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Brief article summaries

- Natural attenuation monitoring programs 2**
 This article describes the elements and strategies of an effective long-term monitoring program at a site undergoing natural attenuation. Of particular importance are sampling frequency and analytical protocols.
- Understanding natural attenuation of MTBE plumes 5**
 Researchers studied five MTBE plumes by examining and comparing rates of plume and source attenuation. The sites selected for this study varied in terms of geographical location, maximum MTBE concentration, plume seepage velocity and methanogenic character.
- Natural attenuation study of BTEX 6**
 Suarez and Rifai recently undertook a comprehensive geochemical study of a BTEX spill at a coastal facility. Their threefold analysis of the plume (to identify a shrinking, stable or expanding plume) and historical data on the plume included analysis of concentration vs. time, Mann-Kendall trend analysis and mass-flux analysis.
- Groundwater velocity effect on biodegradation 9**
 Although many researchers have studied engineered bioremediation and how to efficiently deliver oxidants and nutrients to an aquifer, few studies have reported on the impact of groundwater velocity on pollutant transport and biodegradation. Nakhla and Niaz assessed the fate of BTX compounds in groundwater and the impact of groundwater velocity, DO, as hydrogen peroxide, and BTX concentrations on the efficiency of engineered ISB, or in-situ bioremediation.
- Research notes 10**
 Summaries of published papers are presented.
- Information sources 15**
 Information sources give phone numbers/Web sites of recently published material.

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Natural attenuation monitoring programs

This article describes the elements and strategies of an effective long-term monitoring program at a site undergoing natural attenuation. Of particular importance are the sampling frequency and analytical protocols (Wiedemeier and Haas, 2002).

Sampling point placement

Wiedemeier and Haas (2002) recommend that “all available site-specific data and information developed during site characterization, conceptual model development and groundwater modeling should be used when preparing the monitoring plan.” Factors to be considered when designing a post-characterization monitoring strategy include the following:

- distance to potential receptor exposure points
- groundwater seepage velocity and direction
- contaminant types
- aquifer heterogeneity
- three-dimensional distribution of constituents of concern
- areas of unique geochemical conditions
- surface water interactions
- effects of engineered remediation and other human-constructed systems

In addition, monitoring system designers need to understand the plume’s historical behavior. Secondary factors would include access issues, institutional controls, knowledge of property lines, and contributing offsite contaminant sources. The most crucial factors to a monitoring endeavor, however, are the distance to potential receptors and maximum groundwater seepage velocity.

Some existing monitoring wells may be used; however, “the locations and screened intervals of long-term monitoring wells should be based on site stratigraphy and the three-dimensional plume behavior as revealed during site characterization. This requires a detailed understanding of the three-dimensional relationship between contaminants and stratigraphy to ensure that monitoring wells are screened in the same hydrogeologic unit as the contaminant plume and that they are in the path of contaminated groundwater flow. The geologic complexity of the site and groundwater seepage velocity ultimately will dictate the sampling network density.”

Two types of wells, performance monitoring wells and contingency wells, are important to monitoring programs. Performance monitoring wells (PMWs) are located upgradient, within, and downgradient from the plume. These wells verify that contaminants, plume boundaries and progression toward remedial goals are acceptable over time and space. Contingency (or sentinel) wells, on the other hand, are monitored to ensure that the plume is not expanding. Field workers place them beyond the maximum predicted lateral and downgradient plume boundaries and typically upgradient from known or potential receptor exposure points. A contingency well monitors unexpected plume migration. The authors recommend that contaminant, geochemical and hydrogeological data be used to locate monitoring wells. They also stress that sampling frequency is based on potential receptor points and groundwater seepage velocity.

Site monitors should use geochemical data to confirm that downgradient wells are sampling previously contaminated groundwater. A depleted electron acceptor suite (e.g., dissolved oxygen, nitrate or sulfate) and/or elevated metabolic byproduct concentrations (e.g., iron (II), methane, chloride or alkalinity) that would

be measured relative to background levels would provide evidence that sampled groundwater did flow through the contaminant plume and had been treated, assuming that contaminant levels are also diminished. “These distinct chemical profiles provide fairly conclusive evidence that the groundwater was contaminated at one time and has since been treated” (Wiedemeier and Haas, 2002).

To verify that monitoring wells are placed in the plume flowpath (ideally, they would be aligned parallel to groundwater flow direction, along the plume centerline), remediators need to determine the groundwater biogeochemical signature within the actively biodegrading portion of the plume.

“The distance between the downgradient PMWs and contingency wells and the density of the monitoring network should be based on

- maximum groundwater seepage velocity
- maximum solute transport velocity
- distance to potential receptor exposure points

Distance calculations should be based on maximum groundwater seepage velocity rather than on solute transport velocity; rule-of-thumb suggests that contingency wells be located approximately five years upgradient of the nearest potential receptor.

Wiedemeier and Haas (2002) caution that plumes discharging to surface water bodies require a highly customized monitoring strategy that includes the physical, chemical and biological processes occurring at and beyond the groundwater/surface interface.

Analytical protocols

The site’s analytical protocols will be a function of contaminant type and plume geochemical profile. “A groundwater sampling and analysis plan that specifies a sampling frequency and a list of analytes should be

prepared in conjunction with sampling point placement. The sampling frequency should be appropriate to detect migration of the plume over time and to define trends in groundwater geochemistry accounting for groundwater flow and solute transport rates and monitoring well spacing. Table 1 shows groundwater analytical parameters for PMWs, contingency wells and surface water locations...the analytes listed in this table are used to

- estimate NAPL source composition and strength
- demonstrate that natural attenuation is occurring
- evaluate the relative importance of the various natural attenuation mechanisms"

Location	Purpose	Analytical Parameters	
		Validation Sampling	Long-Term Monitoring
Upgradient/crossgradient	Monitor background water quality	Contaminants, daughter products, full suite of geochemical parameters ¹	Limited suite of geochemical parameters ^{2,3}
NAPL source area	Monitor changing NAPL composition/ source strength and plume behavior over time	Contaminants, daughter products, full suite of geochemical parameters ¹	Contaminants and daughter products in NAPL and groundwater beneath NAPL and limited suite of geochemical parameters ^{2,3}
Downgradient from NAPL source area along plume centerline	Monitor plume behavior over time	Contaminants, daughter products, full suite of geochemical parameters ¹	Contaminants and daughter products ³
Immediately downgradient from plume	Early detection of plume migration	Contaminants, daughter products, full suite of geochemical parameters ¹	Contaminants and daughter products ³
Between contingency wells and the other PMWs	Early detection of plume migration	Contaminants, daughter products, full suite of geochemical parameters ¹	Contaminants and daughter products ³
Downgradient from downgradient PMWs and upgradient from receptor exposure point	Monitor for plume migration toward a potential receptor and trigger contingency plan	Contaminants, daughter products, full suite of geochemical parameters ¹	Contaminants and daughter products ³
At and upgradient and downgradient from discharge point	Determine surface-water impacts	Contaminants and daughter products	Contaminants and daughter products ³

Table 1. Sampling locations, purpose and analytical parameters for groundwater monitoring (from Wiedemeier and Haas, 2002)

¹For fuel hydrocarbon plumes, the full suite of geochemical parameters should include dissolved oxygen, nitrate, Fe(II), sulfate, methane, temperature, pH, conductivity, alkalinity and oxidation/reduction potential.

