

REMEDICATION OF PENTACHLOROPHENOL BY VACUUM SPARGING GROUNDWATER CIRCULATION WELL TECHNOLOGY

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ABSTRACT: As a result of fire in the early 1980's, an undefined volume of PCP solution was released to site soils from a former dip tank at a wooden window frame manufacturing facility in Central Wisconsin. Subsequent to site remediation of this PCP release, a second, older closed dip tank was discovered under a building addition. This addition remains an active part of the current manufacturing operations. Groundwater monitoring data indicated that PCP impacts were limited to the upper sand layer, and that lateral migration of the PCP impacted groundwater plume was somewhat limited by natural attenuation. To enhance the natural attenuation processes through PCP source reduction, a vacuum-sparging (VS)-type groundwater circulation well (GCW) was installed in August 2000. The VS-type GCW technology consisted of a specially constructed bioremediation well that remediated PCP present in the unsaturated zone via bioventing; bioremediation of PCP in the saturated zone and the capillary fringe was accelerated via *in situ* mixing and the introduction of air (oxygen) into the subsurface. The bioremediation system operated from November 2000 until January 2003. Remedial efficacy was determined by collecting groundwater samples semi-annually from the bioremediation well and nearby piezometers and monitoring for PCP along with various biofeasibility parameters such as pH, temperature, conductivity, DO and ORP. The PCP concentrations in the source area decreased 92 to 99% since system start up. Furthermore, no significant rebound of PCP occurred since system shut-off, as evidenced by four consecutive quarterly sampling events conducted in the targeted source area. The longer term trends of enhanced passive remediation and decreasing PCP concentrations were established through continued groundwater monitoring within and outside of the remediated source area.

SITE BACKGROUND

PCP Source Area. A wooden window frame manufacturing facility in northern Wisconsin used pentachlorophenol (PCP) as a wood preservative from the 1960's into the early 1980's. As part of the manufacturing process, wood window components were submerged in a dip tank containing a PCP (5%) and kerosene (95%) solution. The dip tank was filled from an underground storage tank (UST) located under the southeast corner of the building. PCP was delivered to the site by rail or tank truck, and off-loaded to the UST via separate fill lines. Due to an unfortunate plumbing design, the dip tank included an overflow piped to an outlet at the south building exterior, approximately 160 feet west of the rail fill line. This design prevented the PCP/kerosene solution from escaping the dip tank and flowing through the building should the fire sprinkler system activate. When a fire swept through the building in 1967, water from the sprinkler system caused the dip tank contents to overflow onto the soils behind the plant, as designed. PCP released from this incident (and from historic off-loading of PCP from rail road tank cars behind the building) generated localized soil and groundwater contamination. In the mid-1990's, a second, older dip tank was also discovered outside the original manufacturing building footprint. The discharge area and UST area were subsequently covered with concrete when the plant was rebuilt and expanded after the fire; this represents that suspected PCP source

area.

Site Lithology and Hydrology: The site is underlain by fine to coarse sands with gravel and occasional cobbles to a depth of approximately 22 to 30 feet, referred to as shallow soil Unit 1. Groundwater at the site was encountered approximately 15 to 23 feet below ground surface and flows in a southerly direction. Beneath this layer, intermediate soil Unit 2 consists of a very dense sandy silt layer to an approximate depth of 45 to 50 feet. Beneath the dense sandy silt, deep soil Unit 3 consists of a coarse sand layer with some gravel and occasional sandy silt seams, which extends to the maximum depth drilled at the site of 74.5 feet. The hydraulic conductivities of Units 1, 2, and 3 were evaluated with in situ hydraulic conductivity tests, or slug tests. The test results showed an estimated average hydraulic conductivity value for Unit 1 was 1.34×10^{-3} cm/sec and ranged from 1.01×10^{-5} cm/sec to 4.26×10^{-3} cm/sec. The average hydraulic conductivity for Unit 2 was 1.95×10^{-5} cm/sec. The estimated hydraulic conductivity value for Unit 3 was 8.15×10^{-5} cm/sec. In general, the hydraulic conductivity values in Unit 2 underneath the project site are approximately two orders of magnitude lower than those of Unit 1.

