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MTBE plume behavior

MTBE releases have affected nearly 20 California communities in the past five years. At Lake Tahoe, which sits on the California-Nevada border, 13 wells were shut down because of actual or threatened MTBE contamination. This article describes the behavior of an MTBE plume in the Lake Tahoe area as affected by nearby pumping wells.

In the past, remediators used the same strategies designed for BTEX-contaminated wells to delineate MTBE plumes: plume extent was monitored, but not thickness. A more accurate prediction of MTBE plume position, however, could be obtained if remediators could account for factors such as the effect of nearby pumping wells (Dernbach, 2000).

Geohydrologic description of the Lake Tahoe area

Lake Tahoe, on the eastern crest of the Sierra Nevada, sits in a granitic graben with dormant faults. The southern shore of Lake Tahoe, where this study occurred, lies in California; one-third of the lake lies in Nevada. Californians receive water from municipal wells, whereas Nevadans obtain water from intakes that extend 1,000 feet or more into the lake. The largest water purveyor on the southern shore, South Tahoe Public Utility District, has drilled 34 municipal wells, and some were drilled in the 1950s. These wells are susceptible to MTBE contamination for the following reasons:

- because of land limitations, gasoline stations were built close to municipal wells
- the geologically young (less than 10,000 years old) valleys have only 100-260 feet of glacial and alluvial sediments and lack extensive aquitards
- the pre-1970 wells are shallow, about 120 feet deep; they lack sanitary seals and sometimes were screened across thin aquitards
- groundwater here can be as shallow as four feet below ground surface

Dernbach (2000) maintained that gasoline constituents were never detected in drinking water wells from pre-MTBE releases, even at "sites with several feet of gasoline-free product floating on the water table...A likely explanation is that aromatic hydrocarbon characteristics do not lend themselves to extensive migration, as is seen with MTBE." In this area, hydrocarbon plumes extended 300 to 500 feet from the source area, which is about one-third to one-sixth the length of an MTBE plume.

Municipal well contamination

District staff found MTBE contamination of 1.4 µg/L in two municipal wells (Arrowhead wells) that were pumped at a combined rate of 800 gallons per minute. Remediators determined that piping at an active gasoline station released the MTBE, which traveled 1,300 feet in 30 to 50 days. Migration direction to the municipal wells was cross-gradient to the regional groundwater flow direction while capture rate was estimated at 26 to 43 ft/day. Gasoline was detected in groundwater at a 16-foot depth.

The municipal wells were shut down immediately after confirming MTBE detection. Five months later, a groundwater sample from the gas station revealed 28,000 µg/L of MTBE and some other gasoline constituents. An extensive groundwater investigation ensued using a Geoprobe™ on a horizontal grid spacing of 100 feet. Field workers took samples at 20, 40, 60 and 80 feet below ground surface.

An MTBE plume "shadow"

"Investigation results showed trace levels of MTBE, from 0.6 to 1.7 µg/L in groundwater from the gas station toward the municipal wells, in the northeast direction. The results also showed MTBE concentrations up to 3,500 µg/L from the gas station toward the Upper Truckee River, to the northwest, in the expected natural groundwater flow direction. This information indicated that a "shadow" MTBE plume was still detectable in groundwater eight months after the municipal wells ceased pumping. When no longer controlled by the Arrowhead wells, the plume swung about 100 degrees from the east to the expected regional groundwater flow direction in the north."

Investigators also found evidence that "the plume dove in the water column from the gas station when acted on by pumping forces from the municipal wells. Yet when pumping ceased and only the natural groundwater flow was active, the plume acquired a 40-foot thickness from the top of the water table. The plume thickness was likely caused by a combination of surface infiltration of precipitation and a minor vertical gradient component" (Dernbach, 2000).

Remedial actions

Investigators detected MTBE about 70 feet from the Upper Truckee River; thus, the first remedial action specified plume containment. Workers installed three extraction wells that pumped at a combined rate of 60 gal/min. Air stripping and carbon polishing treated groundwater before it was discharged to a constructed subsurface infiltration gallery. These actions pertained only to MTBE on-site; the offsite plume continues to migrate toward Lake Baron, 1,500 feet away. Dernbach (2000) reports that "Plans are underway to install an offsite remediation system to expand plume containment. Further actions, such as excavation and soil vapor extraction, are also being considered to remediate the source area oil, however, beneath the gas station." (*Reviewer's comment: Shell found no evidence of native MTBE biodegraders here*).

MTBE at another well

District staff detected 1.3 μg/L MTBE in another municipal well, Tata Lane well, five miles from the Arrowhead wells. Within a year, MTBE levels increased to 26 μg/L. This well, which had been pumping at 70 gal/min, was undergoing well head treatment–air stripping–to remove chlorinated hydrocarbons. Fifteen months later, while taking water samples between the well and potential gasoline sources, regulators identified the MTBE source as a gas station 1,500 feet away and cross-gradient to the regional groundwater flow direction. MTBE concentrations in groundwater beneath the gas station were 30,000 μg/L. Releases were caused by overfilling USTs, leaky seals in turbine pumps, and poor piping connections beneath dispenser islands.

