RAPID REMOVAL OF TOXAPHENE USING ANAEROBIC BIOREMEDIATION TECHNOLOGY

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ABSTRACT: Field-scale studies were conducted to remove toxaphene from soil at two abandoned livestock dip vat sites and at an abandoned air strip using anaerobic bioremediation technology. The dip vat cleanup studies were conducted in joint collaboration between the Pueblo Office of Environmental Protection (POEP) and the United States Environmental Protection Agency/Environmental Response Team Center (U.S. EPA/ERTC). Composite samples, collected from the Laahty Family Dip Vat (LDV), Henry O Dip Vat (HDV), and Gila River Indian Community (GRIC) sites, were screened for toxaphene-degradative activity in bench-scale studies and found to be active. In field-scale studies, results showed that initial toxaphene levels decreased from 29 mg/kg to 4 mg/kg (86% removal) in 31 days at the LDV site using a standard recipe consisting of blood meal and phosphate buffer. At the HDV site, toxaphene levels in two anaerobic cells decreased from 17-29 mg/kg to 6-9 mg/kg in 61-76 days with the extent of removal ranging from 65-69%. Using a modified phosphate buffer-blood meal recipe for cleanup at the GRIC site, toxaphene levels decreased from 29-34 mg/kg to 4-5 mg/kg in approximately 190 days, with removal levels ranging from 83-88%. Cleanup costs ranged from \$149-\$337/m^3.

INTRODUCTION

Toxaphene is a broad spectrum insecticide which is primarily used to control pests on crops and ectoparasites on livestock (Korte, Scheunert, and Parlor, 1979). The pesticide has been shown to be highly toxic to fish and mammals as well as having mutagenic and carcinogenic properties. Moreover, it is highly stable and can persist in the environment for years. Due to its persistence and toxicity, toxaphene was taken off the market in 1982. Fifty-eight sites, contaminated with toxaphene, were identified and included on the National Priority List by the United States Environmental Protection Agency (U.S. EPA).

Investigations have shown that toxaphene is biodegradable by anaerobic processes (Mirsatari et al., 1987; Parr and Smith, 1976; Smith and Willis, 1978). The U.S. EPA Environmental Response Team Center (U.S. EPA ERTC) and Response Engineering and Analytical Contract (REAC) personnel have successfully developed an anaerobic process for removal of toxaphene from soil (Camacho et al., 1997; Allen et al., 1999). Results of three site cleanup operations are summarized below.

The objective of these studies was to remove toxaphene from contaminated soil using anaerobic bioremediation technology. Composite soil samples, collected from each site, were screened for toxaphene-degradative activity in bench-scale studies using standard recipes. Once activity was identified, plans for site cleanup were initiated.

Site Description. Studies were conducted at three sites: (1) Laahty Family Dip Vat (LDV), (2) Henry O Dip Vat (HDV), and (3) Gila River Indian Community (GRIC) sites. The two dip vat sites were cleaned up under a joint collaborative effort between the Pueblo Office of Environmental Protection (POEP), the U.S. EPA (Region VI), and the U.S. EPA/ERTC. Both sites were former locations of livestock dip vat facilities within the Pueblo of Zuni near Gallup, New Mexico. Each site consisted of a holding corral, a concrete dipping trench having a capacity of 2,500-5,000 gallons (9,464-18,927 liters) of pesticide formulation, a drip pad, and a pesticide disposal area. On an annual basis, livestock were herded into the holding corral, driven through the dipping trench, and held in the drip pad area to dry. After the livestock had been treated, the formulation was drained from the trench to an area used for disposal. Over time, the pesticide disposal area became extensively contaminated with toxaphene and other pesticides. Dip vat sites were prioritized for cleanup based on their proximity to human habitation and to streams and wetlands. Toxaphene levels in soil samples were as high as 800 mg/kg. Contaminated soil at both sites was dug up and stockpiled.

During construction of a trench on Gila River Indian Community (GRIC) property near Chandler, Arizona, workers detected a strong chlorine odor and evacuated the area. Evaluation of old aerial photographs indicated that the area was the former location of an air strip used by crop dusters. It was believed that soil became contaminated due to crop dusters and pesticide transport trucks emptying and rinsing their storage tanks

on or near the runway. High levels of toxaphene were found in site soil samples with contamination levels ranging from 15,000 to 24,000 mg/kg. Contaminated soil was dug up and transported to a designated area for temporary storage pending treatment.

Analytical Procedures. Soil samples were extracted for 16 hours in a Soxhlet apparatus using 1:1 (v:v) hexane:acetone as extracting solvent. Toxaphene was analyzed in solvent extracts using a modified gas chromatography/electron capture (GC/ECD) method developed by ERTC/REAC laboratories (ERTC/REAC, 1994).

