

This document was prepared in conjunction with work accomplished under Contract No. DE-AC09-96SR18500 with the U. S. Department of Energy.

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

This report has been reproduced directly from the best available copy.

Available for sale to the public, in paper, from: U.S. Department of Commerce, National Technical Information Service, 5285 Port Royal Road, Springfield, VA 22161,
phone: (800) 553-6847,
fax: (703) 605-6900
email: orders@ntis.fedworld.gov
online ordering: <http://www.ntis.gov/help/index.asp>

Available electronically at <http://www.osti.gov/bridge>
Available for a processing fee to U.S. Department of Energy and its contractors, in paper, from: U.S. Department of Energy, Office of Scientific and Technical Information, P.O. Box 62, Oak Ridge, TN 37831-0062,
phone: (865)576-8401,
fax: (865)576-5728
email: reports@adonis.osti.gov

**THE USE OF ENHANCED BIOREMEDIATION AT THE SAVANNAH RIVER
SITE TO REMEDIATE PESTICIDES AND PCBs.**

ABSTRACT

Enhanced bioremediation is quickly developing into an economical and viable technology for the remediation of contaminated soils. Until recently, chlorinated organic compounds have proven difficult to bioremediate. Environmentally recalcitrant compounds, such as polychlorinated biphenyls (PCBs) and persistent organic pesticides (POPs) such as dichlorodiphenyl trichloroethane (DDT), have shown to be especially arduous to bioremediate. Recent advances in field-scale bioremediation applications have indicated that biodegradation of these compounds may be possible. Engineers and scientists at the Savannah River Site (SRS), a major DOE installation near Aiken, SC, are using enhanced bioremediation to remediate soils contaminated with pesticides (DDT and its metabolites, heptachlor epoxide, dieldrin, and endrin) and PCBs. This article reviews the ongoing remediation occurring at the Chemicals, Metals, and Pesticides (CMP) Pits using windrow turners to facilitate microbial degradation of certain pesticides and PCBs.

BACKGROUND

The Savannah River Site (SRS) is a 310-square-mile facility owned by the United States Department of Energy (USDOE) near Aiken, South Carolina (Exhibit 1). The SRS has operated since 1950 with the mission to produce nuclear materials for national defense, medical research, and space exploration. Over the last 50 years, five production nuclear reactors have been built and operated. Large amounts of solid and liquid wastes were generated in the course of construction and operation of the reactors and associated fuel fabrication, processing, and waste handling operations. Up until 1970, most of this waste was burned, buried, or dumped in “rubble pits” near the reactor areas or other major facilities.

The Chemicals, Metals, and Pesticides (CMP) Pits are located in the central portion of the Savannah River Site (SRS) (Exhibit 1). The waste unit consists of seven unlined pits that

occupy the top of a knoll at an elevation of 310 ft above mean sea level. The pits were constructed in 1971 to dispose of solvents, pesticides, and lighting ballast components; it received waste until 1979. Subsequent monitoring detected solvents in the groundwater. In 1984, the contents of the pits were excavated, the pits were then back-filled, and an infiltration cover was installed. During excavation of the drums, an area to the west of the pits was used for material staging. This area, which later became known as the ballast area, contains surface soils that are contaminated with low levels of pesticides and polychlorinated biphenyls (PCBs). A maintenance action was conducted in 1996 to minimize erosion by placing six inches of soil over the ballast area, thus improving the perimeter drainage and erosion control. Remediation of the residual subsurface solvent contamination in the vadose zone beneath the pits began in 2000 with the deployment of a soil vapor extraction (SVE) system.

Surface soils in the ballast area are contaminated with pesticides and PCBs that exceed risk-based remediation goals (RG) or clean up levels. The majority of the contamination is confined to the top two feet of soil with a limited amount detected down to 5 ft below land surface. The soil consists of hardpan sandy clay with cobbles, and is lacking organic materials and most normal soil nutrients. Characterization of the site indicates that the soils are only sparsely populated with natural microbial concentrations and are not suitable for bioremediation without substantial amendment additions.

TECHNOLOGY DESCRIPTION

Initial project cost estimates indicated that offsite disposition of the ballast area soils to a permitted facility would be prohibitively expensive. In addition, a subsequent investigation revealed the sporadic presence of 2,4,5-trichlorophenoxypropionic acid (Silvex), which at one time was sold commercially as a herbicide. Silvex is a listed Resource Conservation and Recovery Act (RCRA) waste (code FO27) and has restrictions for off-site disposal, thus severely limiting disposal options for the ballast area soils. Some degree of success in degrading chlorinated organic compounds,

including pesticides, have been achieved commercially with in-situ bioremediation. Deploying an on-site remediation technology at the ballast area would be a more practical and cost-effective solution, provided the technology could be improved upon to degrade PCBs and Silvex to acceptable levels. Due to these factors, a treatability study was performed to determine if enhanced bioremediation would be a viable alternative in remediation the ballast area soils.

Therefore, the objectives for the treatability study of enhanced bioremediation were to 1) reduce contaminant concentrations to levels below the RGs that were established with the regulators for the contaminants of concern (COCs); 2) determine if bioremediation could achieve the RGs within an acceptable time frame; 3) identify the most effective combination of soil amendments and operating conditions that would achieve remediation of the ballast area and also determine any associated factors that might affect the process; and 4) determine the cost of the technology.

Up until recently, one of the limitations with large-scale bioremediation of soils has been the difficulty of achieving adequate homogenization of the correct balance of amendments into the soils to encourage the appropriate microbial reactions to occur. To overcome this limitation, SRS employed a windrow turner known as the Microenfractionator[®] to mechanically improve the effectiveness of homogenizing large quantities of soil with organic composting materials and amendments. The organic materials and amendments encourage the proliferation of microbial communities capable of degrading chlorinated organic compounds.

