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EPA Ground Water Currents

Developments in innovative ground water treatment

Tree Buffers Protect Shallow Ground Water at Contaminated Sites

By L.A. Licht and J.L. Schnoor, University of Iowa

Researchers at the Great Plains/Rocky Mountain Hazardous Substances Research Center (HSRC) are confirming that vegetation—specifically poplar trees (*Populus spp.*)—can help keep toxic herbicides, pesticides and fertilizers out of rivers, streams, creeks and ground water. In addition to agricultural pesticides and nitrate removal, the vegetation is being studied at Superfund sites with other organic contaminants and metals. Trees serve to decrease vertical migration of contaminants to, and in, shallow ground water.

At an agricultural test site on an Iowa farm, a poplar crop, planted by a University of Iowa research team, was found to significantly reduce nitrate levels in the ground water. The trees were planted along a stream bank between a corn field and the stream.

One objective of the project was to reduce the nitrate-nitrogen that was leaching out of fertilized fields into surface water. The test buffer clearly met this objective. In 1990, when the trees were three years old, researchers recorded the average nitrate content of ground water leaving the corn field at 150 milligrams per liter (mg/L), more than three times EPA's permissible limit of 45 mg/L for nitrate in drinking water. In the ground water in the midst of the trees between the field and the stream, the readings were 8 mg/L. Along the creek bank, the nitrate level in the ground water had dropped to only 3 mg/L.

Poplar trees were chosen because they consume such large amounts of nitrogen. The trees take up soluble inorganic nitrogen or ammonium-nitrogen through their roots, converting nitrates into protein and nitrogen gas. After five growing seasons, the average tree contains 33 grams of organic nitrogen in its stem. On land planted with 11,000 trees per hectare, this amounts to 363 kilograms of nitrogen per hectare. The researchers calculated that this means that the trees planted on a hectare of land have transpired, and therefore bioremediated 8.07 million liters of water.

Licht and Schnoor have used poplar trees in a variety of toxicity studies in both controlled chamber and field experiments. In chamber experiments, atrazine labeled with carbon-14 was transformed into CO_2 both in soil and through plant uptake and metabolism. In field studies, the researchers observed that deep-rooted poplars slowed the migration of volatile organic chemicals.

Trees can serve a variety of other functions at a polluted site. They can serve as a wildlife habitat, as a wind screen, as a filter strip to trap sediment and prevent erosion and as a renewable resource that can be harvested for products such as fuel and lumber. At the Iowa farm test site, a second objective was to produce a cash crop, a strategy likely to increase consumer acceptance of the technology, since farmers would be asked to give up land that would normally be planted in crops. Poplar wood can be converted into plywood, lumber or clean-burning wood pellets. Licht has calculated that farmers could grow the equivalent of 9,250 liters of fuel per hectare of poplars per year.

For more information, call L. A. Licht (319–335–5050) or J. L. Schnoor (319–335–5649) at the University of Iowa. The Great Plains/Rocky Mountain HSRC also has several initiatives involving the use of vegetation in bioremediation; for more information, call the HSRC's Director, Larry Erickson (913–532–6519).

This Month in Currents

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Innovative Oxidation Technologies

By Mark Zappi, U.S. Army Corp of Engineers' Waterways Experiment Station

Advanced oxidation processes (AOPs) are ground water remediation techniques that use powerful chemical oxidizers under catalyzing conditions to produce hydroxyl radicals which in turn can destroy a wide variety of organic compounds. The U.S. Army Corps of Engineers' Waterways Experiment Station (WES) has been evaluating both traditional and non-traditional AOPs. This article addresses two non-traditional AOPs—peroxone and ultrasonically (sonolysis) catalyzed oxidation—for treatment of trinitrotoluene (TNT) contaminated ground water. In addition to TNT remediation, peroxone has already been used successfully for treatment of a wide variety of organic contaminants and is being evaluated for additional organic contaminants.

The results of these studies indicate much promise for treating TNT contaminated ground water at a potential cost savings over more traditional AOPs. Although ultrasonically catalyzed oxidation is still in the early stages of development, we do know that peroxone oxidation costs are estimated to range from $0.10 to $1.00 per thousand gallons treated. This is significantly lower than traditional UV based AOP costs which typically range from $1.00 to $5.00 per thousand gallons treated.

Until recently peroxone had been limited to drinking water treatment. However, bench and pilot studies indicate a high potential for utilization of peroxone for treatment of contaminated ground water. Peroxone involves the generation of hydroxyl radicals through reaction of ozone with hydrogen peroxide. Optimal stoichiometric ratios of hydrogen peroxide to ozone are in the 0.25 to 1.5 range, indicating a low dosage of hydrogen peroxide to ozone. Although peroxone have a slower TNT removal kinetics (four times slower) than traditional AOPs, removal is effective and at potentially much lower cost. For the WES study the test influent was a 100 ug/l TNT contaminated ground water. A 10 mg/L hydrogen peroxide dose in the peroxone system indicated potential to remove all of the TNT within 30 minutes of treatment. Subsequent studies indicated that a 100 mg/L dose was able to achieve similar treatment within less than 20 minutes of batch treatment. The addition of ultrasound to the peroxone system substantially enhanced the rate of TNT removal at both the 20 and 40 watt/liter dose.

