

## Intrinsic Bioremediation Of Chlorinated Compounds: An Elegant Approach To Site Remediation

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### INTRODUCTION

Dense, Non-Aqueous Phase Liquids (DNAPLs), such as trichloroethene (TCE), can be dissolved in groundwater, volatilized into soil gas, and exist as a residual or free-product both in the unsaturated and saturated zones. Where each of these DNAPL phases exist in the subsurface is further complicated by how the DNAPL was released (slow continuous releases typically cause the DNAPL to go to greater depth, versus a fast release), the heterogeneity of the geology (DNAPL free phase movement is greatly affected by the permeability and stratigraphy of the geology), and the hydrogeology of the contaminated site.

DNAPLs also have relatively low aqueous solubilities and diffuse into or sorb onto soils more rapidly than they will desorb or diffuse out. Therefore, remediation of DNAPLs is often an expensive and long-term commitment using existing remedial approaches. Current "pump and treat" technologies are often expected to operate for decades or even hundreds of years before the site is cleaned up. The long-term operating costs can run into the million to tens of millions of dollars for a relatively small site. Remediation of bedrock groundwater poses a particularly difficult problem because of the inherent difficulty of assessing groundwater and DNAPL movement in fractured geologies. If DNAPLs can be naturally (intrinsically) biodegraded, and the efficacy of intrinsic biodegradation to contain a DNAPL plume or reduce DNAPL masses can be documented and monitored, then intrinsic bioremediation offers a far more cost-effective means to obtain site cleanup than current pump and treat technologies. The cost savings is realized by working with, rather than engineering around, the natural processes of DNAPL transport and biodegradation.

Chlorinated compounds like TCE do naturally biodegrade in subsurface environments under appropriate conditions. In anaerobic environments, chlorinated ethenes can act as electron acceptors in a process called reductive dehalogenation (specifically, reductive dechlorination). However, the extent of dechlorination has been shown to vary in anaerobic dechlorination studies, depending upon the flow and availability of electrons within the anaerobic microbial community. For example, dechlorinated intermediates such as dichloroethene (DCE) and vinyl chloride (VC) were found to accumulate during the dechlorination of tetrachloroethene (PCE) and TCE (Bower and McCarty, 1983; Parsons *et al.*, 1984; Wilson *et al.* 1986). However, Freedman and Gossett (1989) were the first to observe the complete dechlorination of PCE to ethene in a methanogenic enrichment culture, and DeBruin *et al.* (1992) showed that PCE could be reduced to ethane. The first field observation of the complete dechlorination of PCE to ethene was documented by Major *et al.* (1991). Their laboratory and field study showed that anaerobic microorganisms in a low permeable aquifer were capable of naturally dechlorinating PCE in the presence of methanol. Since then, Wilson *et al.* (1994), and Fiorenza *et al.* (1994) have shown that chlorinated ethenes such as PCE and TCE can be intrinsically biodegraded to ethene under anaerobic conditions by indigenous methanogenic, acetogenic, and sulphate-reducing bacteria. Beeman *et al.* (1994) have

demonstrated that this dechlorination activity can be promoted or enhanced *in situ* under sulphate-reducing conditions. This paper presents evidence of intrinsic biodegradation of TCE in a bedrock aquifer.

## SITE DESCRIPTION

The site is located in the Finger Lakes region of New York. The site is underlain by 3 to 7 metres of overburden which is generally fine-grained and of low permeability. A thick sequence of carbonate strata, consisting of approximately 14 metres of limestone (shallow bedrock) and 37 metres of dolomites (deep bedrock), underlies the overburden. The water table is located in the overburden just below ground surface in the late fall, winter, and early spring. However, significant desaturation of the overburden occurs during the summer as a result of evapotranspiration. A temporally persistent water-table divide occurs immediately to the east of the plant building and is oriented in a north-south direction. The evaporation pits and waste solvent tank are located west of the divide and groundwater flow in these areas is generally to the northwest (see Figure 1a). Horizontal flow velocities of 0.15 and 1.3 metres per day have been estimated for the overburden and shallow bedrock, respectively. Flow in the shallow bedrock is believed to be primarily along bedding planes which may be widened somewhat by solution. The vertical permeability of the shallow bedrock appears to be limited. Downward hydraulic gradients are particularly strong between the shallow and deep bedrock, with waterlevel differences in excess of 12 metres observed during dry periods of the year.