The Microenfractionator[®] developed by H&H Eco Systems Inc., is designed for bioremediation of petroleum contaminated soils and is a modification of commercial and municipal composting operations. It is manufactured with a counter-rotating drum supporting a set of fan-knife blades. The drum is powered hydraulically by a diesel engine and is driven through the soil pile by self-propelled, four-wheel drive power. The fan-knife blade design causes the soil particles to be thrown sideways into each other and

against the stainless steel lining of the Microfractionation chamber at high velocities. This physical action causes the soil particles to fracture into microscopic sizes, exposing more contaminant surface area for treatment.

Although soil particles are thrown aggressively around in the chamber, little potential for fugitive dust to escape exists. The windrow turner enhances the bioremediation process and suppresses fugitive dust in four ways: 1) water is added to the soil to maintain the correct moisture content in the windrows; 2) the physical blending action breaks the soil particles into smaller pieces, thus exposing fresh surfaces and the interior of the previously larger particle; 3) the rubber shields contain dust and airborne particles to the area under the chamber; and 4) the windrows are covered between mixing cycles allowing the retention of moisture and heat from the biochemical reactions.

The windrows are constructed from contaminated soil, organic/agricultural by-products, chemical nutrients, soil amendments, and water. The windrows are trapezoidal in cross-section with the following dimensions: the base is approximately 16 ft wide, the top of the windrows are approximately 5 ft wide, and the height is approximately 5 ft. The windrows vary in length, but are generally longer than 100 ft. The width and height dimensions for the windrows are based on the geometry of the windrow turner. The length of the windrows is based on the available flat test area within the boundaries of the CMP Pits.

Primary Contaminants

Many pesticides and PCBs are complex chlorinated compounds derived from the chemical benzene. Pesticides, particularly insecticides (such as DDT) and herbicides are an integral part of modern agricultural production (Manahan 1994). Due to DDT's ability to control mosquitoes and malarial infection, an exponential increase in the use and production of and use of pesticides became a worldwide phenomenon after World War II. While the public health and economic benefits of synthetic pesticide use of the past 50 years are indisputable, these benefits have not been without costs (Wexler 1998).

Widespread environmental contamination by DDT and other organochlorine pesticides, and their associated deleterious effects on some members of the foodweb heralded the end of an era for their extensive use.

Generally, persistent organic pollutants (POPs), such as DDT and its metabolites, are considered recalcitrant to biological degradation. However, under certain conditions, chlorine atoms on the diphenylethane structure are capable of replacement with hydrogen atoms or hydroxyl groups by microbial action. If the biological reactions are allowed to proceed for a certain time period, eventually the double benzene ring structure can be cleaved, producing a metabolite of the parent compound or some other similar organic compound.

DDT and its metabolites are highly lipophilic and bind strongly to soil particles. Due to their hydrophobic nature, DDT, DDE, and DDD have a tendency to also accumulate in plant tissues and fatty tissues of fish, birds, and mammals (including humans). They have a low acute toxicity to mammals, although there is some evidence that they might be carcinogenic (Manahan 1994).

Other organochlorine pesticides, including dieldrin, endrin, and heptachlor, are structurally similar, are all now banned for application in the United States, and share common characteristics of high persistence and suspicions of potential carcinogenicity (Manahan 1994).

PCBs are considered to be very recalcitrant in the environment. A PCB can contain 1 to 10 chlorine atoms in various positions around the biphenyl rings. With all of the possible combinations of chlorine arrangements on the biphenyl structure, 209 different PCB compounds, or congeners, are likely. The high molecular symmetry and high bond strength between the chlorine and carbon atoms gives PCBs the property of high chemical stability. This property led to widespread industrial application, including coolant-insulation fluids in transformers and capacitors, plasticizers, additives to some

epoxy paints, and lighting ballasts. However, the stability of PCBs is also responsible for their bioaccumulation in the environment and their eventual ban in 1977.

Studies have identified that microbial processes are capable of biodegrading PCBs through aerobic oxidative processes and anaerobic reductive processes. The aerobic dechlorination occurs on the lower chlorinated congeners. Anaerobic dechlorination degrades the highly chlorinated congeners to lightly chlorinated congeners. Aerobic transformation of many congeners has been demonstrated in culture, but evidence for effectiveness in soil is lacking (Focht 1995). In contrast, reductive dehalogenation of Aroclors in incubated sediment has been considerable (Tiedje et al. 1993).

Although highly resistant to biological attack, laboratory research has indicated that limited microbial degradation of PCBs is possible under very specific conditions (Michel et al. 2001). Laboratory evidence suggests that the PCB congeners with 4 or more chlorine atoms can only be degraded under highly anaerobic conditions at very low redox potentials, which must be sustained for protracted periods. These are conditions that are very difficult to replicate in the field. Congeners with 3 or fewer chlorine atoms are believed to be more easily degraded under aerobic conditions, which must be maintained over many months, and the limited number of field trials that have been implemented under this scenario, have met with some degree of success (Michel et al. 2001).

Because of the complexity in measuring PCB degradation in the field, it was decided to take a two-pronged approach to verification for the treatability study (TS) results. Ongoing soil samples would be analyzed for total Aroclor concentrations by a commercial laboratory using EPA Standard Method 8082. Additional verification would be obtained by a supplementary analysis of the congener distribution in samples taken at the beginning and end of the TS. Support for this aspect of the TS has been provided by the Department of Environmental Engineering and Science at Clemson University. Clemson has conducted research over a number of years into the degradation of PCBs in the sediments found in Lake Hartwell, South Carolina, and has developed a substantial

capability in PCB remediation and analytical techniques for complex chlorinated organic compounds.