The Tata Lane well was shut down two years after the initial MTBE detection because MTBE levels had reached 35 μg/L, the California Action Level at this time. Dernbach (2000) asserts that "The length of time that it took for the MTBE plume to first reach the municipal well cannot be calculated because releases at the gas station had been ongoing and it is unknown when MTBE first entered the groundwater. Depth to the groundwater at the gas station ranges from 6 to 18 feet, and the hydraulic gradient is 0.046. The natural groundwater velocity is 0.5-1.5 ft/day" and velocity is seasonally dependent.

Regulators required the responsible party to define the plume in three dimensions, which was accomplished by obtaining multilevel groundwater samples using a HydroPunch and a hollow stem auger rig. Workers sampled groundwater every 20 feet from the water table to the municipal well bottom (at 127 feet) and along the plume's anticipated length and width. The investigation revealed the presence of the following:

- an aquifer
  - that has three water-bearing zones, each about 30 to 40 feet thick
  - whose water-bearing zones are separated by thin clayey-silt aquitards
- a diving plume that
  - began diving beneath the water table at 150 feet from the release area
  - stayed above a laterally extensive aquitard that sloped toward the Tata Lane well
  - was detected at 87 to 127 feet, close to the well screen
  - has an average vertical thickness of 30 feet
  - has a maximum width of 600 feet

Remediation strategy

Workers installed multidepth monitoring wells at every monitoring location. In addition, they shut down six municipal wells nearby because of a potential to encourage plume migration, and the Tata Lane well became a remediation extraction well. Workers also installed 12 smaller extraction wells in each water-bearing zone between the gas station and the municipal well, giving a combined pumping rate of 120 gpm. "Extracted groundwater was sent to three remediation systems and treated with granular activated carbon before being disposed to the sewer system and a constructed leach field."

The remediation plan specified pumping at 70 gpm but pumping actually proceeded at 15 gpm, resulting in a smaller capture zone at the municipal well, thus affecting only 400 feet of the 1,100-foot plume. The following changes occurred:

- the plume renewed migration, and extended 2,000 feet beyond the gas station
- the plume's path shifted about 40 degrees from the northwest to the north
- the former diving plume migrated at the water column depth that it occupied before pumping ceased
- plume width expanded to 1,500 feet
- workers consistently detected the northernmost 1,000 feet of the MTBE plume between 40 and 75 feet below ground surface

(*Reviewer's comment: Lack of MTBE biodegraders in the aquifers maintain a steady mass of MTBE subject to dispersion only.*)

Workers found that screens of offsite extraction wells had become clogged with sediments and iron-fouled, causing pumps to fail and allowing the plume to slip between the offsite wells' capture zones. In addition, when the responsible party began pumping the Tata Lane well at 70 gpm, the well had already been offline for 8 months. Thus, another six offsite extraction wells were installed.

Workers also installed an air sparging soil vapor extraction system, which was not effective because above-average precipitation raised the water table above the remaining soil contamination. The high water table combined with soil temperature of about 40°F (4.4°C) decreased air sparging efficiency.

Two years after the startup of the offsite extraction wells, there was a notable decrease in the MTBE plume size and concentration.

Conclusions

Dernbach (2000) concluded the following:

- delineation of a plume's vertical thickness, which involves collecting multidepth water samples, is just as important as delineation of its horizontal extent
- rate of plume capture by drinking water wells can be fast; for instance, an MTBE plume migrated at an estimated rate of 26 to 43 ft/day toward the Arrowhead wells
- even when unaffected by well pumping forces, MTBE plumes can exhibit a significant vertical thickness caused by infiltrating precipitation and a vertical gradient
- even non-diving plumes will likely require multidepth monitoring wells to evaluate cleanup effectiveness

Reference

Dernbach, L.S., "The Complicated Challenge of MTBE Cleanups," *Environmental Science & Technology*, December 1, 2000; http://www.pubs.acs.org/.

UTTU thanks Lisa Dernbach, California Regional Water Quality Control Board, for her help on this article.

Private water wells at risk

Investigators in eastern New York analyzed water from 74 private wells near 21 gas stations to determine if a correlation existed between

- MTBE contamination of private wells downgradient and close to gasoline stations (< 0.5 mile), as opposed to distant wells (> 1.5 miles)
- MTBE contamination of private wells near gasoline stations selling oxygenated gasoline stations vs. those selling non-oxygenated gasoline

Background information

Lince and others (2001) sought to characterize the increased risks to private wells near gasoline stations. Private wells often lack the groundwater protection that public wells have. Researchers also wanted to determine if gasoline formulation–RFG vs. conventional gasoline–increases the risk of MTBE contamination.