MATERIALS AND METHODS

Bench-Scale Studies. Composited soil samples were initially screened through a #10 stainless steel sieve to remove large particulates, extensively mixed, and then analyzed for toxaphene content. Soil was screened for toxaphene-degradative activity in bench-scale anaerobic reactors using standard recipes. Reactors consisted of 125 mL serum bottles with 100 mL working volumes. Reactors were charged with 25 grams of soil (dry weight) and with varying amounts of dried blood meal. The soil and blood meal were suspended in sodium phosphate buffer to 100 mL. The starting pH ranged from 6.5-7.3. Reactors were incubated at room temperature for up to 56 days with samples collected at Days 0, 28, or 56. At each sampling time, duplicate or triplicate reactors were harvested, analyzed for toxaphene content, and values averaged.

Field-Scale Studies (LDV site). Soil at the LDV site was dug up and stockpiled with a total soil volume of 253 yd^3 (193 m^3). The soil pile was turned over with a backhoe to mix the soil. The anaerobic cell was then constructed with dimensions of 73 ft (22.3 m) by 30 ft (9.1 m) by 4 ft (1.2 m) and then lined with a plastic liner. The soil was added to a concrete mixer with recipe nutrients and water and mixed. The recipe used in this study consisted of blood meal and sodium phosphate at rates of 10 g/kg. Monobasic and dibasic phosphate salts were utilized at a ratio of 3:1 on a weight basis. The nutrient-amended soil slurry was then added to the lined cell. Water was added to a level of 1 ft (0.30 m) over the solids in the cell. The cell was then covered with a plastic sheet and incubated for a total of 60 days with samples collected at 0, 30, and 60 days. Six sampling ports were installed at various points along the cell perimeter. On the date of sampling, three sediment cores were obtained from each port, composited, and a sample collected for toxaphene analysis. A total of six samples were collected at each sampling time, analyzed for toxaphene, and averaged. Samples were collected at later dates to confirm toxaphene removal.

HDV Site. At the HDV site, the soil volume requiring treatment was considerably higher at 660 yd^3 (505 m^3). Two anaerobic cells were constructed for soil treatment. The dimensions of the north cell (Cell #1) were 75 ft (22.9 m) by 35 ft (10.7 m) by 5 ft (1.5 m) while the dimensions of the south cell (Cell #2) were 65 ft (19.8 m) by 30 ft (9.1 m) by 5 ft (1.5 m). After lining both cells with a plastic liner, contaminated soil was mixed with recipe ingredients in a 2 yd^3 (1.5 m^3) bucket and added to a mixing pit. The recipe used was similar to the one described earlier except that the blood meal rate was reduced to approximately 5 g/kg. Water was added to the mixing pit, the soil slurry extensively mixed, and the soil slurry deposited in the lined pits. Additional water was added to each pit to achieve a level of 1 ft (0.30 m) over the cell solids. Each cell was then covered with a plastic sheet and incubated for a total of 61-76 days with samples collected at Days 0 and 61 from Cell #1 and at Days 0 and 76 from Cell #2. Sampling ports and sampling strategies were identical to those used at the LDV site. Samples were also collected at later dates to confirm toxaphene residue removal.

GRIC Site. The largest volume of contaminated soil treated using the anaerobic process was the stockpile located at the GRIC site with a total volume of 3,500 yd^3 (2,676 m^3). Due to the volume of soil requiring treatment, four anaerobic cells were constructed with dimensions of 178 ft (54.3) by 43 ft (13.1 m) by 7 ft (2.1 m). Prior to loading, each cell was filled with water to 25% of its capacity. A recipe with only 50% of the standard recommended nutrient rates was chosen to reduce nutrient costs. The rate of blood meal and sodium phosphate used was 5 g/kg with dibasic and monobasic phosphate salts added in equal amounts. Bench-scale studies previously indicated that the reduced blood meal rate also stimulated toxaphene degradation although degradation proceeded at a slower rate. Sodium phosphate and blood meal were mixed in a nutrient mixing pit. The homogenized nutrients were then added in amounts proportionate to the amount of soil in the bucket of a front end loader and the amended soil transferred to a transportable pug mill with a capacity of 100-300 yd^3/hr (76.5-229.4 m^3/hr) and mixed. The soil-nutrient mixture was then transported and dispensed into the cells with

a front end loader. After loading the units, each cell was flooded with additional water to a level of 1 ft (0.30 m) over the cell solids and covered with a plastic sheet. Six sampling ports were constructed for each cell. Three soil cores were collected from each port and mixed. A composite sample was then collected from each port mixture, submitted for toxaphene analysis, and the values later averaged. Samples were collected from the cells after initial setup and at 3 months, 6 months, and 9 months. During the final sampling event, the cover for each unit was removed and samples were collected at a variety of locations to confirm that there was a uniform removal of toxaphene throughout each cell and not just at the sampling port locations.

