The Xenorem™ process to treat toxaphene contaminated soil

Neil C.C. Gray, Paul R. Cline, Guy P. Moser, Ann L. Gray, Lori E. Moser
Holly A. Guiler, Brian M. Boyd, David J. Gannon
AstraZeneca Canada Inc., Sheridan Park Environmental laboratory
2101 Hadwen Road, Mississauga, L5K 2L3 Canada
Phone: +1 905 403 2748, Fax: +1 905 823 7160
Email: Neil.Gray@astrazeneca.com

Abstract

A commercial-scale demonstration (1,000 yd^3) and a full-scale operation (4,000 yd^3) have been carried out using the Xenorem™ process of the Stauffer Management Company (SMC), a U.S. subsidiary of AstraZeneca PLC., to treat chlorinated pesticide contaminated soil. The soils contained a range of chlorinated organics, thiocarbamate and organophosphorus pesticides, however, toxaphene was the main constituent, typically in the range of 70 to 85% of the total. The goal of the demonstration was to show that the laboratory and pilot-scale results could be scaled-up, and that the enhanced anaerobic/aerobic composting process could remediate the soil to acceptable levels. Toxaphene was utilised as a process marker but analysis of this compound was problematic and required method development to achieve accurate quantitation. The final target levels were achieved for all compounds. Based on the demonstration study, the U.S. EPA recommended in the site Record of Decision (ROD) that bioremediation be used as the preferred technology to treat the pesticide contaminated soil. The technology is now being used to treat soil from two different sites in Florida.

Introduction

For the past eight years SMC has explored bioremediation as a cost-effective technology to treat pesticide and other recalcitrant contaminated soils (Gray *et al*, 2000; Gray *et al*, 1999; Gray and Gannon, 1999; Gray, 1998). In this case, bioremediation is the utilisation of the indigenous microflora associated with the historically contaminated soil, under controlled environmental conditions. The initial target of this research was chlorinated pesticides, including toxaphene. Toxaphene bioremediation became a focus because it was present at high levels and was an effective indicator of good process conditions. However, toxaphene's complex GC profile made its reproducible quantitation problematic and obscured analyses of other chlorinated co-contaminants in soil samples.

Laboratory work using soil from the SMC, Tampa, Florida site, indicated that the toxaphene could be degraded well under controlled environmental parameters. The purpose of the commercial-scale demonstration was to show that the Xenorem™ process could be scaled-up, to investigate potential full-scale logistics and to ensure that appropriate analytical methods were employed for accurate quantitation of toxaphene. With the successful completion of the demonstration, a full-scale operation was initiated at the Tampa site.

Materials and methods

Demonstration study

Initially five highly contaminated (hot) zones were identified from a field-sampling program at the Tampa site. Random samples were collected from each zone and submitted to the laboratory for microcosm evaluations. Based on the sampling verification program and the results from the microcosm studies, two hot zones were selected for the demonstration trial. The soil was excavated, screened, mixed and amended with organics, giving rise to a final volume of ca. 1,000 yd^3. The amended soil matrix was engineered into a compost windrow, built inside a warehouse. Due to potential odour issues from some of the pesticides, and the high groundwater table in the area, it was prudent to carry out the trial inside the warehouse.

Six soil samples were collected from the windrow, on a biweekly schedule. Each soil sample consisted of individual composite (based on depth) samples, which were mixed together to form a single sample. The soil samples were air dried and ground prior to analysis by U.S. EPA Methods 8080 or 8081A. The geomean of the data was plotted on a temporal basis for each chemical. During the investigation/optimisation of toxaphene analysis, gel permeation chromatography (SW846 Method 3640A) and sulphuric acid (based on SW846 Method 3665A) clean-up methods were performed on selected soil samples prior to chemical analysis by EPA Method 8081A.

Temperature, aerobic and anaerobic periods were externally controlled in microcosm studies using an anaerobic incubator and an aerobic environmental chamber. Temperature, aerobic and anaerobic periods in the 1000 yd^3 windrow were controlled by the use of organic amendments and mechanical mixing.

A factorial experiment was designed to assess the impact of the extraction method, extraction solvent and moisture on the quantitation of toxaphene. A 2 kg soil sample from the 1,000 yd^3 windrow was mixed and then sampled wet, after air-drying and then after air-drying and grinding (Agvise, model PB-10). The samples were extracted using three different methods (a) Soxhlet (EPA Method 3540C) using a 1:1 mix of methylene chloride and acetone, (b) wrist action shaker using a 1:1 mix of methylene chloride and acetone (c) wrist action shaker using methylene chloride. EPA Method 8081A was used to analyse the soil extracts.

