IN SITU BIORESTORATION - EFFECTS OF NUTRIENT ADDITION ON AQUIFER PERMEABILITY

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INTRODUCTION

Spills of industrial wastes, leaks from underground storage tanks and improper disposal of industrial, agricultural, and municipal waters and wastes can lead to contamination of important groundwater systems. These systems can constitute the sole supply of potable water for many communities and must be protected from contamination. In the state of Georgia, for example, subsurface injection of wastewater sludges is used in many rural areas where the majority of potable water comes from groundwater sources (Troxler et al., 1981). This and other types of contamination could affect the water supplies of 1,310,000 Georgians using self-supplied groundwater sources (USGS, 1983).

The remediation techniques available for contaminated groundwater sites are numerous. They range from physical removal of contaminated material, followed by subsequent treatment at the surface by physical, chemical, and biological means; to physical containment and in situ chemical or biological restoration.

In situ bio restoration has the potential to be a cost-effective and environmentally-sound technique for reclaiming contaminated groundwaters. Adsorbed organic and inorganic pollutants can be degraded using biologically induced concentration gradients. In solution these contaminants are susceptible to microbial attack and are degraded completely or transformed to more oxidizable compounds. This can occur without expensive removal of contaminated soil and water, costly above-ground treatment systems, or the lengthy time periods often encountered when recirculating treated water (Wilson et al., 1986).

Recent advances in genetic engineering have made commonly-used organic pesticides, such as 2,4,5-T and 2,4-D, microbially degradable (Ghosal et al., 1985) and enzymatic attack and dechlorination of polychlorinated biphenyls (PCB's) are also possible (Unterman et al., 1987). Therefore, where in situ treatment was once considered infeasible, state-of-the-art technology may now enhance its potential for effective full-scale utilization.

Among the factors which may minimize the use and effectiveness of in situ bio restoration is the transport and delivery of essential nutrients and terminal electron acceptors, such as molecular oxygen or nitrate-nitrogen, to in situ microorganisms. This may, for example, be a result of low or non homogeneous aquifer permeability; enhanced microbial activity, where clogging within the formation or around injection wells has been observed; and foaming caused by microbial exopolysaccharides (Wetzel et al., 1985; Raymond et al., 1976).

The on-going focus of this study is to examine effects of microbial stimulation, through addition of essential nutrients and nitrate-nitrogen as a final electron acceptor, on flow characteristics and permeability of groundwater systems during in situ biological treatment. Initial studies on the effects of adding nutrients and a final electron acceptor in the absence of cell growth are presented in this paper. It is proposed that a more thorough understanding of this reclamation option will better improve its effectiveness in contaminant removal and increase its viability as an aquifer restoration option.

MATERIALS AND METHODS

Aquifer permeability, measured as hydraulic conductivity, can be monitored in triaxial permeameters, where a saturated soil sample enclosed in an elastic sleeve is submitted to a constant confining stress from pressurized water. The flow-through liquid or permeant is pressurized to equal or lower stresses so that conditions at any aquifer depth can be simulated. A schematic diagram of a triaxial permeameter being used to study in situ aquifer bio restoration is shown in Figure 1.

Stainless steel plates and acrylic chamber walls are connected by nonreactive flexible tubing. Pressures are maintained using nitrogen gas and a positive displacement pump and liquid-level controller are used to maintain continuous flow with a constant hydraulic gradient.

Hydraulic conductivity can be measured continuously from changes in volume over long periods of time, e.g., 3 to 24 hours, or instantaneously by passing volumes of permeant from influent to effluent site glasses. This first technique allows for measurements without increasing flow, while the latter can be used
when permeability has declined sufficiently to inhibit flow.

Soil material obtained by USEPA-Athens from Watkinsville, Georgia was used in the permeameter and had a cation exchange capacity, CEC, of 3 meq/100 g and organic carbon content of 0.9%. Approximately 275 g (dry mass) was used for this study and confined to a cell pressure of 221 kPa (32 psi). Permeant was pressurized to 155 kPa (22.5 psi). The composition of the permeant was varied in a sequential fashion as various amendments were added to dechlorinated deoxygenated tap water. The pH was adjusted to 7.2 ± 0.2. The concentrations of the amendments are listed in Table 1, along with time of addition.