Ultrasound are soundwaves produced from 20 khz to 100 khz frequency range by electrical devices. Ultrasound is commonly used for cleaning small objects where extremely clean conditions are required in hard to reach areas. Ultrasound has also been used to catalyze slow chemical reactions. Using a directional ultrasonic probe along with one liter, glass reactions, WES has evaluated the feasibility of using ultrasound to increase the reaction rate of TNT during ozonation as well as peroxone oxidation. Much like the peroxone data, as the level of ultrasonic power into the ozonation system is increased, so does the overall TNT oxidation rate. Mechanisms responsible for increasing reaction rates are improved mass transfer, production of hydroxyl radicals and localized pockets of high pressure and temperatures. Because of the paucity of cost information and the absence of large scale ultrasonic chemical reactors to evaluate pilot scale ultrasonic catalyzed oxidation, WES has initiated a collaborative research and development agreement (CRADA) effort with a manufacturer of large scale ultrasonic systems to address these issues.

WES has several other ongoing research activities for both traditional and non-traditional AOPs. As knowledge of the mechanisms involved in contaminant destruction are better understood through current WES research efforts, then treatment costs associated with UV based systems are expected to decrease while the range of applications increases. Of significant note is the definition of oxidation pathways of explosives compounds (TNT, RDX and HMX) during AOP treatment which is currently under investigation by WES in collaboration with Howard University and the University of North Carolina, Chapel Hill. WES is running **(See AOPs, page 4)**

A Word About WES

The U.S. Army Corp of Engineers' Waterways Experiment Station (WES), through its Hazardous Waste Research Center, offers a full service testing and evaluation facility with safety equipment, a high-bay testing area and a fully equipped analytical lab including GC/MS. In addition to extensive analytical equipment and facilities, WES has technical personnel with research experience in a variety of hazardous waste treatment technology types. WES has been involved in best demonstrated available technology development work for the EPA and has conducted treatability testing at Federal facility sites.

In addition, WES is capable of conducting and assisting in treatability testing for other Federal agencies on a cost reimbursement basis and is currently investigating the possibility of government/industry cost sharing for testing and evaluation of hazardous waste treatment technologies. WES has a Resource Conservation and Recovery Act Part B permit for testing hazardous waste treatment technologies.

For more information, call Norman Francinques, Jr. at 601–634–3416.

Canadian Field Study Assesses Biodegradation of PCE

By Alex Lye, GASReP, Environment Canada

Approximately 15 years ago, at a storage and transfer facility in North Toronto, Ontario, releases of tetrachloroethene (PCE) occurred during the coupling and uncoupling of railway tanker cars transporting this chemical. Recent studies revealed that free and dissolved PCE was present in the ground water below the facility but that the PCE was being dechlorinated to ethene and ethane. Laboratory microcosm studies, conducted with aseptically retrieved aquifer sediments from the PCE source area, confirmed that methanol stimulated the anaerobic dechlorination of PCE to ethene. Additionally, the presence of methanol, which was metabolizing to acetate, led to the conclusion that acetogenic microorganisms (or other hydrogen consuming microorganisms) were involved in the biotransformation of PCE to ethene at the site. A field study was conducted to evaluate the specific conditions that contributed to the natural *in situ* PCE biodegradation at this site and to determine if either unenhanced or enhanced anaerobic biodegradation could successfully remediate the site. The field study was financed by Environment Canada, the Ontario Ministry of Environment and Energy, ICI Canada, Celanese Canada, AT&T and General Electric Company.

To evaluate the specific conditions contributing to the *in situ* PCE biodegradation, five *in situ* microcosms (ISMs) were installed in the subsurface at the site, at a depth of approximately seven meters. Each ISM consists of a cylindrical stainless steel test chamber and a detachable equipment chamber that contains and protects the sampling and injection equipment. The test chamber is open at the bottom and separated from the equipment chamber by a set of coarse and fine mesh stainless steel screens. The screens allow even flow of injected test solutions into the test chamber through the injection equipment during experiments. Ground water in the ISM can be sampled through the tip of a stainless steel spike which protrudes approximately 125 centimeters (cm) into the test chamber of the ISM.

