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EPA Ground Water Currents

Developments in innovative ground water treatment

In Situ Degradation of Halogenated Organics by Permeable Reaction Wall

By Stephanie F. O'Hannesin and Robert W. Gillham, Waterloo Centre for Groundwater Research, Canada

The Waterloo Centre for Groundwater Research in Ontario, Canada, consistently is getting good results in the development of a permeable reaction wall that degrades halogenated organic compounds *in situ*. The wall consists of a porous medium containing an iron-based catalyst that degrades the contaminants as they pass through the wall. This passive method of remediation thus prevents further downstream migration of contamination and degrades contaminants many times faster than the natural rate of degradation. Because the degradation occurs in situ, the contaminants are not transferred from the water to a different medium, which is the case with many pump-and-treat methods. The cost of the permeable wall system ought to be much lower than conventional pump-and-treat systems. Once the catalyst is installed, it simply remains in place, unattended, continuing to purify water year after year, with minimal disturbance to the surface environment. The only cost is for some continued monitoring.

First, studies at the University of Waterloo laboratories showed that iron degradation rates were three to six orders of magnitude greater than those reported in the literature for abiotic and biotic degradation. Next, their bench scale laboratory batch experiments and treatability column experiments, conducted with sand aquifer material, confirmed degradation of carbon tetrachloride, chloroform (TCM), trichloroethene (TCE) and tetrachloroethene (PCE).

A pilot test at the Canadian Bases Borden site further confirmed the effectiveness of the permeable wall. The source of the plume was located about 4 meters below ground surface and 1 meter below the water table. The plume was about 2 meters wide and 1 meter thick, with maximum concentrations along the axis of about 250,000 and 43,000 micrograms per liter (μg/L) for TCE and PCE, respectively. The permeable wall was installed about 5 meters downgradient from the source.

Using sealable-joint sheet piling, a rectangular cell was constructed on the surface and driven to a depth of 9.7 meters. The cell was dewatered; and, the native sand was replaced by the reactive material, consisting of 22% by weight iron grindings and 78% by weight concrete sand. The concrete sand, which is coarser than the native materials, was used to insure that the wall would be more permeable than the surrounding sand. After the reactive mixture was installed, the sheet piling was removed, allowing the contaminant plume to pass through the wall. The permeable wall dimensions were 5.5 meters long, 1.6 meters thick; and, it was situated 2.2 meters deep, which is 1.0 meter below the water table. Rows of multilevel monitoring wells were located 0.5 meters upgradient of the wall, at distances of 0.5 and 1.0 meters into the wall and 0.5 meters downgradient of the wall, for a total of 348 sampling points. The plume and its migration through the wall were monitored for over 500 days. Preliminary results indicate that the TCE concentration has been reduced by 95% and PCE by 91%. Mass balance studies confirm an increase in chloride concentration downstream of the wall that is consistent with the quantity of TCE and PCE that has been degraded. Field testing has also been carried out to determine the presence of breakdown products. To date, only trace amounts of dichlorethene (DCE) have been detected; but, no vinyl chloride has been detected. Further research is currently in progress to assess remaining

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This Month in Currents

This month's **Currents** *features news and events from our friends North of the Border.*

Canada's GASReP Promotes Innovative Petroleum Hydrocarbon Research

The Canadian government's Groundwater and Soil Remediation Program (GASReP) promotes research on innovative ways to clean up ground water and soil contaminated with petroleum hydrocarbons. Several Canadian provincial and federal agencies, Canadian and U.S. petroleum industry associations and the U.S. Federal government take part in the program. The group, established as a government/industry venture in 1989, focuses on basic/applied research and/or technology development. Industry partners and those in other government programs are encouraged to carry GASReP's research findings into the final stage of technology demonstration. Additionally, GASReP technology transfer sessions help to enhance knowledge in the field of remediation technologies. These sessions are comprised of an annual GASReP symposium, workshops of GASReP members and other conferences or symposia that GASReP cosponsors.

GASReP has an annual research grants program. GASReP allocates seed money of up to $50,000 per project per year to co-sponsor research with other partners. Under Canadian government guidelines for intellectual property, the government will retain patent rights. However, to ensure that R&D results move into the private sector, contractors will have the first rights to license the technology. GASReP solicits proposals through a two-step process. First, a call for Letters of Interest (short proposal) is issued. The GASReP Technical Committee reviews and ranks the Letters and notifies eligible candidates. The candidates then submit detailed proposals. To help the candidates prepare their proposals, a document entitled *Guidelines for Proposals* is available from GASReP. GASReP evaluates the proposals; and, its Technical Committee makes the final decisions. Finally, GASReP sets up contracts for work after co-sponsors sign agreements for their share of the costs. The research described in the article, "Canada Evaluates In Situ Bioremediation of BTEX in Ground Water" on page 3 of this issue of *Ground Water Currents*, was partially funded by GASReP. For further information on the grants program, call Alex Lye at GASReP (416-336-6438).

