Enhanced bioremediation of trichloroethene contaminated by a biobarrier system

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Abstract: The industrial solvent trichloroethylene (TCE) is among the most ubiquitous chlorinated compounds found in groundwater contamination. The objective of this study was to develop a barrier system, which includes a peat (used as the primary substrates) layer to enhance the aerobic cometabolism of TCE in situ. A laboratory-scale column experiment was conducted to evaluate the feasibility of using this peat biobarrier to remediate aquifers contaminated by TCE. This system was performed using a series of continuous-flow glass columns including a soil column, a peat column, followed by two consecutive soil columns. Activated sludges were inoculated in all three soil columns to provide microbial consortia for TCE cometabolism. Simulated TCE contaminated groundwater with a flow rate of 0.25 L/day was pumped into the system. Effluent samples from each column were analyzed for TCE and its degradation byproducts [cis-dichloroethylene (cis-DCE) and vinyl chloride (VC)]. Average removal efficiency was 96% for TCE over a 60-day operating period. Accumulation of VC was observed due to the depletion of oxygen in the system. Results from this laboratory study reveal that the developed biobarrier treatment scheme would be expected to provide a more cost-effective alternative to remediate chlorinated-solvent contaminated aquifers.

Keywords: Trichloroethylene; aerobic cometabolism; groundwater remediation; biobarrier

Introduction: Groundwater at many existing and former industrial sites and disposal areas is contaminated by halogenated organic compounds that were released into the environment. The chlorinated solvent trichloroethylene (TCE) is one of the most ubiquitous of these compounds. The maximum contaminant level (MCL) (the concentration established under the Safe Drinking Water Act as being protective of human health and the environment) is 5 µg/L for TCE (Federal Register, 1989). At many TCE spill sites, the residual amounts of TCE persists in a pure liquid phase [commonly referred to as dense, non-aqueous-phase liquids (DNAPLs)] within pore spaces or fractures. The slow dissolution of residual TCE results in a contaminated plume of groundwater. Given that it is often not possible to locate and remove the residual TCE, remediation must focus on preventing further migration of the dissolved contamination. This plume control must be maintained for a long period of time. Therefore, some more economic approaches are desirable for groundwater remediation to provide for long-term control of contaminated groundwater.

One cost-effective approach for remediation of contaminated aquifers that is attracting increased attention is the installation of permeable reactive zones or barriers within aquifers. As contaminated groundwater moves under natural or induced hydraulic gradients through a permeable reactive zone, the contaminants are scavenged or degraded, and uncontaminated groundwater emerges from the downgradient side of the reactive zone (Kao and Borden, 1997; Burris, 1995). Reactive media may be designed to remove contaminants from groundwater by either (1) enhanced sorption and/or precipitation, or (2) chemical and biological degradation. The passive barrier concept has several advantages over other remediation technologies currently in use (e.g., pump and treat, air sparging), including lower maintenance costs, treatment in situ, absence of above ground facilities, and no groundwater reinjection.
Current evidence suggests that TCE can be degraded cometabolically by supplying an alternate primary substrate under aerobic conditions (Schollhorn et al., 1997). Several aerobic microorganisms or microbial communities have the ability to synthesize oxygenase enzyme systems that cometabolize TCE and its degradation by-products [e.g., dichloroethylene isomers (DCEs), vinyl chloride (VC), ethylene (ETH), ethane], when the organisms are grown on other substrates. DCE isomers contain 1,1-DCE, cis-1,2-DCE (cis-DCE), and trans-1,2-DCE (trans-DCE) (Gossett and Zinder, 1997; McCarty, 1997). Among those compounds, cis-DCE is the dominant product. Furthermore, VC has been shown to be available as a primary substrate (McCarty, 1997).

Peat has the following characteristics that makes it a good candidate for this type of application: (1) peat is rich in organic/inorganic carbon, an essential energy source for biodegradation; (2) peat could exhibit sufficient carbon bioavailability for reductive dechlorination to occur; (3) peat is readily available and relatively inexpensive; (4) peat can be emplaced in a remediation well or trench by conventional excavation and backfilling technologies. The elemental composition of peat consists primarily of carbon (50-60%), hydrogen (5-6%), oxygen (30-45%), and nitrogen (1-2%). The main components of peat include lignin and derivatives, cellulose, semi-cellulose, ether/alcohol soluble materials, acetate, propionate, and nitrogenous compounds (Martin, 1991; Viraraghavan and Tanjore, 1994). Under aerobic conditions, biodegradation of some simple components of peat will cause the cometabolism of TCE resulting in the formation of subsequent intermediates (Kao and Lei, in press).