## RESULTS AND DISCUSSION

Groundwater samples were collected from twenty existing monitoring wells located along the groundwater flowpath upgradient (background), transgradient, and downgradient from the evaporation pits and waste solvent tank. Groundwater samples were analysed for dissolved oxygen (DO), oxidation-reduction potential (ORP), VOCs, dissolved hydrocarbon gases (ethene, ethane, and methane), oxygenates (methanol, acetone), volatile fatty acids (acetic acid), inorganic anions, and microbiological parameters (biomass, community composition, and metabolic status).

**Redox Conditions:** The groundwater in the overburden and the bedrock downgradient from the former evaporation pits and waste solvent tank was predominantly anaerobic, characterized by negative ORP, and DO depletion.

**Distribution of Selected VOCs and Ethene:** The presence of 1,2-DCE, and VC in groundwater samples collected from the overburden and bedrock provides evidence that TCE is being biodegraded at the site. These TCE degradation products were not used or produced at the site, and thus their presence can only be attributed to the dechlorination of TCE. Ethene was reported in a number of the groundwater samples, at concentrations ranging up to 17,110 µg/L. The presence of ethene provides evidence that VC is being biodegraded to non-toxic end products in the groundwater at the site. The relative distributions of TCE, 1,2-DCE, VC, and ethene in the shallow bedrock, shown in Figures 1a to 1d, suggest that migration of the chlorinated VOCs in the shallow bedrock groundwater is being controlled by biodegradation. The distribution of TCE was much less extensive than the observed distributions for 1,2-DCE, VC, and ethene. However, the distribution of VC was essentially the same as the distribution of 1,2-DCE. The presence of ethene in groundwater samples collected at and downgradient from the VC plume boundary confirms that VC is being dechlorinated.

**Distribution of Oxygenates:** The distribution of acetone was considerably limited in comparison to the distribution of the chlorinated VOCs and ethene (Figure 2). Methanol was only reported in one well (DGC-8B), located in the immediate vicinity of one of the former evaporation pits. Generally, the acetone and methanol distributions coincide with the distribution of TCE. This suggests that acetone and methanol are being biodegraded, in spite of their higher solubility and mobility, and that they may be the substrates that are supporting the dechlorination of TCE. The literature indicates that methanol is an excellent substrate for enhancing anaerobic dechlorinating activity (Freedman and Gossett, 1989; Major et al., 1991). Methanol can be readily metabolized by acetogenic bacteria to acetate and hydrogen, which can

be metabolized by sulphate-reducing and methanogenic bacteria (DiStefano et al., 1992). Acetone is similar to methanol in that it is a slightly oxidized organic chemical, and would likely be a very effective growth substrate for anaerobic bacteria.

**Distribution of Methane, Volatile Fatty Acids, and Inorganic Anions:** The distribution of methane, acetic acid, and selected inorganic anions was used as indirect measures of the activity of functional groups of microorganisms in the bedrock. The distributions of methane, sulphate, and acetic acid are shown in Figures 3a to 3c, respectively. The presence of acetic acid and biotic methane, and the depletion of sulphate, provide indirect evidence that acetogenic, methanogenic, and sulphate-reducing bacteria are active in the shallow bedrock at the site. The activity of each of these groups of microorganisms has been associated with the dechlorination of chlorinated ethenes. In the presence of available sulphate, sulphate reduction tends to suppress methanogenesis because sulphate-reducing bacteria have a greater affinity for hydrogen and acetate and outcompete methanogenic bacteria (Gossett et al., 1992). However, these microorganisms can co-exist in the same habitat in the presence of a complex web of cofactors, end-products, and interspecies hydrogen transfer pathways that promote the establishment of a healthy dechlorinating microbial community. Interestingly, the depletion of acetone and methanol coincide with the higher concentrations of acetate, methane and ethene, and depletion of sulfate. This suggests that acetogenic and methanogenic bacteria may be responsible for the dechlorination of VC to ethene.

**Distribution of Methane Isotopes:** Measurement of the carbon and hydrogen isotope ratios of methane was conducted to separate biotic and thermogenic (abiotic) methane, and to indicate where biological activity may have been occurring. Thermogenic methane deposits have been reported in the vicinity of the site. Microorganisms preferentially use the lighter isotopes of carbon and hydrogen, and therefore, methane derived from biochemical reactions is isotopically lighter than thermogenic methane. Isotopic analysis of methane in the groundwater samples clearly indicated that the methane was produced biotically. More importantly, isotopic analysis of the methane in the groundwater samples clearly showed that the biotic methane was produced in the bedrock and does not result from downward transport from the overburden.