Windrow soil samples were taken at the start and at the end of the aerobic period and also at the end of the anaerobic period during Phase 1, and sent to Clemson for investigation. This was repeated with sampling at the beginning and end of Phase 2. Clemson adopted a dual approach to providing independent verification of biological degradation of the pesticides and PCBs. In addition to the PCB congener speciation, microcosm experiments were performed on the windrow soils under ideal anaerobic and aerobic conditions to determine if the microbes that are known to dechlorinate PCBs were in fact present, and to confirm that PCB dechlorination was feasible under ideal conditions.

Site Preparation

Windrows were constructed with approximately 600 yds³ of the ballast area soils at a location adjacent to the CMP Pits ballast area, on a sand pad base, during early October 2001 (Exhibit 1). The treatment area was constructed on a lower level just to the north of the actual pits but still within the waste unit. A berm was constructed around the perimeter of the treatment area out of railroad ties for erosion control. An 80-mil thick polyethylene sheet was then placed over the ground surface and overlapped the railroad ties to form a containment zone. A 6-inch deep layer of sand was then placed on top of the polyethylene to act as a base for the machine. The windrows were constructed on top of the sand by first placing horse manure in four rows, in a layer approximately 1 ft thick by 15 ft wide for the length of the windrows (Exhibit 2). The contaminated soil (including debris less than 3 inches in diameter) was deposited over the manure layer and constitutes the remainder of the windrow. The ballast area soil was then placed on top of the manure by dumping the dump trucks. The total volume of horse manure and stable sweepings amounted to approximately 240 yds³ or about 40% of the volume of soil. A proprietary mixture of soil micronutrients developed by H&H Eco Systems, Inc. was placed on top of the windrows. Water was added from the machine during windrow

mixing. The last turning event was completed in May 2002 after 6 months of operation, which effectively terminated the process.

Throughout the process, the soil samples were examined for three groups of microbial populations: culturable heterotrophic aerobes, culturable anaerobes, and culturable pseudomonades (Appendices B, C, and D). Microbial plate counts in the ballast area soils were typically low in the unblended soils. Initial plate counts were in the ranges of 10^6 colony forming units per gram dry weight (CFU/gdw) for heterotrophs, 10^3 CFU/gdw for anaerobes, and 10^4 CFU/gdw for pseudomonads. The microbial counts increased by several orders of magnitude by the end of the TS (10^8 CFU/gdw, 10^7 CFU/gdw, and 10^5 CFU/gdw, respectively).

Phase 1 of the Treatability Study

To encourage proliferation of the widest range of microbe and fungi species, the composting process was controlled to operate under mesophilic conditions, thus increasing the likelihood that chlorinated organic compound destroying microbe species would be present. The microbial activity generates sufficient heat to significantly raise windrow temperatures, and the population of mesophilic bacteria is most numerous below 105 °F. Above 125 °F the mesophilic microbes begin to die off and thermophilic microbe populations begin to take over. Throughout the process, the soil samples were examined for three groups of microbial populations: culturable heterotrophic aerobes, culturable anaerobes, and culturable pseudomonades.

Initial COC sampling and analysis of the windrows was conducted at eight discrete locations along each windrow both before and after the first pass of the windrow turner. This sampling schedule was conducted to obtain good baseline information on the distribution of contaminants in the four windrows and to establish the effectiveness of the windrow turner in material homogenization. Each sample was taken by coring the windrows to a depth of about 2 feet with a plastic tube and then placing several smaller samples from along the soil core into a plastic bag. Discrete samples were taken on

weeks 0, 1, 3, 6, 7, 14, 19, and 28; while composite samples were taken on weeks 15, 19, 21, 24, 25, 26, and 27. All the discrete samples, including the final regulatory compliance analyses, were analyzed by utilizing EPA Method 3540 for extraction of semi-volatiles from soils, Method 8081A for pesticide chromatographic analysis and Method 8082 for PCB chromatographic analysis.

In addition, windrow temperatures were monitored to follow the level of microbial activity throughout the winter months. In February, oxygen content measurements in the windrows began in conjunction with the temperature measurements.

Baseline windrow soil moisture levels started out at 13%. Water was added progressively throughout the anaerobic period to levels of 18%. A moisture level of 18% is close to the saturation level for the ballast area soils. Soil pH levels were maintained in the neutral 5 to 8 range, with the occasional addition of lime to neutralize the acids generated by microbial action. Occasional additions of fertilizer were made to maintain an appropriate carbon:nitrogen ratio. Periodically, H&H Ecosystems, Inc. proprietary micronutrient amendments were added to maintain the correct concentrations of standard agricultural elements i.e. potassium, phosphorous, calcium, magnesium, cobalt, copper, iron, boron, molybdenum, sulfur and zinc.

By the end of January 2002, although a general decrease in all contaminant concentrations had been observed under aerobic conditions, the rate of decrease appeared to be leveling off, and would not reach the remedial goals within the contract time frame (Exhibit 3). To accelerate the degradation process, the strategy for the enhanced bioremediation was modified from aerobic conditions, which had been prevalent since start up, to cyclic anaerobic conditions. To promote the necessary anaerobic conditions, molasses and small amounts of manure were added. Molasses, a carbohydrate source that is rapidly consumed along with residual oxygen by aerobic microbes, thus causing a decline in the oxygen content of the windrows which promotes activity within the dormant anaerobic microbial community.