²The limited suite of geochemical parameters should include dissolved oxygen, oxidation/reduction potential, temperature and pH.

³If plume behavior changes or is suspected of changing, then analyze for contaminants and the full suite of geochemical parameters.

Because a NAPL pool can act as a continuing source of groundwater contamination, the U.S. EPA recommends NAPL removal.

The authors also recommend monitoring contaminant concentration and associated daughter products to better determine plume stability and distribution of toxic byproducts. Naturally occurring electron acceptors commonly used in microbial metabolism include dissolved oxygen, nitrate, Fe(III), sulfate, and carbon dioxide. "Measurement of these parameters is useful for evaluating the occurrence of intrinsic bioremediation and the relative importance of the various terminal electron-accepting processes. Iron-reducing microbes use Fe(III) as an electron acceptor. One of the metabolic byproducts of this reaction, Fe(II), is measured to confirm the occurrence of Fe(III) reduction because of the difficulty involved in measuring the concentration of biologically available Fe(III) in an aquifer system. Readily measurable byproducts of microbial metabolism in areas contaminated with organic compounds include Fe(II), carbon dioxide, methane, ethane, ethene, alkalinity, lowered oxidation-reduction potential (ORP), chloride and hydrogen. In addition, pH, temperature and conductivity should be measured."

Sampling frequency

Quarterly sampling of monitoring wells is expected. It is often helpful during the first year to confirm plume migration direction and establish baseline flow direction. Frequency of long-term monitoring should be related to

- natural variability in contaminant concentrations
- the distance and travel time from the source to the location where acceptance criteria are applied
- the reduction in contaminant concentration required to meet the acceptance criteria

Number of wells sampled and sampling frequency will be based on

- complexity of site geology
- distance and estimated time of contaminant travel between long-term monitoring wells
- distance and estimated time of contaminant travel between PMWs and contingency wells

Plume stability and behavior

Perhaps the best line of evidence to show significant plume stabilization is through analysis of the site's historical database. It should be noted, however, that plume stabilization can occur with or without destructive attenuation mechanisms such as intrinsic bioremediation or hydrolysis; thus, using the second line of evidence, chemical and geochemical data, helps to identify the specific processes of natural attenuation.

Graphing techniques often used for evaluating plume stability include

- preparing isopleth maps of contaminant concentration over time
- plotting contaminant concentrations vs. time for individual monitoring wells
- plotting contaminant concentrations vs. distance downgradient for several wells along the groundwater flowpath over several sampling events

Statistical approaches used include

- the Mann-Whitney U test, suitable for every contaminant at every monitoring well
- the Mann-Kendall approach or trend analysis, used to define the stability of a solute plume based on concentration trends at individual wells
- the Thiessen analysis
- other computer analyses

Contingency plans and exit strategies

Because plume conditions change, the authors recommend "a contingency plan that specifies a specific remedy and detailed institutional controls should be an integral part of the monitoring program. A contingency remedy is a cleanup technology or approach specified in the site remedy decision document that functions as a 'backup' remedy in the event that the selected remedy fails to perform as anticipated. A contingency remedy may specify a technology that is different from the selected remedy, or it may simply call for modification and enhancement of the selected technology." Conditions (triggers) that could signal unacceptable performance of the selected remedy include

- contaminant concentrations in soil or groundwater at specified locations that exhibit an increasing trend not originally predicted during remedy selection
- near-source wells that exhibit large concentration increases indicative of a new or renewed release
- contaminants identified in monitoring wells located outside of the original plume boundary
- contaminant concentrations that are not decreasing at a sufficiently rapid rate to meet the remediation objectives
- changes in land and/or groundwater use that will reduce the protectiveness of the monitored natural attenuation remedy

Wiedemeier and Haas (2002) also note that

- remediators should be cautious when analyzing data and take into account sampling variability and seasonal fluctuations
- the most common remedial systems for complementing natural attenuation are source reduction technologies
- contingency plans may require updating

In terms of exit strategies, remediation goals should be established early, which will help establish a purpose for long-term monitoring and define monitoring duration. "According to the U.S. EPA (1999), long-term monitoring should continue until remediation objectives have been achieved, and longer if necessary to verify that the site no longer poses a threat to human health or the environment. Typically, monitoring is continued for a specified period (e.g., one to three years) after remediation objectives have been achieved to ensure that concentration levels are stable and remain below target levels" (Wiedemeier and Haas, 2002).

Reviewer's comments: A significant problem with using the natural attenuation paradigm is that natural attenuation is not always clarified: is natural attention a result of volatilization, biodegradation, absorption or dispersion? Many times, what passes for natural attenuation is simply dispersion. In addition, although natural attenuation may be affirmed from some wells, what about the portion of the plume blasting its way through a highly transmissive layer where there is no well to collect data? If you own a production well and the only site upgradient is undergoing natural attenuation and there is MTBE in your well, what does that mean? The natural attenuation rate wasn't quite right, so the production well needs to be shut down? If a site has thousands of gallons of floating gasoline on the water table, is it possible, in a fast moving groundwater regime, for the natural attenuation rate in groundwater to exceed the mass flux to groundwater? Should you leave the product in place? Practitioners of natural remediation need to consider these issues.

Reference

Wiedemeier, T.H. and P.E. Haas, "Designing Monitoring Programs to Effectively Evaluate the Performance of Natural Attenuation," *Ground Water Monitoring and Remediation*, Summer 2002; <http://www.ngwa.org>

For another perspective on natural attenuation, see "Natural attenuation rate clarifications: the devil's in the details", *UTTU* Vol. 17, No. 2, March/April 2003.



