Biodegradation of PCE and TCE in landfill leachate predicted from concentrations of molecular hydrogen: a case study

Mary E. Gonsoulin1, Barbara H. Wilson2 & John T. Wilson1

1US Environmental Protection Agency, Robert Kerr Research Laboratory, P.O. Box 1198, OK 74820, USA; 2Dynamac, Inc., 3501 Oakbridge Blvd., Ada, OK 74820, USA

Accepted 27 June 2003

Abstract

The Refuse Hideaway Landfill (23-acre) received municipal, commercial, and industrial waste between 1974 and 1988. It was designed as a “natural attenuation” landfill and no provision was made to collect and treat contaminated water. Natural biological degradation through sequential reductive dechlorination had been an important mechanism for natural attenuation at the site. We used the concentration of hydrogen to forecast whether reductive dechlorination would continue over time at particular locations in the plume. Based on published literature, reductive dechlorination and natural attenuation of PCE, TCE, and cis-DCE can be expected in the aquifer if the concentration of molecular hydrogen in monitoring wells are adequate (>1 nanomolar). Reductive dechlorination can be expected to continue as the groundwater moves down gradient. Natural attenuation through reductive dechlorination is not expected in flow paths that originate at down gradient monitoring wells with low concentrations of molecular hydrogen (<1 nanomolar). In three monitoring wells at the margin of the landfill and in five monitoring wells down gradient of the landfill, groundwater maintained a molecular hydrogen concentration, ranging from 1.30 to 9.17 nanomolar, that is adequate for reductive dechlorination. In three of the monitoring wells far down gradient of the landfill, the concentration of molecular hydrogen (0.33 to 0.83 nanomolar) was not adequate to support reductive dechlorination. In wells with adequate concentrations of hydrogen, the concentrations of chlorinated volatile organic compounds were attenuated over time, or concentrations of chlorinated volatile organics were below the detection limit. In wells with inadequate concentrations of hydrogen, the concentrations of chlorinated organic compounds attenuated at a slower rate over time. In wells with adequate hydrogen the first order rate of attenuation of PCE, TCE, cis-DCE and total chlorinated volatile organic compounds varies from 0.38 to 0.18 per year. In wells without adequate hydrogen the rate varies from 0.015 to 0.006 per year.

Introduction

The Refuse Hideaway Landfill (near Madison, Wisconsin, USA) was licensed for waste disposal between 1974 and 1988. Municipal, commercial, and industrial wastes were disposed at the site. This 23-acre landfill was designed as a “natural attenuation” landfill and no provision was made to collect and treat contaminated water that moved through the waste (Wisconsin Department of Natural Resources 1995). As a result, the volatile organic compounds (VOCs), such as Tetrachloroethene (PCE) and Trichloroethene (TCE) moved out of the landfill and into the ground water. The contaminated water existed under the landfill and extended southwest and slightly northwest of the site. The landfill was closed in late 1988 and the waste was covered with a cap. In January 1988, the landfill owner declared bankruptcy and in March 1989, the state of Wisconsin continued the investigation and cleanup of the landfill.

We provided technical assistance to EPA (Region 5) and the State of Wisconsin on the landfill. The Record of Decision (ROD) selected a landfill cap, a gas and leachate extraction system, and ground water pump and treat for ground water contamination exceeding 200 part per billion (ppb) VOCs. The landfill had been capped. We were asked to determine whether other corrective action for the plume in the ground water was necessary, or if the existing landfill cap, gas
and leachate extraction system, and monitored natural attenuation (MNA) would adequately treat the contamination in the plume outside the cap. As one basis for our determination, we sampled ground water and measured hydrogen in selected monitoring wells at the site. Natural biological degradation through sequential reductive dechlorination had been an important mechanism for natural attenuation at the site. We used the concentration of hydrogen to forecast whether reductive dechlorination would continue over time at particular locations in the plume.