Remedial Design Engineering: In 1987, an estimated 421 cubic yards of PCP-containing soil were excavated and shipped off site for disposal. Residual PCP in the groundwater was monitored to demonstrate the stationary and contracting nature of the plume controlled by the natural degradation of PCP. A treatability study conducted in 1996 showed that naturally occurring microorganisms were active toward PCP. Total heterotrophic bacterial populations averaged 2.3×10^5 cfu/ml in the groundwater and PCP-degrading microbial groundwater populations averaged 3.0×10^4 cfu/ml. Heterotrophic and PCP-degrader microbial populations in the saturated soils were approximately 4.9×10^6 cfu/g and 1.2×10^5 cfu/g, respectively. Using this information, accelerated remediation of the suspected source area via enhanced in situ PCP biodegradation was facilitated through the use of a modified biosparging system as described below.

Remedial Solution: The VS-GCW treatment technology for source area reduction consisted of a specially constructed treatment well that simultaneously targeted the unsaturated zone, capillary fringe and the saturated zone of the PCP source area. The system was designed to accelerate PCP biodegradation by introducing air into the groundwater under positive pressure while simultaneously extracting air through the vadose soil via bioventing. Thus, vertical groundwater circulation was established (yielding *in situ* mixing), and groundwater was enriched with dissolved oxygen (to enhance *in situ* aerobic biodegradation of PCP). No groundwater was extracted, hence no *ex situ* treatment was required. Other advantages of the VS-type *in situ* GCW system included: i) effective and accelerated cleanup due to the ability of the well to set up vertical and horizontal components of ground water circulation, ii) very low energy requirements; iii) accelerated remediation time when compared to pump-and-treat; and iv) minimal operational requirements. The following table outlines the design parameters used to size the VS-GCW system.

Design Parameters

Saturated Zone Thickness	10 feet
Treatment Zone Area (ft ²)	4,800 ft ²
Recirculation Flow through VS-GCW Well (gpm)	2 gpm
Zone of Influence (ft)	39 feet (estimated from modeling)

Main Equipment Specifications

Operating Conditions

Blower - 5HP motor	100 scfm
Compressor - ¾ HP motor	6 psi (injection pressure)

Air Sparge Unit with Air Distributor Plate	9 scfm flow
In-well Bioventing Screen	5 feet (long) and 6-in (diameter)

The VS-type GCW and associated equipment were installed in the suspected source area at the active manufacturing facility during August 2000 (Figure 1). The location of the bioremediation well, BRW-1, and two monitoring points, MP-1 (positioned approximately 9 feet north of BRW-1) and MP-2 (installed approximately 5 feet west of BRW-1) are shown in the Figure 2 (inset).