Twelve counties in and around New York City and Long Island participate in the RFG program. This study concerned itself with a seven-county region surrounding Albany, in eastern New York.

Study site and well location selection

Workers used 1994 data from the NYS Office of Real Property Services to locate gasoline service stations and minimarts that were mapped on a geographic information system (GIS). This map was overlaid on a map of 1990 Census data that showed the percentage of households on public water by census block. Using these maps, workers identified 209 facilities that used a low percentage of public water ($\leq$ 20 percent) and consequently relied, to a high percent, on private water. From this list, researchers selected 98 gasoline stations that were evaluated if

- there were a sufficient number of homes, businesses or public buildings near the gasoline facility
- the facility actively sold gasoline
- water in the area was obtained from private wells

Researchers selected 21 gasoline stations: 11 in seven counties that used conventional gasoline, and 10 in four counties that used RFG. A maximum of four wells and a minimum of two wells were sampled at each site. Wells closest to and downgradient from gasoline stations were sampled before other wells; wells less than 0.1 mile from the gasoline station were most often sampled. For each site, field workers sampled a control well that was upgradient and greater than 1.5 miles from any gasoline station. Field workers also followed the usual quality control measures.

Results and conclusions

Workers used EPA method 502.2 to analyze each water sample for 57 VOCs. They sampled 95 wells, 21 of which were control wells–one per facility. "Twenty-one of the 74 case wells (28.4 %) had MTBE concentrations at or above the PQL (practical quantitation limit) of 1.0 μg/L. MTBE detections in case wells ranged from 1.0 to 61 μg/L. The mean detection was 12.0 μg/L with a standard deviation of 18.2 μg/L. The median detection was 4 μg/L and the mode was 1 μg/L. One of the 21 (4.8 %) control wells, located in the oxygenated fuel region, had MTBE at or above the PQL...No MTBE or VOCs were detected at or above their detection limits in any trip, laboratory or field blank. This lends confidence to the assertion that the relatively large portion of detections at or near the PQL accurately represent actual MTBE concentrations" (Lince and others, 2001).

The authors concluded:

- private wells near gasoline stations are at an increased risk for MTBE contamination
- contamination levels in these wells were generally lower than current standards
- MTBE levels in five private drinking water wells did exceed 20 µg/L
- MTBE levels in two private drinking water wells exceeded 50 µg/L
- the probable origin of the MTBE was LUSTs, although research has shown that both stormwater runoff and atmospheric transport may contribute to MTBE deposition in the environment
- four of the 11 gasoline stations with conventional gasoline had one or more private wells contaminated with MTBE concentrations at or above the PQL; seven of 10 gasoline stations supplied with RFG/Oxyfuel had one or more nearby private wells with detectable MTBE concentrations; a Fisher Exact test failed to verify the difference as statistically significant, which might have been achieved had a larger sample been used
- the risk of having MTBE contamination of ≥ 1.0 µg/L in a private well is nearly twice as high when the well is located in a RFG/Oxyfuel county
- the well with the highest MTBE concentration, 61 µg/L, was about 50 yards from a gasoline station; water tested at a kitchen tap showed post-filtration MTBE concentrations of 56 µg/L, and regulators installed granular activated carbon filters; this well also had benzene at the detection limit of 0.5 µg/L
- BTEX was absent in 20 of the 21 control wells tested, indicating MTBE's mobility and persistence

Treating MTBE-contaminated water at private homes

An estimated 42 million people nationwide rely on private wells for drinking water (Greene and Barnhill, 2001). Two technologies that have proved effective for cleaning MTBE to less than 5 µg/L concentration are air stripping and granular activated carbon (GAC).

"An air stripper consists of contaminated water flowing down a column filled with packed material while a stream of air flowing upward strips the MTBE from the water. Some air stripping-specific system technologies consist of spray towers, bubble diffusion strippers, aspirated air strippers, low-profile air stripper and packed towers. Low-profile air strippers have proved to be the most cost effective at lower flow rates, cleaning at a rate of 95.5 percent MTBE removal" (Greene and Barnhill, 2001).

These units, which are easy to install and maintain, are flexible in terms of flow rate modification, but they usually cost more than GAC.

The GAC method uses filters—often made of coconut-shell or coal-based carbon—to remove MTBE to below-detectable levels. Canisters that house the GAC filtering system come in many sizes. Some units have a 6-year warranty and require little maintenance.

References

Greene, J. and T. Barnhill, "Proven Solutions for MTBE in Household Drinking Water," *Contaminated Soil Sediment & Water*, Spring 2001; http://www.aehsmag.com/.

