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

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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 ground water 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, ground water 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 H_2 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 in situ bioremediation for enhanced reductive dechlorination (Capiro et al. 2002; Koenigsberg et al. 2001; Newell et al. 2000).

Dissolved molecular hydrogen (H_2) 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-Muramatsu 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. Reductive dechlorination of PCE and TCE occurs most readily under methanogenic conditions, although methanogens compete with dechlorinators (halorespirators) for H_2 (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)

levels: denitrification (<1 nM), Fe(III) reduction (0.2 to 0.8 nM), sulfate reduction (1 to 4 nM), reductive dechlorination (>1 nM), and methanogenesis (5 to 20 nM) (Fennell & Gossett 1998; Yang & McCarty 1998; Jakobsen et al. 1998; Smatlak et al. 1996; Maymo-Gatell et al. 1995). Halorespiration requires approximately 1 nM of dissolved hydrogen for growth to occur (Smatlak et al. 1996).

Hydrogen is easily created in the environment, and the collection of samples for dissolved hydrogen has several requirements. Dissolved hydrogen cannot be analyzed on newly installed wells, and well installation may affect nearby wells with respect to hydrogen concentrations (Bjerg et al. 1997). Hydrogen is released from mineral and iron surfaces during well installation and development, and a period of at least two months should pass before hydrogen is measured. Hydrogen cannot be measured in steel wells, but well materials consisting of polyvinyl chloride (PVC), Teflon, and probably stainless steel are suitable for use (Bjerg et al. 1997). Submersible pumps cannot be utilized for dissolved hydrogen analysis because hydrogen is produced during sample acquisition; however, piston, positive displacement, or peristaltic pumps are commonly used for collection of hydrogen samples (Microseeps 2002).

Molecular hydrogen is sampled from ground water by equilibrating the hydrogen in ground water with hydrogen in an enclosed bubble that is exposed to large volumes of water. This is often called the bubble strip method because the hydrogen is stripped from the well water and concentrated into the gas bubble, which is then analyzed. Hydrogen is generally the final sample taken at the wellhead because equilibration of the hydrogen in ground water with hydrogen in the bubble requires at least 30 minutes. Due to the time involved in equilibration, duplicate samples are normally not collected. Some practitioners measure the headspace every 15 minutes during equilibration until a stable concentration is reached, but this is still considered one analysis. Due to the substantial requirements for obtaining a dissolved hydrogen sample and its subsequent analysis, dissolved hydrogen measurements are normally made only at selected sites and at selected wells. However, the information obtained can be quite valuable for evaluating sites for natural attenuation, especially those with chlorinated solvents.

We analyzed the long-term monitoring data from the site for trends in the concentration of VOAs in ground water before and after the installation of a landfill cap with vent wells and a leachate collection system under the cap. Also, we requested one round of samples as described in the EPA protocol for evaluating natural attenuation (U.S. EPA 1998). In particular, we requested data on the concentration of hydrogen, to determine if the ground water has sufficient hydrogen to support continued reductive dechlorination.

Nature and extent of contamination

The landfill (23-acre) was a privately owned unlined landfill that received municipal, industrial and commercial waste between 1974 and 1988. The landfill was capped when it was closed. The estimated total volume of waste was 1.2 million cubic yards. Significant erosion at several areas of the landfill cover occurred in 1988 and 1992. Therefore, in the fall of 1992, the cap was repaired and restored (Hydro-Search Inc. 1994). Monitoring wells were sampled for hydrogen in 1998, ten years after the landfill was closed, and six years after the repair of the cap and installation of the leachate collection system. In 1991 the average BOD of the collected leachate was 675 mg/L. At the ground water temperatures in Wisconsin, fill composed of domestic solid waste should continue to produce leachate ten years after landfilling.

A summary of the concentrations of VOCs detected in the ground water monitoring wells is presented in Table 1. Our recommendations were based on the evaluation of the analytical data from the 13 selected monitoring wells to determine whether the data indicated natural attenuation was occurring. Figure 1 depicts the relationship between the landfill and the slope of the water table. The landfill was near a ground water high. The predominant direction of ground water flow is to the southeast. Figure 2 presents the location of monitoring wells that are discussed in Table 1 or elsewhere in the text.