Understanding natural attenuation of MTBE plumes

Researchers studied five MTBE plumes by examining and comparing rates of plume and source attenuation. The sites selected for this study varied in terms of

- geographical location, representing aquifers in Florida, North Carolina, New York, New Jersey and California
- maximum MTBE concentration
- plume seepage velocity
- methanogenic character (three sites were strongly methanogenic)

Four stages of plume formation

Wilson and Kolhatkar (2002) define four stages of plume formation. "The development and the ultimate plume size are controlled by the balance between the processes that create the plume and processes that attenuate the contamination once it is present in the groundwater." The four stages of plume formation are

- stage one: a residual contaminant source is present; mass flux from the source to groundwater exceeds attenuation in groundwater, and the groundwater plume expands
- stage two: residual source is still present, but the mass flux out of the source is in "equilibrium" with attenuation in the dissolved phase, and the groundwater plume is stable

- stage three: residual contaminant source is nearly exhausted; attenuation in groundwater exceeds the mass flux of MTBE from the source to groundwater, and the groundwater plume shrinks
- stage four: the groundwater plume is exhausted, little contamination remains in the residual phase, and the average concentration of the contaminant in the plume is low; in this phase, it is not uncommon for groundwater contamination to be confined to the region that contains the residual source

Plume life cycle and rate constants

To determine a spill's rate of decline, researchers "can use monitoring data from the most contaminated wells at a site...which can be considered as the rate of attenuation of the source area of the plume." Instances wherein MTBE concentrations vary over time include

- a rise or fall in the water table
- a shift in the predominant direction of groundwater flow
- changes in practice in monitoring well purging and sampling

"The rate of attenuation of contamination in a stable or shrinking plume is controlled by natural biodegradation and by dispersion. Natural biodegradation is often first order with concentration in time. The effects of dispersion appear to be first order in distance traveled by the plume. When groundwater moves steadily in one direction at a constant flow rate, the contribution of dispersion can be expressed as a first-order process in time by multiplying the rate of attenuation with distance by the seepage velocity of the plume. In stable plumes, the effects of natural biodegradation and dispersion and dilution are both first-order in time of travel. As a consequence, their combined effect can be described by an overall or bulk first-order rate for natural attenuation" (Wilson and Kolhatkar, 2002).

The rate of attenuation can produce the following scenarios:

- “when the rate of attenuation of the source is faster than the rate of attenuation in the plume, the ‘hot spot’ in concentration will appear to detach from the source and move downgradient over time...this pattern can be expected when active remedial measures have been applied to the source area” (Reviewer’s comment: *Too many uncertainties make this difficult to quantify.*)
- when source rate of attenuation is slower than plume rate of attenuation, the plume will come to steady state and then regress back toward the source over time...the plume’s boundary will appear to recede back toward the source, even though the groundwater and contaminants are moving away from the source

Thus, “if the rate of attenuation of the source and the rate of attenuation in the plume are both known, they can be compared to distinguish between the two possible life cycles. If it can be shown that a plume has reached its maximum extent, and that it is receding back toward its source, additional monitoring wells may not be necessary. When a plume is receding throughout its extent, the interpretation of the long-term monitoring data is more straightforward.”

To determine the source’s rate of attenuation, researchers use long-term monitoring data and data from the most heavily contaminated wells, but not wells with free product. “The rate of change of the source was estimated as the slope of the regression of the natural logarithm of MTBE concentration on the date of sampling. The rate of attenuation is the negative of the rate of change.”

“The rate of attenuation of the plume as a first-order process in time was calculated by multiplying the rate of attenuation with distance by the seepage velocity of the groundwater.” When calculating this plume attenuation rate, researchers did not distinguish between contributions from natural biodegradation and dispersion. “To serve as a boundary on the uncertainty associated with the estimate of the rate of attenuation in the plume, the 90-percent confidence interval on the rate of attenuation with distance was multiplied by the seepage velocity of the groundwater. This calculation assumes that the seepage velocity of the water does not change, and that there is no uncertainty in the calculated seepage velocity” (Wilson and Kolhatkar, 2002).

Natural biodegradation rates of MTBE

Some published reports of natural biodegradation MTBE rates include

- North Carolina plume, 0.37 and 0.30/yr
- large artificial plume in Ontario, 0.44/yr
- industrial landfill in Brazil, 0.28/yr
- South Carolina gasoline spill, anaerobic, 0.04/yr

Conclusion

Researchers sampled wells and calculated plume attenuation rates in Florida, North Carolina, New York, New Jersey and California. These sites encompassed a range of conditions and are likely to be representative of U.S. plumes. Wilson and Kolhatkar (2002) ascertain that “As most plumes progress through their life cycle, they will regress back toward their source. When rates of attenuation of the source have been extracted from long-term monitoring data, the rates under natural conditions are slow (< 1/year). In the absence of active source control, the plumes evaluated in this study should require from one to several decades to reach concentrations below 20 µg/L in the source area.”

Reference

Wilson, J.T. and R. Kolhatkar, “Role of Natural Attenuation in Life Cycle of MTBE Plumes,” *Journal of Environmental Engineering*, September 2002; <http://ojsps.aip.org/eeo>

See also “Natural Gradient Tracer Test to Evaluate Natural Attenuation of MTBE Under Anaerobic Condition,” *Ground Water Monitoring and Remediation*, Winter 2003; <http://www.ngwa.org>.



Natural attenuation study of BTEX

Suarez and Rifai (2002) recently undertook a comprehensive geochemical study at a BTEX spill at a coastal facility. Their threefold analysis of the plume, to identify a shrinking, stable or expanding plume, included

- analysis of concentration vs. time
- Mann-Kendall trend analysis
- mass-flux analysis

Geochemical data are used to demonstrate biodegradation and estimate groundwater capacity to assimilate contaminants. Researchers use groundwater BTEX concentrations to estimate rates of point and plume attenuation. “Biodegradation rates are calculated via spatial and temporal estimates of dissolved BTEX mass within, as well as BTEX mass fluxes across, the plume.” To estimate source lifetime, researchers used four rates of source decay, and to estimate remediation time they relied on analytical modeling of attenuation through natural processes.

Site and plume description

The site, including a facility that produced ethylene, diethylene and ethylene derivatives from raw materials

such as BTEX and naphtha from the 1950s to 1985, is bounded on the south by the ocean, on the east by a river that discharges to a nearby bay, and on the west by refineries. Other relevant site characteristics include

- the water table, which lies at a depth of between 1 and 18 feet below ground surface
- groundwater flow, which is toward the sea
- a subsurface consisting of alluvial deposits with a sand layer that varies in thickness between 7 and 18 feet
- hydraulic conductivities of the alluvial deposits ranging from 1.1×10^{-6} to 7.6×10^{-3} ft/sec
- horizontal gradients, which vary between 0.0008 and 0.002 ft/ft
- an average seepage velocity of 19 ft/yr based on an assumed effective porosity of 0.2 and an average hydraulic conductivity of 6.1×10^{-5} ft/sec
- site contamination covering about 60 acres
- contamination consisting of several oil and other contaminant releases beginning in 1965 and ending in 1995
- a NAPL layer that varies in thickness from 1 to 27 inches, composed predominantly of xylene

There are two plumes at the site, a xylene and a benzene plume. Concentrations varied over the years, and researchers attribute that to a water table rise and a "documented NAPL migration that may be a new source of contamination" (Suarez and Rifai, 2002).

Since 1996

- the benzene plume declined from 1,800 to 1,000 feet
- the xylene plume declined from 2,200 to 1,300 feet

In addition, maximum centerline concentrations of benzene and xylene have decreased by more than 95 percent within 600 feet downgradient from the source area.