The above discussion suggests that a passive peat biobarrier system is a practical method to biodegrade TCE to non-toxic end-products. Peat can be placed in remediation wells or a permeable trench. Figure 1 presents the schematic diagram of this proposed system. The peat barrier will act as a diffusion source for the primary substrate. The biobarrier will be installed perpendicular to the groundwater flow direction. Soluble organic compounds released from the peat biobarrier will enhance the aerobic cometabolism of TCE in the downgradient area. The principal objective of this effort was to develop a cost-effective groundwater treatment technology to bioremediate groundwater contaminated by TCE. This remediation technology has the potential to completely biotransform TCE to nontoxic end-products (ETH and carbon dioxide).

Materials and methods
A laboratory-scale peat biobarrier system was developed using a series of continuous-flow glass columns: the first soil column, a peat column, the second soil column, and the third soil column. The glass columns were 30 cm long with an inside diameter of 4.8 cm. This first soil column was used to equilibrate the feed solution with the aquifer materials and

![Figure 1 Peat biobarrier system](image-url)
evaluate the biodegradability of TCE without the supplement of other carbon sources. The peat column was used to supply the primary substrates and examine the extent of TCE sorption. The second and third soil columns were applied to evaluate the extent of TCE removal and the fate of TCE degradation byproducts in the aquifer downgradient of a peat biobarrier. The flow rate through the laboratory system was 250 mL/d. Depending on the column porosity, the hydraulic retention times for the three soil columns and the peat column were 3 and 6.5 days, respectively. Figure 2 presents the schematic diagram showing the laboratory biobarrier system.

Aquifer materials from a TCE contaminated aquifer were used to pack the soil columns. Previous study had shown that activated sludges collected from an industrial wastewater (pulp and paper wastewater) treatment plant containing microbial communities, which can utilize organics released from peat as the primary carbon source (Kao and Lai, in press). During the primary substrate consumption, oxygenase enzyme was synthesized for subsequent TCE cometabolism. In this study, activated sludge was used as the microbial inoculum and mixed with the aquifer materials before packing. Approximately 900 g of soils and 15 ml of activated sludge were packed in each soil column. The peat column was packed with 80 g of dried peat moss (Lambert Peat Moss Inc., Quebec, Canada).

Preliminary studies had shown that this peat moss maintained adequate permeability after wetting (Kao and Borden, 1997). The synthetic groundwater (feed solution) used in this study contained the following components at the specified concentrations (units are in mg per litre of water): H₂PO₄, 326.4; Na₂HPO₄, 1263.8; Mg₂SO₄·7H₂O, 98.6; CaCl₂·2H₂O, 44.1; NH₄Cl, 10.7; plus 3.35 mg of trace elements which include FeSO₄·7H₂O, 1; MnSO₄·4H₂O, 1; (NH₄)₆Mo₇O₂₄·4H₂O, 0.25; Na₂B₄O₇·10H₂O, 0.25; CoCl₂·6H₂O, 0.25; CuCl₂·2H₂O, 0.25; ZnCl₂, 0.25; NH₄VO₃, 0.1. The pH of this buffer solution was 7.5. The synthetic groundwater was autoclaved before use.

The oxygen-saturated feed solution (purged with air) and TCE stock solution was pumped through the system by peristaltic and syringe pumps so that concentration entering the first soil column was approximately 1 mg/L for TCE. Three pore volumes of the feed solution were allowed to pass through the columns before the TCE injection. The column system was operated for 60 days in the dark at the ambient groundwater temperature (16°C). The effluent from each column was analyzed for TCE, cis-DCE, VC, pH, DO, and COD. An Orion DO meter (Model 840) was used for DO measurements. COD analysis was performed in accordance with the dichromate reflux method described in Standard Methods (APHA, 1995). TCE and its degradation byproduct analyses were performed in...
accordance with U.S. EPA Method 601, using a Tekmer Purge-and-Trap Model LSC 2000 with a Varian Model 3800 Gas Chromatograph (GC). Because cis-DCE is the dominant by-product among DCE isomers during the TCE biodegradation process, only cis-DCE was analyzed in this study.

Results and discussions

Figure 3 presents the concentrations of TCE versus time in the effluent of the four columns. Table 1 lists the average concentrations of TCE, cis-DCE, VC, DO, COD, and pH in the system influent and effluent of each column. Averages are reported for the period from day 18, when breakthrough and stabilization were complete, to the end of the experiment on day 60. Concentrations of TCE and its by-products in all columns reached a quasi-steady state and remained constant after 18 operating days. Results show that TCE broke through the first column by day 2.5, and its breakthrough in the second column (peat column) did not occur until day 12, apparently due to sorption to peat.

No significant TCE removal was observed in the first soil column indicating that TCE cannot be biodegraded under aerobic conditions. The observed pH in the peat column effluent dropped to below 4.3 during the early operation period (from 1–10 days), then it slowly increased to 6 before the end of the experiment. The averaged pH for the peat column with the operation period was 5.2 (Table 2).