The greatest concentrations of contaminants were found near the south and west landfill boundaries. The plume extended to a distance of approximately 370 meters to the northwest from the northwest edge of the landfill and approximately, 1,200 meters to the southwest from the southwest edge of the landfill (Montgomery Watson 1997). Volatile organic compounds detected at concentrations exceeding the Administrative code Chapter Natural Resource 140 Enforcement standards (ESs) included: Benzene, Chloroform, 1,2-Dichloroethane (1,2-DCA), trans-1,2-Dichloroethene (1,2-DCE), Tetrachloroethene (PCE), Trichloroethene (TCE), and Vinyl Chloride.

Table 1. Relationship between the attenuation over time of total volatile organic compounds in selected monitoring wells at the Refuse Hideaway Landfill Site, and the concentration of molecular hydrogen in the monitoring wells

| Monitoring Wells	Highest recorded 1988–1992	1996	2001	Hydrogen concentration February 1998
	Total VOC (μg/liter)	Total VOC (μg/liter)	Total VOC (μg/liter)	Nanomolar
Wells at the margin of landfill				
8 S	1130	Not sampled	Not sampled	9.17
27 S	174	30.3	18.9	3.80
21 S	494	20.7	1.8	3.23
Wells down gradient of the landfill				
22 D	29.8	14.8	14.2	0.52
30 I	Not detected	Not detected	Not dected	1.30
31 I	29	Not sampled	Not sampled	0.33
32 S	Not detected	Not detected	Not detected	1.38
40 I	30	Not sampled	Not sampled	28.3 (?)
41 I	Not detected	Not detected	Not detected	1.71
41 D	Not detected	Not detected	Not detected	3.98
Wells side gradient to landfill and probably never contaminated (background)				
25 S	Not detected	Not detected	Not detected	0.83
34 S	Not detected	Not detected	Not detected	0.66
35 S	Not detected	Not detected	Not detected	0.70
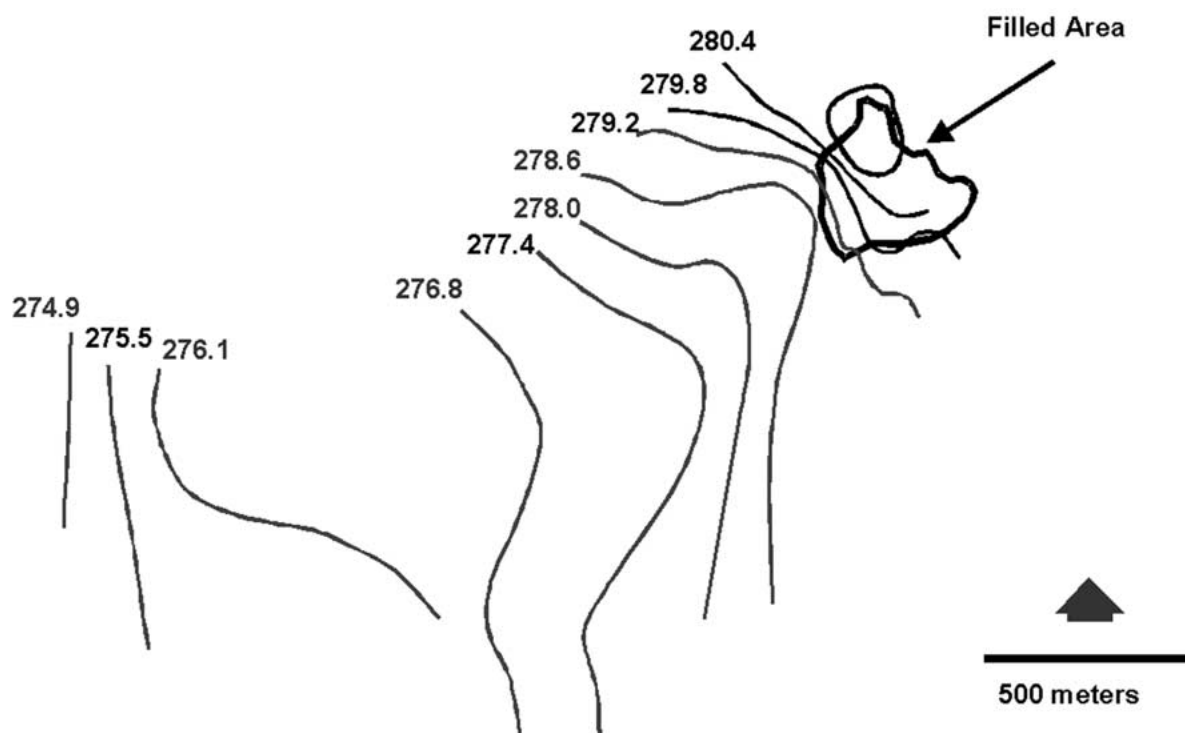
Figure 1. Water table elevations (meters above sea level) and direction of ground water flow down gradient of the Refuse Hideaway Landfill.
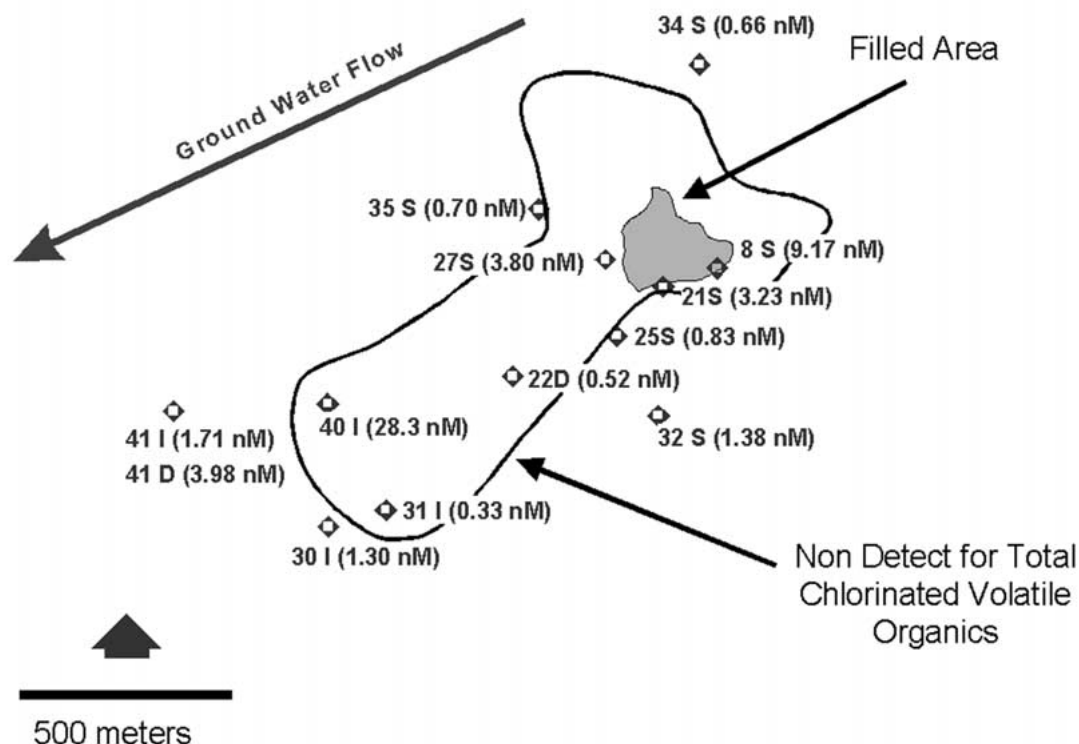
Figure 2. Distribution of monitoring wells near and down gradient of the Refuse Hideaway Landfill. Wells labeled with an **S** are screened across the water table. Wells labeled with an **I** are screened at the midpoint of the aquifer. Wells labeled with a **D** are screened at the bottom of the aquifer. The concentration of dissolved molecular hydrogen is presented in parentheses after the label of the well.

