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Evaluating the fate of chlorinated ethenes in streambed sediments by combining stable isotope, geochemical and microbial methods

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ABSTRACT

The occurrence of chlorinated ethene transformation in a streambed was investigated using concentration and carbon isotope data from water samples taken at different locations and depths within a 15 × 25 m study area across which a tetrachloroethene (PCE) plume discharges. Furthermore, it was evaluated how the degree of transformation is related to groundwater discharge rates, redox conditions, solid organic matter content (SOM) and microbial factors. Groundwater discharge rates were quantified based on streambed temperatures, and redox conditions using concentrations of dissolved redox-sensitive species. The degree of chlorinated ethene transformation was highly variable in space from no transformation to transformation beyond ethene. Complete reductive dechlorination to ethane and ethene occurred at locations with at least sulfate-reducing conditions and with a residence time in the samples streambed zone (80 cm depth) of at least 10 days. Among these locations, *Dehalococcoides* was detected using a PCR method where SOM contents were >2% w/w and where transformation proceeded beyond ethene. However, it was not detected at locations with low SOM, which may cause an insufficient H_2 supply to sustain a detectably dense *Dehalococcoides* population. Additionally, it is possible that other organisms are responsible for the biodegradation. A microcosm study with streambed sediments demonstrated the potential of VC oxidation throughout the site even at locations without a pre-exposure to VC, consistent with the detection of the epoxyalkane:coenzyme M transferase (EaCoMT) gene involved in the degradation of chlorinated ethenes via epoxidation. In contrast, no aerobic transformation of cDCE in microcosms over a period of 1.5 years was observed. In summary, the study demonstrated that carbon isotope analysis is a sensitive tool to identify the degree of chlorinated ethene transformation even in hydrologically and geochemically complex streambed systems. In addition, it was observed that the degree of transformation is related to redox conditions, which in turn depend on groundwater discharge rates.

1. Introduction

Chlorinated ethenes are among the most frequently detected groundwater contaminants in developed countries (Squillace et al., 1999). Due to their high density and viscosity (Pankow and Cherry, 1996), chlorinated solvents can migrate to a substantial depth in aquifers. Chlorinated solvents have a relatively high solubility compared to regulatory values and low tendency to sorb, facilitating the formation of long contaminant plumes (Schwarzenbach et al., 1983; Wiedemeier et al., 1999) that may reach surface water bodies (Ellis and Rivett, 2007). In the vicinity of rivers and lakes, sediment quality may change abruptly compared to the aquifer, leading

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to different geochemical conditions that influence the fate of chlorinated ethenes (Lorah and Olsen, 1999; Chapman et al., 2007). Higher contents of organic carbon can lead to reducing conditions in stream and lake sediments whereas conditions may become oxic again at the surface of streambeds.

Chlorinated ethenes are relatively oxidized compounds due to the presence of electronegative substituents; therefore, they often serve as electron acceptors with natural or anthropogenic organic compounds as the electron donor species. Tetrachloroethene (PCE) with its four chlorine atoms, undergoes reductive dechlorination under all redox conditions expect in oxic aquifers. Reductive dechlorination of trichloroethene (TCE) occurs under Fe(III)-reducing or more strongly reducing conditions, while reductive dechlorination of cis-1,2-Dichloroethene (cDCE) and vinyl chloride (VC) require sulfate-reducing or methanogenic conditions (Vogel and McCarty, 1985; Vogel et al., 1987; Freedman and Gossett, 1989; DiStefano et al., 1991; Maymo-Gatell et al., 1995; Rügge et al., 1999; Bradley, 2000). Hence, the reductive dechlorination of chlorinated ethenes is strongly influenced by the local redox conditions. The transformation intermediates can also be oxidized metabolically and co-metabolically under oxic and/or anoxic conditions (Wackett and Gibson, 1988; Little et al., 1988; Oldenhuis et al., 1989; Tsien et al., 1989; Nelson et al., 1987; Davis and Carpenter, 1990; Fox et al., 1990; Bradley and Chapelle, 1998; Verce et al., 2001). Since the intermediates, especially VC, have a high toxicity, it is important to know whether complete or only partial transformation is occurring at a site.