GASReP will co-sponsor a symposium in Quebec City, September 8-10, 1993, where GASReP members summarize their research on ground water and soil remediation. Papers will be presented on topics such as bioremediation, excavation and treatment, pumping and treatment, off-gas treatment and program initiatives. Vendors are invited to exhibit technical posters. Workshops on topics suggested by attendees will be held after hours. Other co-sponsors include DESRT (the Canadian government's Development and Demonstration of Site Remediation Technology), the Biotechnology Research Institute (part of the National Research Council of Canada), the Quebec Ministry of the Environment and the St. Lawrence Centre. The North Atlantic Treaty Organization's Committee on Challenges of Modem Society will provide papers and posters on some of their remediation pilot projects. To obtain information about this year's meeting, call 416-336-6438. To obtain a copy of the Proceedings from last year's symposium ("Proceedings of the Second Annual GASReP/DESRT Symposium on Groundwater and Soil Remediation," March 25-26, 1992, Vancouver, British Columbia), contact INFO-TECH, Suite 200, 1015 Centre Street North, Calgary, Alberta, Canada T2E 2P8 (telephone: 403-276-7881); the cost for the Proceedings is $65.00 which includes shipping.

GASReP maintains a mailing list of technology vendors, consultants and other interested parties. If you would like to be added to these lists, please send relevant information to: GASReP Manager, Burlington Environmental Technology Office, Canada Centre for Inland Waters, P.O. Box 5050,867 Lakeshore Road, Burlington, Ontario, Canada, L7R 4A6. The telephone number is: 416-336-6438. The FAX number is: 416-336-4858.

Permeable Wall

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questions, such as the long-term integrity and effectiveness of the metal in a range of hydrogeochemical environments, the reaction mechanism and the formation of toxic breakdown products and the most effective means of pH control.

Depending on the installation method utilized, the permeable wall can be placed to depths of 100 feet or more. Application of this technology for above ground treatment is also being developed.

The Waterloo Centre has patents pending on the technology and is linking up with firms to market it in both Canada and the United States. For more information, call Stephanie O'Hannesin (519-885-1211 ex3159) at the Waterloo Centre for Groundwater Research, University of Waterloo, Waterloo, Ontario.

DEMO RESULTS

Chemical Oxidation Destroys Organics in Water

By Norma Lewis, Risk Reduction Engineering Laboratory

The perox-pure™ chemical oxidation treatment technology, developed by Peroxidation Systems, Inc., to destroy dissolved organic contaminants in water, has been demonstrated through EPA's Superfund Innovative Technology Evaluation (SITE) program. The technology uses ultraviolet (UV) radiation and hydrogen peroxide to oxidize organic compounds present in water at parts per million (ppm) levels. The technology does not produce air emissions or generate residue, sludge or spent media that would require further processing, handling or disposal. Ideally, end products are water, carbon dioxide, halides and, in some cases, organic acids. Medium pressure mercury vapor lamps generate the UV radiation. The principal oxidants in the system, hydroxyl radicals, are produced by direct photolysis of hydrogen peroxide at UV wavelengths.

The perox-pure™ system consists of portable, skid-mounted components: a chemical oxidation unit, a hydrogen peroxide feed tank, an acid feed tank, a base feed tank, a UV lamp drive and a control panel. The oxidation unit has a total volume of 15 gallons and contains six reactors in series with one 5-kilowatt UV lamp in each reactor. The UV lamp is mounted inside a UV-transmissive quartz tube in the center of each reactor so that water flows through the space between the reactor walls and the quartz tube.

About 40,000 gallons of ground water contaminated with volatile organic compounds (VOCs) were treated during the demonstration conducted at Lawrence Livermore National Laboratory Site 300 near Tracy, California. The principal ground water contaminants were trichloroethene (TCE) and tetrachloroethene (PCE), which were present at concentrations of about 1,000 and 100 micrograms per liter (μg/L), respectively. The ground water was spiked with 300 μg/L each of chloroform, 1,1-dichloroethane (DCA) and 1,1,1-trichloroethane (TCA). Hydrogen peroxide was added to the contaminated water before it entered the first reactor; however, a splitter could be used to add hydrogen peroxide before any of the six reactors within the oxidation unit. In some applications, acid was added to lower the influent pH and shift the carbonate-bicarbonate equilibrium to carbonic acid. This equilibrium is important because carbonate and bicarbonate ions will scavenge hydroxyl radicals. After chemical injections, the contaminated water flowed through a static mixer and entered the oxidation unit. Water then flowed through the six UV reactors, which were separated by baffles to direct water flow. Treated water exited the oxidation unit through a pipe equipped with a temperature gauge, an effluent sample port and a base injection point. Basic compounds may be added to the treated water to adjust the pH to meet discharge requirements.