Figure 1. The windrow turner SCAT 4932 being used to mix amendments

Figure 2. Big top enclosure with odour abatement system

Full-scale operation

In a similar fashion as to what was carried out for the demonstration study, the soil was excavated from two zones on the site, screened to remove concrete and railway ballast debris, mixed and amended with organics; a total of 4,000 yd^3 of soil was treated. Improved mixing was carried out using a large self-propelled SCAT 4932 windrow turner; this unit was used in all mixing operations (see Figure 1). As with the demonstration study, the operation was carried out within an enclosure (a 300' x 130' Big Top), with an odour abatement system attached (See Figure 2); the system consisted of a set of prefilters, an 8,000 cfm blower and a 10 tonnes activated carbon unit. Soil sampling and analysis was carried out as described above for the demonstration study.

Results and discussion

Preliminary laboratory study

Preliminary treatability studies were performed using grab samples from different hot zones of the site. The microcosms were carried out over a 6-week period, representing one anaerobic/aerobic cycle (4 weeks/2 weeks).

The microcosms were very successful and demonstrated the potential of the enhanced anaerobic/aerobic composting technology to degrade toxaphene (Figure 3). The three soils tested had initial toxaphene levels of 3,155 ppm, 332 ppm and 25 ppm. After one treatment cycle (6 weeks) all 3 soils showed losses of greater than 75%, with 90% loss observed in both soils with lower starting concentrations of toxaphene. No treatment inhibition was encountered at higher levels of toxaphene. These favourable results supported the decision to carry out the field trial at a larger scale.

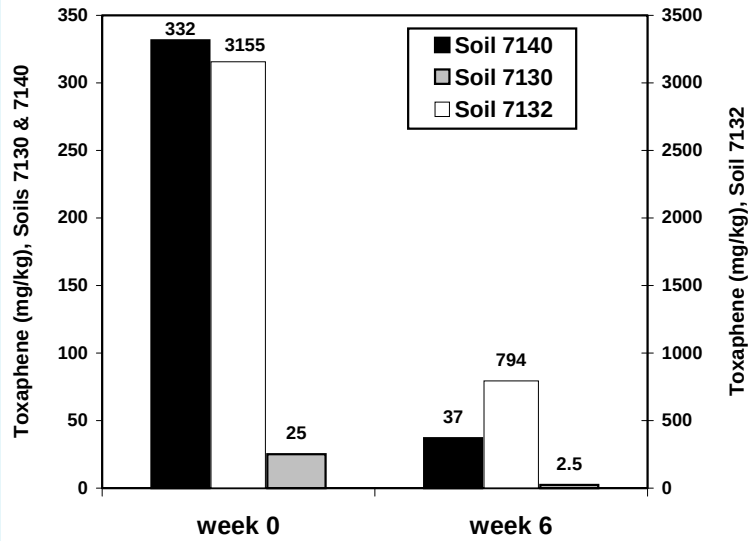

Figure 3. Microcosm toxaphene results after 6 weeks of Xenorem™ treatment

Demonstration study

Toxaphene was the main contaminant of concern, in that it represented nearly 70% of the total contaminants, followed by the DDX family. The overall objective of the study was to determine if the enhanced composting technology could be used to remediate the site contaminated soil to the acceptable clean-up standards listed in the ROD or 90% degradation. For toxaphene, the ROD value is 2.76 ppm.

Toxaphene was analysed by two different methods in order to follow (a) the degradation of the parent compound (technical toxaphene) and the corresponding breakdown products, and (b) to follow only the parent compound (technical toxaphene) degradation (Figure 4). Each data point represents the geomean value of at least 6 samples. Under the optimal environmental conditions, rapid losses of toxaphene and metabolic by-products are seen, giving rise to an overall loss greater than 90%.

