was increased to 1.5 to 2.0 cfm (0.042- 0.057 m³/min)" (*Nimmer and others, 2000*).

Tables 6 and 7 show marked decreases in contaminant levels in MW4 and MW5 after 1 month of sparging. The sparging system was shut down on 9/24/98 for maintenance, and on 12/15/98 sampling resumed. Results from the December sampling event indicated contaminant rebound.

	2/25/98 MW1	5/28/98 MW1	2/25/98 MW2	5/28/98 MW2	8/27/98 MW2	2/25/98 MW3	5/28/98 MW3	8/27/98 MW3
Benzene	2100	240	15,000	19,000	75	2,400	2,400	1,800
Ethylbenzene	260	14	4,300	3,400	90	1,400	1,300	930
Toluene	510	130	33,000	38,000	200	100	69	87
Total xylenes	546	370	20,200	17,300	650	1,200	1,100	1,100

Table 5. Comparison of benzene, ethylbenzene, toluene and total xylene concentrations (ppb). MW1 not sampled on 8/27/98 (*Nimmer and others, 2000*).

MW4 was about 10 feet away from an ozone sparging well. MW5, in contrast, was located on the edge of the contaminant plume, about 20 feet from a sparging well. Remediators suggest that "groundwater circulation and mixing caused by the sparge well moved contaminated water into the MW5 area. This was further evidenced by the results of the 12/15/98 sampling event. With the system shut off, approximately 3 months prior to this sampling event, all parameters in MW5 decreased, most of them to near background levels."

	8/21/97 (Pre-startup)	9/10/98 (1 month sparging)	12/15/98 (System off on 9/24/98)
Benzene	270	33	33
Ethylbenzene	1,100	290	760
Toluene	3,600	320	1,000
Total xylenes	4,900	1,000	2,500

Table 6. Analytical results from MW4 (in ppb) from site 3 (Nimmer and others, 2000).

	8/21/97 (Pre-startup)	9/10/98 (1 month sparging)	12/15/98 (System off on 9/24/98)
Benzene	1	13	12
Ethylbenzene	1,100	150	71
Toluene	3,600	54	5
Total xylenes	4,900	560	100

Table 7. Analytical results from MW5 (in ppb) from site 3 (Nimmer and others, 2000).

Workers noticed bubbling and frothing within sparge wells when flow rates were greater than 2-3 cfm (0.057-0.084 m³/min). "With normal operating flow rates of 0.5-2.0 cfm (0.014-0.057 m³/min) per sparge point, a 3-5 foot (0.910-1.52 m) increase in the water table was noticed in the sparge wells, indicating that the density-driven water recirculation was occurring. A dark precipitate formed a thick layer on the sparge points located within the center of the plume. After 3 months of system operation, the precipitate layer was sufficient to inhibit flow through the sparge points. The sparge points near the edge of the plume had only a thin layer of lightly-colored precipitate suggesting that the precipitate formed from hydrocarbon oxidation." Minor scaling was remedied by submersing sparge points in a weak acid solution.

The remediation system was shut off in the fall of 2000 (after approximately two years of operation) and is currently being sampled. All contaminant parameters in MW4 were below regulatory standards, and so far, rebound has not been observed (Nimmer, personal communication, 3/19/2001).

Costs

Equipment costs for these sites were approximately \$30,000, which included all equipment, programming the PLC, and assembling the ozone generator and all gauges/controls. Operation and maintenance costs were very low, the greatest cost being the air compressor. Since this operation, Nimmer and others (Nimmer, personal communication, March 19, 2001) have switched air compressors, using one normally used for air sparging applications.

Results

Results from these three ozone sparge sites indicated that:

- petroleum contamination decreased significantly within 1-4 months of system startup
- contaminants were converted to inert compounds
- the simple design facilitates quick installation; it has a small equipment footprint and low operating costs
- the technology has the potential to reduce treatment times by
 - creating more uniform ozone distribution in the aquifer by reducing channeling; diffusion limitations are also reduced
 - achieving chemical oxidation of dissolved and absorbed contamination
 - increasing dissolved oxygen levels in groundwater, thereby aiding in biodegradation

Nimmer and others (2000) identified maintenance problems:

- ozone that moved into the piping and controls upstream at shut down; remediators solved this problem by placing a stainless steel solenoid valve directly upstream of ozone introduction point and placing a check valve on the air feed line inside the ozone generator
- malfunctioning diaphragms, which remediators replaced with viton diaphragms
- the air compressor's motors and pumps that required replacement
- excessive cycling of the motor, solved by installing an unloader valve
- automatic condensate release valve on air compressor tank periodically remained open, allowing the tank to depressurize; remediators replaced the valve with a mechanical float valve
- leaking slow-start solenoid valve, replaced with a two-gallon receiver tank and a stainless steel solenoid valve where the ozone joins the main line

Nimmer and others (2000) indicated there has been no long-term evaluation of the system. "The scope of the field applications presented in this paper did not allow for the study or confirmation of reaction rates reported in the literature."