RESULTS AND DISCUSSION

Bench-Scale Studies. Results of soil screening studies are summarized in Table 1. Toxaphene removal levels ranged from approximately 38-48% over a 28- to 56-day period using a recipe consisting of 10 g/kg blood meal and 10 g/kg sodium phosphate. In initial studies, limestone was added to LDV soil at a rate of 25 g/kg, however, due to a progressive increase in culture pH throughout the study period, lime was found to be unnecessary and was removed from further consideration as a recipe ingredient.

TABLE 1. Toxaphene-degradative activity in bench-scale studies.

Site Name	Initial Conc. (mg/kg)	Final Conc. (mg/kg)	Degradation (%)	Time (Days)
LDV	60	37	38.3	56
HDV	100	55	45.0	56
GRIC	25	13	48.0	28

Similar increases in culture pH were noted in studies with HDV and GRIC soil. A time course study of toxaphene removal using LDV and HDV soil is shown in Figure 1.

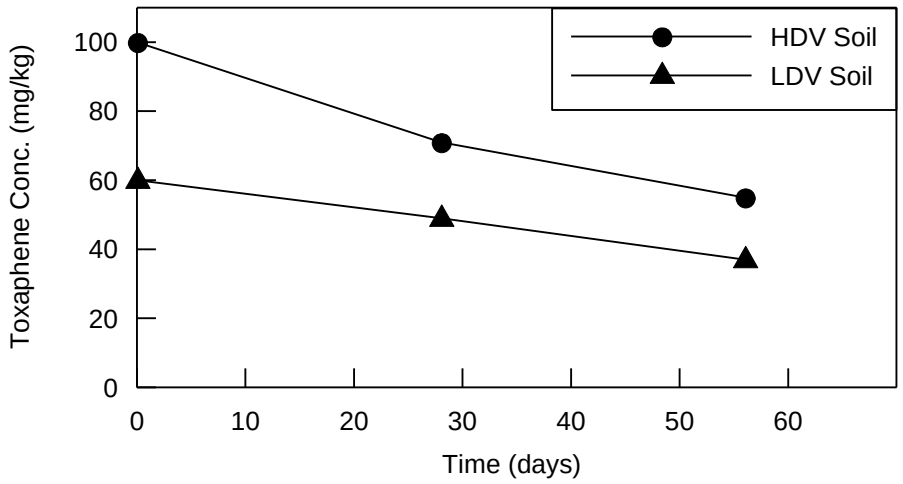

FIGURE 1. Toxaphene removal from HDV and LDV Soil in bench-scale studies.

Field-Scale Studies. Results of the field-scale studies are shown in Table 2. Results showed that toxaphene was rapidly removed from nutrient-amended soil added to test cells. In the cell containing LDV soil, toxaphene was reduced from an initial concentration of 29 mg/kg to 4 mg/kg in 31 days with an overall reduction of 86.2%. In the cells containing HDV soil, toxaphene was reduced from 29 mg/kg to 9 mg/kg with approximately 69% removed in 76 days in Cell #1 and from 17 mg/kg to 6 mg/kg with approximately 65% removed in 61 days in Cell #2. In both studies, the toxaphene was reduced to well below the action level of 25 mg/kg.

TABLE 2. Toxaphene removal in field-scale anaerobic cells.

Site Name	Initial Conc. (mg/kg)	Final Conc. (mg/kg)	Degradation (%)	Time (Days)
LDV	29	4	86.2	31
HDV (Cell #1)	29	9	69.0	76
HDV (Cell #2)	17	6	64.7	61
GRIC (Cell #1)	29	5	82.8	189
GRIC (Cell #2)	31	5	83.9	191
GRIC (Cell #3)	29	4	86.2	190
GRIC (Cell #4)	34	4	88.2	191

Using a nutrient-lean recipe, the removal of toxaphene in GRIC site soil took considerably longer due to an extended acclimation time and a slower rate of removal. Indeed, there was no significant reduction in toxaphene content until approximately 6 months (Days 189-191). At this sampling time, levels were reduced to 4-5 mg/kg with an extent of removal ranging from 83-88%. The samples collected at Days 270-272 confirmed the earlier results with residual levels of 2-4 mg/kg and reduction levels ranging from 86-93%. A time course of this study is shown in Figure 2.