Evidence of intrinsic bioremediation

In March 1999, field workers measured geochemical parameters at 22 locations. Parameters included

- dissolved oxygen
- temperature
- conductivity
- redox potential
- pH
- alkalinity
- ferrous iron
- nitrate
- sulfate
- chloride
- methane

They found the following:

- total alkalinity was high
- oxidation/reduction potential was low, indicating favorable conditions for reduction or anaerobic degradation (*Reviewer comment: This indicates that oxygen has been depleted and that future biodegradation will be slow because it can only be anaerobic.*)
- concentrations of dissolved oxygen (DO) across the site ranged from 0.1 to 6.9 mg/l
- areas of elevated benzene and xylene concentrations have depleted DO concentrations
- background DO values are close to water solubility at ambient temperatures

- nitrate concentrations varied between 0.1 and 8.3 mg/l
- DO was depleted where nitrate was depleted, indicating that denitrification may be promoting BTEX biodegradation
- areas with high xylene concentrations also showed high nitrate concentrations
- areas with high benzene and xylene concentrations have elevated concentrations of ferrous iron, supporting biodegradation via iron reduction
- sulfate concentrations ranged from 0.3 to 532 mg/l and were highest in the most contaminated areas
- methane concentrations were as high as 5.4 mg/l in contaminated site wells but below detection levels in background wells, indicating that methanogenesis is occurring at this site
- methanogenesis is likely not occurring in rich sulfate-reducing bacteria areas because such bacteria typically outcompete methanogenic bacteria

Suarez and Rifai (2002) report that "with the exception of sulfate, the geochemical data support patterns of intrinsic remediation reported at numerous other sites." Biodegradation processes occurring at this site include aerobic respiration, denitrification, iron reduction and methanogenesis. The assimilative capacity of groundwater, based on stoichiometry of these reactions, is at least 11.1 mg/l.

Plume stability

Researchers used three methods to determine plume stability:

- concentration trends in monitoring wells
- Mann-Kendall trend analysis
- mass flux analysis

Concentration trends in monitoring wells. Benzene and xylene concentrations were measured in a number of monitoring wells from 1979 to 2000. Benzene data indicated a decreasing trend whereas some xylene concentrations increased and some decreased.

Mann-Kendall trend analysis. This nonparametric statistical method depends on ranking of individual data and required data from four sampling events. Of the 12 wells analyzed, nine showed decreasing benzene; one indicated stability and the other two showed no trend. Overall, the benzene plume is stable. Eight of 10 wells showed decreasing xylene trends; one well indicated stability, and one showed no trend. "As with benzene, concentrations in the leading wells did not increase with time; thus, the extent of the xylene plume is also not increasing" (Suarez and Rifai, 2002).

Mass flux analysis. Researchers analyzed the total mass of contaminants at specified transects along the plume. "In general, mass fluxes of benzene decreased with time, with the exception of [one] transect" ...The analyses conducted to assess plume stability indicated that the plume had reached a quasi-steady state and exhibited mass flux that was declining spatially and temporally. The stability of the xylene plume, on the other hand, was not confirmed due to increasing concentrations in some of the wells and variable trends of mass flux across the plume."

Researchers performed additional analyses on concentration data "to determine whether the observed spatial and temporal loss of BTEX mass could be attributed to biodegradation and/or source decay." They calculated that the mass loss of BTEX along one transect during a 10-year period (1979 to 1996) due to biodegradation was 12,000 pounds, while attenuation and sorption accounted for a mass loss of 8,000 pounds. Another transect showed a loss of 100,000 pounds of BTEX

between 1979 and 2000, or about 4,760 lb/yr. "In conclusion, analysis of BTEX and geochemical data indicates a plume in a quasi-steady state with declining concentrations of BTEX and mass fluxes. The analyses indicate that source decay and biodegradation are the main loss mechanisms" (Suarez and Rifai, 2002).

Estimating BTEX attenuation and biodegradation rates

Researchers estimated four types of attenuation rates:

- a point decay rate (k_{point}), based on data for individual monitoring wells, used to estimate the time required to meet the remedial goal at plume areas other than source areas
- a bulk attenuation rate (k), based on concentration declines downgradient of the source area, used to evaluate whether the plume will expand or shrink in the future
- a source decay rate (k_{source}), calculated from concentrations in source wells, used to estimate the time required to deplete the remaining sources
- a biodegradation rate derived from mass changes (λ), calculated from changes in the total dissolved BTEX mass over time, used in a solute transport model to estimate cleanup time

The point decay rate, the change of source strength over time, with contributions from biodegradation and dispersion, is derived from the slope of the natural log of concentration vs. time for a monitoring well. From this data, remediators estimated 27 years to clean up benzene and 0.1 year to clean up xylene.

The bulk attenuation rate was estimated from a natural log of benzene concentration vs. distance. This rate, 0.0007/day, means that benzene will travel 900 feet before reaching a concentration of 0.005 mg/l, which is shorter than the plume length (1,000 feet); this suggests possible plume shrinkage in the future.

The source decay rate is derived from source well concentrations in a method similar to the point decay rate. For xylene and benzene, the source decay rate is 0.0001/day, or a half-life of 15 years. Using these estimates, benzene cleanup is expected to take 250 years, and 10 years for xylene. This does not account for fluctuating water levels or bilinear desorption.

Biodegradation rate was determined by plotting dissolved mass as a function of time. Benzene biodegradation occurs at a rate of 0.00019/day (half-life of 10 years).

The four types of rates estimated ranged between 0.0001 and 0.0073, yielding cleanup times of 84 years for dissolved concentrations to up to 250 years for source wells. Inputting data in BIOSCREEN yielded a cleanup time in the source area of 270 years.

Conclusions

Suarez and Rifai (2002) concluded the following:

- analysis of historical data suggests that
 - BTEX concentrations in the monitoring wells are decreasing with time
 - the BTEX plume is at a quasi-steady state
- dissolved BTEX mass biodegradation rate was estimated at 0.00019/day, within the range of mass budgeting of 640 to 6,185 lb/yr
- sulfate concentrations were anomalously high in one part of the facility
- quantification of the biodegraded BTEX mass using aquifer assimilative capacity underestimates the site's actual biodegradation capacity
- most of the site conditions are impacted by biodegradation outside the source areas
- mass flux analyses were suitable for assessing the contribution of biodegradation to natural attenuation

- source well data produced a rate of 0.0001/day (half-life 15 years), suggesting that if no product is removed, remediation by attenuation of source area benzene would take 250 years

Reference

Suarez, M.P. and H.S. Rifai, "Evaluation of BTEX Remediation by Natural Attenuation at a Coastal Facility," *Ground Water Monitoring and Remediation*, Winter 2002; <http://www.ngwa.org>.