They suggested that aquifer conditions and in-situ chemical oxidation reactions should be studied with respect to

- influence of pH, alkalinity, metals, etc. on in-situ chemical oxidation reactions
- determination of conditions that would inhibit in-situ oxidation
- estimation of ozone demand and treatment time based on site-specific aquifer conditions

They have not used this technology at other petroleum-contaminated sites because of regulatory changes; however, they hope to use it to clean up chlorinated solvent-contaminated sites (*Nimmer, personal communication, 2001*).

References

Nimmer, M.A., Wayner, B.D. and A.A. Morr, "In-Situ Ozonation of Contaminated Groundwater," *Environmental Progress*, Vol. 19, No. 3, 2000; <http://www.aiche.org/publications>.

Nimmer, M.A., personal communication, 3/19/2001.

UTTU thanks Mike Nimmer of OMNNI Associates, Appleton, Wisconsin (<http://www.omnni.com>), for his help on this article.



Partitioning tracer tests

Partitioning tracer tests (PTTs), developed by the petroleum industry, are characterization techniques that can detect and quantify NAPL (nonaqueous phase liquid). PTTs have the capability to measure a much larger portion of the aquifer than point sampling methods, such as coring. PTT uses "suites of chemical tracers to detect the presence of NAPL and provide estimates of its effective saturation (S_n) or volume within the swept zone of a flow field... Swept zone refers to the volume of aquifer that is contacted by the tracer pulse during the course of a test" (*Cain and others, 2000*).

Researchers compared results of PTT before and after remedial work to estimate remediation effectiveness. Cain and others (2000) conducted interwell partitioning tracer tests during the summer of 1996 at Hill Air Force Base, Utah, before and after application of two remediation efforts: a cyclodextrin complexing sugar flush (CSF) and an in-well aeration (IWA) system. The goal was to determine extent of LNAPL removal by each technology. Field workers built two hydraulically isolated test cells for the PTT study.

Theory behind PTT

"Partitioning tracer theory is based on the chromatographic separation of two or more selected tracers as they travel with the advecting groundwater through a NAPL-contaminated aquifer. The tracers are typically injected as a single pulse. Degree of temporal separation occurring between the solutes at monitoring locations is dependent on the extent of reversible partitioning of the tracers between the advecting water and the immobile NAPL phase. In essence, the partitioning of the tracers into the NAPL phase retards their transport" (*Cain and others, 2000*).

Field workers use sets of nonreactive (nonpartitioning) and reactive tracers. Effective NAPL saturation can be calculated from the ratio of tracer travel times, or the retardation factor (R) of the reactive tracer:

$$t_p/t_n = R = 1 + (P_b/O_w) K_d + [S_n/(1-S_n)] K_{nw}$$

where

- t_p = travel time of the partitioning tracer
- t_n = travel time of the nonpartitioning tracer
- P_b = bulk density of porous media
- O_w = water-filled porosity
- K_d = water-aquifer solids partition coefficient
- K_{nw} = NAPL-water partition coefficient
- S_n = effective NAPL saturation

Effective NAPL saturation (S_n) multiplied by volume of the tracer-swept zone will give volume of NAPL in the aquifer. "If contaminant mass removal is large, the change in the swept zone between pre- and post-partitioning tracer tests can be significant. Comparing the volume of NAPL removed to the change in V_w (water-filled pore volume) helps determine if the total swept volume of the study changed. This information will help indicate whether the post-PTT flow regime adequately reproduced that of the pre-PTT."

"Tracer travel times are usually determined by moment analysis of tracer breakthrough curves for each sampling location ... Early reports of partitioning tracer studies in the petroleum industry suggest that the 'first arrival' of a tracer or 'landmarks' selected along a breakthrough curve can also be used as characteristic transport times. While useful in some applications, these methods are sensitive to non-ideal transport and variations in experimental conditions. Therefore, they are rarely used for complex, heterogeneous sites" (Cain and others, 2000). Researchers emphasize that compensating for tailing in the breakthrough curves should be included in the moment analysis.

Application of PTT at a contaminated site

The site, a former chemical disposal pit, contained petroleum hydrocarbons from JP-4 jet fuel and chlorinated hydrocarbons. Partition tracer tests took place in a surficial aquifer with interbedded sand and gravel alluvium and silt and clay stringers. Average hydraulic conductivity was 4.5×10^{-2} cm/s. Clay served as a relatively impermeable barrier for the base of the two cells. Field workers created cells by driving corrugated steel sheet piling into the clay and grouting the joints. The workers then installed a line of four injection wells and three extraction wells along opposite ends of each cell.

