Full-Scale Removal of PCP from Pringle Post and Pole Site Soil

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ABSTRACT: In August 2005, full-scale cleanup of pentachlorophenol (PCP)-contaminated soil at the Pringle Post and Pole site was initiated using solid-phase bioremediation technology. Two land treatment units (LTUs), having a total capacity of 4,000 yd^3 (3,058 m^3), were constructed and bioaugmented with an indigenous PCP-degrading *Sphingomonas sp.* at a rate of 10^7 CFU/kg of soil. Soil cleanup was not completed until May 2006 when PCP levels were reduced to below the action level of 48 mg/kg in both units. PCP levels ranged from 33 to 44 mg/kg with the extent of removal ranging from 74 to 81%. In June 2006, remaining stockpiled soil was loaded into the LTUs, amended with recipe ingredients, and inoculated. After 116 days, cleanup of soil in LTU #1 was achieved with an average PCP concentration of 20 mg/kg and an extent of removal of 81%. Starting PCP levels in LTU #2 were highly variable due to incomplete mixing of stockpiled soil. Performance in this unit was difficult to assess although PCP levels were reduced to 102 mg/kg with the extent of removal at 48%. Current plans are to complete the cleanup of LTU #2 in 2007.

INTRODUCTION

Pentachlorophenol (PCP) is a biocide that has been extensively used as a preservation agent for the production of treated lumber and timber. It has also been used in other industrial applications as a fungicide, bacteriocide, herbicide, insecticide, algicide, and molluscicide (Crosby 1981). PCP was listed as a priority pollutant by the U.S. EPA (U.S. EPA 1989), and it is designated as a persistent organic pollutant (POP) because of its toxicity and environmental stability.

Site Background. The Pringle Post and Pole site is located in Custer County, South Dakota, near the town of Pringle on U.S. Highway 385. The site, covering approximately 10 acres (4 hectares), is the former location of a wood treatment business that produced treated wood products for over 50 years. State records show that wood products were treated with PCP, creosote and chromated copper arsenate (CCA). After treatment, the wood products were placed on racks to dry. The site has been under investigation by the State of South Dakota as well as the U.S. EPA since the early 1990s. Site investigations showed that soil and stream sediments were extensively contaminated with PCP, creosote and CCA. Currently, the wood treatment business is not active.

In late August 2005, two land treatment units (LTUs) were constructed on-site to treat stockpiled contaminated soil using solid-phase bioremediation technology. Each unit was amended with ingredients from a standard recipe developed by Response Engineering and Analytical Contract (REAC) personnel. Each unit was also augmented with an indigenous PCP-degrading microorganism that was isolated in an earlier activity screening study. The purified culture, isolate PPP-1, was sent to a commercial laboratory for characterization and identified as a *Sphingomonas sp.* Bench-scale solid-phase studies

later showed that this culture rapidly degraded PCP in site soil over short incubation periods with concomitant, stoichiometric production of chloride (Cl).

In a previous communication, results were presented that summarized the performance of the field units during their operation from September 2005 to May 2006. By May 2006, soil cleanup goals in both units were achieved with PCP levels reduced to below the action level of 48 mg/kg (Allen et al. 2006). The purpose of this report is to assess the performance of the LTUs in the 2005 and 2006 field seasons and to outline strategies planned for the 2007 field season to complete site cleanup.

MATERIALS AND METHODS

Bench-Scale Studies. Bench-scale solid-phase studies were conducted to assess the performance of the REAC recipe in promoting the removal of PCP from site soil. Two soil sources were used in these studies and included highly contaminated soil collected near the retort process building and from LTU #1. The latter soil source was used in a study to determine if elevated DRO levels were responsible for sluggish PCP removal rates observed in LTUs during the 2005 field season.