Two of the five ISMs were installed in aquifer materials in which high concentrations of PCE and methanol had been detected. The remaining three ISMs were installed downgradient of the PCE and methanol source area in anaerobic aquifer materials which contained trace concentrations of PCE breakdown products of *cis*-1,2-dichloroethene (*cis*-1,2-DCE), vinyl chloride (VC) and ethene, but no detectable PCE, trichloroethene (TCE), methanol or acetate. Two of the ISMs in each study location were used for anaerobic treatments and received amendments of methanol (1,500 mg/L) in addition to PCE [10 to 130 micromoles per liter (μM/L)] and bromide (100 mg/L as a tracer). The remaining ISM in the downgradient location would serve as a live control; so, only bromide and PCE—but no methanol—were added to this ISM. Any PCE loss in this ISM would be due to sorbtion. PCE biotransformation in the four anaerobic and single unamended control ISMs was monitored at given times over a period of up to 29 days.

It was expected that a portion of the injected PCE would sorb to the soil matrix in the ISMs; and, the study calculated the amount of soil sorption in determining the mass loss of PCE by biodegradation. The observed mass loss in the unamended control ISM was approximately 60%. PCE mass loss in the four anaerobic treatment ISMs averaged approximately 90%. In the amended ISMs, methanol depletion was accompanied with the production of acetate and methane and an increase in chloride concentrations. These changes were not observed in the control ISM. Further, the concentration of PCE continued to decrease as long as methanol or acetate was present. These results suggest that a continuous supply of methanol (or suitable alternate electron donor) would be required to completely dechlorinate all of the PCE mass to ethene or carbon dioxide (CO_2) at this site.

The production of TCE, *cis*-1,2-DCE and VC was observed in several of the anaerobic ISMs. However, these dechlorination products were only detected at trace concentrations; and VC did not accumulate in any of the anaerobic ISMs during the study, thus confirming that PCE can be biotransformed at this site without the accumulation of VC. Ethene and ethane were detected at low concentrations in the ISMs but did not accumulate during the study. CO_2 was not quantified, but was assumed to be the end product based on the results of similar studies (Cox and Major, 1993; Vogel and McCarty, 1985).

This field study demonstrated that the depletion of methanol in the anaerobic ISMs was accompanied by the production of acetate and methane in several of the anaerobic ISMs. These results provide evidence that a consortia of acetogenic (acetate-producing) and methanogenic microorganisms were likely involved in the observed PCE mass loss. Methanol was likely converted to acetate and an intermediate pool of hydrogen by the acetogenic microorganisms in the anaerobic ISMs. This hydrogen pool then served as a supply of electron donors for the rapid dechlorination of PCE and its daughter products.

For more information, call Alex Lye, Manager, GASReP, Environment Canada at 905–336–6438.

NEW FOR THE BOOK SHELF

Complex Mixtures

The occurrence of organic chemicals in soil and ground water has become an issue of great interest and importance. Research on the transport and fate of organic contaminants in subsurface environments has expanded greatly in recent years. Much of this research has been focused on dissolved constituents in aqueous systems. However, the behavior of "complex mixtures" is beginning to receive increased attention. By complex mixture we mean any system other than the simple system of water containing a single solute. Examples of pertinent problems involving complex mixtures include the transport of oxygenated gasoline in the subsurface, the dissolution of diesel fuel and coal-tar and the use of chemical agents such as surfactants or solvents to enhance the removal of contaminants by pump-and-treat remediation.

M. L. Brusseau of the University of Arizona has prepared an "Environmental Research Brief" for EPA on complex mixtures and ground water quality. As discussed in the brief, these mixtures may affect contaminant behavior through a variety of mechanisms. Because many c mechanisms are not we derstood, approaches for u ing with complex mixtures in the subsurface often involve direct application or untested extrapolation of knowledge derived from relatively simple aqueous systems.

The primary purpose of Brusseau's brief is to identify and discuss, in a generic sense, some of the important processes which must be considered when dealing with complex mixtures in the subsurface, and to illustrate how these may impact ground water quality. From the discussion, it is apparent that complex mixtures may play a role in ground water reclamation as well as degradation of ground water quality. Equally apparent, however, is the need for improved scientific understanding of the process- ssociated with the trans- of complex mixtures and the influence that chemical mixtures have on the behavior of specific contaminants.

A copy of the "Environmental Research Brief; Complex Mixtures and Groundwater Quality" can be ordered from EPA's Center for Environmental Research Information (CERI) at 513–569–7562. When ordering, please refer to the Document Number: EPA/600/S-93/004.

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three pilot studies on three contaminated ground water sites at Rocky Mountain Arsenal in Colorado with a WES designed and constructed Peroxone Oxidation Pilot System (POPS). POPS has a 0.5 to 15 gallons per minute flow rate and is completely mobile. WES is also developing other non-traditional UV based AOPs, such as semiconductor catalyzed photolysis and second generation hydrogen peroxide/UV based AOPs.

Call Mark Zappi at 601–634–2856 for more information on WES's research on both non-traditional and traditional AOPs.

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 45242–0419. Please refer to the document number on the cover of the issue if available.

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