Strategies for *in situ* bioremediation of chlorinated solvent contaminated groundwater

P. L. MCCARTY

Department of Civil and Environmental Engineering, Stanford University, Stanford, California 94305-4020, USA
e-mail: mccartv@cee.stanford.edu

Abstract Chlorinated solvents such as TCE and TCA can be biologically degraded aerobically through cometabolism. PCE and TCE can be degraded anaerobically while being used as electron acceptors in energy metabolism. *In situ* bioremediation strategies may be directed either towards containing a plume or cleaning it up completely. The DNAPL source for PCE and TCE can also be biodegraded, resulting in enhanced dissolution due to higher reaction rates and toxicity to competing methanogens. All *in situ* biodegradation processes require the addition of electron donors, and perhaps bioaugmentation. Added materials, the contaminants, and the degrading organisms must be brought together so that the transformation can be effected. This may be accomplished using liquid injection/extraction systems, gas injection, and bioreactive barrier walls.

Key words biodegradation; chlorinated solvents; cometabolism; dehalorespiration; DNAPL; *in situ* groundwater remediation; PCE; TCA; TCE

INTRODUCTION AND BACKGROUND INFORMATION

Chlorinated solvents are among the most widespread and difficult to remediate organic groundwater contaminants (McCarty, 1999). Included are tetrachloroethene (PCE), trichloroethene (TCE), 1,1,1-trichloroethane (TCA), and carbon tetrachloride (CT). All are biodegradable, but by unusual pathways. TCE and TCA can be degraded aerobically through cometabolism by organisms grown on different primary substrates, such as methane, propane, toluene and phenol. Here, oxygenases produced by microorganisms to initiate oxidation of these primary substrates fortuitously bring about expoxidation or hydroxylation of the chlorinated solvents, leading to their subsequent chemical and/or biological degradation. All the chlorinated solvents can also be degraded anaerobically, but the pathways tend to differ. PCE and TCE can be used as electron acceptors in energy metabolism through reductive dehalogenation (dehalorespiration), with hydrogen and sometimes certain organic compounds as electron donors. The pathways for TCA and CT anaerobic transformation are not as clear, but often involve cometabolism.

Chlorinated solvent contamination can often be characterized as consisting of a source of dense non-aqueous phase liquid (DNAPL) that penetrates groundwater, and a plume of groundwater that becomes contaminated as it flows by the source, leading to a downgradient contaminated plume (Cherry et al., 1997). *In situ* bioremediation strategies may be directed towards containing the plume or cleaning it up completely. In addition, recent studies indicate the DNAPL source for PCE and TCE itself can also be biodegraded, resulting in enhanced dissolution rates (Carr et al., 2000; Nielsen & Keasling, 1999; Yang & McCarty, 2000a).
Remediation of chlorinated solvent contamination can at times be achieved through natural processes (natural attenuation). This requires that sufficient organics, which serve as electron donors for dehalogenation, and necessary dehalorespiring organisms are already present in the aquifer. If these necessary conditions do not exist, then in situ bioremediation can be achieved through addition of electron donors and/or through bioaugmentation (McCarty, 1999). In either case, a remediation strategy must be designed to ensure that the electron donor, the chlorinated solvents, and degrading microorganisms all are brought together in the same location and at the same time. Groundwater flow has a low Reynolds number and hence represents laminar flow, meaning that natural processes are not likely to accomplish the mixing required to bring them together. Thus, one cannot generally rely on the natural processes alone, but must design specifically for adequate mixing to occur. Strategies that have been successfully used and recent findings for DNAPL biodegradation are discussed here.

**MIXING APPROACHES**

The limitations of dispersive forces in laminar-flow groundwaters for mixing injected substrates with organisms and contaminants needs to be recognized. Adequate mixing for efficient use of substrates and resources requires more rigorous approaches, several possibilities of which are depicted in Fig. 1 (Cherry et al., 1997; McCarty, 1999). The choice for a given site depends upon a number of factors such as anticipated reaction rate, site hydrogeology, remediation objectives, and treatment system capital vs operating costs.

