Chlorinated Solvent Contaminants in Arizona Aquifers

Part II: Innovative Remediation Methods and Site Characterization Strategies.

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Preface

SciTransfer research bulletins are produced by The University of Arizona Superfund Basic Research Program (UA SBRP) Research Translation Core. Each issue is dedicated to providing a brief introduction to a current environmental contaminant or issue, while highlighting current UA SBRP biomedical and environmental remediation research.

In Part I of the SciTransfer series on Chlorinated Solvent Contaminants in Arizona, we discussed the sources, properties, health effects and fate of trichloroethene (TCE) and tetrachloroethene¹ (PCE). Part II is devoted to describing innovative methods for treating chlorinated-solvent contamination both below and above-ground. This issue will also present advanced site characterization methods that can be used to enhance the design, implementation and operation of remediation projects.

Introduction

In the past, groundwater remediation techniques have focused primarily on the physical containment and removal of these chemicals followed by above-ground treatment. This approach, termed pump and treat, requires contaminated groundwater to be pumped from the aquifer to the ground surface where it is treated via air stripping or activated carbon removal to lower trichloroethene (TCE) concentrations below drinking water standards (5 ppb or 5 µg/L). The treated water may be re-injected back into the outer limits of the aquifer contamination plume to control the spread of TCE. Pump and treat has proven to be very effective at containing contaminant plumes. However, it is now clear that in many cases complete site cleanup can not be achieved using pump and treat alone. This is especially true for sites that have immiscible liquid forms of contamination (for example liquid TCE) trapped in portions of the subsurface (we refer to these areas as “source zones”). Remediation of sites that have immiscible-liquid² source zones is limited by the several contaminant mass transfer issues outlined in Part I. In response to these issues, other remediation methods have been and are being developed to specifically address contaminant source zones.

One method that has proven to be very successful is soil vapor extraction (SVE) or soil venting, which is used to remove volatile, immiscible liquid phase contaminants trapped above the groundwater (vadose zone). Soil vapor extraction has been used successfully at many chlorinated solvent contaminated sites in Arizona. Other, newer methods being tested for remediation of source zones include using reagents such as surfactants (detergents) and alcohols to increase the solubility of the organic compounds, using thermal methods such as injecting steam to enhance contaminant movement (mass transfer), injecting reagents to promote chemical (abiotic) transformation of contaminants in place (rather than bringing the contaminants to the surface for treatment), and injecting reagents to promote biotransformation of contaminants by the resident microorganisms. We will discuss some of these methods in the following sections, focusing on efforts associated with the UA SBRP investigators.

¹ Also known as perchloroethene or perchloroethylene.
² Refers to organic liquids with very low water solubilities.
Innovative Site Treatment

Regeneration of GAC Filters in the Field using Fenton’s Reagent

As noted above, soil vapor extraction is used when volatile, immiscible liquid phase contaminants are trapped in the vadose zone. This technique uses air injection and air recovery (vacuum) wells that maintain moderate to high air flows through the contaminated zone. Solvent vapors are swept and collected in the recovery wells and passed through an activated charcoal (also known as granular activated carbon (GAC)) filter that traps the TCE or PCE. When charcoal filters are saturated with chlorinated solvents, these must be either regenerated with heat or incinerated at considerable expense. To eliminate expensive offsite regeneration or disposal costs of carbon filters, three UA SBRP researchers are exploring novel approaches to mitigate this problem.

Drs. Robert Arnold and Wendell Ela are exploring the use of a chemical called Fenton’s reagent to regenerate the GAC filters in the field, thereby avoiding expensive offsite regeneration or disposal. This process is based on the well known oxidation reaction between carbon-based chemicals like solvents (TCE, PCE) and highly reactive chemicals (radicals) that are produced when hydrogen peroxide (a chemical commonly available in drugstores) and metal ions (such as iron (Fe)) are mixed with water. The chemicals (reagents) and benign products that result from this reaction can be briefly summarized as follows:

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\text{Ferrous Iron ions (Fe}^{2+}\text{)} + \text{hydrogen peroxide (H}_2\text{O}_2) \rightarrow \text{Ferric Iron ions (Fe}^{3+}\text{)} + \text{hydroxyl ions (HO}^-\text{)} + \text{radicals (OH}^-\text{)}
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which when reacted with TCE \(\rightarrow\) \text{carbon dioxide (CO}_2\text{)} + \text{chloride ions (Cl}^-\text{)} + \text{acidity (H}^+\text{)} + \text{water (H}_2\text{O)}

