

Ground Water Currents

Developments in innovative ground water treatment

Innovative Measures Distinguish Natural Bioattenuation from Dilution/Sorption

By John Wilson and D. H. Campbell, Robert S. Kerr Environmental Research Laboratory

The EPA's Robert S. Kerr Environmental Research Laboratory (RSKERL) recently demonstrated natural bioattenuation of organic contaminants from a gasoline spill in ground water at the Sleeping Bear Dunes National Lakeshore site near Honor, Michigan. The results of the demonstration offer conclusive quantitative evidence of natural bioattenuation distinct from dilution and sorption. Additionally, nitrate depletion, sulfate depletion and increased methane production (methanogenesis) under anaerobic conditions are found to be important indicators of natural bioattenuation, which should be measured in addition to the traditional measure of oxygen depletion.

The geology of the Sleeping Bear site is characteristic of many urban and industrial sites where BTEX compounds (benzene, toluene, ethylbenzene and xylenes) are found. The water table aquifer is in highly transmissive glacial sands and gravels; and, water flow is rapid. The ground water is cold (10 to 11 degrees Centigrade), hard (alkalinity 200 to 350 milligrams per liter (mg/L)) and well-buffered (pH 6.1 to 7.6). Ambient concentrations of oxygen, nitrate and sulfate in uncontaminated

ground water are 2.4, 67, and 21 mg/L, respectively.

A gasoline service station had been operated for many years on a corner lot where Michigan Highway M-22 crosses the Platte River. The National Park Service acquired the land and removed the service station. On December 11, 1989, three underground storage tanks were excavated and removed. Fill and excavated soil around the tanks smelled of gasoline. The excavation was backfilled with the same soil that had been removed to prevent injuries to visitors to the open pit. The distance from the source of the plume to the Platte River is only 70 feet.

The following strategy was used to acquire information that would allow a quantitative assessment of natural bioattenuation at field scale. A soil gas survey for hydrocarbon vapors was used to identify those areas that still contained oily phase hydrocarbons and could act as a source of ground water contamination. Core samples were taken in the areas that showed hydrocarbon vapors in order to define the vertical extent of gasoline contamination and to determine the depth to which the spill penetrated moving ground water. Most of the spill was

above the water table. The core data and soil gas data were used to estimate the total amount of gasoline remaining in the subsurface (1,200 gallons).

Clusters of monitoring wells were installed at three locations in the plume of contaminated ground water - at the source of the plume, at the bank of the river and at an intermediate point. Concentrations of contaminants and potential electron acceptors were monitored in the plume over time.

Attenuation of contaminants in ground water plumes may be due to dilution or sorption. Unless the contribution by dilution and sorption can be quantified, it is impossible to evaluate the contribution of biodegradation. One of the goals of this

demonstration was to determine the extent to which bioattenuation is responsible for the reduction in the concentration of BTEX compounds.

The strategy was to identify an innocuous component of the plume that sorbs as strongly as the contaminants and that should not be biodegraded, at least not anaerobically. The contaminant plume contained several low molecular weight branched alkanes that should not biodegrade in the absence of oxygen, and should sorb at least as strongly at the BTEX compounds. One of the alkanes, 2,3-dimethylpentane, was used as a tracer.

For example, in November, 1992, the concentrations of benzene and toluene in the

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PILOT RESULTS

Surfactant Flushing of Ground Water Removes DNAPLs

By John C. Fountain, Ph.D., State University of New York at Buffalo

Recent research results from a field test have demonstrated that the surfactant flushing process is capable of rapid removal of dense nonaqueous phase liquids (DNAPLs) from a contaminated aquifer. The surfactant solution successfully removed perchloroethylene (PCE) at a rate far greater than it could have been removed by conventional pump-and-treat methods. Surfactants have the ability to greatly increase the solubility of organic compounds in water and thus to increase the efficiency of pump-and-treat operations. It has been shown that pump and treat alone is not always effective for restoring aquifers contaminated with organic compounds.

The research began just four years ago at bench scale at the State University of New York at Buffalo and has been field tested at the Canadian Forces Base Borden at Alliston, Ontario, Canada. It is believed to be the most carefully controlled field test of an aquifer remediation surfactant flushing process conducted to date. The field test of surfactant flushing was considered successful enough to warrant a pilot scale demonstration at a contaminated site at Corpus Christi, Texas.

At the Borden field test, a three-meter-square cell was built in a four-meter-thick surficial sand aquifer by driving sheet piling walls into the underlying clay. A second sheet piling wall was then installed one meter beyond the first wall for secondary containment. Five injection wells were installed on one side of

the cell and five extraction wells on the other side. Ten multi-level monitoring wells were also installed.

