Performance and Process Economics of Anaerobic Bioremediation of Toxaphene

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ABSTRACT: In January 2001, field-scale studies were initiated at the Gila River Indian Community (GRIC) site in Chandler, AZ, to clean up toxaphene-contaminated soil using anaerobic bioremediation technology. The anaerobic process was developed by United States Environmental Protection Agency/Environmental Response Team (U.S. EPA/ERT) and Response Engineering and Analytical Contract (REAC) personnel and has been successfully used over the past ten years. Four anaerobic cells were constructed to treat approximately 2,700 m^3 of contaminated soil. Results showed that the extent of removal of toxaphene ranged from 86 to 93% after approximately 9 months, with the toxaphene concentration falling below the action level of 17 mg/kg. The cost for soil cleanup was assessed at \$271/m^3. In October 2002, another site, the Gila River Boundary (GRB) site, was identified on the reservation and is currently finishing full-scale cleanup. The GRB site contained approximately 6,100 m^3 of contaminated soil, which was treated in six anaerobic cells. After 6 months of treatment, the toxaphene concentration had been reduced below the action levels in each of the treatment cells, with the average extent of removal ranging from 66 to 82%. The cost for soil cleanup was approximately \$130/m^3. The cost breakdown of the different elements involved in the development, implementation, and operation of a large-scale anaerobic bioremediation process is presented.

INTRODUCTION

Toxaphene is a broad spectrum insecticide that has been used for the control of insect pests in the agriculture and forestry industries. It has been heavily used in the southern United States for pest control on cotton but has also been used on a variety of agricultural commodities and crops. Although primarily used in agriculture, it has also been used to control exoparasites on cattle, sheep, and goats (Korte et al. 1979).

Toxaphene is highly toxic to fish and mammals. It has been shown to be teratogenic, mutagenic, and carcinogenic in animal studies. Not only highly toxic, it also has been shown to be persistent in the environment and tends to degrade very slowly. Due to its toxicity and environmental persistence, the U.S. EPA banned its use in 1982 (Saleh 1991).

A number of studies have shown that this pesticide is susceptible to anaerobic biodegradation (Mirsatari et al., 1987; Parr and Smith, 1976; Smith and Willis, 1978). The U.S. EPA/Environmental Response Team (ERT) and Response Engineering and Analytical Response (REAC) personnel have developed an anaerobic bioremediation process which has been successfully used to remove toxaphene from soil at a variety of sites throughout the United States (Camacho et al. 1997; Allen et al. 1999).

In 2001, the bioremediation process was used to clean up 2,700 m^3 of contaminated soil located at the Gila River Indian Community (GRIC) site (Allen et al. 2002). This site was the former location of an abandoned air strip used by crop dusters during application of pesticides to crops. More recently, another abandoned crop duster facility was identified on the reservation and referred to as the Gila River-Boundary (GRB) site. Site soil was extensively contaminated with toxaphene and, after preliminary bench and pilot testing to confirm toxaphene-degradative activity in site soil, full-scale treatability studies were initiated in May 2004.

The objective of the studies was to assess the performance of removing toxaphene from contaminated soil at both sites. A cost breakdown of the process during cleanup of both sites will be discussed and summarized below.

Site Description. A description of the GRIC site has been discussed previously (Allen et al. 2002). The site was the former location of an airstrip used by crop dusters during the application of pesticides to crops. The soil was extensively contaminated from runoff generated when storage tanks on crop dusters and pesticide transport trucks were emptied and rinsed out with water. Contaminated soil was transported to a designated area on the reservation for treatment.

The GRB site is the former location of a commercial establishment involved in the aerial application of pesticides. The site consists of airstrips used by crop dusters during pesticide application. Soil was contaminated from spills of pesticide formulation when loading the tanks on crop dusters and when emptying the tanks after completing pesticide application. In October 2002, the site assessment phase was initiated to determine the extent of contamination and to estimate volumes of contaminated soil requiring treatment. Soil analysis showed extensive contamination with toxaphene especially at airplane "turnaround" areas on the airstrips. In October 2003, on-site bench- and pilot-scale studies were conducted to assess the performance of the anaerobic process in removing toxaphene from site soil. During these studies, cost effective second generation nutrient recipes were evaluated to further reduce process costs. Results showed that up to 73% of available toxaphene was removed in approximately 6 weeks using the new recipes. Full-scale treatability studies were initiated in May 2004.