Note that this reaction has numerous competing and intermediate steps not described here. The overall efficiency of this reaction is affected by several chemical conditions. Site pH is perhaps the single most important variable that limits the use of this approach for in-situ degradation of chlorinated solvents in Arizona aquifers (alkaline in nature), as this reaction is most efficient at low pH (<4) where Fe ions are more soluble. Both the type and quantity of soluble metal ions present affect this reaction. Since Fe\(^{3+}\) in particular is very insoluble in water, Dr. Ela’s group is researching the use of copper (Cu\(^{2+}\)) ions to improve the efficiency of the Fenton’s reaction. The efficiency of this reaction is also dependent on the type of organic chemical that must be destroyed. Field regeneration studies of spent GAC filters (saturated with TCE and PCE) at a Superfund site in Tucson have shown that the destruction of these two chemicals in GAC filters is limited by their low water solubilities (see Part I), and the diffusion rates of these chemicals out of the carbon filter particles. However, multiple regeneration cycles do not appear to affect the sorption capacity of GAC filters treated with Fenton’s reagents.
To make this chemical treatment a viable, cost-effective alternative for field regeneration of GAC filters, further research is needed to reduce the regeneration times of these filters using modified Fenton’s reagents and iron-amended, modified porosity GAC filters (Arnold and Ela, 2006).

**Destruction of TCE and PCE from SVE Systems**

Another approach for handling the contaminant vapors generated from SVE systems is to convert them to non-hazardous compounds, thus eliminating the need for GAC filters. Dr. Eric Betterton is exploring an onsite method of direct TCE destruction using heat and a catalyst similar to those used to treat hydrocarbons in car exhaust (also known as a catalytic converter). This process employs simultaneous oxidizing and reducing conditions. The reducing conditions created at the catalyst surface convert chlorinated chemicals into hydrochloric acid in a hydrocarbon rich environment, see diagram. However, the oxygen from the air-stripping stream also allows for the complete combustion of residual hydrocarbons into carbon dioxide and maintains a clean catalyst surface. The process requires heat, but is self-sustaining once the catalyst reaches its optimum operating temperature (>450°C). Finally, hydrochloric acid vapors are scrubbed out and neutralized before the air is released into the atmosphere, see figure 2.

![Field diagram of catalytic TCE destruction system](image)

Figure 2. Field diagram of catalytic TCE destruction system installed at the Park - Euclid State Superfund Site.

**Innovative Approaches to Enhance TCE Removal**

In Part I we showed that the low water solubility of chlorinated chemicals severely limits their timely removal from contaminated aquifers. Surfactants and other solvents (co-solvents) like alcohols have been shown to enhance the water solubility of chlorinated solvents and speed up their removal, requiring less flushing. Pump and treat systems can benefit from the additions of these chemicals which enhance contaminant removal rates. However, to be effective, large concentrations (>3%) of these chemicals must be pumped into the contaminant source zones. Also, the recovered mixture (water + surfactant/co-solvent + TCE) must be treated to separate the TCE and surfactant chemicals from the water before it can be re-injected, at an additional expense. Unfortunately, many surfactants and co-solvents can be toxic, are very soluble in water and can end up as unwanted residual contaminants in the treated water. In some situations, surfactants may unexpectedly increase the mobility of dense non-aqueous phase liquids (DNAPLs), which can lead to extended downward TCE contamination.

Research by the UA SBRP investigator Dr. Mark Brusseau has shown that an organic compound called cyclodextrin, a sugar produced from microbial degradation of starch and used as a food additive, offers several advantages for the facilitated removal of TCE, see Figure 3. Cyclodextrin is a water soluble, non-toxic, stable chemical that enhances the removal of low soluble organic contaminants like TCE and is easy to separate from water. A pilot scale research project (Tick et al., 2003) demonstrated that cyclodextrin is efficient in enhancing the removal of PCE. A cyclodextrin solution increased the solubility of PCE 22 times, and removed nearly 50% of the total PCE in nearly 13 times fewer pore volumes than with water. This sugar also proved safe for soil microorganisms as it is biodegradable. However, the use of this chemical is limited to highly contaminated aquifer zones since high concentrations of this chemical (>10%) are needed to maintain its co-solvent³ efficiency.

³ Ability to enhance the solubility of chlorinated solvents in water.

**In-Situ Abiotic Degradation of Chlorinated Contaminants**

Numerous laboratory research and field studies have demonstrated that it is possible to enhance the chemical degradation (abiotic) rates of chlorinated chemicals in situ with the help of strong chemical oxidants or reducing agents, without having to pump the contaminated water to the surface. For example, Fenton’s Reagent (hydrogen peroxide and iron) as described previously has been successfully utilized in other parts of the United States (U.S.) for in-situ degradation of chlorinated solvents.