Different methods have been proposed to evaluate the occurrence of complete reductive dechlorination of chlorinated ethenes including: 1) characterization of geochemical conditions (availability of electron donors such as H_2, Luijten et al., 2004; assessment of redox conditions, Witt et al., 2002; Lu et al., 2006), 2) characterization of parent and daughter product patterns (Witt et al., 2002) and 3) assessment of the presence and activity of key organisms such as *Dehalococcoides* (Fennell et al., 2001; Hendrickson et al., 2002; Müller et al., 2004; Duhamel and Edwards, 2006; Rahm and Richardson, 2008; Imfeld et al., 2008; Lee et al., 2008). While geochemical conditions and the presence of certain organisms can indicate whether the conditions are favorable for reductive dechlorination, these parameters usually do not provide information about the degree of transformation. Furthermore, assessment of concentration patterns can be ambiguous since they are also affected by physical processes such as dilution, especially at the surface-groundwater interface, and because non-unique end products may be formed such as CH_4 and CO_2 (Bradley and Chapelle, 2000). Recently compound-specific isotope analysis was proposed as a complementary tool to assess the degree of reductive dechlorination (Hunkeler et al., 1999; Sherwood Lollar et al., 2001; Hunkeler et al., 2002; Song et al., 2002). The method relies on differences in reaction rates between molecules with light and heavy isotopes, which lead to the enrichment of heavy isotopes in the remaining substrate. Previous studies have suggested that the method is particularly sensitive to assess reduction dechlorination of cDCE and

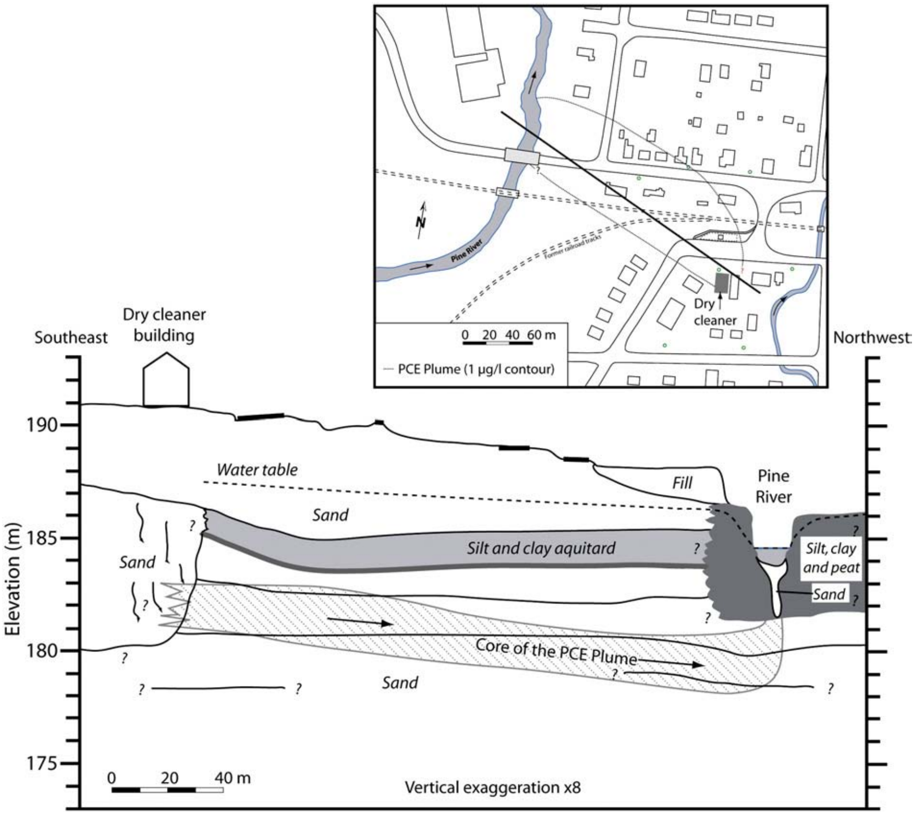

Fig. 1. Schematic illustration of study site with PCE plume migration pathway. Modified from Conant et al. (2004), Hunkeler et al. (2004).