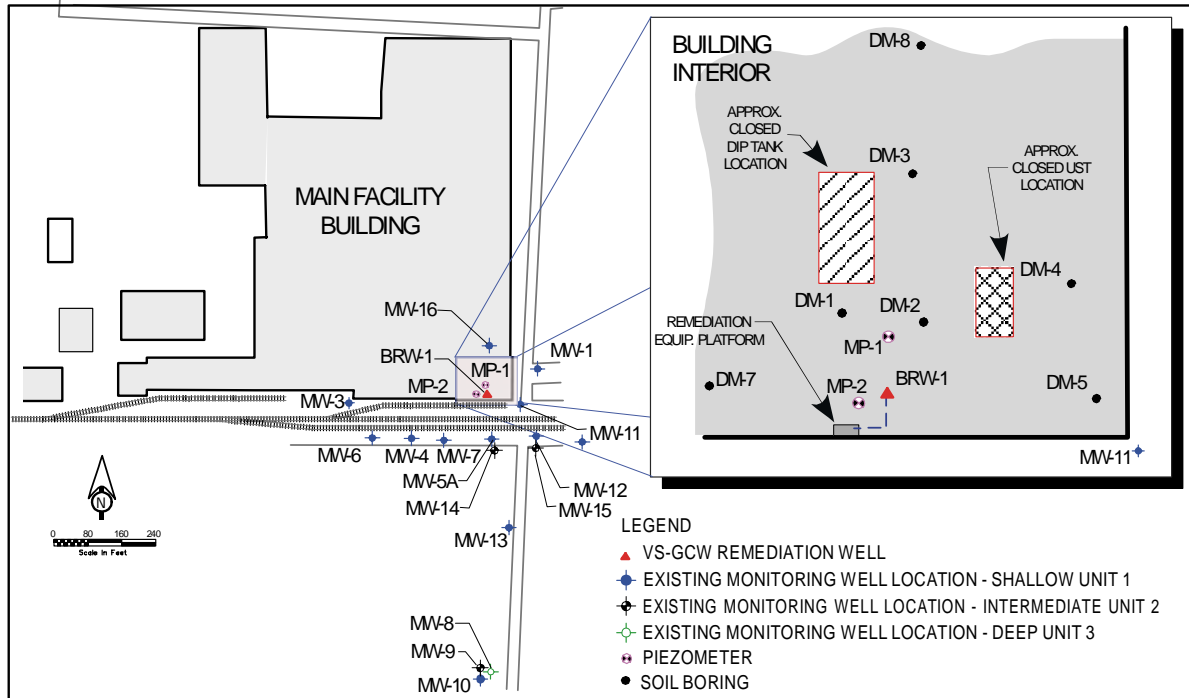


FIGURE 1: Monitoring Well and Remediation System Locations

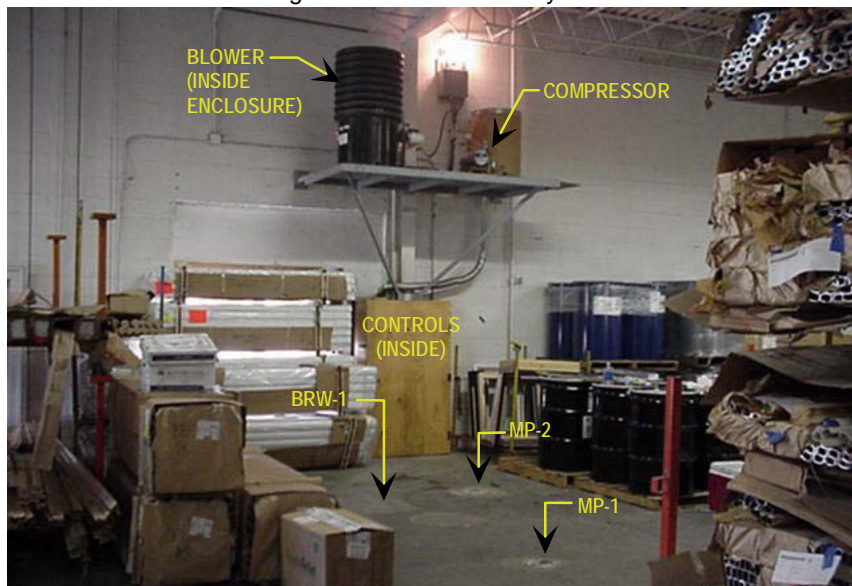


FIGURE 2: Photograph of VS-GCW System and Well Points

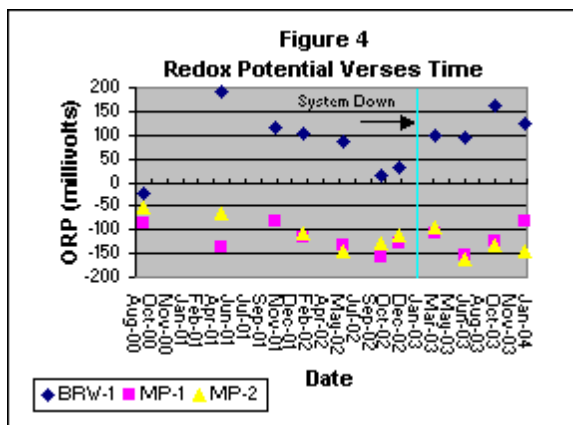
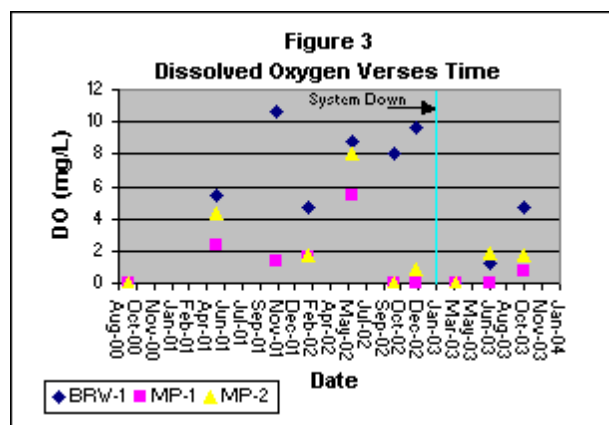
Operational and Performance Monitoring: Baseline sampling was conducted in September 2000. System operation was initiated in November 2000 and continued for approximately two years (November 2000 to January 2003). General system monitoring