Lince, D.P., Wilson, L.R., Carlson, G.A. and A. Bucciferro, "Effects of Gasoline Formulation on Methyl tert-Butyl Ether (MTBE) Contamination in Private Wells near Gasoline Stations," *Environmental Science & Technology*, Vol. 36, No. 6, 2001; http://www.pubs.acs.org/.

UTTU thanks Daniel Lince, Michigan Department of Community Health, Division of Environmental Epidemiology, for his help on this article.

Oxygenated gasoline dissolution

Using batch equilibrium tests, researchers determined the equilibrium aqueous concentration of 12 organic compounds of gasoline in gasoline-water and gasoline-ethanol-water systems. Other research prerogatives included:

- investigating equilibrium concentrations at different gasoline-to-water ratios
- fitting data to models and comparing these data for pure gasoline and oxygenated gasolines
- investigating the long-term dissolution behavior of gasoline constituents in flow-through systems with and without ethanol, using column studies

The 12 organic compounds investigated are listed in Table 1 on the next page.

Compound	Aqueous solubility at 25°C (mg/L)	Molecular weight (g/mol)	Log K_{ow} at 25°C	Weight (percent)	C (calculated concentration in mg/L)	Log K_{fw} (calculated gasoline/ water partition coefficient)
Hexane	50.0	64.17	3.39	2.07	1.33	4.07
Benzene	1,780.0	78.11	2.13	1.80	44.30	2.49
Toluene	534.8	92.10	2.69	8.30	52.05	3.08
Ethylbenzene	161.2	106.17	3.15	3.41	5.58	3.67
p-Xylene	156.0	106.17	3.18	8.00	12.69	3.68
o-Xylene	170.5	106.17	3.12	1.50	2.60	3.64
Propylbenzene	55.0	120.20	3.63	1.00	0.49	4.19
1,2,4-TMB	59.0	120.19	3.65	7.20	3.82	4.16
1,2,3-TMB	75.2	120.19	3.41	1.42	0.96	4.05
1,3,5-TMB	48.2	120.19	3.42	1.50	0.65	4.24
Indan	109.1	116.16	2.92	0.72	0.72	3.88
Naphthalene	111.1	128.16	3.36	1.46	1.47	3.91

Table 1. Selected properties of investigated compounds (Reckhorn and others, 2001).

Raoult's law

Water solubility affects soil sorption, desorption and volatilization from aquatic systems. High-solubility compounds are more likely to desorb from soils and less likely to volatilize from water. Furthermore, "dissolution of compounds from mixtures, such as gasoline and diesel fuel, behaves differently from single compounds when brought into contact with water. Each component in the mixture will partition between the aqueous phase and the mixture, as approximately described by Raoult's law. At equilibrium, the chemical potential of each solute is uniform among all phases. Using Raoult's law convention, the aqueous concentration of each solute in gasoline-water mixtures at equilibrium can be expressed as:

$C^w_i = X^o_i Y^o_i S^w_i$

Where

C^w_i = solute concentration in the aqueous phase in equilibrium with the organic phase

X^o_i and Y^o_i = mole fractions of the solute i and the activity coefficient in the organic phase (in most studies involving hydrocarbons, Y^o_i is considered close to 1 because interactions between components with similar chemical structures are assumed to be insignificant)

S^w_i = aqueous solubility of the pure solute i

Researchers here used gasoline containing 10 and 20 percent ethanol and employed applied column tests to analyze the cosolvent effects arising from residual phases.

Previous studies have shown:

- with increasing volume fraction of a completely miscible organic solvent in a binary mixed solvent, hydrophobic compound solubility increased essentially in a log-linear way, although deviations from the log-linear behavior are more apparent for some cosolvents than for others; increased solubility results in decreased sorption and increased contaminant mobility in soil
- to predict aqueous solubility, vapor pressure and octanol/water partition coefficient, models have been used; one relies on the fact that compounds may be structurally decomposed into functional groups, each one contributing toward a compound's activity coefficient; discrepancies of up to four orders of magnitude have been reported
- a cosolvency power, σ, can be computed: this is the log ratio of the solute solubility in pure cosolvent over the solute concentration in the aqueous phase in equilibrium with the organic phase
- the cosolvency power, σ, can be correlated to octanol/water partition coefficient (K_{ow}) and two empirical constants that are unique for a given cosolvent; in complex mixtures such as gasoline, the complexity of determining moles of each component involves theoretically infinite combinations

Laboratory study

Reckhorn and others (2001) performed batch tests to quantify the aqueous solubility of the 12 compounds listed in Table 1. They used sandy soil samples collected at 2 meters below the surface from Ribeirao Preto, Sao Paulo. The soil was composed of

- 74-79 percent sand
- 6-7 percent silt
- 14-18 percent clay
- organic carbon, f_{oc}, 0.006 percent

For the column tests, these three systems were investigated:

- a two-component system with gasoline and water
- a three-component system with gasoline and 10 percent ethanol and water
- a three-component system with gasoline containing 20 percent ethanol and water

Cosolvent mixtures were prepared in volumetric gasoline-to-water ratios of

- 1:1
- 1:10
- 1:100
- 1:10,000
- 1:100,000

Researchers equilibrated samples on a rotator for 12 to 24 hours, then centrifuged. They acquired samples with a glass syringe. Depending upon the gasoline-to-water ratio, these samples were used for either direct injection into a gas chromatograph or head space analysis, followed by GC detection.