![Cyclodextrin](image)
Other oxidants effectively used throughout the U.S. include permanganate (MnO₄⁻), and ozone gas (O₃) that once spent, leave non-toxic chemicals (like iron oxide and manganese oxide) in the treated (aquifer) zone. SBRP funded laboratory and field studies have demonstrated that permanganate is a very efficient oxidant for the removal of TCE in Arizona aquifers. A recent pilot study demonstrated that permanganate is a viable and effective oxidant for TCE contamination in an aquifer located in the Tucson International Airport Superfund Site (Brusseau et al., 2006). This chemical offers the advantage of being very water soluble and stable (unlike Fenton’s reagent and ozone gas), and its efficiency is not affected by the high pH and alkalinity conditions typical of Arizona aquifers. One potential drawback of this method is the reduction in aquifer water flow (hydraulic conductivity) due to the precipitation of manganese oxide.

Chlorinated solvents can be degraded, transformed, trapped by soil particles, and diluted to levels below detection limits in the groundwater. These processes are collectively described as the natural attenuation (NA) that occurs in aquifer environments. In Part I we described the mechanisms and difficulties involved in the biodegradation of chlorinated solvents. TCE is known to degrade in aquifer environments. PCE has not been found to degrade at all under aerobic conditions common in Arizona aquifers, though PCE has been found to degrade under anaerobic conditions at the Park-Euclid State Superfund Site (UA SBRP Field Demonstration Booklet, 2007). Biodegradation may be an important component of MNA for other solvents like TCE. Thus, it is important to know whether this process is occurring in solvent-contaminated aquifers and how significant it is. To distinguish between physical and biological attenuation, Dr. Mark Brusseau is researching the use of two novel techniques, PCR – DNA⁴ screening and compound specific isotope (CSI)⁵ analysis, to determine the presence of microbes that can degrade chlorinated solvents, and the presence of carbon (C) isotopes associated with the degradation of chlorinated solvents in Arizona aquifers. If direct evidence of microbes capable of degrading TCE (via PCR-DNA) or indirect evidence of chlorinated solvent degradation (via CSI analysis) is found, then it may be possible to predict the removal of these contaminants in the near future with this low cost MNA approach. For example, at the Park-Euclid State Superfund Site, PCR-DNA screening confirmed that Dehalococoides, the only anaerobic bacterium known to transform PCE all the way to ethene (other anaerobic bacteria stop at vinyl chloride a highly toxic intermediate) is present at the site. In addition, the results of CSI analysis of the groundwater revealed evidence of PCE/TCE transformation. Finally, chemical analysis of groundwater revealed the presence of ethene, the ultimate anaerobic degradation product of PCE (UA SBRP Field Demonstration Booklet, 2007).

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The development and implementation of efficient, cost-effective groundwater contamination remediation schemes requires detailed site-specific information (National Research Council 1994). Thus, besides the rate of groundwater flow and direction, it is very important to know other specific site characteristics including:

- Contaminant distributions (location and amounts)
- Aquifer permeability (hydraulic conductivity)
- Aquifer heterogeneity (example: distribution and size of clay zones in the contaminated aquifer)
- Contaminant mass transfer and transformation processes

Current site characterization techniques rely primarily on the collection and analysis of samples from wells. This approach is limited by the costs of installing new monitoring wells, the limited number of soil and samples collected, and often-inadequate site background information. In short, too often not enough samples are collected and little information is available about the contaminated aquifer zone. Although the costs of this approach are moderate and it identifies the types of pollutants present and general locations of contaminants, this approach often fails to identify the true quantities and extent of the pollution or pollutant(s). For example, the measurement of water-

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⁴ Polymerase Chain Reaction (PCR) based – DNA screening to determine the presence for microbes capable of degrading chlorinated solvents.

⁵ Compound Specific Isotope (CSI) analysis is used to characterize microbial degradative activity in groundwater by measuring specific chemical isotopes released.
phase contamination provides no information about the presence of a separate phase or DNAPL. As discussed in Part I, TCE and PCE have low solubilities in water and are about 1.5 times denser than water. These heavy liquids can sink to the bottom of aquifers and can also be trapped inside the pores of soils and aquifers. Thus, relying primarily on the collection and analysis of samples from wells may not lead to the selection of the best and most efficient remediation methods. For example, the text below presents a summary of selected innovative site characterization tools available to remedial project managers that were utilized at the Tucson International Airport Area (TIAA), a National Priority List (Superfund) Site in Tucson, Arizona.