parameters including weekly measurement of air flow rate, system vacuum/pressure and temperature. The off-gas flow rate was measured using a permanently fixed pitot tube and magnehelic gage, and also with a hand-held velocity meter for confirmatory purposes. Vacuum/pressure and temperature readings were monitored using fixed gages. At quarterly intervals, groundwater samples from BRW-1 and nearby piezometers MP-1 and MP-2 were analyzed for PCP (Method SW 8270B), chloride (Method EPA 325.2), total and dissolved iron (Method EPA 236.1), total dissolved solids (EPA 160.1), calcium and magnesium [hardness] using Method SW 6010B, carbonate (Method EPA310.1), sulfate (Method EPA 300.0) and nitrate/nitrite (Method EPA 353.2). Various physical parameters were also recorded, including water level, temperature, DO, pH, ORP, specific conductivity and turbidity using a Horiba U-22 Flow-thru cell (pH-DO-C-T-S-ORP-TDS-Turbidity). Finally, an air discharge sample was collected approximately every six months and analyzed by the Wisconsin Occupational Health Laboratory using the Occupation Safety and Health Administration (OSHA) Method 39.

RESULTS AND DISCUSSION

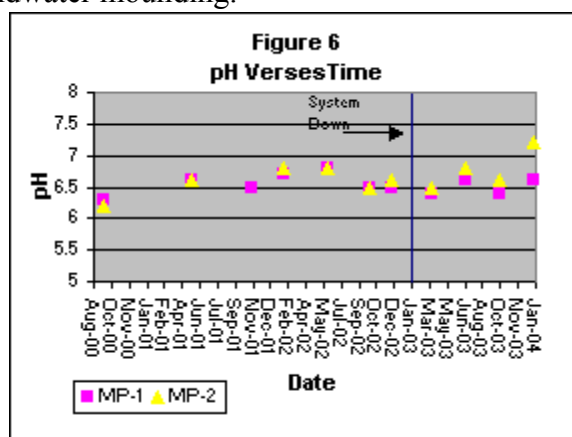
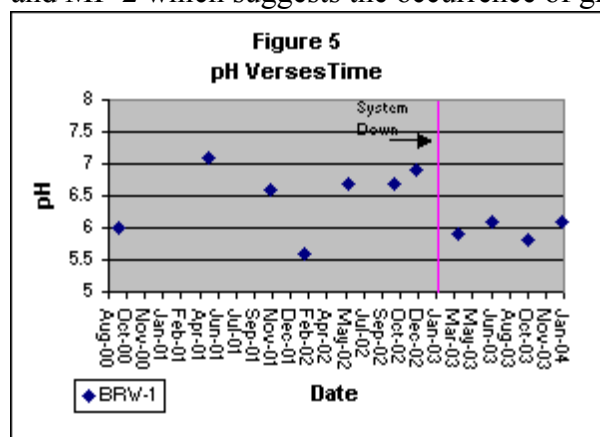
Physicochemical Parameters: During the two-year VS-GCW operational period, DO levels in BRW-1 increased from 4.7 mg/L to 10.6 mg/L (Figure 3). However, DO levels in MP-1 and MP-2 fluctuated at levels consistently lower than BRW-1, ranging from 0 mg/L to 5.5 mg/L and 0 mg/L to 8 mg/L, respectively. Due to compressor problems experienced between January 2002 to March 2002, DO levels measured during that period were generally low. With the replacement of the compressor in April 2002, higher DO levels were subsequently observed. During the rebound monitoring and sampling conducted in 2003 the detected DO levels in MP-1 and MP-2 ranged from 0.7 mg/L to 1.8 mg/L; DO ranged from 1.2 mg/L to 4.7 mg/L in BRW-1.