Tracers

Cain and others (2000) used bromide and PFBA (pentafluorobenzoic acid) as the primary nonreactive tracer. Ethanol was also a nonpartitioning tracer. The partitioning tracers were hexanol and 2,2-dimethyl-3-pentanol (DMP) and 6-methyl-2-heptanol. Field workers put into chilled coolers the samples collected from the tracer tests and shipped them overnight for analysis at the University of Arizona. Depending on the tracer, samples were analyzed by the colorimetric method or a gas chromatograph equipped with a flame ionization detector.

First remedial effort: complexing sugar flush (CSF)

Remediators used a 10 percent solution of cyclodextrin, a complexing sugar, to enhance LNAPL solubilities. Solubility enhancement of NAPL components—not mobilization—was the primary mechanism of mass removal. Solubilities of the various contaminant compounds varied. In addition, "Mass

loss, presumably due to biodegradation, prohibited the use of several tracers for the accurate estimation of NAPL saturations. The mass loss observed for ethanol (nonpartitioning) and hexanol (partitioning) caused overestimation and underestimation of S_n values, respectively. The most reliable tracer pair in the preliminary PTT (pre-PTT) consisted of bromide as the nonreactive tracer and 2,2-dimethyl-3-pentanol (DMP) as the partitioning tracer. This pair was also included in the post-PTT tracer suite and again proved dependable. The partitioning tracer, 6-methyl-2-heptanol, included in the post-PTT, also provided robust results. All three tracers indicated recoveries above 90 percent" (Cain and others, 2000).

Ethanol and hexanol experienced significant mass loss during the tests, which researchers attributed to biodegradation; therefore, using ethanol as a nonreactive tracer yields travel times that are erroneously small, and consequently producing S_n values that are erroneously large. In contrast, using hexanol as a partitioning tracer yields travel times that are erroneously small, and average S_n values that are erroneously small. Researchers suggest that "the large degrees of uncertainty in travel times derived from data influenced by degradation supports the careful selection of tracers for a microbially active site."

Second remedial effort: in-well aeration (IWA) test cell

"A standard IWA system creates a vertical flow field that brings contaminated groundwater into the lower portion of a dual-screened vertical circulation well, which is equipped with an in-situ air-stripping system. Volatile contaminants are stripped from the groundwater into a gas phase that is drawn out of the well casing into a contaminant collection system. The treated water then moves back into the aquifer through an upper screen. Note that this system does not enhance the solubilities of the LNAPL components nor is it designed to mobilize the LNAPL to the well and volatilize it. Due to the low solubilities and dissolution rates of many organic compounds, the remediation efficiency of this technology was expected to be much lower than that of the CSF."

"The operation of the IWA remediation system created significant vertical flow and caused temporal fluctuations in the elevation of the water table. It is possible that these flow transients altered the NAPL distribution. Thus, the post-technology PTT may not have experienced the same conditions as the pre-PTT. This inconsistency between tracer tests may constrain the accurate determination of remediation efficiency" (Cain and others, 2000).

Conclusions

Researchers conclude the following:

- using interwell PTT at Hill AFB to determine remediation efficiencies for a complexing sugar flush and an in-well aeration system provided results of varying usefulness
- site heterogeneity and rate-limited partitioning between the NAPL and aqueous phases can cause tailing of solute breakthrough curves
- for this site, the degree of heterogeneity was large relative to the scale of the experiment, making it necessary to extrapolate all tracer response curves to zero to produce results that were more consistent and accurate
- the PTT-derived remediation efficiency for the CSF test was similar to the value determined using core samples
- biodegradation precluded the use of several tracers for determining NAPL saturations
- the past presence of hydrocarbons at this site "appears to have produced an active population of microbes that readily used both contaminants and partitioning tracers as a carbon source"
- the loss of mass from the tails of breakthrough curves caused erroneous saturation estimates, thus, only the branched alcohols had mass recoveries large enough to be useful in moment analysis and estimation of NAPL saturations
- design of a partitioning tracer study should include a flow system similar or identical to that of the remediation technology; if not, tracer study results could reflect regions of the aquifer not accessed by the technology or vice versa
- if the remediation system significantly alters the distribution of the NAPL, it would be difficult if not impossible to directly compare post-remediation data with that of a pre-PTT

Reference

Cain, R.B., Johnson, G.R., McCray, J.E., Blanford, W.J. and M. L. Brusseau, "Partitioning Tracer Tests for Evaluating Remediation Performance," *Ground Water*, September-October 2000; <http://www.ngwa.org>.



Innovative partition, interfacial and biogeochemical tracers

Remediators generally use soil coring data to determine if a site has been adequately remediated. Because the number of samples required for statistical validity may be cost-prohibitive, tracer use is being explored as a less expensive option. Tracers can estimate spatial patterns for the following:

- NAPL saturation (S_n), the volume of NAPL trapped by capillary forces in a porous medium, expressed as a fraction of the total volume of the porous medium
- NAPL-water interfacial area (a_{nw}), the area of contact between two immiscible fluids (here NAPL and water), distributed in a complex manner
- biogeochemical reactivity (k_c), the transformation rate

At present, remediators use four general categories of tracers in contaminant site studies:

- non-reactive tracers for hydrodynamic characterization
- partitioning tracers that selectively partition into the NAPL
- interfacial tracers that only accumulate at the NAPL-water interfaces but do not partition into the NAPL
- biogeochemical tracers to quantify abiotic and biotic reactivity

Aqueous and gaseous tracers are also available. Remediators use aqueous tracers for investigating the saturated and vadose zone, and gaseous tracers for vadose zone studies.