**Case Study entitled: A Manager's Tool Kit: Site Characterization and Evaluation of a Chlorinated-Solvent Contaminated Superfund Site in Tucson, Arizona.**

**Tool: Partitioning Tracer Tests**
The injection of minute amounts of chemicals (tracers) to estimate the average geologic properties between two points (injection-collection) has been used in the oil industry for decades. The chemical tracers are inert (unreactive), do not degrade and can be detected and quantified at very low concentrations. Therefore, these chemicals can be injected into aquifers in very small amounts without a significant risk of contamination. As noted previously, DNAPL are extremely difficult to remove due to their very low water solubility. This also means that the presence of DNAPL zones is often not reflected in the water contaminant concentrations. However, if one considers the total amount of contamination of TCE for example, on a mass basis, TCE DNAPL zones often contain the bulk (>90%) of the contaminant. We noted that one kilogram of TCE or PCE can contaminate 52 million of gallons of water. Therefore, it is very important to establish early on the presence and amounts of DNAPLs to estimate the efficiency, duration and types of remediation efforts.

The use of partitioning tracers to characterize DNAPLs distributions in TCE contaminated aquifers has been studied by UA SBRP researcher Dr. Brusseau. Since these tracers prefer (like to partition into) non-aqueous liquids, their movement is retarded in proportion to the amount of DNAPLs they encounter along their flow pathways. Thus, tracers can be used to estimate the mass of DNAPLs in aquifer zones located between two wells (a tracer injection well and recovery well), see Figure 1. The capacity of multi-solute, bio and partitioning tracer tests were demonstrated during an advanced site characterization study at the TIAA site. Tracer use for site characterization is a proven state-of-the-art approach that is more expensive than the standard method described earlier. However, chemical tracers can provide a much better understanding of the site complexities and true extent of the pollution. It should be noted that these higher initial characterization costs would likely be offset by lower clean up costs. This is because better initial site information will allow for the use of more efficient remediation methods.

**Tool: Laboratory Tests**
Laboratory studies are also considered part of innovative (state-of-the art and science) site characterization efforts. To understand and model the behavior of pollutants, it is necessary to use actual site materials or engineered porous media with controlled additions of DNAPLs under controlled laboratory conditions. Laboratory studies have shown that flushing contaminated systems containing heterogeneous pore media produces lower concentrations (mass flux) of TCE in water, but the residual DNAPL (source zone mass) of this pollutant left behind is high. These studies found that the nature or “architecture” of the source zone has a significant impact on mass removal behavior (DiFilippo and Brusseau 2006).

**Tool: Depth-specific Sampling**
By studying soil samples (cores) from contaminated areas, detailed information about site characteristics and specific pollutant behavior can be obtained. For example, soils cores can be used to study the ways TCE interacts (sorption, desorption and dissolution behavior) with a particular aquifer material. This information can in turn, help develop state-of-the-art and science computer models that can be used to predict the behavior of pollutants, see Figure 5.

**Tool: Contaminant Transport Modeling**
Computer modeling can lower the costs of remediation since they can be used to simulate innovative cleanup strategies without having to test them in the field. Unfortunately, this tiered approach is not commonly used in conjunction with standard site characterization efforts. This is primarily due to its high initial costs and lack of trained scientists and specialized tools.

Using the site characterization and evaluation of the TIAA site in Tucson, Arizona as a case study, relatively high aqueous concentrations, extensive elution tailing, and strong rebounding were observed for TCE and dichloroethene during induced-gradient contaminant elution tests conducted within a source zone at the site. Several lines of evidence indicate that immiscible liquid is likely present in the saturated zone at the site. In such cases, source-zone management becomes of central importance to successful remediation efforts.

The use of advanced site characterization methods and modeling throughout the duration of this field project helped refocus the TCE cleanup priorities at the TIAA site. By establishing the presence of DNAPL in the aquifer using tracers, modeling and aquifer material laboratory studies, the effort was shifted from the TCE plume to the removal of the source (zone), while controlling the dissolved TCE (plume). Advanced modeling also showed that the observed TCE concentration tailing, see figure 5, was due primarily to the presence of TCE in the form of DNAPL in the source zones. The results show that controlling the source zone can reduce the time required to remove TCE from the subsurface.

In conclusion, The UA NIEHS SBRP researchers have been very successful at developing and implementing basic and field scale research aimed at the remediation of TCE contaminated groundwater sites in Arizona. They have shown that the use of new on site, above ground TCE destruction techniques could significantly reduce the off-site disposal/regeneration costs associated with traditional activated carbon trapping methods. In-situ subsurface TCE destruction using the permanganate oxidant has been shown to be successful for DNAPL removal in Arizona aquifers and is now being used in full scale aquifer remediation projects. The combined use of traditional and research in advanced site characterization methods such as field tracer tests, laboratory bench scale studies and mathematical modeling employed at the TIAA Superfund site, have proven to be an effective approach to manage and optimize remediation activities at TCE contaminated sites in Arizona.
References


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