Column tests

Researchers used column tests to simulate subsurface conditions. Cosolvent mixtures contained either 10 or 20 percent ethanol in gasoline. The glass column used had a 430-cm^3 volume and a 6-cm diameter. "The volumetric porosity was between 0.42 and 0.44. Until breakthrough, gasoline was pumped from the top to the bottom of the columns with a velocity of 0.73 m/day. From here the columns were flushed again by pumping degassed water from bottom to top. When residual saturation of the gasoline was achieved, the degassed water was pumped from top to bottom and leachate samples were collected in predetermined time intervals. These types of experiments were carried out for 113 days to investigate the change in composition of the gasoline due to aqueous dissolution of the constituents (aging effects)" (Reckhorn and others, 2001).

Researchers found that gasoline dissolution rate in columns depended on

- effective solubilities and diffusivities of the gasoline compounds; compounds are depleted from the mixtures in a decreasing order of solubility in both gasoline and oxygenated gasoline column tests
- physical distribution of the gasoline-NAPL in the porous medium
- rate of water flow through and around the gasoline-NAPL; higher water velocities reduce dissolved concentrations

Thus, benzene is depleted from the column first, but it shows relatively high effluence concentrations for extended periods of time. "This is attributed to the slow dissolution of some residual blobs still containing benzene ('tailing')" (Reckhorn and others, 2001). Data from long-term dissolution experiments suggest that for water flow velocities of 1 m/day, initial equilibrium is achieved in the column effluent. Compounds with relatively high water solubilities (benzene, toluene, ethylbenzene) had contact times of 30 and 202 minutes.

Other results

This research also indicated the following:

- compounds with relatively high water solubilities fit Raoult's law better than the compounds with lower aqueous solubilities
- for water in contact with a non-aqueous-phase liquid (NAPL), the dissolved concentrations often approach effective solubility values in minutes to hours, depending on the NAPL-to-water volume ratio
- compounds with highest aqueous solubility, such as benzene and toluene, rapidly equilibrated and were less sensitive to small changes in the aqueous phase concentrations as measured by GC/FID
- the columns showed a higher concentration of benzene and toluene in the effluent; both of these could have caused enhanced dissolution of low-solubility compounds ("cosolvent effect"); these results give a first approximation of the prediction of maximum solute concentrations that may be present in aqueous leachate leaving a gasoline-contaminated zone

Conclusions

Researchers concluded that

- the solubility of a solute in gasoline-ethanol-water mixtures is a function of the ethanol in the aqueous phase

- a significant cosolvency effect is observed only at a water-to-oxygen gasoline ratio of <10:1 and when f_c>0.1 (f_c is volume fraction of cosolvent in the aqueous phase)
- the fit of high-solubility compounds to the model (Raoult's law and studies) is better than for low-solubility compounds
- when ethanol is present, compounds with lower aqueous solubilities will show the highest concentration enhancements

"Only volume fractions of ethanol in water > 0.1 cause significantly enhanced aqueous concentrations of gasoline constituents. This may occur during the first pore volume displaced in a column test ('first flush'); later dissolution behavior is not influenced by the cosolvent that was present initially. Aqueous leaching of residual gasoline caused dramatic changes in the aqueous concentration due to a change in gasoline composition ('aging'). Results of the column dissolution experiments indicate that at sufficiently high residual saturations, equilibrium concentrations prevail for a considerable period of time, which can be estimated in a first approximation by the retardation of the dissolution front... Based on present test results, gasoline with 26 percent ethanol will increase aqueous concentrations of gasoline constituents, but only at very early leaching times when ethanol is flushed out. Later (e.g., in aged gasoline spills), it does not significantly change the dissolution of gasoline constituents" (Reckhorn and others, 2001).

Reference

Reckhorn, S.B.F.R., Zuquette, L.V. and P. Grathwohl, "Experimental Investigations of Oxygenated Gasoline Dissolution," *Journal of Environmental Engineering*, March 2001; http://ojps.aip.org/eeo.