Significant anaerobic microbial activity generally requires a 1 to 2 weeks incubation time to become really effective and anaerobic conditions must be sustained within the windrows for at least this period and longer. However, from the beginning of February, the general level of microbial activity in the windrows had begun to decline indicating that most of the organic material had been consumed. This was indicated by a gradual drop in windrow temperatures from 90 - 100 °F range to the 75 - 85 °F range throughout February/March.

During the February/March time frame, measurements of the oxygen content within the windrows were taken in order to gauge the effectiveness of the anaerobic process. In general terms, the transition from aerobic and anaerobic conditions, takes place at around 5% oxygen. Typically within 24 hours of turning the windrows after the molasses additions, the oxygen content would drop sharply to the 1-8% range coupled with a corresponding temperature rise of 5-10 °F. This trend is indicative of a rapid burst of activity within the anaerobic microbial community. However within the following 2-3 days, the oxygen content would increase to the 12-18% range, and the windrow temperatures would decrease, These conditions are indicative of a rapid return to aerobic conditions. Furthermore, visual inspections based on the windrow soils characteristics indicated that the organic material had been consumed. Thus, insufficient organic material remained in the windrows to sustain anaerobic microbial activity for more than 2-3 days.

A more intensive effort to sustain anaerobic conditions began in April in three out of the four windrows. Contaminant concentrations in windrow 3 were already below the RGs, therefore no further work was conducted with this windrow. To determine if repeated windrow turnings were more effective after molasses additions versus non-turning, two of the windrows were turned twice per week throughout April with molasses additions at each turning event, while the remaining windrow was turned with its molasses additions once, and then left undisturbed. Fresh manure, consisting of 50% horse stable sweepings and 50% cow manure (to increase the nitrogen content in the compost mixture), was

added to the two active windrows at two intervals, Oxygen content and temperature were measure daily. Weekly composite sampling, pH, and moisture content measurements were conducted, as well.

Following the initial windrow turning in April, the two windrows rapidly became anaerobic, with a corresponding evolution of reducing gases such as methane, ammonia, and hydrogen sulfide. The reducing gas concentrations were measured using Draeger tubes to measure gas concentrations. These concentrations were therefore only indicative of the types of biochemical reactions that were occurring, and were not quantified to formulate a mass balance.

Phase 2 of the Treatability Study

The objective of Phase 2 was to redesign the process in order to achieve faster biodegradation rates for the contaminants. Based on the results obtained from Phase 1, the bioremediation process was modified as discussed below.

The windrows were turned at least twice per week, during both aerobic and anaerobic cycles, to improve contaminant/microbe/nutrient interaction. Anaerobic conditions were difficult to sustain for a prolonged period of time without multiple turnings possibly due to accumulation of by-products (i.e. alcohols) within the windrows, which effectively hinders the bioremediation processes. In order to overcome this buildup, windrow operations were cycled from anaerobic to aerobic conditions depending on the oxygen and temperature measurements for the windrows. Aerobic and anaerobic parts of the cycle were each expected to last several weeks, with the caveat that multiple cycles might be necessary. Furthermore, the increase in mixing allowed the windrows to achieve anaerobic conditions. Although this statement seems contradictory, the additional mixing and amendments provides the aerobic microbes with abundant food sources causing an increase in aerobic microbial activity. This increase in activity forces the piles anaerobic due to the consumption of oxygen by the aerobic microbes.

In addition, increased and continuous monitoring of the principal parameters was

completed in order to make the necessary adjustments for optimum windrow conditions. Measurements included temperature and oxygen (daily), pH and moisture (weekly), COC concentrations (weekly under anaerobic conditions), PCB congener analysis (start and end of phase 2), and soil nutrients (monthly).

Similar to Phase 1, 600 yds³ of contaminated soil was used for Phase 2. Phase 2 commenced August 2002 with the first mixing event. Following the initial mixing, molasses and additional manure were mixed into the windrows. Operations continued in the anaerobic mode with twice-weekly turnings of the windrows and molasses additions. Cottonseed hulls and manure were added to supplement the organic material content. Additional inorganic soil amendments were added in October to balance the pH, nutrient and nitrogen depletion.

During mid-October, windrow temperatures began to decline signifying the end of the composting process (Exhibit 4). Minor manure additions were mixed into the windrows in an attempt to continue the bioremediation process.

PHASE 1 RESULTS

Mean DDT concentrations decreased by 95% in windrow (WR)1 over the 28-week duration of the TS. Mean DDT concentrations in WR2, WR3, and WR4 could not be calculated due to questionable data associated with the initial (WR4) and final (WR2 and WR3) data, therefore, specific results cannot be discussed. However, over the 28-week period, the concentrations of DDT generally decreased. A significant portion of the DDT reduction occurred during the period of anaerobic operation in April in WR1 and WR2. During the intensive anaerobic period, oxygen and temperature measurements were taken twice daily. Temperatures during this period averaged 100 °F with a standard deviation of 8 °F. During the third week, windrow temperatures peaked at an average of 106 °F, with a standard deviation of 8 °F. The twice weekly turning of windrows 1 and 2 kept their window oxygen contents in the <5% range and many readings were <1%. Additional water elevated moisture levels to 25%. DDT concentrations decreased rapidly

until the third and fourth weeks, when the biochemical reactions appeared to slow, ammonia production decreased and the rate of DDT reduction slowed dramatically. Several reasons have been postulated for this apparent process slowdown namely, formulation of alcohols and phenols generated from the fermentation process which would poison the anaerobic microbes, poisoning of the anaerobic microbes by the ammonia and also the rapid depletion of nitrogen from the compost process by the ammonia generation. Activity in WR4, which had minimal amounts of DDT throughout Phase 1 (400 ug/kg) and was not mixed during the aggressive period, was minimally affected by the anaerobic period. These results imply that DDT concentrations were not significantly decreased. Mean DDE concentrations decreased by 76% in WR1 and WR2, 60% in WR3, but slightly increased in WR4. The DDD results indicate that levels remained above the RG. Concentrations of DDD increased over time in WR1 and WR2, especially during the April anaerobic period. These results suggest that as the microbes degrade DDT into its anaerobic daughter product, an increase in DDD concentrations is occurring. The increase in DDD levels was not in direct proportion to the decrease in DDT concentrations. In addition, concentrations of chlorodiphenylchloroethylene (DDMU), a degradation product of DDD, were detected. The presence of DDMU suggests that the bioremediation continued the biodegradation process past the daughter product of DDT.