Analytical Procedures. Soil samples were analyzed for toxaphene as previously described (Allen et al. 2002) using analytical methods developed by ERTC/REAC laboratories (ERTC/REAC, 1994).

MATERIALS AND METHODS

Bench-Scale Studies. Bench-scale studies using GRIC soil have been previously described (Allen et al. 2002). For studies with GRB site soil, site soil was extensively mixed in a 5-gallon bucket and dispensed in 250-g aliquots into 1-liter polyethylene bottles. Nutrients from standard and newly developed recipes were added as dry ingredients and the reactors filled with distilled water, sealed, and mixed. The lids from each reactor bottle were loosened to allow venting of gases. The bottles were placed in a 5-gallon bucket, sealed, and buried on-site. A control sample was collected from the soil composite and analyzed to determine the initial toxaphene concentration. The bottles were later recovered after 41 days and the soil analyzed for toxapahene content.

The second generation recipes were considerably different from standard recipes. These recipes consisted of reduced levels of sodium phosphate (6 g/kg), a starting pH of 7.8, the addition of starch (4 g/kg) and varying levels of blood meal (2.5-10 g/kg.).

Pilot-Scale Studies. At the GRB site, two pits were constructed on-site and lined with polyethylene sheets. Two hundred pounds (91 kg) of toxaphene-contaminated soil were added to each lined pit and then amended with blood meal and sodium phosphate. Blood meal and sodium phosphate were added at a rate of 10 g/kg. Sodium phosphate was added as a combination of dibasic and monobasic salts at a ratio of 1:1 on a weight basis. The nutrient-amended soil was extensively mixed and then flooded with tap water. Prior to water addition, duplicate or triplicate samples were collected as Day 0 control samples. The liners on each reactor were then sealed and the pits filled in with soil. Duplicate or triplicate core samples were collected from each reactor after 41 and 111 days. The toxaphene concentrations found at Days 41 and 111 were compared with the concentration found at Day 0 to determine the extent of toxaphene removal.

Field-Scale Studies. The construction of field cells at the GRIC site has been described previously (Allen et al. 2002). A 3,500 yd^3 (2,676 m^3) stockpile of contaminated soil was dispensed in four anaerobic cells with dimensions of 178 ft (54.3) by 43 ft (13.1 m) by 7 ft (2.1 m). The rate of blood meal and sodium phosphate used was 5 g/kg with dibasic and monobasic phosphate salts added in equal amounts. Nutrient addition and sample collection have been described previously (Allen et al. 2002).

Approximately 8,000 yd^3 (6,116 m^3) of toxaphene-contaminated soil are being treated at the GRB site in six field cells. The field cells had dimensions of 142 ft (43.3 m) by 22 ft (6.7 m) by 5 ft 1.5 m). Each cell was lined with a plastic liner before the addition of nutrient-amended contaminated soil. The liner was constructed such that it could be folded over to create a cover after each cell was loaded.

The soil was dug up, stockpiled, and sieved through a 3-in. (7.62-cm) vibrating screen. The screened soil was then amended with nutrients in proportional amounts and mixed in a pug mill. The mixed amended soil was transported to the lined field cells with a front-end loader. Approximately 900 yd^3 (688 m^3) of amended contaminated soil was added to each field cell. Each field cell was then flooded with water until a free-standing water depth of 6 to 12 in. (15.2 to 30.5 cm) was achieved. Each field cell was covered by folding over a portion of the cell liner and then glued together. The sealed liners were then buried in ditches surrounding the perimeters of each unit.

Sampling ports were then installed which permitted sampling without having to remove the cover. These ports consisted of five-ft. (1.5 m) pieces of 4-in. (10.2 cm) diameter polyvinyl chloride (PVC) pipe. The pipe was inserted through the cover, the cover sealed around the pipe, and the end of the pipe positioned above the surface of the cell. The other end was covered with a threaded PVC cap that had been fitted with a check valve. The venting pipe was attached to a vertical metal rod embedded in the soil adjacent to the cell. Three ports were installed in each field cell.

Sampling devices consisted of a 15 ft. (4.6 m) PVC pipe with a diameter of 1.5 in (3.8 cm). The pole was inserted through the sampling/venting port pipe into the flooded soil to a depth of three feet. The pole was removed from the port pipe and the soil core transferred to a resealable plastic bag. The sample was manually mixed and a subsample

collected in glass sampling jars. Samples collected from each cell were analyzed for toxaphene content and the results averaged. The rate and extent of toxaphene reduction was determined for each cell by comparing test toxaphene levels with the control (Day 0) toxaphene level. Contaminated soil was considered "clean" if the toxaphene content was reduced to below the action level of 17 mg/kg.