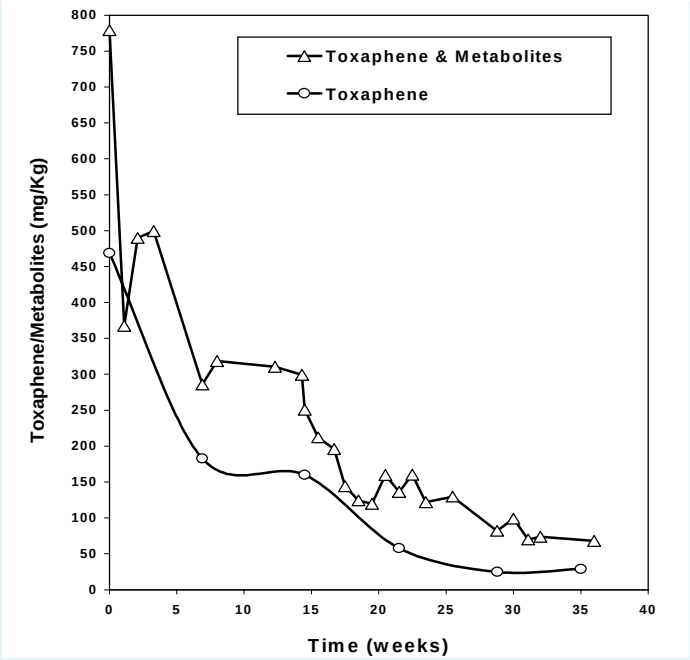

Figure 4. Toxaphene degradation in the 1,000 yd^3 windrow

GC/ECD chromatograms (Figure 5) from soil samples taken during the Xenorem™ process substantiate the degradation of toxaphene observed in the 1,000 yd^3 windrow. Over time, there were significant reductions in both the component peak heights and the characteristic toxaphene hump of unresolved compounds, decreases in the higher chlorinated congeners present at the longer retention times and a migration towards lower chlorinated congeners/ metabolites at the earlier retention times.

To confirm the toxaphene endpoint observed in the 1,000yd^3 windrow, soil samples from the 35-week time point were submitted to 5 commercial analytical laboratories for toxaphene quantitation by EPA Method 8081. The results (Table 1) were highly variable with toxaphene levels as low as < 0.2 ppm and as high as 105 ppm reported representing a greater than 500 fold difference.

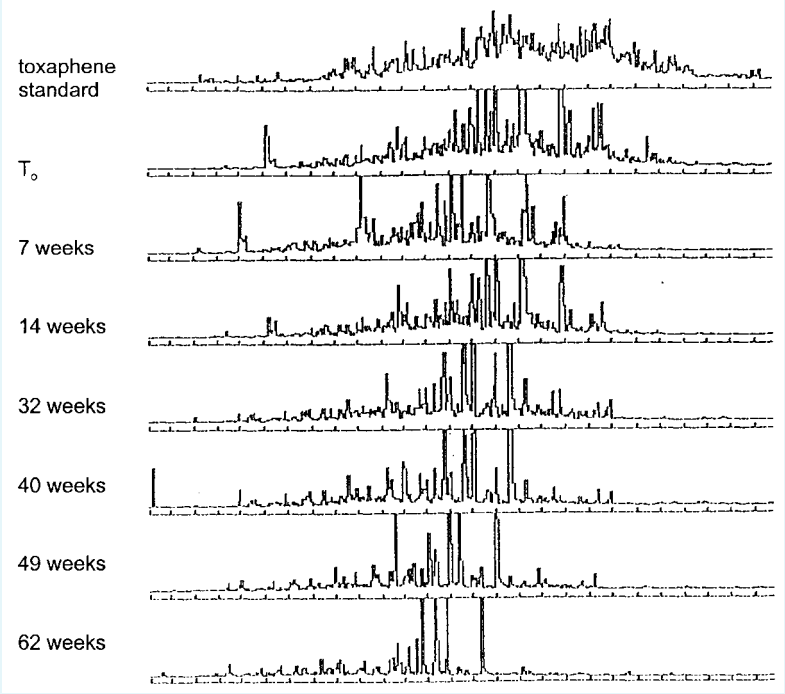

Figure 5. GC/ECD chromatograms (13-40 minutes) showing toxaphene degradation with time in the 1,000 yd^3 windrow