See also "Calculation and Use of First-Order Rate Constants for Monitored Natural Attenuation Studies," Newell, C.J., Rifai, H.S., Wilson, J.T., Connor, J.A., Aziz, J.A. and M.P. Suarez, U.S. Environmental Protection Agency, *Ground Water Issue Paper*; <http://www.epa.gov/ada/pubs/issue.html>.



Groundwater velocity effect on biodegradation

Although many researchers have studied engineered bioremediation and how to efficiently deliver oxidants and nutrients to an aquifer, few studies have reported on the impact of groundwater velocity on pollutant transport and biodegradation. Specifically, Nakhla and Niaz (2002) wanted to "assess the fate of BTX compounds in groundwater and the impact of groundwater velocity, DO, as hydrogen peroxide, and BTX concentrations on the efficiency of engineered ISB, or in-situ bioremediation. Ultimately, we wanted to develop a correlation for biokinetic constants as a function of the aforementioned variables."

Experimental set-up and design

Researchers built an 8.6 m long, 30 cm x 30 cm Plexiglas tank with the following characteristics:

- two piezometer ports, located at the box's two ends
- sampling ports in the center located at every meter
- inlet and outlets
- a metering pump to inject nutrients
- a syringe pump for injecting BTX and hydrogen peroxide
- sand with a hydraulic conductivity of 0.35 m/s and a porosity of 0.36

They initiated the system by "recirculating settled raw wastewater from a local municipal treatment plant through the sand bed." They then fed into the tank, at pore water velocities of 0.5 m/d for two weeks, groundwater containing 5 mg/l BTX and 50 mg/l hydrogen peroxide.

Experimental runs varied according to

- groundwater velocity; researchers used velocities of 1, 2 and 4 m/d
- BTX concentration levels; concentrations of 10 mg/l and 50 mg/l, typical of contaminant levels in hot spots, were used
- hydrogen peroxide to oxygen-to-BTX mass ratios; researchers used ratios of 1.5:1 and 3.2:1

Nakhla and Niaz (2002) assert that "...the ratio of O:BTX mass required for complete aerobic biodegradation has been estimated to range from the 3:1 ratio used in the BioPlume II model to 1.7:1... A carbon:nitrogen:phosphorous ratio of 100:10:1, typical for biodegradation of petroleum hydrocarbons, was used. Thus, 12 runs with six duplicates were performed. Furthermore, at each velocity, a control run using sodium azide was performed to evaluate abiotic loss. The control runs were conducted prior to the bioremediation runs using clean, unseeded sand; the primary objective was to determine the solute loss due to volatilization, chemical oxidation, and sorption on the aquifer media,

and to ascertain biodegradation impact" (2002).

Monitoring

Researchers collected groundwater samples during each run from each of the eight sampling ports. They measured influent and effluent DO concentrations to determine if oxygen was depleted, not limited. Researchers analyzed piezometer readings to compute hydraulic conductivity, porosity and pore water velocities. They also analyzed soil samples taken from five different locations along the length of the tank and analyzed for total bacterial plate counts and volatile suspended solids.

Results

Researchers obtained concentration profiles following two turnovers of the mean hydraulic residence time, HRT, in the tank, computed as the aquifer length divided by the pore water velocity. "Numerical modeling indicated that contaminant concentrations reached a quasi-steady state after two to three turnovers of the HRT... At an initial concentration of 10 mg/l and O:BTX ratio of 1.5:1, toluene decreased continuously throughout the aquifer for all three velocities. Toluene removal efficiencies ranged from 98 percent at a velocity of 1 m/d to only 42 percent at 4 m/d, with a major drop occurring between the 2 and 4 m/d velocities where final concentrations rose from 2.9 to 6.0 mg/l. Final effluent concentrations of toluene as low as 200 µg/l were achieved at a velocity of 1 m/d. Benzene and o-xylene behaved similarly with almost identical removal efficiencies. That is, all three contaminants were reduced to the µg/l at a velocity of 1 m/d when the influent concentration was 10 mg/l."

With an o-xylene concentration of 50 mg/l and O:BTX ratio of 3.2:1, removal efficiencies drop from around 98 percent at 1 m/d to only 37 percent at 4 m/d. As velocity increases from 2 to 4 m/d, removal efficiencies

deteriorate. At low velocities of 1 m/d, concentrations showed a rapid decline within the first 2-3 m, followed by a slower drop; at high velocities, the concentration drop is nearly linear. Nakhla and Niaz (2002) state, "The observed concentration at any point in the aquifer is the net result of two main processes: transport or dispersion, and biodegradation. At low velocities, transport is slow, thus allowing sufficient time for biodegradation. On the other hand, at high velocities, the rate of transport far exceeds the biodegradation rate, and thus the contaminant profile is mostly governed by dispersion and advection and follows a pseudo-linear relationship. In this case, the intrinsic bioremediation rate, even though much slower than the rates observed in this study, is still fast relative to the extremely slow groundwater flow."

When hydrogen peroxide was added at a concentration of 50 mg/l and a velocity of 1 m/d, essentially increasing the concentration by more than two-fold, only a marginal improvement in bioremediation resulted. (Reviewer's comment: A hydrogen peroxide concentration of 50 mg/l could kill any microbes it comes in contact with.) Researchers attribute this marginal enhancement to higher biomass density in the aquifer. Researchers report that DO concentrations at the aquifer's end ranged from 3.5 to 4.3 mg/l, indicating that oxygen was not limiting biological activity.

With respect to biomass accumulation and hydraulic conductivity, researchers found the following:

- plate counts decreased throughout the aquifer length
- at the highest groundwater velocity tested, 4 m/d, both plate count and contaminant concentration decreased almost linearly
- at 1 m/d velocity, plate count and contaminant concentration showed an initial rapid decline within 3 m, then a declining rate of drop

- the plate count at any given point in the aquifer is dependent on rate of solute transport, biodegradation kinetics and biomass shearing
- hydraulic conductivity dropped rapidly from an initial clean sand value of 262 cm/s to 80 cm/s in about 45 days, then stabilized for one month before decreasing to 50 cm/s
- while mean plate counts increased by approximately ten-fold, hydraulic conductivity dropped by 80 percent

Conclusions

Researchers conclude the following from this study:

- at groundwater velocities of 1 m/d, BTX removal efficiencies were 96 to 99 at concentrations of 10 and 50 mg/l
- at velocities of 2 m/d, BTX removal efficiencies dropped to 70 to 85 percent
- at velocities of 4 m/d, BTX removal efficiencies dropped 37 to 53 percent
- final BTX concentrations for all velocities were low enough to categorize hot spots as bioremediated
- both BTX and plate counts in the aquifer were impacted by groundwater velocity; distribution of BTX and plate counts indicated a rapid decline in the first 2-3 meters while at 4 m/d, linear profiles were observed
- hydrogen peroxide levels up to 1,020 mg/l did not have an adverse effect on bioremediation
- BTX removal efficiencies generally followed first-order kinetics with respect to BTX concentrations
- plate counts increased by an order-of-magnitude over the seven-month experiment; this was accompanied by an 80 percent drop in hydraulic conductivity, with nearly 90 percent of that occurring in the first six weeks