The ORP was measured in BRW-1, MP-1 and MP-2 during baseline sampling at -23 mVolts (mV), -86 mV and -53 mV, respectively (Figure 4). Generally, an ORP potential of greater than +50 mV is an indicator of an aerobic environment. During the two-year operational period, the ORP measured in MP-1 and MP-2 ranged between -80 mV to -156 mV and -53 mV to -145 mV, respectively, indicating anoxic or reducing conditions. In BRW-1, the measured ORP ranged between -23 mV to 193 mV, generally indicating an oxidizing and, therefore, aerobic environment. During the rebound monitoring and sampling conducted in 2003, oxidizing conditions existed in BRW-1 and reducing conditions existed in MP-1 and MP-2.



The pH values measured during the operational period in BRW-1, MP-1 and MP-2 remained constant at values ranging from approximately 6.0 to 7.1 (Figures 5 and 6). During the rebound monitoring in 2003, pH values in MP-1 and MP-2 were constant and similar to values observed during system operation. However, pH decreased in BRW-1 and ranged from 5.8 to

6.1. Also, temperature values initially ranged between 14°C to 18°C and remained relatively stable through the 24 months of operation. Initial measurements of conductivity and TDS values during the first year of operation ranged between 23 and 39 milliSiemens /cm (mS/cm) and 170 mg/L to 220 mg/L. These measured values remained stable in MP-1 and MP-2 during the first year, but both parameters decreased significantly in BRW-1 following baseline sampling. No trends were observed from conductivity and TDS measurements during rebound monitoring in 2003. Salinity measurements were below the detection limit of the instrument for all samples collected. Lastly, review of the field data shows fluctuations in water levels observed in MP-1 and MP-2 which suggests the occurrence of groundwater mounding.



Additional parameters analyzed include TDS, calcium and magnesium. These parameters were collected primarily for assessment of solids formation within the subsurface formation. Calcium and magnesium are both present and were fairly constant in both MP-1 and MP-2. In BRW-1, there were fluctuations in concentrations of calcium and magnesium. These concentrations compare well with TDS readings collected using the field instrument.

Groundwater PCP Data: During baseline sampling conducted prior to operation of the bioremediation system, PCP was detected in BRW-1, MP-1 and MP-2 at concentrations of 1,100 µg/L, 130 µg/L and 86 µg/L (Table 1). PCP concentrations decreased rapidly during the course of bioremediation system operation. During the sampling conducted in June 2002, the PCP concentration in MP-1, MP-2 and BRW-1 decreased to below laboratory detection limits (BDL < 2 µg/L). The October and December 2002 groundwater sampling also indicated PCP concentrations to be below laboratory detection limits. Post-closure rebound sampling was conducted for four consecutive quarters during 2003. PCP levels remained BDL (< 2 µg/L) in BRW-1 and have rebounded to only very low concentrations in MP-1 and MP-2. The calculated PCP mass removal in the groundwater based on the assumed zone of influence (ZOI) of 20 feet was approximately 12 pounds (Table 1). The assumed ZOI was approximately 50% of ZOI based on modeling.

Biodegradation Kinetics. As discussed earlier, frequent monitoring of DO and ORP during the two-year operational period suggested that oxidizing conditions and hence aerobic degradation occurred proximal to BRW-1. However, in MP-1 and MP-2 the data suggested reducing conditions with spikes of oxygen observed during the operation of the VS-GCW system. It therefore appears that a combination of anaerobic and aerobic PCP biodegradation was possible. The first-order biodegradation rate constant calculated from BRW-1 data is approximately 0.010 day⁻¹ with a half life of 70 days (see Table 1). This rate constant is at the lower end of many values reported in the literature, which range from 0.01 to 0.03 day⁻¹ (Howard

et al., 1991). On the other hand, first-order rate constants calculated from MP-1 and MP-2 are approximately 0.006 and 0.008 day⁻¹, respectively, with a half life of 84 to 108 days. These values are in between aerobic and anaerobic rate constants reported in the literature. The rate constant reported in the literature under anaerobic conditions is 0.0045 day⁻¹ (IEPA, 2002).