Next, 231 liters of reagent-grade PCE were released into the cell through a shallow injection well in the center of the cell. The well penetrated to a depth of about 30 centimeters (well below the water table). Thus, the entire contaminated zone was below the water table. Prior to starting surfactant flushing, all free-phase PCE that could be directly recovered was pumped out; approximately 47 liters of PCE were recovered by this process. When direct pumping was no longer recovering significant volumes of free-phase PCE, water flushing was begun to flush any free-phase PCE that could be so mobilized and to determine the vertical and horizontal variations in hydraulic conductivity within the cell. Twelve liters of PCE were recovered by water flushing.

After recovery of free-phase PCE by water flushing ceased, surfactant injection began. A 2% (by weight) aqueous solution was used, composed of equal weights of nonyl phenol ethoxylate and a phosphate ester of the nonyl phenol ethoxylate. The surfactant solution containing the PCE was then pumped from the extraction wells into a holding tank, through two air strippers, into a second tank where additional surfactant can be added to bring the surfactant concentration to 2% if it is necessary to repeat the surfactant injection again.

The pool of DNAPLs, originally 50 centimeters thick, was only 3 millimeters thick at the end of the pilot. Additionally, out of the 231 liters of PCE injected into the cell, only 8 liters remained, spread between the thin layer above the treatment zone, the DNAPL pool and in the probe holes in the aquitard.

Data from the field study show that the surfactant flushing method circulation of 18 pore volumes would require 90 days of pumping at a standard rate of 500 gallons per day. By comparison, it would take many years to clean the same

volume using conventional pump-and-treat methods. Once the free-phase PCE is removed by surfactant flushing, aquifer restoration can be accomplished by circulating water, using a conventional pump-and-treat operation. Results from the pilot scale demonstration at Corpus Christi are expected in March 1993. Preliminary data from surface cores show DNAPLs below detectable limits. For more information call John Fountain at 716-645-3996 at the State University of New York at Buffalo. ▲

THE REG RACK

EPA Directive Updates Ground Water Policy to Include DNAPLs

By Kenneth Lovelace, Office of Solid Waste and Emergency Response

EPA's Office of Solid Waste and Emergency Response (OSWER) has updated a 1989 ground water policy to address nonaqueous phase liquid (NAPL) contaminants, including dense NAPLs (DNAPLs). The policy directive promotes a consistent ground water cleanup approach for both Superfund sites and Resource Conservation and Recovery Act (RCRA) Corrective Action sites. The policy reinforces EPA's commitment to clean up ground water contamination at hazardous

waste sites to the fullest extent possible while acknowledging at the same time that, in some situations, complete ground water restoration may be technically impracticable. The directive builds on previous policies and good science to address special problems associated with NAPL contamination. It recognizes that DNAPLs may be more widespread at hazardous waste sites than previously realized. The presence of NAPLs, especially

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Bioattenuation (from page 1)

spill area were 253 micrograms per liter ($\mu\text{g}/\text{L}$) and 31,400 $\mu\text{g}/\text{L}$, respectively. The concentration of 2,3-dimethylpentane was 23.3 $\mu\text{g}/\text{L}$ in the spill and 1.6 $\mu\text{g}/\text{L}$ at the river bank, 6.9% of the original concentration in the spill area. Based on the attenuation of 2,3-dimethylpentane, the expected concentrations of benzene and toluene due to dilution or sorption would be 17.4 and 2,170 $\mu\text{g}/\text{L}$, respectively; the actual concentrations were 23.3 and 1.69 $\mu\text{g}/\text{L}$.

A pumping test was conducted to measure the hydraulic conductivity of the aquifer. The hydraulic gradient was monitored over time to estimate the direction and velocity of ground water flow. Information on flow was used to predict the average time elapsed since the water sampled in the well clusters left the source area of the plume. The information on time

elapsed and extent of attenuation in ground water was used to calculate bioattenuation rate constants.

Bioattenuation of toluene ranged from 16% to 47% per week, ethylbenzene from 2.2% to 7.7% per week, p-xylene 1.7% to 6.7% per week, m-xylene 1.0% to 2.6% per week and o-xylene 1.1% to 2.8% per week. These results are consistent with those seen in other methanogenic aquifers contaminated with petroleum hydrocarbons. The rate constants for individual compounds at sites at Bemidji, Minnesota, and Traverse City, Michigan, and at the Sleeping Bear Dunes site do not vary more than an order of magnitude. The agreement is remarkable, considering the level of uncertainty introduced into these field scale estimates from variation in ground water flow and changes in plume geometry.

Oxygen consumption, nitrate and sulfate reduction, methane production and iron solubilization were measured

to estimate the extent of bioattenuation of BTEX compounds that could be expected from these processes. Typically, as BTEX compounds are degraded, there is a decrease in oxygen followed by anaerobic degradation supported by nitrate and sulfate. After depletion of nitrate and sulfate, methanogenesis occurs and methane concentrations increase as BTEX compounds are further degraded.