**Microbiology:** The microbial biomass in the groundwater ranged from  $1.6 \times 10^2$  cells/mL to  $4.2 \times 10^4$  cell/mL. The total biomass was orders of magnitude higher near VOC source areas, and areas with measurable concentrations of acetone and methanol, as compared to downgradient or background (upgradient) locations. The microbial biomass distribution, along with the chemical data, suggests that a biologically active zone (BAZ) has developed in response to the presence of VOCs, including acetone, and methanol. Analysis of respiratory quinones indicated that the microbial populations at the site are strictly anaerobic.

## CONCLUSIONS

This study provides evidence that microbial populations can exist and function in bedrock groundwater environments. Furthermore, these populations possess an intrinsic capability to anaerobically dechlorinate TCE to ethene when suitable substrates are present to support their growth. At this study site, an active and diverse anaerobic microbial community, consisting of sulphate-reducing, methanogenic, and acetogenic bacteria has been established and is being maintained by acetone and methanol. This anaerobic microbial community is controlling the distribution and migration of TCE, its biodegradation products, and other chemicals at the site.

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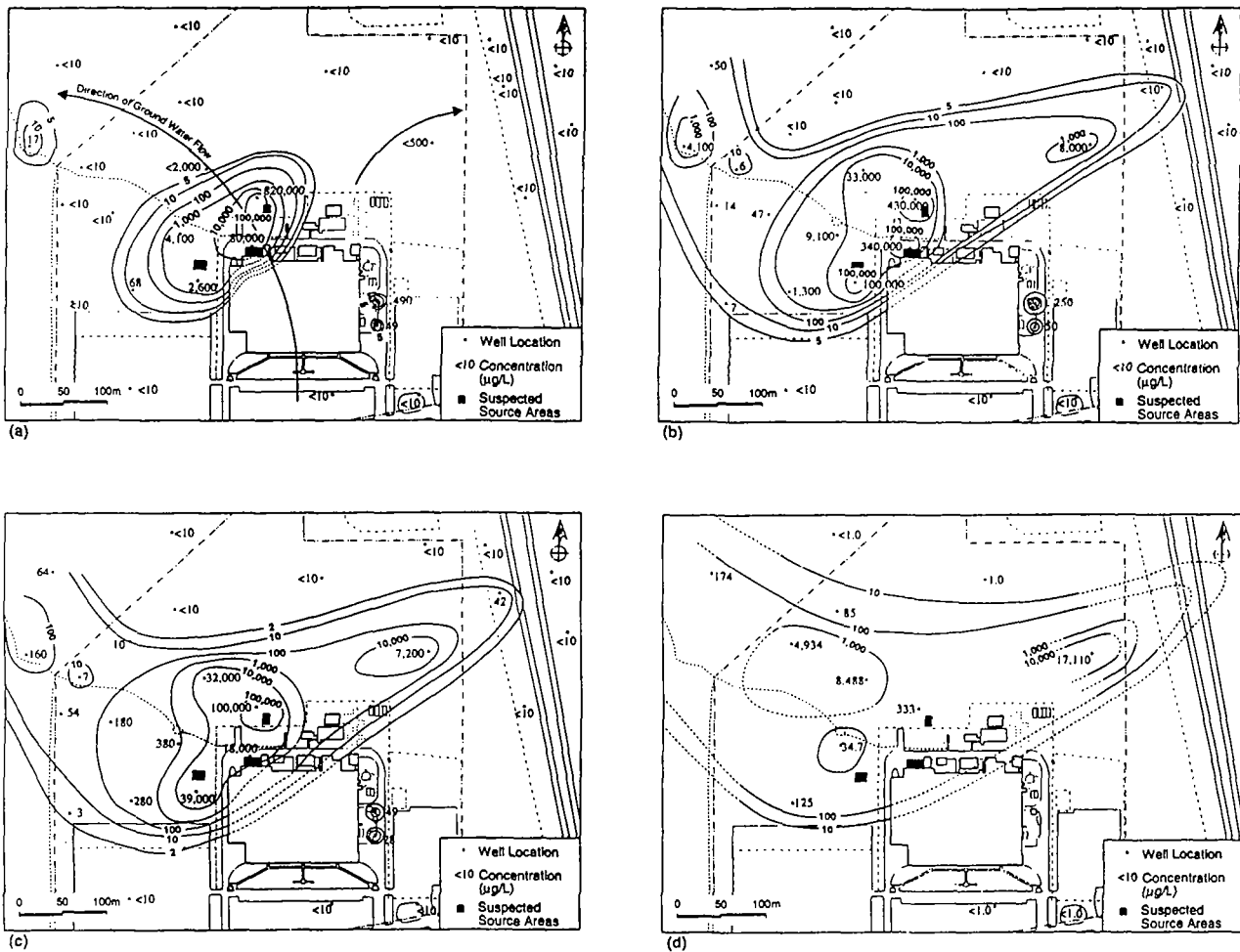


FIGURE 1. Isoconcentration contours of (a) trichloroethene, (b) 1,2-dichloroethene, (c) vinyl chloride, and (d) ethene in the shallow bedrock groundwater (contours dashed where inferred).