Reductions in mean dieldrin concentrations of 73%, 62%, and 89% were achieved for WR1, WR2, and WR3, respectively. Initial concentrations of dieldrin in WR4 slightly increased throughout Phase 1. Final concentrations of dieldrin in all four windrows, including WR4, were below the RG.

Reductions in mean endrin concentrations of 76%, 88%, and 72% were achieved for WR1, WR2, and WR3, respectively. Concentrations of endrin in WR4 were non-detects throughout Phase 1. Final concentrations of endrin in WR2, WR3, and WR4 were below the RG (60 ug/kg) at the end of Phase 1. The concentration in WR1 was only slightly higher than the RG at the end of Phase 1 (70 ug/kg).

Reductions in mean heptachlor epoxide concentrations of 93% and 42% were achieved for WR2, and WR4, respectively. Concentrations of heptachlor epoxide increased in WR1 (25 to 67 ug/kg) and WR3 (4 to 11 ug/kg) throughout Phase 1. The only Phase 1 windrow not to meet the RG at the end of the 28-week period was WR1.

Based on comparisons between initial and final concentrations, slight reductions in the mean concentrations of PCBs occurred in all four windrows (Table 6). WR2, WR3, and WR4 were below the RG (1000 ug/kg) at the end of Phase 1 with final concentrations of 996, 736, and 290 ug/kg, respectively. The final mean WR1 concentration (1605 ug/kg) was somewhat below the initial concentration of 1614 ug/kg. The mechanism for degradation of PCBs is more complex and less easily understood than the chlorinated pesticides. Based on visual observations, PCBs appeared to exist in the form of hard pea sized 'pellets' in the ballast area soils. During the first 5-7 weeks of Phase 1, it is possible that these 'pellets' were fractured in the aggressive mixing environment of the windrow turner allowing the PCBs to be more bioavailable for sampling and remediation. Furthermore during the first few turning events, a number of lighting ballasts and electrical capacitor cans were ejected from the windrows via the rotating action of the fan blades. Enough of the electrical components from Phase 1 were collected to nearly fill a 55-gallon drum. This rationale provides one explanation for the initial rise in PCB concentrations. The PCB congener analysis for samples taken at 4, 22 and 28 weeks indicate that the average number of chlorine atoms per biphenyl molecule remained unchanged in the range of 3.2 to 3.8. These results suggest that anaerobic dechlorination for Phase 1 was minimal, perhaps due to the low redox conditions, short duration of the anaerobic environment, and/or an absence/latency of the appropriate dechlorinating microorganisms in the windrows. The distribution of di-, tri-, tetra-, penta-, hexa-, and heptachlorobiphenyls in Phase 1 soil samples suggests a decrease in the percentage of dichlorobiphenyls relative to the other higher chlorinated congeners. In the December 2001 soil samples, dichlorobiphenyls comprised a 10-52 mole percent of the total congener distribution; whereas, the April 2002 soil samples consisted of 15-19 mole

percent of dichlorobiphenyls. It is possible that the apparent decrease in the mole percentage of dichlorobiphenyls is due to oxidative biodegradation, presumably under aerobic conditions (which predominated during operation of the Phase 1 windrows). Approximately 5-29 mole percent of the dichlorobiphenyls in the December 2001 samples consisted of a non-chlorinated ring. Under aerobic conditions, these non-chlorinated rings are typically hydroxylated causing the non-chlorinated ring to break (dichlorobenzoates). Therefore the potential for aerobic oxidation does exist. Dichlorobenzoates are less hydrophobic than PCBs and are amenable to aerobic oxidation, making them less likely to persist in the windrows.

Silvex, which is not a COC for the CMP Pits OU (WSRC 2003), was considered for this TS due to its RCRA listing (F027 waste). Results from Phase 1 data indicate non-detects for Silvex within weeks of beginning Phase 1. These results suggest that Silvex is bioremediated through aerobic processes

PHASE 2 RESULTS

Reductions in mean DDT concentrations were 96%, 83%, 96%, and 90% for windrows 1, 2 and 4N and 4S, respectively, over 12-week period of operation. These Phase 2 results, when compared to the Phase 1 results (95% reduction in WR1), validates the theory that the bioremediation can be accelerated by frequent windrow turning. The Phase 2 results for DDT concentrations are below the RG of 1620 ug/kg. The mean concentrations of DDT for all of the windrows are below the RG. The degradation of DDT that occurred during weeks 2-6, produced a corresponding increase in concentrations of DDE in all four windrows. Mean concentrations of DDE increased slightly in WR1 and WR2, and decreased slightly in WR4N & S between the initial and final concentrations. However, the mean concentrations do not portray the increases and decreases in concentrations of DDE as DDT was degraded. In addition, DDE concentrations are below the RG of 554 ug/kg in all four windrows. Likewise for DDD, the degradation of DDT that occurred during weeks 2 through 6, produced a corresponding increase in concentrations of DDD

in all four windrows. Mean concentrations of DDD increased in all four windrows between the initial and final concentrations. Concentrations in WR1 were 37 to 266 ug/kg; WR2 were 67 to 468 ug/kg; WR4N were 95 to 149 ug/kg; and WR4S were 39 to 94 ug/kg. Despite the increases in DDD concentrations at the end of Phase 2, final concentrations were below the RG of 287 ug/kg, except in WR2. It is conjectured that WR2 concentrations would also have decreased had Phase 2 operated for a longer time period.