Rao and others (2000) recently summarized the new tracer techniques for NAPL source zone characterization, that is, those tracer categories mentioned above minus the non-reactive tracers. These researchers examined the reliability of the new tracer techniques and their ability to depict aquifer condition before and after cleanup.

Partitioning and interfacial tracers

Partitioning tracers are commonly low-molecular-weight compounds, methyl-substituted alcohols, or natural tracers such as Radon-222 that measure NAPL residual saturation. Interfacial tracers consist of anionic and cationic surfactants and high-molecular-weight alcohols that measure interfacial area. Experimental approaches for both tracer types are the same. "A small pulse of non-reactive and reactive tracers is displaced through the test zone, and the retardation of the reactive tracer(s) with respect to non-reactive tracer(s) is measured. The non-reactive and reactive tracers experience

the same hydrodynamic conditions during displacement through the swept zone, but the average travel time for the reactive tracers is delayed due to specific interactions with the NAPL. The ratio of average travel times for non-reactive and reactive tracers is defined as the retardation factor R and is used to calculate S_n or a_{nw} " (*Rao and others, 2000*).

"The mechanism responsible for retardation of partitioning tracers is fluid-fluid phase partitioning due to differential solubilities in the two fluid phases. Retardation of the interfacial tracers is the result of accumulation at the interfaces between immiscible fluids (water-air; water-NAPL)... A linear isotherm is used for describing the reversible phase distribution of partitioning tracers if the NAPL-water partition coefficient (K_n) is constant over a significant range of tracer concentrations... The issue of non-linear tracer partitioning must be carefully considered, however, in selecting tracers and the appropriate concentration range. While the use of n-alcohols and methylated alcohols as aqueous partitioning tracers has been popular, the use of natural tracers (e.g., 222Rn) has been successfully explored."

Multi-level samplers can help to determine tracer travel times at several locations within a three-dimensional flow domain, which will allow spatial distribution of S_n or a_{nw} . Rao and others (2000) relate that "partitioning tracer field tests have been conducted using various flow configurations and employing different patterns of multiple injection and extraction wells under forced-gradient steady fluid flow conditions. ... Most of the aggressive NAPL-remediation technologies implemented in the saturated zone depend on extraction of the NAPL constituents generating a dissolution driving force across the NAPL-water boundary. Thus, the ratio of NAPL volume to total NAPL-water interfacial area accessible to mobile water is of particular interest. Similarly, some vadose-zone remediation techniques (e.g., soil vapor extraction) rely on vapor-phase mobilization of contaminants, and the mass transfer rate of the contaminants from soil water to soil gas is a critical parameter. The dynamics of air-water exchange of contaminants are a strong function of specific air-water interfacial area in the system." Using partitioning and interfacial tracers together during some point of a remedial effort gives a more accurate evaluation of NAPL presence.

Biogeochemical tracers

Biogeochemical tracers include low-molecular-weight alcohols, benzoate, sugars and electron donors or acceptors that are labile or reactive compounds used to estimate the kinetics of microbial or abiotic reactions. Testers can estimate the transformation rate constant (K_s) by measuring tracer loss during displacement through a specified area. Using "an appropriate, spatially distributed, multi-level monitoring network" helps. The biogeochemical characteristics of the flow system defined will depend on the nature of the tracers.

Examples of tracer applications: laboratory studies

Remediators have used both NAPL-partitioning gaseous and aqueous tracers to determine NAPL volume in the source zones under laboratory and field studies. Following are summaries of these efforts.

A tracer technique employed sand and glass-bead columns and sodium dodecylbenzene-sulfonate (SDBS), an anionic surfactant, as the interfacial tracer for estimating the interfacial area between two immiscible fluids (NAPL-water or air-water) present at residual saturations in porous media. Based on the data obtained, an empirical linear relationship was derived to show the relationship between interfacial area and degree of NAPL (or air) saturation.

Aqueous tracers can be used over a wide range of S_n , but "at sufficiently large S_n , the discontinuous 'ganglia' of the immiscible fluid (NAPL or air) begin to join and form a continuous phase; aqueous permeability decreases, causing significant experimental difficulties, such as long travel times. Flow rates can be increased by increasing the hydraulic gradient" (*Rao and others, 2000*).