Both studies included the use of isolate PPP-1 as a bioaugmenting agent. The culture was grown in shake flask culture in minerals salts-glutamate medium at 30ºC for 48 hours. The culture growth was monitored daily by spectrophotometric methods, measuring the absorbance at 560 nanometers (nm). After 48 hours, an aliquot of the culture was diluted to 1.25×10^7 Colony Forming Units (CFU)/mL and the diluted culture placed in an ice bath until used.

One-gallon (3.78 L) stainless steel trays fitted with stainless steel lids were used as bench-scale reactors. Soil blends were prepared in each reactor and consisted of contaminated soil (1,175 g), sawdust, and calcium carbonate at rates of 50 g/kg and 10 g/kg, respectively. The total soil blend weight (dry weight) was 1,250 g.

Due to the presence of elevated levels of diesel range organics (DRO) in LTU soil, inorganic nitrogen (ammonium nitrate) and phosphorus (dibasic sodium phosphate) sources were added to the soil beds to stimulate the growth of DRO-degrading microorganisms. The nitrogen and phosphorus sources were added at rates based on the estimated total organic carbon (TOC) content of the soil beds. The carbon to nitrogen (C:N) and carbon to phosphorus (C:P) ratios were 30:1 and 400:1, respectively.

An aliquot of the diluted culture was added to deionized water used to hydrate the soil beds. Upon soil hydration, the theoretical population density of the bioaugmenting agent was 1×10^4 CFU/g with a target moisture level of 20%.

Soil PCP, Cl, pH, and moisture content (MC) were monitored over test periods ranging from 28 to 63 days. PCP and pH were measured biweekly while Cl and MC were measured weekly. The incubation temperature ranged from ambient temperature (18ºC to 22ºC) to 30ºC.

Scale-up of the Bioaugmenting Agent. Scale-up studies were conducted to produce sufficient biomass to inoculate the LTUs. Medium development studies were conducted to develop a nutrient medium recipe capable of promoting high cell densities over short incubation periods. The culture was bulk produced in pilot fermentors and in shake flasks using the optimized medium recipe. The cell suspensions were concentrated by

centrifugation, the cell concentrates suspended in 50% v/v aqueous glycerol, and then frozen at –80°C until shipped to the site.

Field-Scale Studies

Soil Treatment Cycle (Lift) 1. Contaminated soil was transferred into each of the two field cells and then amended with sawdust and calcium carbonate at the same rates used in bench studies. To reduce DRO concentrations, ammonium nitrate and dibasic sodium phosphate were added to stimulate the growth of indigenous oil-degrading microbial populations. The final depth of the soil bed was approximately 1.5 ft (0.46 m). Once applied, the amendments were homogenized using mechanical soil mixing equipment.

The field units were also bioaugmented with isolate PPP-1. The microbial cells were dispensed into the soil beds using a cell dispensing apparatus fastened to the frame of a spring tooth harrow. The harrow was pulled by a tractor to apply the microbial cells. The apparatus consisted of a 300-gallon (1,137 L) plastic feed tank, a diaphragm pump, and a custom-made manifold-tubing assembly to dispense the microbial suspension. A PVC pipe exiting the feed tank was fitted with a gate valve and attached to a diaphragm pump. The diaphragm pump was connected to the manifold-tubing assembly with Teflon® tubing attached to the back of the teeth of the harrow. As the spring teeth created furrows in the soil, cell suspension was trickled into the furrows to be covered as the soil collapsed.

The flow rate of the cell dispensing apparatus was initially calibrated using un-chlorinated well water. The cell suspension was then prepared by suspending the thawed cell concentrate in well water added to the 300 gallon feed tank. Assuming a 4-foot (1.2 m) wide applicator, and setting a 4.5 gpm (17 L/min) flow rate, 250 gallons (945 L) of irrigation water containing a 55 g cell suspension could be dispensed over an LTU by driving the tractor at a speed of 2 mph (3.2 kmph). The apparatus was refilled as needed until both units were inoculated. The soil was then further mixed using a disk harrow attached to a tractor. Each LTU was then hydrated to specification with well water using a sprinkling system. Each field unit was tilled weekly and watered daily for defined time periods using the sprinkling system.