Overall mean concentrations of dieldrin increased very slightly in WR1 and WR2; and decreased slightly in WR4N and S throughout Phase 2. However, a more sporadic degradation nature seems to correlate with mixing and amendment additions. Despite this erratic nature, windrow concentrations for dieldrin are at or below the RG of 68.4 ug/kg.

Mean concentrations of endrin decreased in all four windrow to below detection limits. In addition, endrin concentrations were non-detects before the end of Phase 2. The RG for endrin is 40 ug/kg.

A situation similar to that of endrin exists for heptachlor epoxide. Mean concentrations of heptachlor epoxide have degraded to levels at or below 1 ug/kg. The RG for heptachlor epoxide is 21 ug/kg.

Mean concentrations of total PCBs were below the RG (1000 ug/kg) in all four windrows. In addition, total PCB concentrations in the soil were at or below the RG. However, soil samples collected for congener analysis showed no significant difference in the average number of chlorine atoms per biphenyl molecule detected in samples taken at the beginning and end of Phase 2 for all windrows. Nonetheless, a change in the mole percent and weight distribution of specific congeners throughout Phase 2 was detected. It appears that the average mole percentage of dichlorobiphenyls decreased which is indicative of some degree of aerobic biodegradation. In addition the mole percentage of penta-, hexa- and heptachlorobiphenyls decreased with a corresponding increase in the

mole percentage of tri- and tetrachlorobiphenyls, which is indicative of a degree of anaerobic activity. However the changes were relatively small and somewhat inconsistent between windrows.

Because Silvex results from Phase 1 showed successful degradation during the aerobic portion of Phase 1, Silvex was not analyzed for in Phase 2 and will not be discussed as part of Phase 2.

CONCLUSIONS

With the discrete samples for individual windrows, COC concentrations were reduced to less than the new RG levels in nearly all cases (Exhibit 5). In a few discrete sample cases, the COC levels did not quite achieve the RG levels, but would almost certainly get below RG levels with additional time.

Enhanced bioremediation based on horse manure, molasses, appropriate soil amendments and moisture is a process that can be duplicated to give reproducible results within an acceptable time frame.

Contract costs for Phase 1 were \$690,000 to remediate 600 yd³ of soil or \$1,150/yd³. Because of the increased efficiencies achieved in Phase 2, the same quantity of soil was remediated in three months instead of six for \$350,000 or \$585/ yd³. These unit costs are relatively high for enhanced bioremediation and are principally due to two factors. The quantities of soil involved in Phase 1 and Phase 2 are relatively low. Full-scale bioremediation is normally conducted on soil quantities much higher than deployed in this TS, which would reduce the unit cost. In addition, the largest individual component of the cost of this process is the rental or capitalization of the Microenfractionator[®] machine itself.

ACKNOWLEDGMENTS

SRS would like to thank Clemson University's Department of Environmental Engineering and Sciences (Dr. Cindy Lee and Dr. David Freedman) for their work on the

PCB congener analyses and microbial microcosm experiments. We would also like to thank H&H Ecosystems, Inc. for the use of their Microenfractionator[®] and proprietary soil amendments.

REFERENCES

Focht, D.D. 1995. "Strategies for the improvement of aerobic metabolism of polychlorinated biphenyls. *Current Opinion in Biotechnology*. 6:341-346.

Manahan 1994. *Environmental Chemistry* Lewis Publishers, CRC Press, Boca Raton, LA.

Michel, F., J. Quensen, C.A. Reddy. 2001. "Bioremediation of a PCB-Contaminated Soil Via Composting", *Compost Science and Utilization*, 4:274-284.

Tiedje, J.M, J.F Quensen, S.J. Chee, J.P. Schimel, and S.A. Boyd. 1993. "Microbial reductive dechlorination of PCBs. *Biodegradation*. 4:231-240.

Wexler, 1998. *Encyclopedia of Toxicology*. Academic Press, San Diego, CA.

Catherine M. Lewis is a geologist with the Soil and Groundwater Closure Projects at the Savannah River Site. She is a technical lead for environmental activities within the Reactors Team and has over 15 years of professional experience.

Amitava Ganguly is a Principal Engineer with the Soil and Groundwater Closure Projects at the Savannah River Site. He is a technical lead for environmental activities within the

Reactors Team and has more than 25 years of professional experience in Civil/Structural and Environmental Engineering.

Alvin G. Morrow is an Environmental Engineer with the Soil and Groundwater Closure Projects at the Savannah River Site. He is the Design Authority for environmental activities within the Reactors Team and has over 4 years of professional experience in environmental remediation.

Lisel R. Shoffner is a characterization engineer with the Soil and Groundwater Closure Projects at the Savannah River Site. She has over 3 years of professional experience in geologic characterization of waste units and groundwater monitoring of environmental activities within the Reactors Team.

Robert F. Blundy is a Senior Technical Advisor with the Soil and Groundwater Closure Projects at the Savannah River Site specializing in the introduction of innovative technologies into the Reactors Team environmental projects, and has over 25 years of professional experience.

Patrick F. Nakagawa is a nuclear engineer with the Soil and Groundwater Closure Projects at the Savannah River Site. He has over 8 years of professional experience in environmental remediation with the Reactors Team.