Methods and materials for hydrogen sampling

Ground water for analysis of dissolved hydrogen was collected through polyethylene tubing. Water was lifted by a peristaltic pump at land surface. Hydrogen samples were collected in the field using the bubble strip method. This method takes advantage of the large Henry's constant for hydrogen (McInnes & Kampbell 2000; Kampbell et al. 1998; Chapelle et al. 1997). Water was pumped from the monitoring wells. A 250-mL glass gas-sampling bulb was attached to the tubing on the outflow side of the pump. The bulb was filled with water, and then 20 mL of commercially available ultra high purity grade N_2 was injected to create a headspace for concentration of the H_2 gas into the N_2 bubble. The bulb was adjusted to an angle of 45 degrees, and well water was pumped through the bulb at a constant flow rate of between 400 and 700 mL/min for 30 minutes. This equilibrated the hydrogen in the N_2 bubble with the hydrogen dissolved in the flowing ground water. After equilibration, the bulb was closed, and a 10-mL sample was withdrawn from the N_2 bubble using a gas tight syringe. The 10-mL sample (at atmospheric pressure) was immediately injected into a sealed 25-mL serum bottle containing nitrogen at atmospheric pressure, resulting in a dilution of 3.5 fold (10 ml to a total volume of 35 ml). The sample bottles had been previously prepared by displacing the air with a stream of ultra pure hydrogen-free N_2, then immediately capped with a Teflon-lined, gray butyl rubber septa. The septum was sealed with a crimp cap seal; the entire top and neck were further sealed by a minimum of 5 mm silicone rubber caulking compound. The hydrogen samples were placed in a cooler with gel blue ice packs and shipped to R.S. Kerr Environmental Research Center, Ada, OK, for analysis.

The hydrogen samples were analyzed using a Trace Analytical RGA3 Reduction Gas Analyzer with a column temperature of 100 °C, a detector temperature of 265 °C, and an injection volume of 2 mL. The carrier gas was high purity nitrogen at a flow rate of 22 mL/min; the retention time of H_2 was 0.5 minutes. Strong absorption of UV light by mercury vapor is
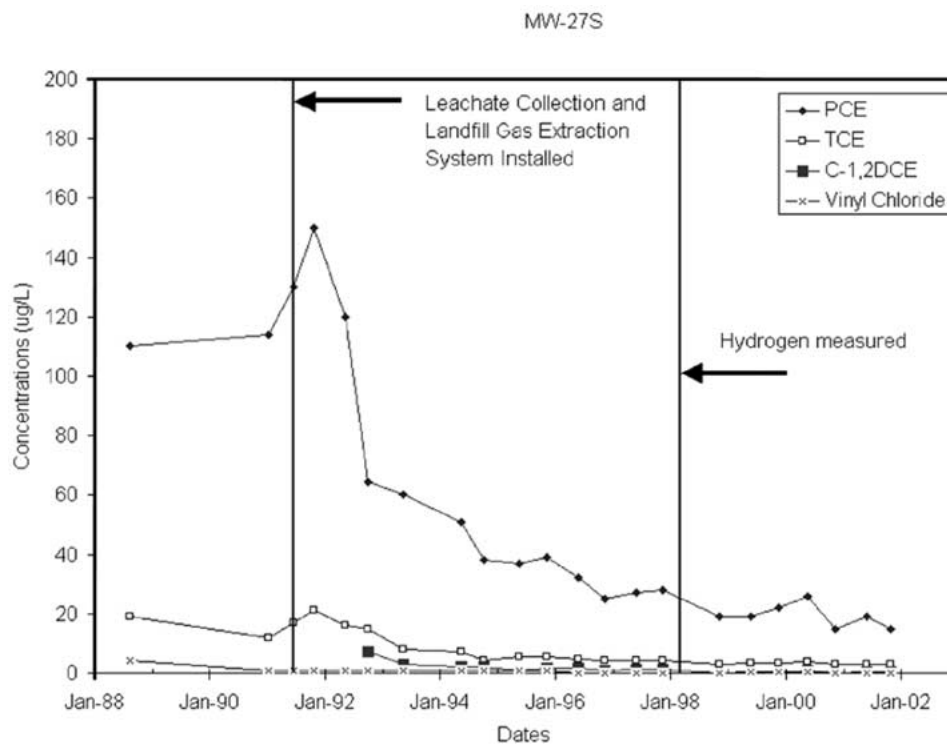
MW-27S