Soil Treatment Cycle (Lift) 2. The remainder of the stockpiled soil was added on top of Lift 1 in each of the LTUs to prepare Lift 2 in June 2006. Preparation, inoculation, process parameters, and operation of each unit were identical to procedures used in Lift 1.

Field Sampling. Each unit was divided into four quadrants and designated as Northwest (NW), Northeast (NE), Southwest (SW), and Southeast (SE). Samples were collected from a number of random locations within each quadrant and a composite sample for each quadrant prepared. These samples were analyzed for PCP and DRO content.

RESULTS AND DISCUSSION

Bench-Scale Studies. Results of the two bench-scale solid-phase studies are summarized in Figures 1 and 2. In both studies, PCP was rapidly degraded over short incubation periods at starting concentrations ranging from approximately 70 to 140 mg/kg. The rapid degradation of PCP was confirmed by the rapid increase in soil Cl content. The Cl levels reached a maximum level at the same time period when PCP levels were reduced to minimal concentrations. Further incubation showed no significant decreases in PCP or increases in Cl. Earlier shake flask studies had shown that isolate PPP-1 was capable of completely degrading PCP with production of stoichiometric levels of Cl as an end product. PCP is comprised of approximately 66.6% Cl by weight.

The initial solid-phase study was conducted to demonstrate that the REAC recipe could promote the rapid degradation of PCP after bioaugmentation with isolate PPP-1. The highly contaminated soil source (1,850 mg/kg) was mixed with site clean soil to reduce the PCP concentration to a level where PCP could be rapidly degraded. From an initial concentration of 144 mg/kg, the PCP concentration was reduced by over 50% (67 mg/kg) in 14 days and over 93% (10 mg/kg) by Day 42. The Cl production curve shows that Cl was continually produced until Day 42. These data indicated that PCP was continually degraded suggesting that the Day 28 PCP measurement is inaccurate, perhaps due to extraction error. The PCP concentrations measured at Days 42 and 63 were 10 and 19 mg/kg, respectively, and were well below the action level of 48 mg/kg established for this site.

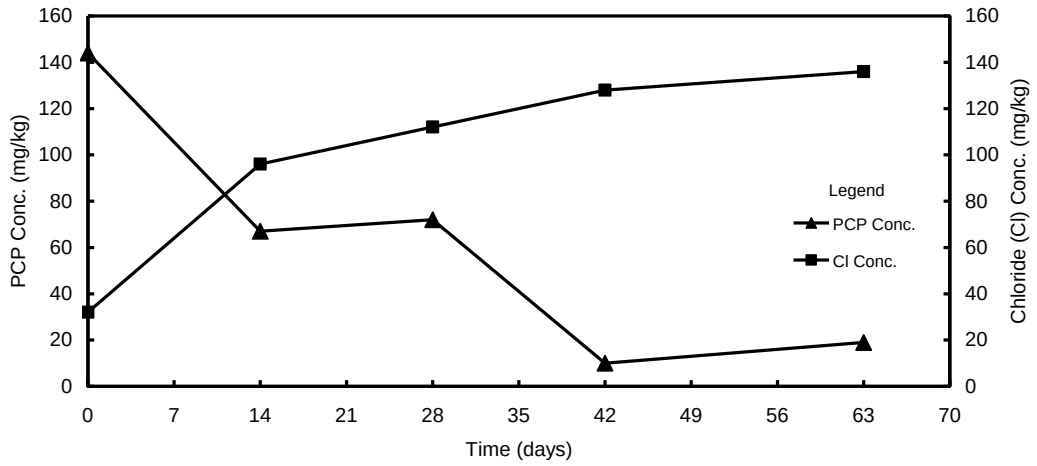

FIGURE 1. Biodegradation of PCP in contaminated soil.