Circular wipers attached to the quartz tubes housing the UV lamps were used periodically to remove any solids that accumulated on the tubes. Solids may accumulate as a result of metals oxidized by the treatment system (such as iron and manganese), water hardness or suspended solids that may precipitate out of the water. Accumulated solids could eventually coat the tubes, thus reducing treatment efficiency.

During the demonstration, removal efficiencies for TCE

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NEW FOR THE BOOKSHELF

Canada Evaluates *In Situ* Bioremediation in Ground Water

The Waterloo Centre for Groundwater Research at the University of Waterloo in Canada has evaluated six approaches to *in situ* bioremediation of benzene, toluene, ethylbenzene and xylene (BTEX) in ground water. They are: passive bioremediation, oxygen addition, acclimated microorganisms, the vacuum-vaporizer-well, land surface application and subsurface volatilization and ventilation (SVVS™). The evaluations consisted of a review of the literature and constitute an important first research step in our understanding of these technologies, pending further research in laboratories and in real life circumstances that deal with a host of varying site conditions. The Waterloo Centre's evaluation findings are presented in a report, *Reviews of Six Technologies for In Situ Bioremediation of Dissolved BTEX in Groundwater.*

The report highlights principles and limitations of each approach and identifies the site information that should be gathered. Case studies illustrate how some of the techniques are applied and emphasize the need for thorough demonstrations. A summary of the report's findings follows.

Passive Remediation. The study found that passive remediation (remediation that relies on natural processes) takes longer than active approaches. Baseline data on passive bioremediation will provide a benchmark for measuring the effectiveness of active approaches.

Oxygen Addition. Oxygen addition enhances biotransformation of BTEX. A system that can deliver oxygen where it is needed in the subsurface influences the outcome. While natural dispersive processes promote transformation by

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Evaluations

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mixing oxygenated and contaminated water, some geochemical reactions may compete for the oxygen and hinder cleanup.

Acclimated Microorganisms. Where a population of indigenous microorganisms cannot perform desired biotransformations, adding acclimated species provides a desirable option. This method can be ineffective if the introduced microorganisms die or are not delivered to the contaminated area.

Vacuum-Vaporizer-Well. The vacuum-vaporizer-well technique incorporates air stripping and *in situ* biorestoration below the surface. If physical conditions at a site restrict ground water flow near this treatment well, or oxygenation of the water causes adverse chemical interactions, remediation will be limited.

Land Surface Application. Land surface application involves pumping contaminated ground water to the surface, then trickling it through relatively well-drained soils. This technique can economically treat large amounts of ground water contaminated with low levels of BTEX. Despite its benefit, the system arouses political and environmental sensitivities because it introduces contaminated water into clean soil and may release volatiles to the atmosphere.

SVVS.™ By combining air sparging to strip volatile contaminants from ground water, and vacuum extraction to remove contaminant vapors, the SVVS removes dissolved BTEX from ground water. While this approach works well for relatively shallow water table aquifers, treatment is restricted to water in a small area near the well.

A copy of the Waterloo report can be obtained by contacting the GASReP Manager at 416-336-6438

[Editor's Note: This article is based primarily on excerpts from GASReP PRESSC, a newsletter on Environment Canada's Groundwater and Soil Remediation program.]

Chemical Oxidation

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and PCE were greater than 99.7% and 97.1%, respectively. Removal efficiencies for chloroform, DCA and TCA were 93.1%, 98.3% and 81.8%, respectively. The treatment system effluent met California drinking water action levels and Federal drinking water maximum contaminant levels for TCE, PCE, chloroform, DCA and TCA at the 95% confidence level. The treated effluent, however, did not pass bioassay tests for acute toxicity to freshwater organisms.

The perox-pure™ technology has been used to treat landfill leachate, ground water and industrial wastewater containing a variety of organic VOCs, including chlorinated solvents, pesticides, polynuclear aromatic hydrocarbons and petroleum hydrocarbons. When contaminant concentrations are too high for the system to handle alone (about 500 milligrams per liter), the system can be combined with other treatment technologies.

For more information, call Norma Lewis of EPA's Risk Reduction Engineering Laboratory at 513-569-7665. The Applications Analysis Report and the Technology Evaluation Report will be available in the Fall of 1993.

To order additional copies of *Ground Water Currents,* or to be included on the permanent mailing list, send a fax request to the National Center for Environmental Publications and Information (NCEPI) at 513-891-6685, or send a mail request to NCEPI, 11029 Kenwood Road, Building 5, Cincinnati, OH 45242. Please refer to the document number on the cover of the issue if available.

Ground Water Currents welcomes readers' comments and contributions. Address correspondence to:
Managing Editor, *Ground Water Currents* (OS-110W), U.S. Environmental Protection Agency,
401 M Street S.W., Washington. DC 20460.

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