Figure 3. Change in concentrations of chlorinated organic contaminants in monitoring well 27 S over time.
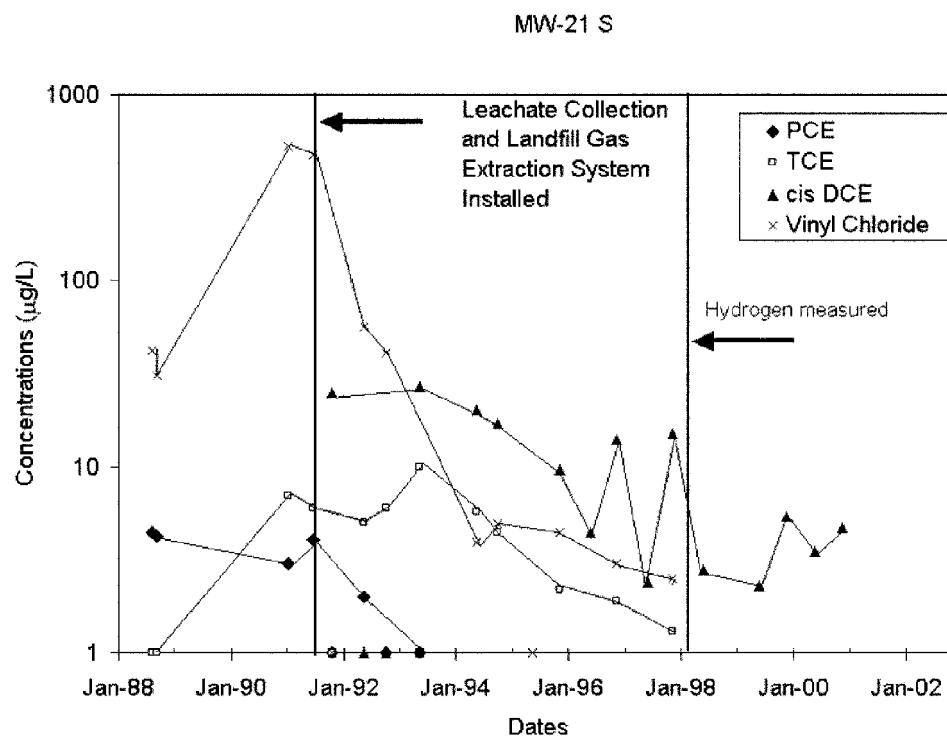
MW-21 S

Figure 4. Change in concentrations of chlorinated organic contaminants in monitoring well 21 S over time.

the basis for the detector used in the chromatograph. The reducing compounds, to be analyzed, were passed through a heated mercuric oxide bed and reacted with mercuric oxide, releasing mercury vapor. The free vapor is measured in a photometric cell as a change in the absorption of UV light, with the change directly proportional to the concentration of the reducing compound quantified.

A seven-point calibration curve was prepared using hydrogen standards ranging from 0.0 to 20.0 ppm v/v in nitrogen. The hydrogen standards were prepared by adding appropriate volumes of a hydrogen mixture (100 ppm in nitrogen) into sealed serum bottles containing nitrogen (Kampbell et al. 1998). The bottles were equilibrated for one hour before gas chromatographic analysis was initiated. Gas tight syringes were used in all phases of the standard preparation and hydrogen analysis procedures.

Results

The Technical Protocol for Evaluating Natural Attenuation of Chlorinated Solvents in Ground Water (U.S. EPA 1998) predicts that reductive dechlorination is possible when the molecular hydrogen concentration exceeds 1 nM (their table 2.3, p. 29). Table 1 presents the relationship between the attenuation of chlorinated solvents in the monitoring wells over time and the concentration of molecular hydrogen in the well water in 1998, which was ten years after the installation of the landfill gas and leachate collection system. The concentration of molecular hydrogen in three wells at the margin of the landfill was high enough to support reductive dechlorination, ranging from 3.2 to 9.2 nM. See Figure 2 for location of the monitoring wells.

The hydrogen in the ground water samples was probably formed by natural fermentation reactions supported by the dissolved organic carbon in the leachate from the landfill. Mormile et al. (1996) collected active fill material from two landfills in the United States and determined the steady state concentration of hydrogen sustained by the fill material. The median steady-state concentrations of hydrogen in the gas in the fill corresponded to concentrations in ground water of 1,400 and 5,200 nM respectively. The hydrogen concentrations in the monitoring wells at the Refuse Hideaway site were approximately one thousand fold lower than the concentration of hydrogen that might be expected in active fill material.

At monitoring well 27 S, screened at the water table at the margin of the landfill, the maximum concentration of total VOCs was 174 μg/L (Table 1). After the installation of the leachate and gas collection system, the concentrations of chlorinated organic compounds began to decline (Table 1 and Figure 3). All three transformation products were present in water from well 27 S (Figure 3), but their concentrations were less than 10% of the concentration of the parent compound PCE. The concentration of vinyl chloride was less than the concentration of cis-DCE, which was less than the concentration of TCE. The concentration of hydrogen in 1998 was 3.8 nM. The decline in concentration of PCE, TCE, and cis-DCE can be associated with concentrations of hydrogen higher than 1 nM.