- analysis of variance indicated that groundwater velocity was the most significant parameter, accounting for approximately 80 percent of the variability

Reference

Nakhla, G. and M. Niaz, "Pilot-Scale In-situ Bioremediation of Gasoline-Contaminated Groundwater: Impact of Process Parameters," *Environmental Progress*, Vol. 21, No.1, 2002; <http://www.aiche.org/publications>



Research Notes

Aerobic and Cometabolic MTBE Biodegradation at Novato and Port Hueneme

Magar, V.S., Hartzell, K., Burton, C., Gibbs, J.T. and T.J. Macchiarella, *Journal of Environmental Engineering*, September 2002; <http://ojsps.aip.org/eeo>

Researchers conducted a microcosm study using groundwater and saturated soils from the Novato and Port Hueneme plumes in California. They investigated the following biodegradation processes:

- aerobic
- anaerobic
- aerobic cometabolic

Growth substrates used included those produced by propane, butane and nitrate.

Researchers concluded the following:

- the potential for aerobic MTBE biodegradation and mineralization exists at both sites
- in the commingled, or upgradient portion of the Novato plume, nitrate facilitated MTBE biodegradation

- in the absence of nitrate or under anaerobic conditions, MTBE degradation was insignificant
- downgradient, where groundwater was MTBE-contaminated, MTBE readily degraded with and without nitrate addition, and without external amendments
- MTBE, according to mineralization studies, was mineralized at both sites, with maximum recoveries approaching 80 percent of the radiolabeled carbon added to the microcosms
- in the downgradient MTBE portions of both sites, addition of propane and butane did not improve aerobic conditions; when nitrate was not present, propane and butane inhibited MTBE degradation
- in the upgradient MTBE/BTEX commingled plume, propane plus nitrate-fed microcosms outperformed the aerobic, nitrate-fed microcosms; in the absence of nitrate or under anaerobic conditions, MTBE degradation was insignificant
- the potential for aerobic biodegradation here suggests that technologies such as biosparging, aerobic biobarriers and in-situ oxygenation would be useful at this site

Effects of Ethanol vs. MTBE on Benzene, Toluene, Ethylbenzene, and Xylene Natural Attenuation in Aquifer Columns

Da Silva, M.L.B. and P.J.J. Alvarez; *Journal of Environmental Engineering*, September 2002; <http://ojs.aip.org/eeo>

Da Silva and Alvarez (2002) performed breakthrough studies using laboratory aquifer columns to compare the effects of ethanol on BTEX retardation factors. They fed the columns continuously with benzene, toluene and o-xylene. Two additional columns were fed with either 1 or 50 percent (by volume) ethanol, to simulate ex-

pected ethanol levels near the source, or neat releases at bulk terminals. Researchers also ran a sterile control column to distinguish biodegradation from potential abiotic losses.

According to researchers, "The addition of ethanol to gasoline could affect the equilibrium partitioning for BTEX compounds between aqueous, fuel and solid phases (i.e., cosolvency effect). Specifically, ethanol could reduce water polarity, allowing higher concentrations of moderately hydrophobic compounds (e.g., BTEX) in the aqueous phase. This cosolvent effect could also enhance the mobility of dissolved BTEX compounds by decreasing sorption-related retardation, as shown for methanol in M85 fuel. Such effects, however, are concentration dependent and were not observed when ethanol was fed continuously to sterile aquifer columns at 10,000 mg/l... Since this ethanol concentration is unlikely to be exceeded in gasohol-contaminated sites, adding ethanol to gasoline (e.g., <15 % v/v) should not have a significant impact on BTEX retardation factors. Nevertheless, neat spills of ethanol (as at a bulk terminal) could result in a very high ethanol concentration in a localized area, exerting a significant cosolvent effect that could exacerbate groundwater pollution by mobilizing preexisting petroleum releases. At 50 percent, ethanol enhanced the migration of toluene, as well as of benzene and o-xylene, which traveled unretarded at the same velocity as the bromide tracer."

At the same time, researchers caution others that "ethanol is unlikely to spread over relatively large areas and persist for extended periods of time. Therefore, the adverse impacts of ethanol on BTEX degradation are likely to be of relatively short duration and perhaps more manageable than impacts associated with MTBE" (Da Silva and Alvarez, 2002). They also assert that gasohol spills use up oxygen; thus, most ethanol will

be degraded anaerobically, and the resulting byproducts (such as butyrate), although not toxic, could adversely affect taste and odor of groundwater. A buildup of ethanol-derived volatile fatty acids and acetate could cause a decrease in pH, which could inhibit microbial activity and contaminant degradation. Another concern is accumulation of ethanol-derived methane; "some gasohol spills could pose an explosion risk if site-specific conditions favor extensive methanogenesis and methane accumulation (e.g., low concentration of alternative electron acceptors and adequate interspecies hydrogen transfer, and low methanotrophic activity)."

Researchers concluded that

- benzene, toluene, ethylbenzene and xylene were completely degraded within the first 3 cm of the column inlet when fed alone or in the presence of MTBE
- the presence of ethanol adversely affected degradation of benzene, toluene, ethylbenzene and xylene
- ethanol was degraded before the BTEX compounds
- ethanol depleted the system of oxygen, nitrate and sulfate
- ethanol's high electron-acceptor demand created strongly reducing conditions, which reduce the thermodynamic feasibility of BTEX oxidation
- enhanced BTEX migration due to a decrease in sorption-related retardation is unlikely to occur at retail sites contaminated with gasohol but could be important at bulk terminals
- the preferential degradation of ethanol and accompanying depletion of oxygen and other electron acceptors suggest that ethanol could hinder the natural attenuation of BTEX plumes

Ethanol Fuel Benefits Questioned

J. Pelley, *Environmental Science & Technology*, Nov. 1, 2002; <http://www.pubs.acs.org>

Corn ethanol, after MTBE, is the second leading fuel oxygenate used in the United States. At present ethanol appears to have a relatively benign image. If the full life-cycle analysis of ethanol were revealed, however, it would become apparent that ethanol consumes significant amounts of fossil fuel, could degrade water quality, and could become too costly if production is expanded.

The NEV—the fuel's net energy value—"compares the amount of energy produced by a gallon of ethanol to the energy it takes to fertilize, grow, harvest, transport and distill the corn. Nearly a dozen studies of NEV have come up with estimates ranging from an unfavorable value of -33,562 to a high of 30,589 British thermal units per gallon (Btu/gal), depending on the biases and assumptions of the researcher... A USDA (U.S. Department of Agriculture) study also shows that significant amounts of fossil fuel, mainly coal and natural gas, are burned to produce ethanol fuel, making it a net emitter of greenhouse gases. For that reason, corn ethanol is not really sustainable or renewable... In addition, using fertilizers to grow more corn could worsen water quality problems."