RESULTS AND DISCUSSION

Bench-Scale Studies. Results of soil screening studies with GRIC and GRB site soil are summarized in Table 1. The toxaphene content in GRIC was reduced by approximately 50% in 28 days using the standard recipe of 10 g/kg blood meal and 10 g/kg sodium phosphate.

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

Site Name	Recipe	Initial Conc. (mg/kg)	Final Conc. (mg/kg)	Degradation (%)	Time (Days)
GRIC	Standard	25	13	48.0	28
GRB	Standard	895	570	36.3	41
	1	895	240	73.2	41
	2	895	310	65.4	41
	3	895	260	70.9	41

In GRB soil, significant removal of toxaphene was observed using the standard recipe with the toxaphene content reduced by over 36%. Addition of starch resulted in a 2-fold increase in toxaphene removal regardless of the blood meal concentration utilized. In these studies, Recipes 1, 2, and 3 contained 10, 5, and 2.5 g/kg of blood meal, respectively.

Pilot-Scale Studies. Results of the pilot study are summarized in Table 2. The toxaphene content was reduced by approximately 50% in both reactors in approximately four months.

TABLE 2. Toxaphene-degradative activity in pilot-scale studies.

Site Name	Recipe	Initial Conc. (mg/kg)	Final Conc. (mg/kg)	Degradation (%)	Time (Days)
GRB	Standard	2,767	1,467	47.0	111
		2,650	1,300	50.9	111

Field-Scale Studies. Results of the field-scale studies for the GRIC and GRB sites are shown in Table 3. Toxaphene was rapidly removed from soil in anaerobic cells constructed at both sites.

TABLE 3. Toxaphene removal in field-scale anaerobic cells.

Site Name	Initial Conc. (mg/kg)	Final Conc. (mg/kg)	Degrad. (%)	Time (Days)
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
GRB (Cell #1)	51	15	70.6	203
GRB (Cell #2)	42	10	76.2	203
GRB (Cell #3)	110	20	81.8	203
GRB (Cell #4)	29	9	69.0	187
GRB (Cell #5)	29	10	65.5	187
GRB (Cell #6)	23	5	78.3	187

Toxaphene degradation in GRIC soil has been reported previously (Allen et al. 2002). From an initial concentration ranging from 29 to 34 mg/kg, the toxaphene content was reduced to a level of 4 to 5 mg/kg with the extent of toxaphene removal ranging from 83 to 88% in approximately six months.

Similar results were observed at the GRB site. From an initial concentration ranging from 23 to 110 mg/kg, the toxaphene content was reduced to levels ranging from 5 to 20 mg/kg with the extent of removal ranging from 66 to 82% in approximately six months. The toxaphene content was reduced to concentrations below the action level of 17 mg/kg in five of six cells.

Site Cleanup Costs. Table 3 summarizes the costs for cleanup of the two sites. Cleanup costs ranged from \$130-\$271/m^3 for the two sites. These costs are very competitive compared to other cleanup methods, such as incineration or thermal desorption.

TABLE 4. Cleanup costs using anaerobic bioremediation technology.

Site Name	Cost ($)	Soil Volume (m^3)	Cost ($/$m^3$)
GRIC	725,000	2,676	271
GRB	793,000	6,116	130

CONCLUSIONS

Simple nutrient recipes, composed of phosphate buffer and blood meal or phosphate buffer, blood meal, and starch, promoted the rapid removal of toxaphene in

bench-scale, pilot-scale, or field-scale studies at the GRIC and GBR sites. In studies with GRIC soil, toxaphene levels were reduced by 48% in bench studies and by 83-88% in field studies. In studies with GBR soil, toxaphene levels were reduced by 36-73% in bench studies, 47-51% in pilot studies, and 66-82% in field studies. The toxaphene content was reduced to below the action level of 17 mg/kg in field cells at the GRIC site and in five of six cells at the GBR site in approximately six months. Process costs ranged from \$130-271/m^3 suggesting that toxaphene removal using anaerobic bioremediation technology is cost competitive when compared to other cleanup methods. Additional sites are being targeted for cleanup based on EPA's success in these and similar studies.

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