TABLE 1: PERCENT PCP REDUCTION WITH TIME IN GROUNDWATER

Date	Days	MP-1			MP-2		
		PCP (mg/L)	% Reduction	First Order	PCP (mg/L)	% Reduction	First Order
9/6/2000	0	0.1135	0%	Rate Constant (day ⁻¹) 0.0064	0.358	0%	Rate Constant (day ⁻¹) 0.0082
5/15/2001	251	0.017	85.0%		0.041	88.5%	
11/1/2001	421	0.2	-76.2%		0.044	87.7%	
6/3/2002	635	0.0019	98.3%	Half Life (days) 108	0.0019	99.5%	Half Life (days) 84
10/3/2002	757	0.0034	97.0%		0.007	98.0%	
12/12/2002	827	0.0016	98.6%		0.0016	99.6%	

Date	Days	BRW-1			Mass Removal (lbs)	
		PCP (mg/L)	% Reduction	First Order		
9/6/2000	0	1.1	0%	Rate Constant (day ⁻¹) 0.0099	For ZOI = 20' 12	
5/15/2001	251	0.012	98.9%		Half Life (days) 70	For ZOI = 39' 46
11/1/2001	421	0.0055	99.5%			
6/3/2002	635	0.002	99.8%			
10/3/2002	757	0.0018	99.8%			
12/12/2002	827	0.0016	99.9%			

Note: 9/6/00 and 9/7/00 data were averaged for calculation of percent PCP reduction and rate constants
Zone of Influence (ZOI) = 20' (observed from system operation); ZOI = 39' (from numerical modeling)

Oxidizing conditions were observed in MW-11 (closer to the source area) and reducing conditions in MW-12 (further from the source area) and as expected rate constants are lower in MW-12 compared to MW-11. The first-order natural attenuation rate constant for MW-11, located approximately 60 feet southeast of the treated source area, is approximately 0.005 day⁻¹ (Table 2) and correlates well with rate constants calculated from MP-1 and MP-2. The first-order natural attenuation rate constant for MW-12, located approximately 120 feet southeast of the treated source area is approximately 0.00046 day⁻¹ and correlates well with published first-order rate constant of 0.00045 day⁻¹.

TABLE 2: PCP Degradation Constants Outside of Source Area

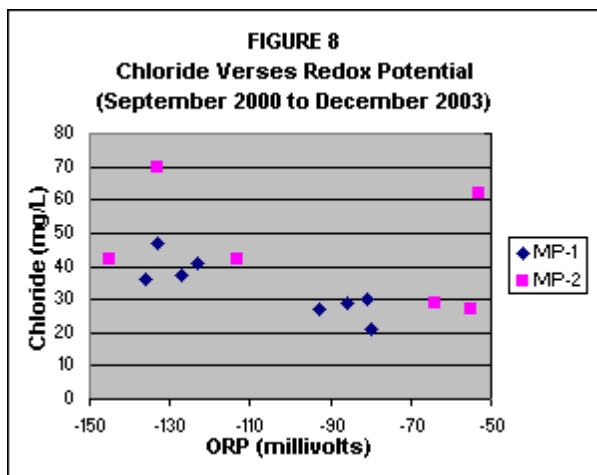
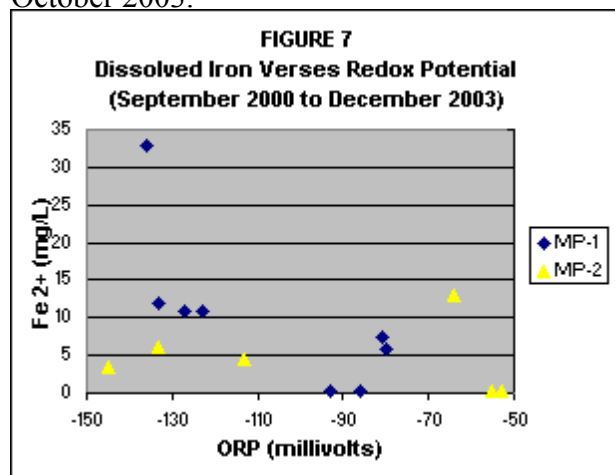
Date	Days	MW-11		MW-12	
		PCP (ug/L)	First Order	PCP (ug/L)	First Order
Dec-94	0	520	Rate Constant (day ⁻¹) 0.0049	150	Rate Constant (day ⁻¹) 0.00046
May-96	517	170		910	
Dec-96	731	4.5		22	
Apr-97	852	7.72	Half Life (days) 140	86	Half Life (days) 1494
Jul-97	943	ND		48	
Dec-97	1096	ND		610	
Jun-98	1278	ND		260	
Jan-04	3318	ND		100	

Note: ND - Non Detect

Biodegradation is essentially a microbially catalyzed oxidation-reduction reaction.