Impact of Ethanol on Benzene Plume Lengths: Microbial and Modeling Studies

Deeb, R.A., Sharp, J.O., Stocking, A., McDonald, S., West, K.A., Laugier, M., Alvarez, P.J.J., Kavanaugh, M.C. and L. Alvarez-Cohen, *Journal of Environmental Engineering*, September 2002; <http://ojsps.aip.org/eeo>

Researchers conducted a microbial degradation study using a pure culture isolated from a toluene-enriched culture from a gasoline-contaminated aquifer to determine the effect of ethanol on benzene degradation. The culture used in this study was *Rhodococcus ruber*, designated here as RR1. "Experiments that evaluated substrate interactions in mixtures of benzene and ethanol revealed that the presence of ethanol severely inhibited the biodegradation of benzene by benzene-grown cells of RR1. When a bottle containing 25 mg/l of benzene was spiked twice with ethanol at initial concentrations of 25 mg/l, benzene degraded very slowly until most of the ethanol was depleted from the bottles. The observed lag in the biodegradation of benzene due to the presence of ethanol indicates that ethanol is preferentially degraded over benzene by RR1 although the culture was grown on benzene."

Researchers modeled the data using the 1987 Domenico, two-dimensional fate and transport equation and concluded the following concerning biodegradation rate constants:

- ethanol's half-life, λ , was defined at laboratory conditions of 28°C; however, a temperature of 15°C is more representative of subsurface conditions because groundwater temperatures are usually within 2°C of mean annual temperatures
- ethanol's λ was determined in a lab using a liquid culture with a high concentration of biomass; "biomass activities in field soils are generally much lower than those reported for laboratory cultures. In addition, only a small fraction of microorganisms within subsurface environments contact dissolved contaminants, and only a fraction are capable of degrading ethanol...thus, the expected field biodegradation rate for benzene is at least an order of magnitude less than measured rates from laboratory experiments under a range of conditions"

- degradation rates in fields are typically lower than laboratory-derived rates because of mass transfer limitations in the field

Thus, researchers adjusted the average ethanol biodegradation rate, literature-derived, from 0.28/day to 0.014/day.

Results from model simulations indicated that "the presence of ethanol is predicted to cause increases in benzene plume lengths of between 7 and 150 percent... The ethanol biodegradation rate constant strongly influences the length of benzene plumes. By using a literature-derived ethanol biodegradation rate constant, and by correcting for projected temperature and biomass activity in the field, stable benzene plumes were predicted by the model to travel approximately 27 percent farther under typical California groundwater conditions when ethanol is present in gasoline (5% on a volume basis). Benzene plume lengths were generally observed to increase with increasing values of groundwater velocity and organic carbon content." (Reviewer's comment: *Usually, increasing organic carbon content has the opposite effect.*)

In addition, researchers report that their laboratory results correlate well with previous studies showing that ethanol degrades faster than other gasoline components and inhibits BTEX biodegradation. It should be pointed out that these experiments took place in microcosms that had high concentrations of ethanol, although the oxygen and the nutrient supply were limited. In field situations, releases of oxyfuels are .3 and 5.4 percent ethanol by volume and are less likely to lead to large increases in benzene plume length. At fuel terminals, however, where ethanol-oxygenated fuels are splash-blended, "high concentrations of ethanol in source zones are likely to increase the mobility of other gasoline constituents in subsurface environments via cosolvency. In addition, the large amount of ethanol

introduced into subsurface environments is likely to exert an exorbitant biochemical demand for oxygen and other electron acceptors that potentially inhibit the biodegradation of BTEX compounds and other gasoline components over large areas."

In general, model simulations indicated a plume length increase of 16 to 34 percent in the presence of ethanol.

Importance of Nonequilibrium Sorption Conditions: Contaminated Soil

Opdyke, D.R. and R.C. Loehr, *Ground Water Monitoring and Remediation*, Summer 2002; <http://www.ngwa.org>

This article describes the rate of release (ROR) of hydrocarbons from soil and how ROR influences sorption equilibrium. "Most models assume that sorption equilibrium exists between the chemicals in the soil and the aqueous phase. For groundwater, this local equilibrium assumption is valid when the rate of sorption is more rapid than the rate of aqueous chemical changes by other processes such as advection or biodegradation. However, for some chemical/soil matrices, this equilibrium assumption is not necessarily correct. This observation has led to considerable research to understand

- the extent and rate of release (ROR) of chemicals from contaminated soils
- the factors that affect the release of chemicals from soil
- how to incorporate chemical release information in fate and transport evaluations"

Opdyke and Loehr (2002) examined these issues and developed a three-tiered procedure designed to make decisions about

- whether equilibrium sorption conditions could be assumed at a site

- the relative value of expending resources (time and money) to obtain kinetic as well as equilibrium sorption data
- the level of effort that should be expended to use kinetic sorption data for site decisions

The first tier uses three power-law relationships between site parameters and rate of release kinetics to estimate the importance of these kinetics at a site. The second tier, which involves running a groundwater model, evaluates the model's deterministic component of a fate and transport model, whereas the third tier evaluates the probabilistic component.

Researchers developed a model, the Probabilistic Rate Limited Sorption in Saturated Zone Transport model (PRSST), to investigate the impact that kinetic chemical release parameters would have on site remediation decisions. This one-dimensional model assumes that groundwater flow is steady and that chemical decay is primarily due to biodegradation and occurs only in the aqueous phase.

In addition, to provide a comparison with results from PRSST and define the specific contributions of release kinetics, researchers developed an equilibrium model. Model testing led researchers to conclude that "...ROR kinetics may be important for possible site decisions using the measured, high biodegradation rate constant. ROR kinetics were predicted to be unimportant if the biodegradation rate constant was markedly lower. These results highlight the influence of other chemical removal processes (e.g., advection and biodegradation) on ROR kinetics at a site" (Opdyke and Loehr, 2002).

Oxygen Revisited

Nyer, E.K., Davis, J.S. and I. King, *Ground Water Monitoring and Remediation*, Vol. 22, No. 3, Summer 2002; <http://www.ngwa.org>

Authors of this article discuss the various ways to deliver oxygen to the subsurface. Methods include vacuum extraction, vacuum-enhanced recovery, air sparging, oxygen diffusion, dilute hydrogen peroxide solutions, oxygen-releasing materials, pure oxygen injection, and electrolytic oxygen generation. They compared these methods, and their ability to deliver 450 pounds of oxygen, based on total cost of delivery, time to deliver and cost per pound. They found vacuum extraction to be not only the most economical but also the quickest way to deliver the oxygen.