A stoichiometric relationship was observed between the extent of PCP degraded and the amount of Cl produced. These data suggest that soil PCP was being completely mineralized with no significant buildup of partially dechlorinated metabolites of PCP.

The second solid-phase study was set up to determine whether elevated DRO concentrations were responsible for the sluggish removal of PCP observed in the field units in late 2005. The results of this study are summarized in Figure 2. Soil, collected from LTU #1, was used as the source of contaminated soil for the study. Results showed that PCP was again rapidly removed with concomitant production of soil Cl. By contrast,

DRO concentrations remained unchanged throughout the study. From a starting concentration of 72 mg/kg, PCP concentrations decreased to 21 mg/kg by Day 28 with the extent of removal at approximately 71%. PCP removal was virtually completed by Day 14 with relatively minor decreases in PCP concentration over the next 14 days while Cl production approached its maximal value by Day 14 with only slight increases observed thereafter. It was concluded that the sluggish rates of PCP removal in the field were not caused by elevated DRO levels but were probably due to low temperatures experienced in late September and October of 2005. Good agreement between the theoretical and measured Cl was not observed in this study.

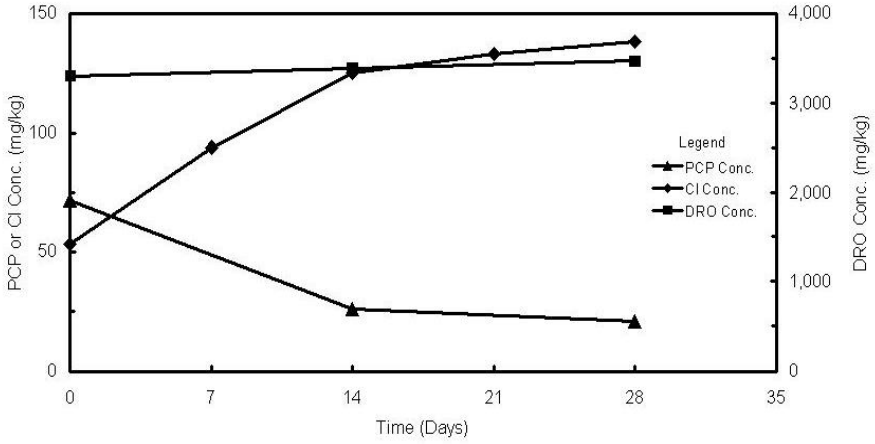

FIGURE 2. Biodegradation of PCP in DRO-contaminated soil.

Field Studies

Soil Treatment Cycle (Lift) 1. The performance of the two field units during Lift 1 is summarized in Table 1. The initial field units were set up in late August 2005 and monitored for 55 days before cold weather shut down operations for the season. Over the 55-day test period, the extent of PCP removal LTUs #1 and #2 was 21% and 17%, respectively. At the start of the 2006 field season (May 2006), samples were again collected to determine the extent of PCP removal. Results showed that PCP levels were dramatically reduced to concentrations ranging from 33 to 44 mg/kg with the extent of removal ranging from 74 to 81%. PCP concentrations were generally uniform throughout the quadrants in each of the LTUs, indicating that stockpiled soil was well mixed during the setup of each unit. The respective average temperatures for August through October, which is the end of the 2005 growing season were as follows: August 63^{o}F (17^{o}C), September 58^{o}F (14^{o}C), and October 45^{o}F (7^{o}C). In Spring 2006, the respective averages for April and May were 44^{o}F (7^{o}C) and 50^{o}F (10^{o}C), with daytime temperatures as high as 80^{o}F (27^{o}C) in May. The warm temperatures might explain the apparently excellent biodegradation activity observed after the October 2005 sampling event.

TABLE 1. Biodegradation of PCP in lift 1.