The decreased pH also inhibited the bacteria activity, and therefore, no obvious TCE degradation was observed after the breakthrough of TCE in the peat column. For the future field application, pH will not be a concern because the pH effects could be minimized by the nat-

Table 1  Averaged influent/effluent concentrations for TCE and other parameters from day 18 to 60

<table>
<thead>
<tr>
<th>Influent/Effluent</th>
<th>TCE µg/L</th>
<th>cis-DCE µg/L</th>
<th>VC µg/L</th>
<th>pH</th>
<th>DO mg/L</th>
<th>COD mg/L</th>
</tr>
</thead>
<tbody>
<tr>
<td>Influent</td>
<td>1103</td>
<td>BDL</td>
<td>BDL</td>
<td>7.5</td>
<td>8.5</td>
<td>BDL</td>
</tr>
<tr>
<td>1st Column Effluent</td>
<td>989</td>
<td>BDL</td>
<td>BDL</td>
<td>7.4</td>
<td>7.6</td>
<td>BDL</td>
</tr>
<tr>
<td>2nd Column Effluent (Peat Column)</td>
<td>951</td>
<td>BDL</td>
<td>BDL</td>
<td>5.2</td>
<td>7.2</td>
<td>25</td>
</tr>
<tr>
<td>3rd Column Effluent</td>
<td>689</td>
<td>132</td>
<td>43</td>
<td>6.1</td>
<td>1.2</td>
<td>19</td>
</tr>
<tr>
<td>4th Column Effluent</td>
<td>48</td>
<td>27</td>
<td>78</td>
<td>7.1</td>
<td>0.3</td>
<td>18</td>
</tr>
</tbody>
</table>

% of Removal → [(Inf - 1st)/Inf]×100
% of Removal → [(Inf - 2nd)/Inf]×100
% of Removal → [(Inf - 3rd)/Inf]×100
% of Removal → [(Inf - 4th)/Inf]×100
% of Removal → [(1st - 2nd)/Inf]×100
% of Removal → [(2nd - 3rd)/Inf]×100
% of Removal → [(3rd - 4th)/Inf]×100

1NA: not available
2BDL: below detection limit

Figure 3  TCE concentrations vs. time
ural soil/groundwater buffer and dilution capacity. The initial decrease in DO concentrations (decreased from 8.5 mg/L to 7.6 mg/L) in the first column might be due to the degradation of organics contained in activated sludge and soils. DO decrease was not noticeable in the peat column. DO concentrations dropped from 7.6 mg/L to 1.2 mg/L in the third column then dropped to 0.3 mg/L in the fourth column (Table 1). The decrease in DO concentration indicates the occurrence of active aerobic biodegradation in the soil columns. Approximately 25 mg/L of COD was detected in the peat column due to the release of organics from peat. Part of the organics was degradable and caused the decrease in COD from 25 to 19 mg/L in the third column.

For the period from day 18 to 60, the average removal efficiencies in the third and fourth columns were 38% and 58%, respectively (Table 1). Therefore, a total of 96% of TCE was removed via this biobarrier system. No cis-DCE and VC were detected in the first two column effluents. Approximately 132 µg/L of cis-DCE and 43 µg/L of VC were detected in the third column, and 27 µg/L of cis-DCE and 78 µg/L of VC were detected in the fourth column. VC degradation is usually facile under aerobic conditions, and its conversion to ethylene is usually the rate-limiting step in the anaerobic dechlorination pathway. Therefore, the accumulation of VC in the last soil column might be due to the decrease in DO concentrations. Most of the time, at the downgradient fringe of the TCE plume with VC present, complete degradation of VC via aerobic cometabolism (or direct metabolism) can occur because of the intrusion of oxygen from the vadose zone and the edge of the plume. Therefore, the accumulation of VC in the TCE contaminated sites may not cause a serious environmental problem.

**Conclusions**

The objective of this laboratory-scale study was to develop and evaluate a peat biobarrier system to passively remediate TCE contaminated groundwater. Conclusions of this study include the following:

1. The released organics from peat biobarrier can serve as the primary substrates and enhance the aerobic cometabolism of TCE.
2. Using the preexamined activated sludge as the inoculum can significantly minimize the acclimation time and lag period.
3. Because of its low sorption capacity, peat is not a suitable material for TCE removal by sorption.
4. Occurrence of aerobic cometabolism can be verified by (1) depletion of TCE (96% removal); (2) production of cis-DCE and VC; (3) decrease in DO and COD.
5. Complete TCE and VC removal can be achieved by extending the retention time and providing sufficient oxygen.
6. Because organic materials are released from peat continuously, peat can remain active for a long period of time in the proposed system.

Significant TCE removal from this system indicates that the proposed biobarrier has the potential to become a cost-effective remediation alternative. This system is able to clean up TCE and other chlorinated-solvents contaminated aquifers. Results from the study will aid in designing a scale-up system for field application.

**References**