Evaluating indoor air vapors

Nichols and Ettinger (2001) recently developed a course to evaluate the impact of indoor vapors near a release site. This article is a brief summary of the *Indoor Air Pathway and Risk-Based Decision Making* course given in Portland, Oregon, in the spring of 2001. The course focuses on

- risk-based management
- vapor intrusion modeling, which includes fate and transport and the conceptual model
- sampling procedures and modeling program design

Risk-based process

The risk-based process consists of the following elements:

- site characterization (nature of the release, site condition, exposure pathways)
- site conceptual model (which pathways are complete, current and potential land/water use, hydrogeologic characteristics, sources, pathways, receptors)
- target risks and cleanup goals (based on policy decisions, risk calculation using toxicity, exposure and fate and transport)
- tiered analysis (conservative vs. site-specific)
- risk management and remediation options: remove source, control pathway and control receptor

Fate and transport analysis and conceptual model

Fate and transport concepts/mechanisms depend on the conceptual model, which focuses on determining a chemical's attenuation factor (0 to 1). The model incorporates ideas such as

- mixing in the breathing zone
- convective transport into the building
- aerobic biodegradation zone
- diffusive transport to the breathing zone
- impacted soil and/or groundwater in equilibrium with soil gas

Important mechanisms include the following:

- partitioning, where chemicals partition between the various phases depending on moisture content, sorbed equilibrium, sorption coefficient, and residual hydrocarbon
- diffusion, which is a function of diffusive flux, moisture impact, and residual water saturation, which is a function of soil type
- convection, which is a function of basement crack diameter and crack depth
- building effects, which depend on indoor/outdoor air mix and building volume
- biodegradation, which is a function of the types and amounts of chemicals and microorganisms present, and environmental conditions; determination of rates involves such elements as kinetics and criteria to determine aerobic biodegradation

The conceptual model has several assumptions:

- one-dimensional transport
- steady-state conditions
- no preferential pathways

- contaminant below the structure
- single contaminant source
- biodegradation (often neglected)
- vadose-zone heterogeneity
- constant or depleting source concentration

The authors also give formulas for determining the impact of these mechanisms at a particular site.

Transport models

Transport models addressed by the course include:

- Farmer model
- Jury model
- Orange County model
- Little, Daisey and Nazaroff model
- Johnson, Kemblowski and Johnson model (dominant layer model)
- Oxygen-limited model
- Johnson, Hermes and Roggemans model

The authors also describe the EPA Spreadsheet, GSI RBCA Toolkit, and BP RISC software.

Air quality sampling analyses and guides

Air quality sampling concerns include a description of the following:

- passive vs. active sampling and the use of Tedlar bags, canisters and grab samples
- sources of variability and what constitutes conservative sampling conditions
- which media to sample and over what time scale
- existing sampling guides from Massachusetts, San Diego and New Jersey

Other topics

Other topics discussed in the course include field data interpretation and case studies, model parameter estimation and sensitivity and data reliability.

Reference

"Indoor Air Pathways and Risk-Based Decision Making" CD.

UTTU thanks Wally Moon, U.S. EPA Ground Water Protection Unit, Portland, Oregon, moon.wally@epa.gov, for his help on this article.

Leak detection evaluation list

This article describes the 8th edition of *List of Leak Detection Evaluations for USTs* , a compilation of reviews conducted by the National Work Group on Leak Detection Evaluations (NWGLDE). The group, composed of state and EPA staff, compiled both UST and piping leak detection system evaluations.

The evaluations were often based on one-time events conducted in lab settings, and as such, the evaluations took place under artificial conditions rather than actual field conditions; consequently, the systems may not perform in the field as predicted by the lab tests. Furthermore, NWGLDE reviewed only those evaluations that followed an EPA protocol, an alternative protocol such as a national voluntary consensus standard, or a test developed by an independent third party. Changes to a listed protocol and/or other deviations that developed during testing required approval by the Work Group.

A leak detection system may be listed as "under review" if:

- the vendor must re-test the system to correct the problem
- the vendor fails to meet the Work Group's time frame
- the vendor fails to respond to a Work Group request

Information required

Some information the NWGLDE required to perform an evaluation included the following:

- a complete third-party evaluation
- an outline of the manufacturer's operating procedures for the equipment/system
- a complete installation/operations manual
- a sample of the test report
- an outline of the test procedures in high-groundwater areas
- an outline of the test procedures for manifolded tank systems
- an affidavit from the manufacturer confirming there are no mutual financial interests between the equipment manufacturer and the third-party evaluator
- a resume, including all applicable formal training and experience, from those who conducted the evaluation
- equipment calibration procedures and manufacturer-recommended schedule of calibration
- contact information of the technical personnel serving as the manufacturer's representative

- correspondence from state agencies who have reviewed the equipment/system
- other information from permanently installed leak detection equipment, such as installer list, list of service personnel authorized to conduct the annual functional test, outline of the maintenance procedure, outline of "Equipment Check Guidelines for Inspectors", sample reports, information on how control panel modules are connected to various probes
- documentation for systems using tracer analysis (e.g., a laboratory that analyzes vapor samples), quality assurance manual, method and amount of tracer injection, vapor sample collection method and chain of custody records, third-party certification

In addition, each participant was required to fill out a 10-question survey.