LTU #	Time (Days)	PCP Conc. Range (mg/kg)	Avg. PCP Conc. (mg/kg)	Degradation (%)
1	0	150-190	168	0.0
	55	110-160	132	21.4
	192	17-44	44	73.8
2	0	130-250	175	0.0
	55	99-150	145	17.1
	192	34-61	33	81.1

Soil Treatment Cycle (Lift) 2. The performance of field units in Lift 2 is summarized in Table 2 and Figure 3. Lift 2 was constructed in June 2006 after the cleanup goals were achieved in Lift 1. The units were operated for approximately four months (116 days) with samples collected monthly for the initial two months and a final set of samples collected after four months in October 2006. Results showed that there was significant reduction of PCP in both units but that cleanup goals were only achieved in LTU #1.

TABLE 2. Biodegradation of PCP in lift 2.

LTU #	Time (Days)	PCP Conc. Range (mg/kg)	Avg. PCP Conc. (mg/kg)	Degradation (%)
1	0	89-122	104	0.0
	27	12-59	32	69.2
	54	18-49	37	64.4
	116	3-62	20	80.8
2	0	102-450	195	0.0
	27	25-84	58	70.3
	54	21-144	63	67.7
	116	42-200	102	47.7

The cleanup goal was achieved in LTU #1 by Day 27 with an average PCP concentration of 32 mg/kg. The PCP concentration decreased slightly thereafter to 20 mg/kg over the next 89 days. Varying PCP concentrations were observed in several of the quadrants over the 116-day test period. For example, PCP concentrations in the SW quadrant were progressively reduced to 18 mg/kg after 54 days but increased to 62 mg/kg by Day 116. The overall extent of PCP removal in LTU #1 was approximately 81%. The average temperatures for these five months of the 2006 growing season were as follows: June 62^{o}F (17^{o}C), July 69^{o}F (21^{o}C), August 65^{o}F (18^{o}C), September 51^{o}F (10^{o}C), and October 40^{o}F (4^{o}C).

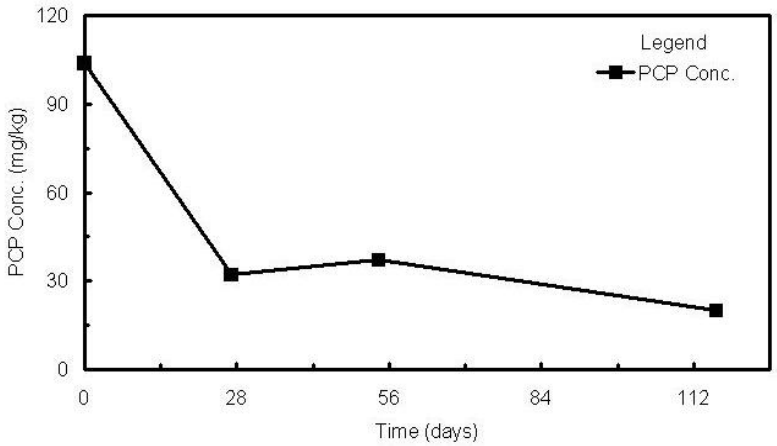

FIGURE 3. Biodegradation of PCP in LTU #1 (lift 2)

The performance of LTU #2 was more difficult to assess due to apparent incomplete mixing of contaminated soil during the setup of Lift 2. The PCP concentrations ranged from 102 to 450 mg/kg at Day 0 depending on the quadrant measured (Table 2). The PCP concentration in the NE quadrant was particularly important because of the presence of high concentrations of PCP (450 mg/kg). High levels of PCP can dramatically reduce the rate of degradation due to toxic effects on microbial populations. In field studies at the Yavapai-Prescott wood treating site in Prescott, AZ, PCP levels ranging from 130 to 160 mg/kg were reduced to below the action level of 62 mg/kg in 42 to 60 days, while PCP levels at 520 mg/kg required 156 days to achieve the same level (Allen et al. 2000, Allen et al. 2005). Thus, it would be expected that the rate of PCP removal would be much slower in this quadrant and that the cleanup goal (48 mg/kg) would require longer periods of time to achieve. The PCP concentration was highly variable in the NE quadrant over the 116-day period with concentrations of 84, 144, and 200 mg/kg at Days 27, 54, and 116 days, respectively. Varying PCP concentrations were also observed in the SE quadrant in this unit. PCP concentrations progressively decreased from 118 mg/kg at Day 0 to 60 mg/kg by Day 54 but then rose to 110 mg/kg at Day 116. The high PCP levels found in the NE and SE quadrants were responsible for the high average PCP levels of 102 mg/kg at Day 116.