Between the spill and the bank of the river, 42.6 mg/L BTEX compounds were consumed after correction for dilution. Methane that accumulated would account for removal of 39 mg/L of BTEX, nitrate reduction for 14 mg/L, sulfate reduction for 4.2 mg/L, iron reduction for 1.1 mg/L and oxygen respiration for 0.8 mg/L BTEX removed.

The amount of nitrate, sulfate, oxygen and iron reduction and methanogenesis was greater than would be expected from the quantity of BTEX compounds removed from the plume. The actual

electron acceptor demand was slightly greater than the theoretical supply of electrons. Thus, other compounds in the plume, such as trimethylbenzenes and naphthalenes, may have also been biodegraded. The ground water also contained large concentrations of non-volatile total organic carbon, presumably of natural origin. Total organic carbon was reduced from 58 mg/L in the well cluster at the spill to 47 mg/L 30 feet down gradient and 21 mg/L 70 feet down gradient.

Although benzene failed to degrade, benzene degradation has been observed at two other field sites where the plume was longer. The failure of benzene to degrade (after correction for dilution) at the Sleeping Bear site is inconsistent with these other two field studies where benzene was biodegraded. Because the plume at Sleeping Bear was short (less than 100 feet) and the residence time of the

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Directive (from page 2)

DNAPLs, will significantly affect the time and likelihood of achieving ground water cleanup standards.

Ground water contamination is found at more than 70% of Superfund National Priorities List sites and almost 50% of permitted RCRA land disposal facilities. The directive emphasizes the need to determine the likelihood of NAPL contamination - especially DNAPLs - early in the site investigation. Where NAPLs are likely, the nature and extent of contamination should be characterized to determine appropriate remedial actions (both early and long term actions). Early remedial

actions should be used to minimize further migration of dissolved or NAPL contaminants. Early response actions should also include extraction of free-phase NAPLs, whenever possible. Careful ground water monitoring should be included in all cleanup efforts in order to measure effectiveness and to allow for warranted design improvements. Because NAPLs dissolve slowly, they are a potential long term source of significant contamination.

Accumulations of free-phase NAPLs, which are not removed as an early action, should generally be removed during the final remedy, to the extent practicable. The directive envisions NAPL remedial actions as part of a

larger phased approach to allow coordination with later cleanup efforts. Furthermore, because the mass proportion and spatial extent of residual NAPLs are usually much greater than that of free-phase NAPLs, new conventional and innovative technologies should be considered for enhanced recovery of residual NAPLs from the subsurface.

For those sites where hydrogeologic or contaminant characteristics may ultimately make long-term ground water cleanup targets unattainable, EPA reserves the right to issue technical impracticability waivers for National Priority List sites and to modify RCRA permits or enforcement orders. In such cases, EPA will identify alternative remedial

requirements, which will protect human health and the environment and that are appropriate for each site's specific conditions.

For a copy of the full directive, contact the National Technical Information Service at 703-487-4640 and ask for NTIS Publication No. PB92-963358, which is OSWER Directive 9283.1-06 "Considerations in Ground Water Remediation at Superfund Sites and RCRA Facilities - Update." The directive lists the names and phone numbers of contacts at EPA. ▲

EPA's Multi-Faceted Efforts to Improve Ground Water Remediation

EPA has several efforts underway to enhance ground water remediation. The Robert S. Kerr Environmental Research Laboratory (RSKERL) will evaluate innovative technologies related to ground water remediation, including technologies with the potential to remove nonaqueous phase liquids (NAPLs) from the subsurface. The Office of Solid Waste and Emergency Response (OSWER) will work closely with RSKERL to develop fact sheets and guidance on site characterization, remediation and performance monitoring for sites contaminated with dense nonaqueous phase liquids (DNAPLs). Additionally, OSWER has initiated a survey to determine the potential number of existing Superfund

sites where DNAPL contamination is likely. This survey, to be completed by March, 1993, will help to assess the extent of this problem for the Superfund program.

OSWER is also supporting a National Research Council (NRC) study, "Alternatives for Reducing Risk from Existing Ground Water Contamination", that will assess the current state-of-the-science concerning ground water remediation and look at alternative approaches for addressing ground water contamination. The NRC study is scheduled for completion by September, 1993.

Additionally, OSWER recently inventoried alternatives to pump-and-treat technologies. For more information on that

study, see the September, 1992, issue of *Ground Water Currents* (Document No. EPA/542/N-92/005).

A technical work group within OSWER is developing further guidance concerning waivers due to technical impracticability for ground water. Another work group, led by the Office of Enforcement, is

developing model consent decree language addressing a technical impracticability waiver process for implemented pump-and-treat remedies at Superfund sites.

Look for news of the availability of products from all of these efforts in future issues of *Ground Water Currents*. ▲

Bioattenuation (from page 3)

ground water was short (5 to 35 weeks), there may not have been adequate opportunity for anaerobic degradation of benzene.

For more information, call John Wilson at EPA's Robert S. Kerr Environmental Research Laboratory at 405-332-8800. ▲

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