Table 1. Toxaphene determinations from different analytical laboratories

Analytical Laboratory	Toxaphene Standard	Extraction Procedure	# of peaks used in quantitation	Where peaks selected	Toxaphene (mg/kg)
A	Riedel-de Haën	Shaking	10	Across whole toxaphene pattern	105
	Riedel-de Haën	Shaking	4	Back half of toxaphene pattern	29
B	Restek	Soxhlet	10	Across whole toxaphene pattern	75
C	Restek	Ultrasonication	4	Back half of toxaphene pattern	4.6
D	Ultra Scientific	Soxhlet	10	Middle & back half of toxaphene pattern	< 0.2
	Ultra Scientific	Ultrasonication	10	Middle & back half of toxaphene pattern	< 0.2
E	Supelco	Soxhlet	4 - 6	Across whole toxaphene pattern	< 69
	Supelco	Ultrasonication	4 - 6	Across whole toxaphene pattern	< 45.5

Optimising toxaphene analysis in soil

To identify factors influencing the variation in toxaphene quantitation by EPA Method 8081, soil sample preparation, sample extraction methods and the reference standard used in quantitation were investigated.

The variation in toxaphene reference standards was investigated by comparing GC/ECD profiles from four commercial sources under identical GC conditions. From the resulting chromatograms (Figure 6), it was visually evident that significant differences in the component peaks profiles and relative proportions existed between different sources of toxaphene standards. The differences in commercially available toxaphene standards have impacted the accurate identification and reproducible quantitation of toxaphene between laboratories. Other researchers have observed inconsistent toxaphene results caused by the variability among toxaphene reference standards (Carlin and Hoffman, 1997). The Ideal toxaphene standard, that identically matches the weathered GC/ECD profile in soil samples from contaminated sites, does not exist. So, a suitable toxaphene reference standard, from one commercial supplier, should be selected and consistently used when trying to achieve reproducible and accurate toxaphene quantitation. This will reduce the variability in toxaphene values reported within one or between different analytical laboratories.

Different extraction methods, extraction solvent systems and moisture levels were studied to investigate their impact on toxaphene quantitation in soil. The quantitation of toxaphene in soil samples was effected by moisture level, the physical processing and extraction procedure used prior to analysis by EPA Method 8081A. Soxhlet extraction with methylene chloride and acetone was superior to less rigorous wrist-action extraction procedures studied, resulting in significantly (using a = 0.05) higher levels of toxaphene being detected. Other studies comparing Soxhlet and ultrasonic extraction methods produced similar results when the same extraction solvent was used.

Lower moisture levels and physical processing of soil samples also had a significant effect on the toxaphene concentration measured. Highest levels of toxaphene were measured in soil samples that were dried (11% moisture) and ground. The same trend was observed for three other chlorinated co-contaminants present in the soil samples.

The quantitation of toxaphene in soil is challenging enough because of its complex GC/ECD profile. The presence of chlorinated co-contaminants makes accurate quantitation even more problematic. Sulphuric acid clean-up is commonly used to remove a number of single component organochlorine and organophosphorus pesticides prior to PCB analyses by EPA Method 8082. Sulphuric acid clean-up was investigated as a means to remove co-contaminants in soil samples prior to toxaphene analysis by Method 8081A. A 500 ppm reference standard, containing twenty OCP's measured by EPA Method 8081A, was subjected to sulphuric acid clean-up. Of the twenty components studied, DDE, endosulfan I, endosulfan II, endrin, endrin aldehyde and methoxychlor were completely removed by the acid clean-up. The four components; aldrin, beta-BHC, endosulfan sulphate and heptachlor epoxide were partially removed (losses between 47 and 64%). The ten components alpha-BHC, delta-BHC, gamma-BHC, alpha-chlordane,

gamma-chlordane, DDD, DDT, dieldrin, heptachlor and toxaphene were not affected by the acid clean-up. This confirmed that toxaphene quantitation would not be affected by sulphuric acid clean-up. As 10 of the 20 organochlorine pesticides were completely or partially removed by sulphuric acid clean-up, this method was considered a benefit for toxaphene quantitation in soils co-contaminated with OCPs.