Future Studies. The main focus of the 2007 field studies will be to monitor the quadrants in LTU #1 and LTU #2 which have PCP levels greater than the action level of 48 mg/kg. Initially, samples will be collected from all quadrants to confirm removal results from the 2006 field study. Quadrants within field units requiring further treatment will be amended with recipe ingredients, bioaugmented with isolate PPP-1, and monitored until PCP levels have been reduced to desired cleanup levels.

CONCLUSIONS

Solid-phase bioremediation technology performed well in removing PCP from site soil in the 2005 and 2006 field seasons. Temperature played a significant role in the performance of the LTUs in the 2005 field season. Treatment time was significantly extended (192 days) to achieve cleanup goals due to a late start in the field season and the onset of low temperatures which are unfavorable to microbial growth. Lower

temperatures resulted in a reduced rate of removal of PCP and extended the time required to achieve cleanup goals until May 2006. When the LTUs were recharged early in the 2006 field season under a more desirable temperature range, excellent performance was observed in LTU #1 with PCP concentrations reduced to below the action level (48 mg/kg) in 27 days after startup.

Soil mixing during LTU construction in the 2006 field season played a role in LTU performance, especially in LTU #2. Due to incomplete mixing of stockpiled soil during LTU #2 setup, a wide range of PCP concentrations was found throughout the unit. One quadrant had PCP levels so high that the rate of PCP removal was significantly reduced, which resulted in high residual PCP concentrations at the end of the 2006 field season. The broad range of starting PCP concentrations also made it difficult to accurately determine the starting Day 0 PCP concentration in this unit as well as to assess the performance of the unit throughout the 116-day study. These difficulties resulted in the need to extend the treatment time into 2007 to achieve cleanup goals.

REFERENCES

Allen, H.L., J. McKeown, and T.F. Miller. 2006. Effects of Bioaugmentation on Removal of Pentachlorophenol from Contaminated Soil. Abstracts of *The Fifth International Conference on Remediation of Chlorinated and Recalcitrant Compounds*, Battelle Press, Columbus, Ohio.

Allen, H.L., K. Lawrence, D. Zuroski, S. Journell, W. Wellendorf, K. Harris, and T.F. Miller. 2005. "Performance and Process Economics of the Aerobic Bioremediation of Pentachlorophenol." Paper F-05. In B.C. Alleman and M.E. Kelley (ed.), In Situ and On-Site Bioremediation – 2005, *Proceedings of* the *Eighth International In Situ and On-Site Bioremediation Symposium*, Battelle Press, Columbus, Ohio.

Allen, H.L., K. Lawrence, S. Journell, W. Wellendorf, K. A. Harris, and T.F. Miller. 2000. "Field-Scale Studies on Removal of Pentachlorophenol from Contaminated Soil." In G. B. Wickramanayake, A. R. Gavaskar, J. T. Gibbs, and J. L. Means, (Eds.), *The Second International Conference on Remediation of Chlorinated and Recalcitrant Compounds*, pp. 161-168, Vol. C2-7, Battelle Press, Columbus, Ohio.

Crosby, D.G. 1981. "Environmental Chemistry of Pentachlorophenol." *Pure Appl. Chem.* 53: 1051-1080.

United States Environmental Protection Agency. 1989. "Hazardous Wastes from Non-Specific Sources." 40 CFR Subpart 261.31. U.S. Environmental Protection Agency, Washington, D.C.