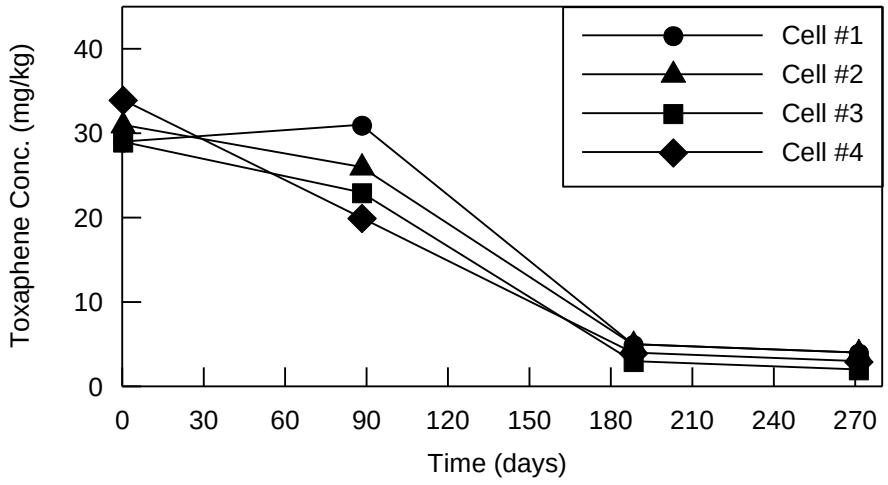

FIGURE 2. Toxaphene removal in field-scale anaerobic cells at the GRIC site.

The residual values are well below the 17 mg/kg action level established for the site. After confirmation of site cleanup, the cells were backfilled and site restoration activities initiated and completed.

Site Cleanup Costs. Table 3 summarizes the costs for cleanup of the three sites. Cleanup costs ranged from \$149-\$337/m^3 for the three sites. These costs are very competitive when compared to other cleanup methods such as incineration or desorption methods.

TABLE 3. Cleanup costs using anaerobic bioremediation technology.

Site Name	Cost ($)	Soil Volume (m^3)	Cost ($/m^3$)
LDV	65,000	193	337
HDV	75,000	505	149
GRIC	725,000	2,676	271

CONCLUSIONS

A simple recipe, composed of phosphate buffer and blood meal, promoted the rapid removal of toxaphene in both bench-scale and field-scale studies. In bench-scale studies, toxaphene was reduced by 38-48% in 28 to 56 days while in field-scale studies, toxaphene levels were reduced by 65-88% in 31 to 191 days. The toxaphene content was reduced to well below the action level established for each site. Process costs ranged from \$149-337/m^3 suggesting that toxaphene removal using anaerobic bioremediation technology is cost competitive when compared to other cleanup methods.

Future studies will involve the development of more cost effective nutrient recipes which promote rapid degradation of toxaphene. Additional sites are being targeted by the POEP for cleanup.

REFERENCES

Allen, H.L., R.M. Mandel, M. Torres, D.G. Crouse, and T.F. Miller. 1999. "Anaerobic Bioremediation of Toxaphene-Contaminated Soil." In A. Leeson and B.C. Alleman, (Eds.), *The Fifth International In Situ and On-Site Bioremediation Symposium*, pp. 89-94, Vol. 5(6), Battelle Press, Columbus, Ohio.

Camacho, J.M., W. Joyner, R. Vemuri, and B. Holderness. 1997. "Anaerobic Degradation of Toxaphene in Soils: A Pilot Study." In B.C. Alleman and A. Leeson, Symposium Chairs, *The Fourth International In Situ and On-Site Bioremediation Symposium*, pp. 251–256, Vol. 4(2), Battelle Press, Columbus, Ohio.

EPA/REAC. 1994. SOP #1802 *Routine Analysis of Toxaphene in Soil/Sediment by GC/ECD*.

Korte, F., I. Scheunert, and H. Parlar. 1979. "Toxaphene (Camphechlor). A Special Report." *J. Pure Appl. Chem.* 51:1583–1601.

Mirsatari, S.G., M.M. McChesney, A.C. Craigmill, W.L. Winterlin, and J.N. Seiber. 1987. "Anaerobic Microbial Dechlorination: An Approach to On-Site Treatment of Toxaphene-Contaminated Soil." *J. Environ. Sci. Health.* B22 (6):663–690.

Parr, J.F., and S. Smith. 1976. "Degradation of Toxaphene in Selected Anaerobic Soil Environments." *Soil Sci.* 121(1):52–57.

Smith, S., and G.H. Willis. 1978. "Disappearance of Residual Toxaphene in a Mississippi Delta Soil." *Soil Sci.* 126(2):87–93.