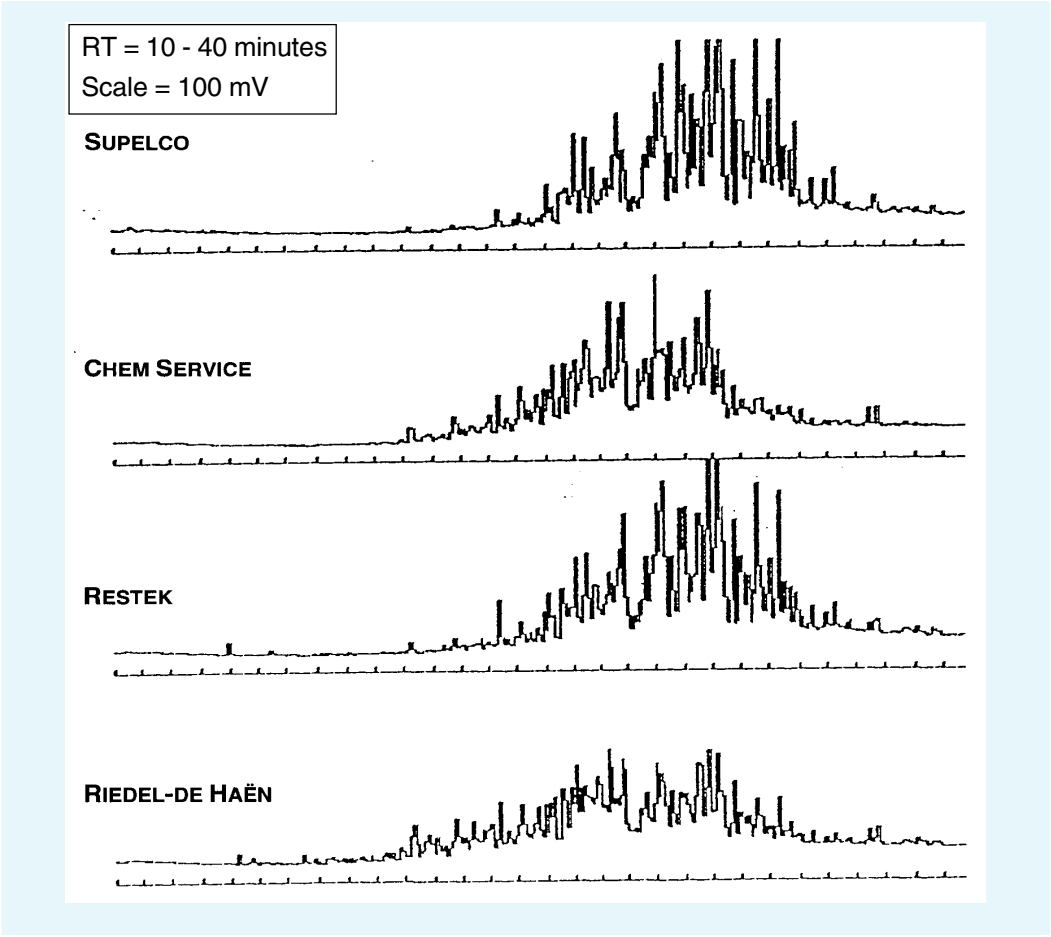

Figure 6. GC/ECD chromatograms of toxaphene standards

Since the majority of soil samples being analysed for toxaphene originated from a windrow compost technology that uses organic amendments, gel permeation chromatography (GPC) clean-up was also employed during method optimisation. GPC is a size exclusion procedure commonly used on soil/sediment samples for the elimination of lipids, polymers, copolymers, proteins, natural resins, cellular components, viruses, steroids and dispersed high-molecular weight components in sample extracts. In those soil samples where GPC clean-up was used, lower analytical detection limits were achieved.

Based on the optimisation data, accurate quantitation of technical toxaphene by Method 8081A would be possible at different analytical laboratories by standardising (a) sample preparation, (b) sample extraction procedures, (c) reference standard, (d) defining clean-up procedures and (e) selecting peaks from the later retention time window of the toxaphene standard (back-half) where there are fewer interference from matrix and co-contaminants effects. Table 2 provides data from two analytical laboratories where toxaphene was quantified using a standardised procedure.

Table 2. Toxaphene quantitation using a standardised EPA 8081A procedure

Analytical Lab	Toxaphene (ppm) T = 0	Toxaphene (ppm) T = 35 wk	% Degraded
C	212	4.6	98
F	212	20	91

Samples from the same time points as in Table 2 were sent to the USEPA Region IV laboratory in Athens, Georgia for toxaphene analysis using a new GC/ECD congener method being developed (Revells, 1999). A mixture of 22 purified and characterised congeners were used as standards to quantitate toxaphene in soil samples and can be applied to "weathered" samples. The results estimated a toxaphene value of 130 ppm for the time zero sample and a toxaphene value of < 8 ppm for the week 35 sample. Toxaphene levels determined by the congener method support the results presented in Table 2 using the standardised GC/ECD method. The 22 toxaphene congener method being developed by the EPA is an improved procedure for toxaphene quantitation since it is less subjective and quantifies toxaphene based on defined component peaks. Presently, this is not an official method; the congener standards are expensive and it is not a routine analytical procedure used to quantify toxaphene. Since the standardised GC/ECD method produces similar results and is cost-effective, this method was recommended for toxaphene analysis in soil samples for the 1,000 yd^3 field demonstration and the full-scale operation.