Sara T. Mundy is a chemical engineer with the Soil and Groundwater Closure Projects at the Savannah River Site. She is a project lead for environmental activities within the Reactors Team and has over 18 years of professional experience in environmental compliance and engineering.

Sadika M. Baladi is a senior engineer/toxicologist with the Soil and Groundwater Closure Projects at the Savannah River Site. She is involved with many projects associated with environmental activities within the Reactors Team and has over 5 years of professional experience in environmental risk assessment and remediation.

Larry Anderson is a Construction Engineer with Soil and Groundwater Closure Projects at the Savannah River Site. He is the Person-In-Charge of many remediation projects associated with environmental activities within the Reactors Team and has over 27 years of professional experience in construction and environmental remediation.

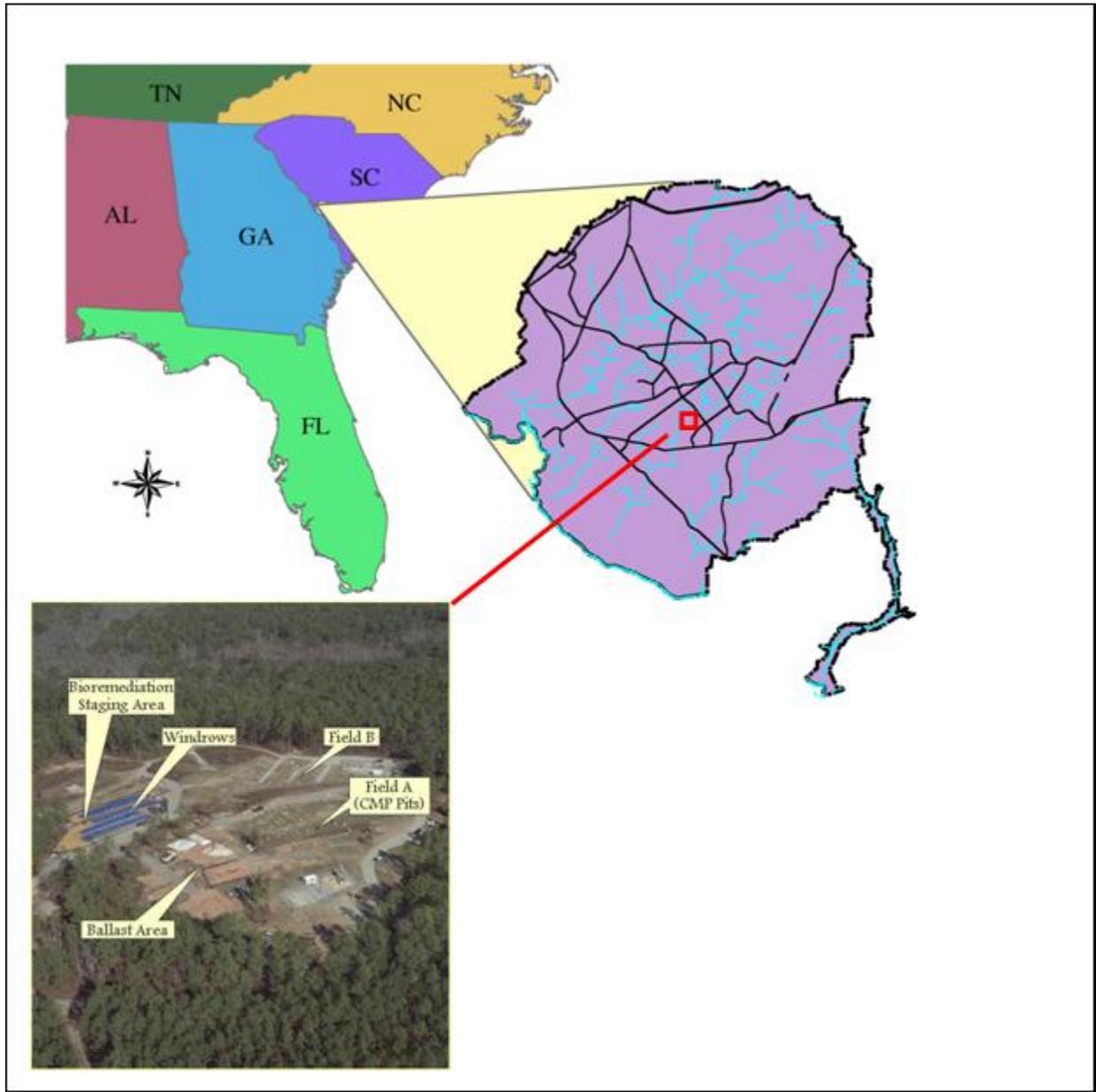


Exhibit 1. Location of CMP Pits at the SRS.



Exhibit 2. Windrows located on the treatment pad near the CMP Pits.