"Our analysis shows that there is a good dichotomy between low oxygen demand situations and high oxygen-demand situations. The problem is to determine which situation exists at your site." Authors also caution readers that the analyses presented in this article are not applicable to every site: every site is unique and must be treated as such.

Treatment of MTBE-Contaminated Water in Fluidized Bed Bioreactor

Vainberg, S., Togna, A.P., Sutton, P.M. and R.J. Steffan, *Journal of Environmental Engineering*, September 2002; <http://ojps.aip.org/eec>

Researchers examined MTBE biodegradation in a laboratory-scale, granular activated carbon (GAC)-based fluidized bed bioreactor (FBR). Factors that varied in the reactor include

- MTBE loading rate
- hydraulic retention
- co-contaminant loading (butyl and BTEX)
- temperature

Researchers concluded that both moderate MTBE concentrations (10 mg/l) and TBA (1 mg/l) were treated effectively in the FBR. Performance was reduced at a temperature below 25°C; groundwater temperatures can be as low as 10-15°C, and heating the reactor, modifying the loading or increasing reactor size can compensate for some of this.

This study "demonstrates that FBR systems inoculated with an appropriate MTBE-degrading culture are suitable for treating MTBE-contaminated water over a wide range of MTBE concentrations. An added advantage of these systems is that they can remove other common co-contaminants such as BTEX and TBA with little or no effect on MTBE removal efficiency. The study also reveals that care must be taken when designing full-scale systems with particular attention to operating temperature, loading rates and biomass control."

Other articles of interest include the following:

"A Continuous Fibrous-Bed Bioreactor for BTEX Biodegradation by a C-Culture of *Pseudomonas Putida* and *Pseudomonas Fluorescens*," Shim, H., Shin, E.B. and S.T. Yang, *Advances in Environmental Research*, Vol. 7, No. 1, 2002; <http://www.elsevier.com>.

"A New Multilevel Ground Water Monitoring System Using Multichannel Tubing," Einarson, M.D. and J.A. Cherry, *Ground Water Monitoring and Remediation*, No. 4, Fall 2002; <http://www.ngwa.org>.

"Anaerobic, Sulfate-Dependent Degradation of Polycyclic Aromatic Hydrocarbons in Petroleum-Contaminated Harbor Sediment," Rothermich, M.M., Hayes, L.A. and D.R. Lovley, *Environmental Science & Technology*, Vol. 36, No. 22, 2002; <http://www.pubs.acs.org>.

"Aqueous Vapor Extraction: A Previously Unrecognized Weathering Process Affecting Oil Spills in Vigorously Aerated Water," Prince, R.C., Stibrany, R.T., Douglas, G.S. and E.H. Owens, *Environmental Science & Technology*, Vol. 36, No. 13, 2002; <http://www.pubs.acs.org>.

"Biodegradation of Aromatic Compounds by White Rot and Ectomycorrhizal Fungal Species and the Accumulation of Chlorinated Benzoic Acid in Ectomycorrhizal Pine Seedlings," Dittmann, J., Heyers, W. and H. Bucking, *Chemosphere*, Vol. 49, No. 3, 2002; <http://www.elsevier.com>.

"Bioremediation of Oil Sludge-Contaminated Soil," N. Vasudevan and P. Rajaram, *Environmental International*, Vol. 26, No. 506, 2001; <http://www.elsevier.com>.

"Burial, Exportation and Degradation of Acyclic Petroleum Hydrocarbons Following a Simulated Oil Spill in Bioturbated Mediterranean Coastal Sediments," Grossi, V., Massias, D., Stora, G. and J.C. Bertrand, *Chemosphere*, Vol. 48, No. 9, 2002; <http://www.elsevier.com>.

"Effects of pH, Moisture and Flow Pattern on Trickle-Bed Air Biofilter Performance for BTEX Removal," Lu, C., Lin, M.R. and C. Chu, *Advances in Environmental Research*, Vol. 6, No. 2, 2002; <http://www.elsevier.com>.

"Electron-Beam Treatment of Aromatic Hydrocarbons That Can Be Air-Stripped from Contaminated Groundwater: 1. Model Studies in Aqueous Solution," Mark, G., Schuchmann, H.P., Schuchmann, M.N., Prager, L. and C. von Sonntag, *Environmental Science & Technology*, Vol. 37, No. 2, 2002; <http://www.pubs.acs.org>.

"Environmental Contamination and Cancer Rates," R. Arnold, *Journal of Environmental Engineering*, August 2002; <http://ojps.aip.org/eeo>.

"Evaluation of Granular Activated Carbon Technology for the Removal of Methyl Tertiary Butyl Ether (MTBE) from Drinking Water," Shih, T.C., Wangpaichitr, M. and M. Suffet, *Water Research*, Vol. 37, No. 2, 2003; <http://www.iwahq.org.uk>.

"Fate of the Oil Residuals in Patagonian Soils, Effects of the Environmental Exposure Time," Nudelman, N.S., Rios, S.M. and O. Katusich, *Contaminated Soil, Sediment and Water*, April/May 2002; <http://www.aehsmag.com>.

"Initiation of MTBE Biotreatment in Fluidized-Bed Bioreactors," Stringfellow, W.T. and K.C. Oh, *Journal of Environmental Engineering*, September 2002; <http://ojps.aip.org/eeo>.

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"Numerical Simulations of Groundwater Recovery Systems to Optimize Contaminant Plume Capture," Gagon, M. and J.L. Osiensky, *Contaminated Soil, Sediment and Water*, September/October 2002; <http://www.aehsmag.com>.

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

"Petroleum Product Identification in Environmental Samples: Distribution Patterns of Fuel-Specific Homologous Series," Galperin, Y. and H. Camp, *Contaminated Soil, Sediment and Water*, April/May 2002; <http://www.aehsmag.com>.

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Information sources

U.S. EPA publications and information

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

- New York/New Jersey Harbor: Alternative Methods for Ex-Situ Sediment Decontamination and Environmental Manufacturing

Other U.S. EPA documents:

Alternative Landfill Cover Profiles On-line; <http://clu-in.org/products/altcovers>.

Calculation and Use of First-Order Rate Constants for Monitored Natural Attenuation Studies, <http://www.epa.gov/ada/pubs/issue.html>.

Other documents and Web sites

Groundwater Central® consists of a resource-links database and several integrated communication components, <http://www.groundwatercentral.info>.

Solidification/Stabilization Web site, <http://solidificationstabilization.org>.

Technology Status Report: Treatment Trains for Remediation of Soil and Groundwater (TS-03-01), http://www.gwrtac.org/pdf/train_full.pdf

UTTU obtained this information from *Ground Water Monitoring and Review* (<http://www.ngwa.org>), *Environmental Science & Technology* (<http://www.pubs.acs.org/>) and *TechDirect* (<http://clu-in.org/techpubs.htm>). UTTU thanks the editors and writers for allowing us to reprint this information.