Full-scale operation

Based on the earlier analytical results, the analytical lab which gave the most consistent results, and who employed a standard that closely mimicked the toxaphene profile found in the contaminated soil, was used as a third-party contract laboratory. As with the demonstration study, excellent results were obtained; a comparison is provided in Figure 7.

Even though there were a number of differences between the demonstration study and the full-scale operation, including source of soil, concentration of contaminants, methods employed to mix and the amount and type of amendments used, there was very good agreement between the results.

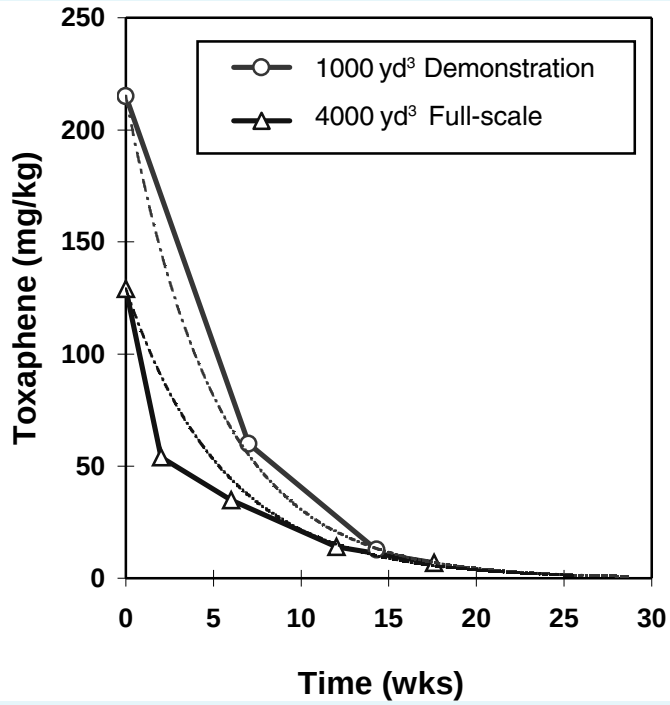

Figure 7. A comparison of the demonstration study and the full-scale operation data for the degradation of toxaphene

Conclusions

The 6-week Tampa soil microcosms were predictive of the toxaphene treatment observed for the 1,000 yd^3 windrow, and the full-scale operation. The full-scale operation also performed, as predicted, from the demonstration study.

Based on GC/ECD data using a standardised EPA Method 8081A, the 1,000 yd^3 windrow demonstrated greater than 90% removal of toxaphene from soil after treatment with the Xenorem™ technology. In the case of the full-scale operation, 95% was achieved after 17 weeks; this is expected to improve by the end of the operational period (a total of 24 weeks) to less than 2.76 ppm, which is the target end-point. This demonstrated that the process could remediate

soil to acceptable levels. However, the accurate quantitation of toxaphene in bioremediation samples can be problematic and requires controlled analytical methodology.

Toxaphene produces a complex GC/ECD chromatogram and soil samples taken from contaminated sites or active bioremediation processes have added analytical complications. As toxaphene is weathered and degraded, the standard toxaphene profile changes as the higher chlorinated congeners are degraded to lower chlorinated congeners. Furthermore, the presence of chlorinated co-contaminants and the addition of organic amendment add to quantitation difficulties. Variation in data between contract analytical laboratories can be controlled and accurate quantitation of technical grade toxaphene can be achieved.

Using a step-wise approach, from laboratory to field demonstration to full-scale operation, it has been successfully demonstrated that toxaphene can be readily biodegraded using the Xenorem™ technology.

Note

This paper covers information that was presented at an earlier Battelle Conference in 2000, plus new information since that time. The photographs have never been published, but most of the graphs have been shown and placed in the conference proceedings; in some cases they have been updated.

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