Another researcher used gaseous partitioning and interfacial tracers to determine the immiscible fluid volumetric content and the fluid-fluid contact area. Data indicated that while the fluid (water content) estimated by gravimetric and gas-tracer techniques agreed, air-water interfacial areas measured using aqueous and gaseous tracers did not display the same trends. "Within a range of water contents where both types of tracers could be used, a_i values estimated using the gaseous tracers were larger than those estimated using the aqueous tracers" (*Rao and others, 2000*). This difference increased with increasing water content, and researchers attributed this disparity to

- the differences in access to the fluid-fluid interfaces for the two tracer types
- the mobility of the air-water interface during aqueous tracer displacement
- gaseous tracer adsorption by the soil, especially at low water contents

Field applications of tracer studies

The petroleum industry developed and still uses partitioning tracer studies (see Cain and others, 2000, in this issue of *UTTU*). Researchers in this study used cosolvent and single-phase micro-emulsion flushing in hydraulic isolated test cells to estimate S_n and a_i for site characterization and cleanup efficiency. Test results were then compared with soil-core analysis and mass balance calculations for some NAPL constituents.

Tracer test in the field: results and concerns

Conventional methods such as soil coring can measure NAPL content, but there is no standard method for measuring the NAPL-water interfacial area and the "actual" fluid-fluid interfacial area. The latter "can only be surmised from theoretical models assuming some type of pore-network geometry and fluid saturation. Tracer technique validation must be based not only on agreement with more traditional methods but also on the uncertainty in the estimated parameter values for both types of methods" (Rao and others, 2000). Discrepancies among the different methods will depend on

- spatial heterogeneity in hydrologic properties
- NAPL content
- magnitude of the parameter values given a tracer

Tracer tests likely will underestimate values because of "constraints in hydrodynamic accessibility of tracers to NAPLs and non-equilibrium mass transfer" (Rao and others, 2000). This is especially pronounced for partitioning and interfacial tracers used in

- hydrologically homogeneous media with sparse NAPL distribution
- hydrologically heterogeneous media with non-uniform NAPL distribution
- zones with high NAPL saturation

In these cases, tracer breakthrough curves are highly skewed with extensive tailing. "Extrapolation of these tails is necessary to estimate NAPL content or interfacial area; however, extrapolation introduces estimation errors that require evaluation. The magnitude of uncertainty in an estimated parameter value is likely to vary with the magnitude of the estimated value. Researchers have shown that "for low NAPL saturation and sparse NAPL distribution, optimizing k_n by selecting an appropriate suite of tracers can minimize the estimation errors. Also, the mass loss of NAPL via dissolution and the associated changes in S_n and NAPL accessibility during the tracer tests may need to be accounted for in cases where sparsely distributed NAPL has a significant aqueous solubility" (Rao and others, 2000).

In pre-remediation testing, organic matter and mineral interference is likely to be small; however, testing during or after remedial efforts indicates that estimated S_n or a_{nw} values may be impacted. For example, Rao and others (2000) assert that "removal of NAPL via in-situ flushing may 'unmask' sorptive domains that were otherwise inaccessible to the tracers. A recalcitrant, insoluble fraction of the NAPL (referred to as the 'pitch' component) may be left behind as thin coatings on soil surfaces after aggressive source zone remediation. Tracer partitioning into this hydrophobic carbon matrix may yield a false-positive signal for presence of NAPL."

In addition, agents used for aggressive remediation of NAPL source zones "may impact tracer retardation in post-flushing tracer tests. For example, the residual amounts of alcohol or surfactant left behind by an in-situ flushing treatment may alter tracer partitioning or degradation. While residual cosolvents or surfactants can decrease sorption of the partitioning tracers, such effects are likely to be small unless the residual alcohol or surfactant concentrations are excessively high. However, surfactants might be adsorbed on the aquifer solids and thus increase the tracer adsorption. Post-remediation tracer tests conducted after in-situ flushing with oxidants can also be problematic:

- the residual oxidant can cause abiotic degradation of the tracers, complicating interpretation of tracer data
- microbial degradation of tracers during pre- or post-remediation tests can also introduce additional uncertainties in parameter estimates, especially critical for tracer tests conducted in source zones with sparse heterogeneous NAPL distribution"

Conclusions

Researchers concluded the following:

- the experimental and theoretical basis for tracer techniques is well established
- limited field-testing, however, contributes to concerns about their reliability and valid representation of tracer results
- tracer techniques can give reliable estimates of NAPL volumes and biogeochemical reactivity "within the test zone hydrodynamically accessible to the mobile fluids"; thus, parameter values estimated are conservative, that is, minimum value
- highly heterogeneous NAPL distribution can complicate data interpretation and introduce uncertainties
- agents used in aggressive remediation may also complicate interpretation of tracer data

Rao and others (2000) recommended that more field-scale testing would help solve some of these problems. In addition, they recommended evaluating biogeochemical tracers for estimating potential rates of geochemical and microbial processes.