At monitoring well 21 S, also screened at the water table at the margin of the landfill, the maximum concentration of total VOCs was 494 μg/L. Dechlorination in monitoring well 21 S was extensive. Vinyl Chloride was the chlorinated VOC that was present at the highest concentration prior to installation of the leachate and gas collection system. Concentrations of VOCs declined after installation of the gas and leachate collection system (Table 1 and Figure 4). The concentration of hydrogen in 1998 was 3.23 nM. This high concentration of hydrogen is consistent with the extensive dechlorination in water from monitoring well 21 S.

The concentrations of hydrogen in monitoring wells down gradient or cross gradient of the landfill were variable. Concentrations were high in some wells and low in others. In monitoring well 22 D, the concentration of molecular hydrogen was only 0.52 nM. Monitoring well 22 D is 500 meters down gradient of the landfill. The estimated travel time of ground water from the landfill to monitoring well 22 D is approximately 13 years. Apparently, the capacity of the leachate to generate hydrogen was exhausted by the time the water reached monitoring well 22 D. There was no significant change in the concentration of PCE, TCE, or cis-DCE after installation of the leachate and gas collection system (Table 1 and Figure 5). The failure of the chlorinated VOCs to attenuate in water from monitoring well 22 D is associated with a low concentration of hydrogen. In contrast to the behavior of PCE, TCE, and cis-DCE, concentrations of vinyl chloride attenuated after installation of the leachate and gas extraction system. This may be due to anaerobic microbial oxidation of vinyl chloride carried out by iron
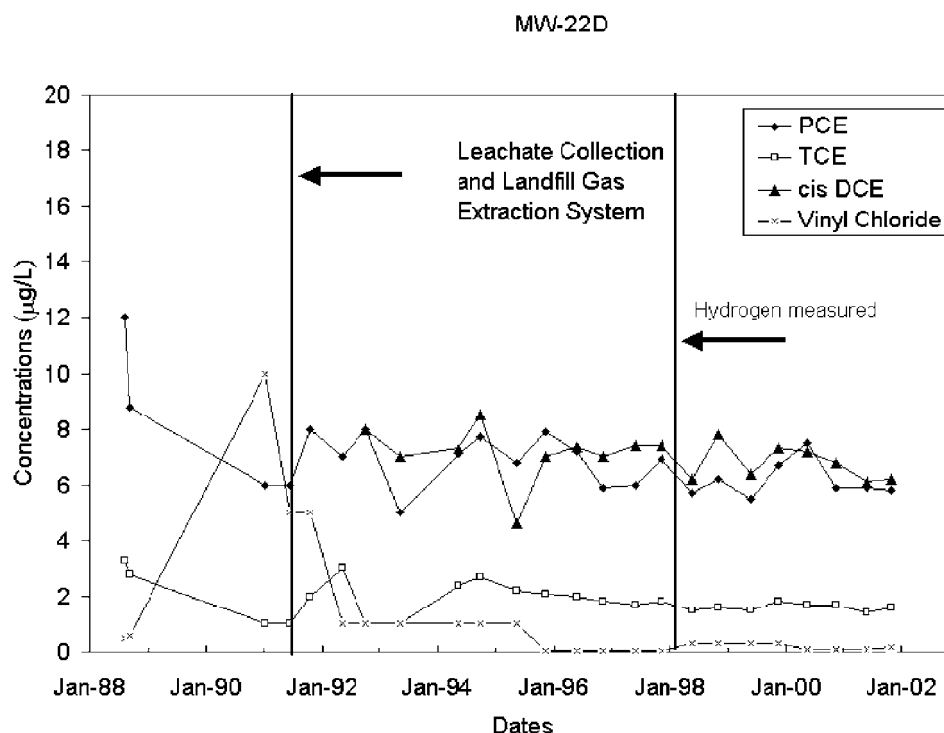
MW-22D

Figure 5. Change in concentrations of chlorinated organic contaminants in monitoring well 22 D over time.

reducing or manganese reducing bacteria (Bradley et al. 1997, 1998b).

The concentration of molecular hydrogen in monitoring well 22 D was slightly lower than the concentration in monitoring wells 25 S, 34 S, and 35 S. These wells are side gradient to the plume and are thought to have never been impacted by the landfill (Table 1).