**Role of molecular hydrogen in natural biodegradation of chlorinated solvents**

The measurement of molecular hydrogen in ground water to accurately describe predominant in situ redox reactions has recently been utilized to overcome the limitations imposed by traditional redox measurements (Lovley & Goodwin 1988; Lovley et al. 1994; Chapelle et al. 1995). Field evidence suggests that dissolved H₂ concentrations in ground water can be associated with specific microbial processes, and these concentrations can be used to identify zones of methanogenesis, sulfate reduction, and iron reduction in the subsurface (Chapelle 1996). Dissolved hydrogen may also be used to describe the functioning of fermentation reactions in landfills (Mormile et al. 1996), hydrogen metabolism in sedimentary ecosystems (Goodwin et al. 1988), the bioremediation of petroleum hydrocarbons in a gas condensate contaminated aquifer (Gieg et al. 1999), and chromate reduction in aquifer sediments (Marsh & McInerney 2001). Direct delivery of molecular hydrogen or addition of lactic acid to the subsurface may also be used during situ bioremediation for enhanced reductive dechlorination (Capiro et al. 2002; Koenigsberg et al. 2001; Newell et al. 2000).

Dissolved molecular hydrogen (H₂) plays a significant role in the fate of chlorinated solvents in the subsurface because it can serve as an electron donor during reductive dechlorination (Maymo-Gatell et al. 1997; DiStefano et al. 1992; Wiedemeier et al. 1999). When the organisms use hydrogen to produce ATP, the process is termed halorespiration (Hollinger et al. 1998; Scholz-Muraiatsu et al. 1995; Maymo-Gatell et al. 1999). The DNA from *Dehalococcoides*, an organism that carries out halorespiration, is widely distributed in contaminated ground water in Europe and North America (Hendrickson et al. 2002.). Biological reductive dechlorination requires sufficiently reduced subsurface conditions to support fermentation for the generation of hydrogen from fermentable compounds such as native organic matter, volatile fatty acids from landfill leachate, and soluble constituents of petroleum hydrocarbons (benzene, toluene, ethylbenzene, and xylenes). Although PCE and TCE can be reductively dechlorinated using a variety of electron donors, dechlorination of DCE and vinyl chloride requires molecular hydrogen. The hydrogen produced during fermentation is valuable as a high-energy electron donor, and competition for hydrogen exists between halorespiring, methanogenic, sulfate-reducing, iron-reducing, and denitrifying bacteria (Fennell & Gossett 1998; Ballapragada et al. 1997). Halorespiration can degrade chlorinated ethenes (PCE, TCE, DCE, VC), chlorinated ethanes (TCA, 1,2DCA), and chlorinated benzenes (Wiedemeier et al. 1999).

Identification of the predominant geochemical process is important in ground water impacted by chlorinated solvents because iron reduction, sulfate reduction, and methanogenesis can occur simultaneously at the same location in landfills (Cozzarelli et al. 2000; Jakobsen et al. 1998), hydrocarbon plumes (Vroblesky et al. 1996), and marine sediments (Canfield et al. 1993). The identification of the predominant geochemical process is especially important in understanding the behavior of chlorinated solvent plumes. Reduction dechlorination of PCE and TCE occurs most readily under methanogenic conditions, although methanogens compete with dechlorinators (halorespi-rators) for H₂ (Smatlak et al. 1996).

Oxidative processes may also affect the fate of chlorinated solvent. The daughter products, cis-dichloroethylene and vinyl chloride, of reductive dechlorination of PCE and TCE can be oxidized under the less reducing conditions of iron-reduction (Bradley et al. 1998a; Bradley & Chapelle 1996, 1997). Vinyl chloride and, at some sites, cis-dichloroethylene, can be degraded aerobically (Bradley & Chapelle 1998a, b; McCarty & Semprini 1994; Hartmans & de Bont 1992). The predominant geochemical process occurring at specific locations can be identified using dissolved hydrogen concentrations. This will assist evaluation of the behavior of the parent and daughter products at those locations and may help predict their future performance.

The concentration of dissolved hydrogen in ground water is a sensitive indicator of the dominant electron acceptor of the system measured. Concentrations of dissolved hydrogen correlated with important geochemical processes are present at nanomolar (nM)