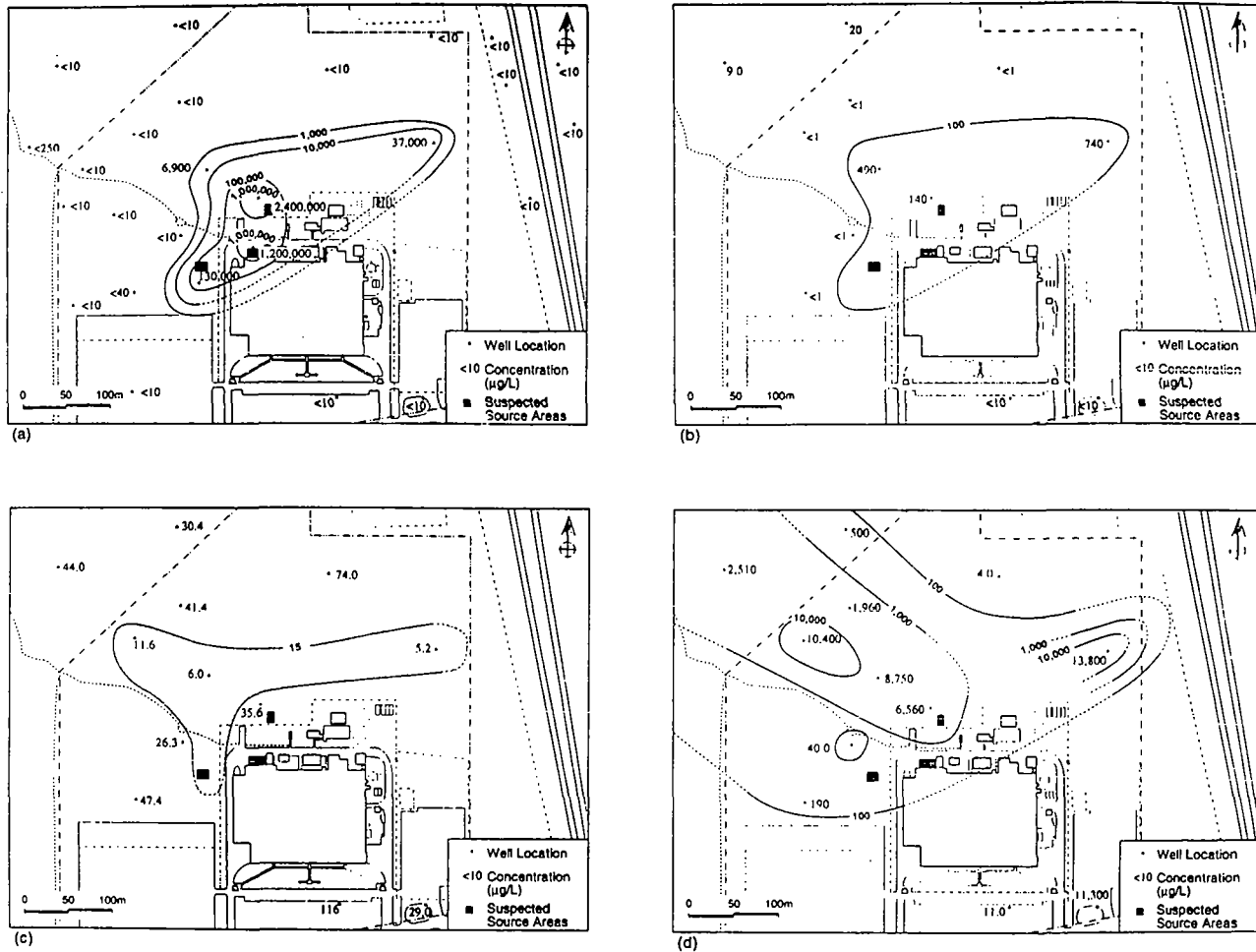


FIGURE 2. Isoconcentration contours of (a) acetone, (b) acetic acid, (c) sulfate, and (d) methane in the shallow bedrock groundwater (contours dashed where inferred).