List organization

The list is organized by

- company
- test method
- equipment model
- leak rate

Evaluations vary in the amount of information presented, but most give leak threshold/detection limits, applicability, tank capacity and reviewer's comments.

Finally, approval of a system for use at any site is not within the jurisdiction of EPA or NWGLDE but the responsibility of the implementing agency, which is usually the state environmental agency.

The list was first created in January 1995. The current 8th edition was distributed in March 2001 and is available at http://www.epa.gov/OUST/pubs/index.htm. This 311-page edition, which reviewed 275 systems, is available only in electronic format.

Research notes

Flow Dynamics and Potential for Biodegradation of Organic Contaminants in Fractured Rock and Vadose Zones

Geller, J.T., Holman, H.Y., Su, G., Conrad, M.E., Pruess, K. and J.C. Hunter-Cevera, *Journal of Contaminant Hydrology*, Vol. 43, p. 63-90, 2000; http://www.elsevier.com/locate/jconhyd.

Previously, deep fractured rock vadose zones in arid regions have been thought to be biologically inactive, due to dry conditions and minimal organic matter. Researchers investigated this premise by using VOC-contaminated rock samples and indigenous microorganisms to:

- establish a conceptual model for fluid and contaminant distribution in the geologic matrix of interest
- identify important features of liquid distribution by means of seepage experiments in the fracture plane
- identify the presence and activity of microorganisms by non-destructive monitoring of biotransformations on rock surfaces at the micron scale
- integrate flow and biological activity in natural rock geocosms

Researchers found that "a mixed culture of viable bacteria exist on the surface of rock samples." Furthermore, they hypothesized that contact with liquid water and organic contaminants would stimulate bacterial activity. Currently, researchers are using high-resolution spectroscopic techniques to map bacteria, mineral and contaminant distributions. They are also quantifying any potential isotopic shifts caused by contaminant biodegradation.

Interaction of Soil Air Permeability and Soil Vapor Extraction

Farhan, S., Holsen, T.M. and J. Budiman, *Journal of Environmental Engineering*, January 2001; http://ojps.aip.org/eeo/.

Remediators need to know soil air permeability values to effectively design soil venting systems. "Although soil air permeability increases during the venting process, it is usually assumed to be a constant during soil venting due to the lack of a fundamental approach to trace its variation with time." Farhan and others (2001) performed soil column venting experiments to calculate contaminant removal and soil air permeability as a function of time. Their end result was a model that can be calibrated with measured values of mass removal and sample permeability.

Investigation of a Long-Term Sampling Period for Monitoring Volatile Organic Compounds in Ambient Air

Uchiyama, S. and S. Hasegawa, *Environmental Science & Technology*, Vol. 34, 2000; http://www.pub.acs.org/.

Researchers sampling for VOCs maintained non-stop sampling periods of four weeks, seven days, and 24 hours using a multisorbent sampling tube packed with Carbotrap C, B and 1000. Using a GC/MS to evaluate VOC concentration, researchers found wide variation in daily concentrations and suggested that "long-term, nonstop sampling is necessary for measuring accurate average concentrations of VOCs in the ambient atmosphere." Factors that affect a VOC's concentration (such as benzene) include wind direction, automobile traffic density, industrial work rate, and weather conditions. This paper describes, in detail, the experimental setup and data collection and analysis.

A Numerical Model (MISER) for the Simulation of Coupled Physical, Chemical, and Biological Processes in Soil Vapor Extraction and Bioventing Systems

Rathfelder, K.M., Lang, J.R. and L.M. Abriola, *Journal of Contaminant Hydrology*, Vol. 43, 2000; http://www.elsevier.com/locate/jconhyd.

Researchers examined soil vapor extraction (SVE) and bioventing (BV) systems with respect to remediation of unsaturated zones. They developed a Michigan soil vapor extraction remediation model (MISER) that integrates the concepts of multiphase flow, multicomponent compositional transport with non-equilibrium interphase mass transfer, and Monod kinetics for aerobic biodegradation. Field investigations along with model applications allowed them to conclude the following about contaminant removal efficiency:

- removal is controlled by gas flow through regions of organic liquid-contaminated soil and by mass transfer to the gas stream
- the ability to engineer gas flow through regions of contaminated soil poses design and operation difficulties
- biodegradation is a minor consideration; researchers attributed only 6 percent or less of the total mass of lost contaminant to SVE biodegradation
- effective supply of oxygen may not be the sole criterion for efficient BV performance: chemical partitioning and biological growth characteristics will determine "optimal" substrate and oxygen supply
- efficiency and contaminant removal pathways can be significantly influenced by interdependent dynamics that involve growth factors, interphase mass transfer rates and air injection rates

Articles of additional interest include:

"BTX Biodegradation in Activated Sludge Under Multiple Redox Conditions," Ma, G. and N.G. Love, *Journal of Environmental Engineering*, June 2001; http://ojps.aip.org/eeo.