### TABLE 1. NUTRIENT AMENDMENTS IN GROUNDWATER PERMEANT

<table>
<thead>
<tr>
<th>Compound</th>
<th>Conc. mg/L</th>
<th>Day added</th>
</tr>
</thead>
<tbody>
<tr>
<td>KH₂PO₄</td>
<td>15 as P</td>
<td>47</td>
</tr>
<tr>
<td>NaNO₃</td>
<td>25 as NO₃⁻</td>
<td>62</td>
</tr>
<tr>
<td>NH₄Cl</td>
<td>15 as N</td>
<td>90</td>
</tr>
</tbody>
</table>

For tracer analyses, lithium chloride was initially used at 5 mg/L as Li⁺. These were run after all nutrients had been added and after an organic contaminant was introduced and then removed from the permeant. However, once NO₃⁻ was shown to pass completely through the system, its application as an anionic tracer was utilized.

2,4-dichlorophenol (DCP) was used as the organic contaminant. DCP is an organic acid listed as a priority pollutant and can be biotically and abiotically formed from degradation of phenoxy herbicides (Krijgsheld and van der Gen, 1986).

**RESULTS AND DISCUSSION**

For the first 200 days of the study, the average flow through the sample was 34.5 mL/hr. Hydraulic conductivity, as shown in Figure 2, averaged $5.7 \times 10^{-3}$ cm/sec (16.2 ft/d). The hydraulic conductivity, which was normalized to 20 °C to account for viscosity fluctuations due to room temperature changes (22 ± 0.5 °C), changed relatively little over this period. However, a slight decline over the 200 days occurred from an initial high of $6 - 7 \times 10^{-3}$ to a low of $3 \times 10^{-3}$ cm/sec. It is possible that cationic exchange between amendments and soil, long-term soil consolidation, and abiotic reactions resulted in these minor changes in conductivity.

**Effects of Amendments**

Prior to nutrient addition (0 to 47 days), hydraulic conductivity was stable at an average value of $7.7 \times 10^{-3}$ cm/sec. Once sequential addition ensued, a declining trend developed starting with the first amendment, KH₂PO₄. Contributions by NaNO₃ and NH₄Cl to this effect cannot be measured due to detection limits of the permeameter and time required.

Results from a tracer study are shown in Figures 3 and 4. NO₃⁻ appeared in the effluent nearly 1.5 hours before Li⁺, indicating a possible holdup of the cation. From a normalized time distribution in Figure 4, residence times for each were 2 and 4.8 hours, respectively, showing a relative retardation of lithium due to cation exchange and possibly anionic exclusion of nitrate.

Input of DCP began on day 109 and continued at a concentration 13.5 mg/L for 40 days. DCP was detected in the effluent in a few hours, after which effluent concentrations slowly approached influent levels. Slow, nonlinear adsorption contributed to this effect, since microbial activity did not take place.

The hydraulic conductivity remained near the levels prior to DCP addition, indicating no
significant interactions occurred. This could be due to the low concentration used in this respect. Adsorption accounted for 67 mg of the roughly 450 mg that flowed through the reactor giving an adsorbed DCP concentration of 0.24 mg/g.

CONCLUSIONS

To this point in our studies, amendment introduction for in situ biorestoration caused only slight changes in soil permeability. At most, a steady, slow decrease has resulted, possibly from cation exchange and abiotic reactions. For typical values of CEC associated with soils or aquifer materials (e.g., ≤ 50 - 100 meq/100 g), cation exchange can be insignificant. Any abiotic reactions taking place are likely the result of amendment interaction with soil constituents. Therefore, the impact of this phenomenon will be site specific, based on soil chemistry, types and amounts of amendments used, and conditions induced by in situ treatment (e.g., ORP or pH).

After 200 days of continuous flow under the operating conditions used, the effects of nutrient supplementation on permeability were minor. Hydraulic conductivity remained above 10⁻³ cm/sec and was considered to be sufficient for in situ biological treatment. Therefore, essential amendments could be transported to contaminated regions of an aquifer with the intrinsic properties simulated.

Current Research

For efficient use of in situ biological treatment, delivery of the necessary nutrients and electron acceptor must proceed unimpeded. Therefore, future and on-going study is focused on direct effects of microbial growth. This can be the result of cell mass accumulating on solid surfaces; blockage associated with extracellular reactions; and formation of gases during metabolic processes.

At this writing, an enriched culture has been adapted to phenol under denitrifying conditions and phenol uptake is being monitored. Stimulation of microbial growth in a phenol-contaminated aquifer is to be studied.

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LITERATURE CITED