Different possible site remediation objectives might be: (a) prevention of plume migration, (b) clean-up of entire plume, or (c) removal or containment of contaminant source. The least expensive alternative often is to prevent plume migration. This might be accomplished for example by longitudinal extraction/injection (Fig. 1(b)) with in situ or ex situ treatment, by lateral multiple injection (Fig. 1(d)), or by a barrier wall that may or may not include a funnel and gate (Fig. 1(e)). Either would accomplish the same objective. The barrier wall is likely to involve a high initial capital cost for construction, but a smaller yearly operating cost. The other two systems involving substrate injection would be much lower in capital cost for construction, but would involve higher yearly operating costs. The barrier wall might be more favourable with shallow contamination, but the injection systems would tend to be more favoured with deeper contamination since here building a deep wall could be prohibitively expensive.

Complete plume cleanup may at times be required. Here, some form of pump and treat is generally used, such as a longitudinal injection/extraction (Fig. 1(a)), because of the large areal extent of a plume. This approach is often used to isolate and treat only the water within the contained area. Multiple injection and extraction wells (Figs 1(b), 1(c), 1(d)) may also be used with various possible configurations. In such cases, care must be taken to ensure that contaminants are not simply moved downgradient faster to cause a larger problem. Entire plume remediation requires a higher investment in wells and operation than prevention of plume migration alone. In comparing treatment alternatives, regulators often are willing to accept a barrier wall, with its function of preventing plume migration, but then insist that a pump and treat system must be designed to effect complete plume cleanup. This is not a fair comparison. The
correct comparison would be between a barrier wall and a longitudinal extraction/injection system where the objectives are the same. In this case, the lateral extraction/injection system would be much cheaper in capital cost, and perhaps cheaper in total cost when considered on a present worth basis.

A TWO-AQUIFER LONGITUDINAL EXTRACTION/INJECTION SYSTEM

A full-scale demonstration of in situ aerobic cometabolic biodegradation of a TCE contaminated plume was carried out at the Edwards Air Force Base in Southern California through addition of toluene and oxygen (McCarty et al., 1998). This modification of the longitudinal extraction/injection system (Fig. 1(b)) took advantage of the fact that two adjacent aquifers were contaminated. This allowed chemical injection, mixing with contaminants, and biological treatment all to take place in the subsurface as illustrated in Fig. 2. Two treatment wells were installed, each with screens in both aquifers. Pumping was downward in the first well at a flow rate of 25 to 38 l min⁻¹, and upward in the second well at a similar flow rate. Treatment chemicals (toluene, oxygen, and hydrogen peroxide) were injected into both wells and mixed with the contaminants in the pumped groundwater using a static mixer. Biodegradation of trichloroethene through cometabolism was effected in the aquifer near the well effluents by microorganisms growing on the injected toluene and oxygen. The hydrogen peroxide provided a disinfectant at the well to prevent clogging near the screens, and then hydrolyzed as it moved into the aquifer to provide additional oxygen.

Fig. 1 Different schemes for introducing and mixing substrates with contaminants and microorganisms for efficient treatment.
Once steady-state treatment was obtained at a pumping rate of 25 liters per minute, TCE removal in the upper aquifer through biodegradation was 86 ± 9%, and in the lower aquifer was 83 ± 16% with each pass through the treatment system. Since there was much recycling between treatment wells as they were relatively close to one another (10 m), the overall treatment efficiency of upgradient water passing through the system was much higher. The upgradient TCE concentrations were 1188 ± 112 µg l⁻¹ (n = 83) in the upper aquifer and 981 ± 213 µg l⁻¹ (n = 82) in the lower aquifer. The treated water moving downgradient from the treatment system had concentrations of 26 ± 6 µg l⁻¹ (n = 129) in the upper aquifer and 16 ± 7 µg l⁻¹ (n = 121) in the lower aquifer. The overall efficiency of TCE removal in the aquifer water passing through the treatment system was thus 97.8 ± 0.6% in the upper aquifer and 98.4 ± 0.8% in the lower aquifer.