"Effective Air Delivery from a Horizontal Sparging Well," Lundergard, P.D., Chaffee, B. and D. LaBrecque, *Ground Water Monitoring and Review*, Spring 2001; http://www.ngwa.org.

"Empirical Model for Biofiltration of Toluene," Strauss, J.M., Plessis, C.A. and K.H.J. Riedel, *Journal of Environmental Engineering*, July 2000; http://ojps.aip.org/eeo.

"Enhanced Degradation of a Model Oil Compound in Soil Using a Liquid Foam-Microbe Formulation," Ripley, M.B., Harrison, A.B., Betts, W.B., Dart, R.K. and A.J. Wilson, *Environmental Science & Technology*, Vol. 34, No. 3, 2000; http://www.pubs.acs.org.

"Enhanced Solubility and Biodegradation of Naphthalene with Biosurfactant," Vipulanandan, C. and X. Ren, *Journal of Environmental Engineering*, July 2000; http://ojps.aip.org/eeo.

"Modeling Transport of Gaseous Ozone in Unsaturated Soils," Hsu, I.Y. and S.J. Masten, *Journal of Environmental Engineering*, June 2001; http://ojps.aip.org/eeo.

"Photolytic Behavior of Polycyclic Aromatic Hydrocarbons in Diesel Particulate Matter Deposited on the Ground," Matsuzawa, S., Nasser-Ali, L. and P. Garrigues, *Environmental Science & Technology*, Vol. 35, No. 15, 2001; http://www.pubs.acs.org.

"Practical Modeling of SVE Performance at a Jet-Fuel Spill Site," El-Beshry, M.Z., Gierke, J.S. and P.B. Bedient, *Journal of Environmental Engineering*, July 2001; http://ojps.aip.org/eeo.

"Proposal for Including What is Valuable to Ecosystems in Environmental Assessments," D.E. Campbell, *Environmental Science & Technology*, Vol. 35, No. 14, 2001; http://www.pubs.acs.org.

Information sources

U.S. EPA publications and information

Publications that can be viewed or downloaded at http://clu-in.org/techpubs.htm include

- The State-of-the-Practice of Characterization and Remediation of Contaminated Ground Water at Fractured Rock Sites (EPA 542-R-01-010)
- Innovations in Site Characterization–Technology Evaluation: Real-Time VOC Analysis Using a Field-Portable GC/MS (EPA 542-R-01-011)
- Monitored Natural Attenuation: USEPA Research Program–An EPA Science Advisory Board Review (EPA-SAB-EEC-01-004)
- Tech Trends (EPA 542-N-01-002)

U.S. EPA Web sites

Innovative cleanup technology, EPA CLU-IN, http://clu-in.org/, and sites that can be reached from CLU-IN include:

- Air Force Center for Environmental Excellence (AFCEE), http://www.afcee.brooks.af.mil/, has a link to *CenterViews*, which recently contained an article on diffusion sampling
- EPA Kerr Lab, http://www.epa.gov/ada/kerrcenter.html, contains reports, research papers, modeling reports and issue papers
- EPA REACH IT, http://www.epareachit.org/
- In-Situ Thermal Treatment Site Profile Database, http://clu-in.org/thermal_060700/
- *Soil & Groundwater Cleanup Online Magazine*, http://www.sgcleanup.com/
- U.S. EPA Technology Innovation Office, http://www.epa.gov/swertio1/index.htm, contains publications, site characterization information and information on groundwater and soil contaminant technologies
- Watershed Assessment, Tracking and Environmental Results, http://www.epa.gov/waters, integrates water quality information from several state and EPA databases; the site will eventually add links to ambient water quality, drinking water quality, polluted runoff, fish consumption advisories, facility discharge outfalls and other information

In addition, the EPA CLU-IN studio, http://clu-in.org/studio, has a collection of archived Internet seminars covering the following topics:

- diffusion sampling
- geophysical characterization techniques and data uses
- installation of iron-based permeable reactive barriers and non-iron-based barrier treatment material
- in-situ chemical oxidation
- in-situ thermal treatment

EPA Remediation Grant Project Summaries, http://es.epa.gov/ncer/publications/topical/remediation.html, has a searchable database of remediation-related research projects.

UTTU obtained many of these sites and other information from TechDirect (http://clu-in.org/techdrct/). UTTU thanks Jeff Heimerman for allowing us to reprint this information.