Oxidation-reduction reactions are those in which there is a transfer of electrons from an electron donor (generally the substrate) to an electron acceptor. The primary electron acceptors analyzed in the site groundwater were dissolved oxygen under aerobic conditions and nitrate/nitrite, iron (total and dissolved), and sulfate under anaerobic conditions. Dissolved iron shows a trend of increasing concentrations with decreasing ORP and is consistent with expectations (Figure 7). However, BRW-1 has oxidizing conditions, and the dissolved iron concentrations in BRW-1 have remained relatively stable since start-up of the system and were below the detection limit (<0.042 mg/L) during the December 2002 and October 2003 (<0.016 mg/L) sampling events. Nitrate levels were very low and no trends were observed during both the operational and rebound sampling periods.

The PCP biodegradation end-products analyzed were carbonate (measured as alkalinity) and chloride. Carbonate was not detected at concentrations greater than 10 mg/L in any of the groundwater samples, which suggests that no significant mineralization of the available substrate (PCP) has yet occurred. During baseline sampling, chloride was detected in all of the sampled monitoring wells at concentrations ranging from 22 mg/l to 62 mg/l. Chloride concentrations have remained relatively constant in MP-1 and MP-2 during the three years of monitoring. Using chloride as an indicator of reductive dehalogenation of PCP, it can be seen that lower ORP corresponds to higher concentrations of chloride (Figure 8). This is to be expected, since highly reducing conditions promote reductive dehalogenation. In BRW-1, the chloride concentration decreased to below detection in 2001 and the first three quarters of 2002. In December 2002, the chloride concentration in BRW-1 increased to 32 mg/L but decreased to below detection in October 2003.



Also, complete mineralization of PCP under aerobic conditions will yield CO₂ and HCl. CO₂ was not monitored but groundwater pH decreased slightly in BRW-1 during rebound monitoring conducted in 2003 suggesting some mineralization of PCP has occurred (see Figure 5).

CONCLUSIONS

The primary objective of the *in situ* bioremediation system was to achieve source area reduction and hence, facilitate the natural attenuation of PCP residuals (*i.e.*, enhanced passive remediation). Enhanced biodegradation of PCP in the dissolved phase occurred via distribution of oxygen to the indigenous microflora thereby stimulating *in situ* bioremediation processes. ORP and DO measurements collected during VS-GCW system operation showed that aerobic conditions (Eh >50 mV) were sustained in the area proximal to bioremediation well BRW-1.

Combined anaerobic/aerobic conditions were observed in the vicinity of monitoring points MP-1 and MP-2, as evidenced by ORP and fluctuating DO levels measured throughout the period of system operation. Within two years of system operation, groundwater PCP concentration decreased significantly in the targeted source area. Post-closure “rebound” monitoring during four consecutive quarters showed that groundwater PCP levels remained BDL in BRW-1, and have rebounded to only very low concentrations in MP-1 and MP-2. These data support the conclusion that the VS-type GCW system enhanced the in situ biodegradation of PCP in the source area.

Due to budget constraints, PCP intermediate breakdown products in BRW-1, MP-1 and MP-2 were not evaluated. Relatedly, the monitoring network was recognizably limited. During post-closure rebound monitoring in 2004, the number of sampling points will be expanded and the groundwater will be analyzed for the presence of recognized PCP catabolites.

The total cost for system installation, startup and 2.5 years of operation followed by one year of rebound monitoring and sampling was approximately \$199,000. The VS-GCW system therefore represents a very cost-effective and efficient remedial solution for saturated and unsaturated source zones, especially when compared to other conventional treatment technologies.

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