The original modelling of the treatment system, based upon the limited data then available, indicated the plume capture zone at 25 liters per minute pumping rate in the two wells was 62 m wide in the upper aquifer and 53 m wide in the lower aquifer. However, more rigorous modelling using detailed results from one year of operation, including drawdown data from the 19 monitoring wells in the upper and lower aquifers, bromide tracer studies, and 7213 TCE concentration measurements, indicated that much less capture was effected, about 40 m wide in the upper aquifer and much less than this in the lower aquifer, perhaps 15 to 20 m (Gandhi et al., 2002a, 2002b). Part of the reason for the lower capture was the presence of a leaky connection between the two aquifers through a well just east of the treatment system, which effectively increased the recycle rate.
Closer well spacing results in an increased recycle rate and increased overall system treatment efficiency, but lower capture of regional groundwater. Consider a single aquifer with extraction and injection at flow rate $Q_p$, which captures a regional groundwater flow of $Q_g$. If the recycle flow $Q_r$ is defined such that $Q_r + Q_g$ equals $Q_p$, and the recycle ratio $R$ is defined to equal $Q_r/Q_g$, then:

$$Q_g = Q_p/(1 + R)$$  \hspace{1cm} (1)

Using mass balance for this case, the overall treatment efficiency ($E$), when the removal efficiency for each pass through the system is $e$, becomes:

$$E = e(1 + R)/(1 + eR), \quad \text{and} \quad R = (E - e)/(e(1 - E))$$  \hspace{1cm} (2)

The high overall treatment efficiencies of the Edwards system (97–98%) resulted from a high recycle rate. A more efficient design, however, would use further spacing of the treatment wells to reduce recycle and installation of a complementary two-well system downgradient of the present system as in Fig. 1(c). With such series operation, overall treatment efficiency ($E_T$) would be:

$$E_T = 1 - (1 - E)^m, \quad \text{and} \quad E = 1 - (1 - E_T)^{1/m}$$  \hspace{1cm} (3)

where $m$ is the number of well pairs in series. As an example, assume $e = 0.84$, and the desired overall removal efficiency $E_T$ is 0.99. With a single well pair ($m = 1$), $R$ would equal 18 and $Q_g$ would equal $Q_p/19$. However, with two well pairs in series ($m = 2$), each with the same $Q_p$, $E$ would equal 0.9, $R$ would equal 0.71, and $Q_g$ would equal $Q_p/1.71$. Thus, for a given pumping rate for the treatment systems, the groundwater capture zone for the overall treatment system would be larger by a factor of 16 for the two well pairs in series. This is an obvious large advantage of using extraction/injection pairs in series.

**ENHANCED DNAPL DISSOLUTION**

A problem with anaerobic dehalogenation of contaminants such as PCE and TCE is that the electron donors added to effect treatment are generally used as well by competing methanogenic and sulphidogenic microorganisms. However, PCE dehalogenation can occur with little inhibition to dehalogenation at saturated solution concentrations (0.8 mM or 133 mg l$^{-1}$) (Nielsen & Keasling, 1999; Yang & McCarty, 2000a). Additionally, such concentrations, as well as the intermediate and ethene end products of dehalogenation, are all inhibitory to the competing methanogens. A further advantage is that biodegradation near DNAPLs enhances DNAPL solubilization by maintaining a low PCE solution concentration (Carr et al., 2000; Yang & McCarty, 2000a). In this manner, the sum total concentration of PCE plus its degradation products emerging from a soil column containing PCE DNAPLs equalled 4.5 mM, or about 5 times PCE solubility (Yang & McCarty, 2000a). Thus, DNAPL removal through a pump and treat system can be greatly enhanced when coupled with *in situ* biodegradation, and at the same time, inhibition of methanogenesis increases substrate utilization efficiency. Only about 1 gram of pentanol was required for each gram of PCE dehalogenated.

For DNAPL biodegradation a longitudinal substrate injection/extraction system (Fig. 1(a)) might be used to obtain recycling through the DNAPL for substrate
addition, and diversion of regional groundwater flow around the DNAPL site. Thus, containment together with enhanced biodegradation would be achieved. The enhanced dissolution resulting from biodegradation would reduce the overall time for remediation considerably. Other possibilities are the direct injection of hydrogen gas into the DNAPL zone (Newell et al., 1998), or the introduction of substrates, such as oleate or biomass, to effect slow substrate utilization and hydrogen release within the aquifer (Yang & McCarty, 2000b).

Whatever the scheme selected, a mixing process that permits efficient substrate utilization and reduces the clogging potential in the aquifer is of importance. There are many alternatives available to achieve good mixing, the best of which depend upon the individual characteristics of the site, remediation objectives, and economic comparisons. There is no system available that is best for all sites; each circumstance requires a thorough comparison of the alternatives.

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