Reference

Rao, P.S., Annable, M.D. and H. Kim, "NAPL Source Zone Characterization and Remediation Technology Performance Assessment: Recent Developments and Applications of Tracer Techniques," *Journal of Contaminant Hydrology*, Vol. 45, 2000; <http://www.elsevier.com/locate/jconhyd>.

UTTU thanks Dr. Suresh Rao, School of Civil Engineering, Purdue University, for his help on this article.



VOCs from a parking lot

Lopes and others (2000) investigated non-point sources of VOCs (volatile organic compounds) from a parking lot in Minnesota. Non-point VOC sources include

- spills trapped in the pore space of concrete and asphalt
- nonaqueous phase (asphalt, oil and grease) particles that accumulate on impervious areas
- VOCs from the atmosphere, auto exhaust and leaking gas tanks, which may partition into asphalt, oil, grease, vehicle soot, vegetation and other organic particles

VOCs from parking lots are the most important non-point sources contributing to stormwater runoff from a parking lot, adding each year "almost 500,000 tons of oil and grease in urban stormwater" which is discharged into streams, lakes, reservoirs and coastal waters (Hoffman and Quinn, 1987, in Lopes and others, 2000)

Researchers used a mass balance approach to identify the most important VOC sources in stormwater runoff from a parking lot. The parking lot investigated has a drainage area of 10,030 m². Investigators identified spots where oil and grease had dripped from car engines; they found no other point sources of VOCs such as gasoline stations.

Mass balance was based on inflow, outflow and change in mass stored within a defined area. "When all components are accounted for and accurately quantified, the outflow equals the inflow plus change in storage... For stormwater discharged from the parking lot, the mass balance of VOCs is

$$\begin{aligned} \text{VOC}_{\text{stormwater}} &= \text{VOC}_{\text{precip}} + \text{VOC}_{\text{particle}} + \text{VOC}_{\text{ia}} \\ \text{VOC}_{\text{stormwater}} &= \text{mass of VOCs discharged in stormwater} \\ \text{VOC}_{\text{precip}} &= \text{mass of VOCs in precipitation} \\ \text{VOC}_{\text{particle}} &= \text{mass of VOCs sorbed to particles} \\ &\quad \text{on the parking lot} \\ \text{VOC}_{\text{ia}} &= \text{mass of VOCs flushed from} \\ &\quad \text{impervious areas} \end{aligned}$$

The fraction of VOCs flushed from a particle will depend on many factors such as

- the physical/chemical properties of each VOC
- temperature
- amount of precipitation

VOC_{ia} consists of VOCs sorbed to fine-grained particles too small to sweep, VOCs in oil and grease, and VOCs that may diffuse from asphalt. This value was estimated as a residual of the mass balance because it "was not possible to quantify the total mass of VOCs in the impervious area or the fraction of VOCs that is flushed" (Lopes and others, 2000).

To obtain samples for VOC_{particle}, researchers used a precleaned wirebrush and metal dustpan to sweep up loose particles from the parking lot. They analyzed particles for VOCs and organic carbon, and composite samples for particle size, surface area and uptake of gaseous MTBE.

The researchers took stormwater and precipitation samples from the parking lot one morning in the summer after 2 cm of rain. Fifteen VOCs were detected in one or more discrete particulate samples. Samples were taken from a flat area, an oily flat area, an oily dry puddle and a dry puddle. "Most of the detected VOCs were gasoline-related compounds such as benzene, toluene, ethylbenzene and xylenes... eight of the 15 VOCs were detected in more than 50 percent of the samples and, except for benzene, in one or both of the composite samples." The highest mean concentration of any VOC was acetone. Acetone, emitted in vehicle exhaust, is a byproduct of reacted organic compounds. BTEX compounds, except for two measurements, indicated concentrations less than 3 µg/L.

Researchers developed uptake isotherms for MTBE on particles <63 µm and identified two sorption mechanisms. At low vapor pressure there appears to be "site-specific interaction between MTBE and a particulate component similar to soot... the nonlinearity of the isotherms (and corresponding high-distribution coefficients) observed at low-vapor pressure for MTBE on chimney soot and parking lot particles suggests that soot particles contribute more to the total sorption of MTBE than their fraction of the total mass might suggest. This also suggests a mechanism for dry depositions of MTBE from the atmosphere. Although MTBE was not detected during this study, most VOCs partition into organics to a greater extent than MTBE. Thus, dry deposition is likely to be a mechanism for concentrating other VOCs. At higher pressures, the curve is similar to the isotherm for asphalt, which indicates infinite dissolution of MTBE into asphalt and oil and grease in particles. However, these pressures are much higher than those in urban air, indicating transfer of MTBE from air to asphalt is not an important mechanism" (Lopes and others, 2000).