The concentration of molecular hydrogen in monitoring well 31 I was 0.33 nM. This well is 1100 meters down gradient of the landfill. The concentrations of PCE, TCE, and cis-DCE were very similar to the concentrations in monitoring well 22 D. In monitoring well 31 I, PCE was present at the highest concentration, followed by cis- DCE, then TCE. In contrast, all of the other wells that are down gradient of the landfill had hydrogen concentrations greater than 1 nM, and the chlorinated organic compounds were not detected (Table 1). High concentrations of hydrogen don't necessarily mean that dechlorination is active, but they do mean that dechlorination is possible. When the concentration of hydrogen was high in the monitoring wells, the chlorinated VOCs were absent; when the concentration of hydrogen was low, the VOCs were present.

There was one well down gradient of the landfill that contained chlorinated VOCs, but had an anomalous high concentration of molecular hydrogen. The concentration of hydrogen was high enough to support methanogenesis (Chapelle et al. 1995). The high concentration of hydrogen in monitoring well 40 I may be caused by the presence of steel in the screen or riser of the well (Bjerg et al. 1997).

Trends in ground-water monitoring data from the site suggest that concentrations of chlorinated VOCs have significantly decreased since completion of the landfill cap in 1988, and the leachate collections and landfill gas extraction systems in 1991. At the time of the ROD, all of the wells at the margin of the landfill had high concentrations of chlorinated VOCs; in two of the wells the concentrations were above the action level that would trigger a pump and treat remedy (200 ppb total VOCs). By 1996 all of the monitoring wells at the site were below the action level.

Table 2 presents first order rate constants for attenuation of PCE, TCE, cis-DCE and total VOCs over time in selected wells. The rates were calculated from the data presented in Figure 3–5, for the time interval after installation of the leachate and gas collection system (June 1991). In wells with adequate hydrogen the

Table 2. Rate of attenuation (per year) of contaminants over time in monitoring wells

Monitoring Wells	PCE	TCE	Cos-DCE	Total VOC
Wells at the margin of the landfill with adequate concentrations of hydrogen				
27 S	0.20	0.18	0.30	0.19
	± 0.036	± 0.039	± 0.101	± 0.034
	± 0.023	*± 0.025*	*± 0.063*	*± 0.022*
21 S			0.30	0.38
			± 0.241	± 0.123
			± 0.127	*± 0.094*
Well down gradient of the landfill without adequate concentrations of hydrogen				
22 D	0.015	0.003	0.012	0.006
	± 0.019	± 0.043	± 0.025	± 0.019
	± 0.012	*± 0.027*	*± 0.016*	*± 0.012*

Rate of attenuation per year ± 95% confidence level.
Rate of attenuation per year ± 80% confidence level.

first order rate of attenuation of PCE, TCE, cis-DCE and total chlorinated VOCs varies from 0.38 to 0.18 per year. In the well without adequate hydrogen the rate varies from 0.015 to 0.006 per year. With adequate concentrations of hydrogen, the rate of attenuation over time was at least 10 times faster.

Conclusions

Ground water moving away from the Refuse Hide-away Landfill maintained a molecular hydrogen concentration that is adequate for reductive dechlorination in eight of the 13 selected monitoring well sites. The concentration of molecular hydrogen ranged from 1.30 to 9.7 nM in three monitoring wells at the margin of the landfill (wells 8 S, 27 S and 21 S in Figure 2) and in five monitoring wells down gradient of the landfill (wells 30 I, 32 S, 40 I, 41 I and 41 D in Figure 2). In two of the monitoring wells far down gradient of the landfill (wells 22 D and 31I in Figure 2) and in three of the monitoring wells side gradient to the landfill (wells 25 S, 34 S and 35 S in Figure 2), the concentration of molecular hydrogen ranged from 0.33 to 0.83 nM. These concentrations of molecular hydrogen were not adequate to support reductive dechlorination. In wells with adequate concentrations of hydrogen, the concentrations of chlorinated VOCs were attenuated over time, or concentrations of chlorinated VOCs were below the detection limit. In wells with concentrations of hydrogen <1 nM, the rate of attenuation of chlorinated VOCs was less than 10 percent of the rate of attenuation in wells with concentrations of hydrogen >1 nM.

Notice

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