VOCs of benzene, toluene, ethylbenzene, m- and p-toluene, o-xylene, 1,2,4-TMB, naphthalene, acetone, MEK (methyl ethyl ketone) and MIK (methyl isobutyl ketone) were detected in particulate water extracts in extremely small amounts. VOCs detected in precipitation included toluene, acetone, MEK and chloroethane. Analysis of stormwater indicated eight detected VOCs; however, benzene, toluene, acetone and MEK were detected in all stormwater samples. Other VOCs collected included MIK, chloromethane and styrene. Researchers found that correlations were statistically significant between oil, grease, MEK and total organic carbon, and between TOC, MEK and toluene. Correlations indicate that MEK was associated with both organic fractions, whereas toluene was associated with a fraction of organic carbon other than oil and grease.

Conclusions

Researchers concluded the following:

- the atmosphere is an important source of soluble, oxygenated VOCs
- the parking lot surface is an important source for the more hydrophobic VOCs
- VOCs in the parking lot surface appear to be concentrated in oil and grease, soot and other organic material
- except for spills, asphalt does not appear to be an important source of VOCs
- VOC concentrations in precipitation and in stormwater from parking lots without obvious point sources may be too low (0.1 mg/L), except for ketones, to explain concentrations measured in urban stormwater, streams, rivers and groundwater
- VOCs detected in this study were likely from point sources that had been dispersed and possibly from non-point sources from industrial and commercial areas

Researchers indicated that future studies would be helpful to

- confirm the mechanism for dry deposition of VOCs
- determine how temperature, surface type and presence of gasoline stations affect these results
- develop a method for directly measuring VOC_{ia} , determining whether VOCs are associated with fine-grained particles, vehicle soot, oil and grease or asphalt, and identifying mechanisms of concentrating VOCs on landsurface

Reference

Lopes, T.J., Fallon, J.D., Rutherford, D.W. and M.H. Hiatt, "Volatile Organic Compounds in Stormwater from a Parking Lot," *Journal of Environmental Engineering*, December 2000; <http://www.pubs.asce.org>.



Information sources

U.S. EPA publications and information

The following documents are available from <http://clu-in.org/techpubs.htm>:

- *NATO/CCMS Pilot Study Evaluation of Demonstrated and Emerging Technologies for the Treatment of Contaminated Land and Groundwater (Phase III): 2000 Annual Report (EPA 542-R-01-001)*
- *Technologies for Clean-Up of Contaminated Ground Water in the United States: Current Practice and Information Resources*

MTBE Treatment Case Studies and Web site
<http://www.epa.gov/oust/mtbe/mtberem.htm>

This site presents 18 case studies with performance and cost data and an additional study site. Technologies used include air stripping, carbon adsorption, in-situ and ex-situ bioremediation, in-situ chemical oxidation, soil and dual phase extraction and pump and treat. Those needing more information can contact Linda Fiedler at 703-603-7194.

Physical and Chemical Factors Affecting Contaminant Hydrology in Cold Environments (ERDC/CRREL TR-00-21)
http://www.crrel.usace.army.mil/techpub/CRREL_Reports/reports/TR00-21.pdf.

RCRA Cleanup Reforms II: Fostering Creative Solutions (EPA 530-F-01-001; <http://www.epa.gov/epaoswer/hazwaste/ca/reforms/reforms2.pdf>)

Response videos produced by the EPA Environmental Response Team (ERT) are available at <http://clu-in.org/studio>.

Statistical Estimation and Visualization of Ground Water Contamination Data (EPA 600-R-00-034); http://www.epa.gov/ada/download/reports/epa_600_r00_034.pdf.

Tri-Service Site Characterization and Analysis Penetrometer System-SCAPS: Innovative Environmental Technology from Concept to Commercialization (SFIM-AEC-ET-TR-99073)
<http://aec.army.mil/prod/files/scaps99073.pdf>.

Treatment Technologies for Site Cleanup: Annual Status Report (ASR), Tenth Edition (EPA 542-R-01-004)
<http://clu-in.org.asr>.

Updated Citizen Guide Series from the EPA Technology Innovation Office; <http://www.clu-in.org/techpubs.htm>

Several two-page fact sheets are also available by calling 800-490-9198 or 513-489-8190. The fact sheets include:

- *A Citizen's Guide to Bioremediation (EPA 542-F-01-001)*
- *A Citizen's Guide to Phytoremediation (EPA 542-F-01-002)*

- *A Citizen's Guide to Thermal Desorption* (EPA 542-F-01-003)
- *A Citizen's Guide to Natural Attenuation* (EPA 542-F-01-004)
- *A Citizen's Guide to Permeable Reactive Barriers* (EPA 542-F-01-005)
- *A Citizen's Guide to Soil Vapor Extraction/Air Sparging* (EPA 542-F-01-006)
- *A Citizen's Guide to Chemical Oxidation* (EPA 542-F-01-013)

The site, <http://www.clu-in.org/techpubs.htm>, also has a listing of 124 documents published since February 1977.

Other publications

Engineering and Design—Requirements for the Preparation of Sampling and Analysis Plans (EM 200-1-3); <http://www.usace.army.mil/usace-docs/eng-manuals/em200-1-3/>

Recent publications from Lewis Publishers (800-272-7737, <http://www.crcpress.com>) include the following:

- *Applications of Environmental Chemistry: A Practical Guide for Environmental Professionals*
- *Aquatic Effects of Acidic Deposition*
- *Contaminant Hydrology: Cold Regions Monitoring*
- *Environmental Toxicology: Impacts of Environmental Toxicants on Living Systems*
- *Groundwater and the Environment: Applications for the Global Community*
- *Groundwater Chemicals Desk Reference—Third Edition*
- *Microbiology of Well Biofouling*

- *Phytoremediation of Contaminated Soil and Water*
- *Principles of Hydrogeology*
- *Practical Atlas for Bacterial Identification*
- *Restoration of Contaminated Aquifers: Petroleum Hydrocarbons and Organic Compounds*
- *Sequenced Reactive Barriers for Ground Water Remediation*

Books from Battelle Press, 800-451-3543 or <http://www.battelle.org/bookstore>

- *Biopile Design, Operation, and Maintenance Handbook for Treating Hydrocarbon-Contaminated Soils*
- *Cost-Effective Remediation and Closure of Petroleum-Contaminated Sites*
- *The Environmental Impact Statement Process and Environmental Law—2nd Edition*
- *Options for Remote Monitoring and Control of Small Drinking Water Facilities*
- *Permeable Barriers for Groundwater Remediation: Design, Construction and Monitoring*
- *Vadose Zone: Science and Technology Solutions*

Geophysical Prospecting for Groundwater and Groundwater Flow and Contaminant Transport in Carbonate Aquifers is available from A.A. Balkema; <http://balkema.ima.nl/>.

The American Chemical Society and Oxford University Press <http://www.oup-usa.org/>

- *Innovative Subsurface Remediation: Field Testing of Physical, Chemical Characterization Technologies—ACS Symposium Series 725*

Subscriptions and address corrections

Any person or organization wanting a subscription to *Underground Tank Technology Update (UTTU)* should send this form and the subscription fee (free to state government employees) to

Debbie Benell
432 North Lake Street
Madison, WI 53706
Phone: 608/263-7428

Subscriptions begin with the first issue of each year; those who subscribe during the year will receive all issues in the volume.

Please send address corrections to the above address. Back issues (bimonthly from April 1987) are available. Please check the form.

- YES, put me on the *UTTU* mailing list
 - I'm enclosing \$30 for a 1-yr subscription (paper version only).
 - I'm enclosing \$20 for a 1-yr subscription (electronic version only).
 - I'm enclosing \$35 for a 1-yr subscription (paper and electronic versions).
 - Please send me one free electronic issue as a sample.
 - Free: ELECTRONIC PAPER See my state government employer below.
- YES, send me *UTTU's* previous issues.
 - I am enclosing \$30 (paper versions).
 - Free. See my state government employer below.

NAME _____

TITLE _____ PHONE _____

COMPANY/ STATE GOV. AGENCY _____

ADDRESS _____

E-MAIL _____

CITY _____ STATE _____ ZIP _____

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

Make checks payable to University of Wisconsin—Madison

From Marcel Dekker, Inc.; <http://www.dekker.com>

- *Multilayered Aquifer Systems: Fundamentals and Applications*
- *A Manual of Field Hydrology: Fundamentals and Applications*

Books from the National Ground Water Association (<http://www.ngwa.org>, 800-551-7379) include:

- *Groundwater Contamination: Transport and Remediation*
- *Groundwater Hydraulics and Pollutant Transport*

Websites and web courses

Delaware's DNR and Environmental Control page
<http://www.dnrec.state.de.us/DNREC2000/ust.asp>

GeoTracker, California's online Geographic Information System; <http://geotracker2.arsenaultlegg.com>

On-Site On-Line Tools for Site Assessment, developed by the U.S. EPA ORD, gives site assessment information to help regulators and others monitor and assess plumes.
<http://www.epa.gov/athens/onsite>

Phytoremediation, a fairly comprehensive site that lists review articles, books and journals, a glossary, and links
<http://www.mobot.org/jwccross/phytoremediation/>

Tank School, co-authored by Marcel Moreau and Bill Reeves, is an online training school. For more information, contact Bill Reeves at Br1009@aol.com or call him at 850-385-9443.

The University of California at Davis has an annotated list of MTBE sites including sites from the EPA OUST, American Petroleum Institute, U.S. Geological Survey, and Health Effects Institute.
http://www.tsrtp.ucdavis.edu/mtbe/page_4.htm

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

Underground Tank Technology Update



COLLEGE OF ENGINEERING
UNIVERSITY OF WISCONSIN-MADISON

Engineering Professional Development
432 North Lake Street
Madison, Wisconsin 53706

Nonprofit
Organization
U.S. Postage
PAID
Madison, WI
Permit No. 658