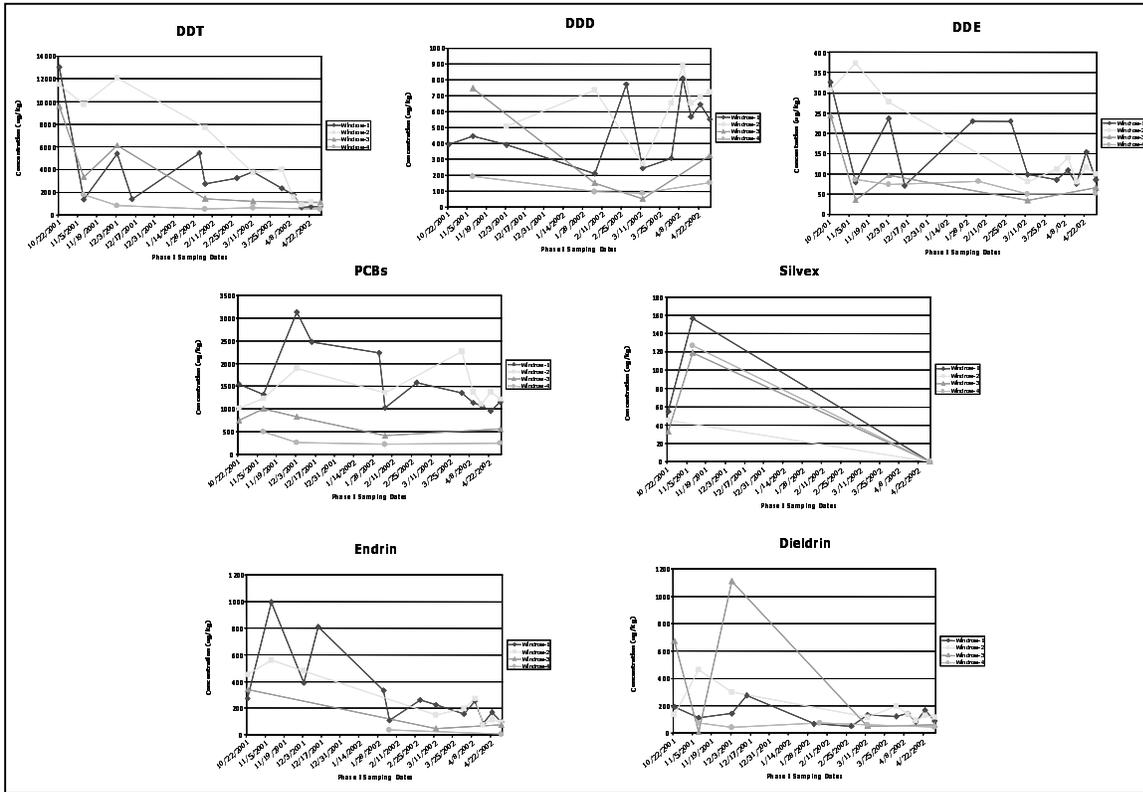


Exhibit 3. Phase 1 Sampling Results.

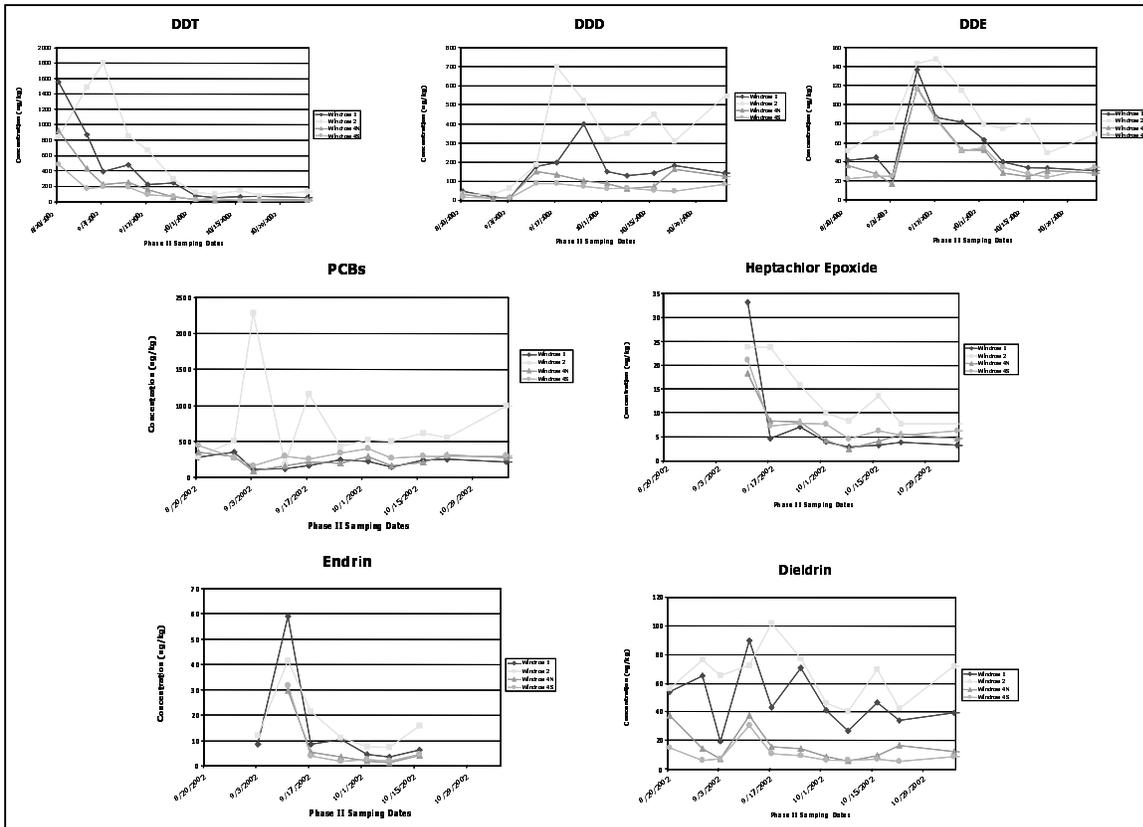


Exhibit 4. Phase 2 Sampling Results.

Exhibit 5. Summary of Overall Treatability Study Results

COC	Remedial Goals (ug/kg)	Mean Phase 1 results (ug/kg)	Mean Phase 2 results (ug/kg)	Type of COC
PCBs	1,000	857.6	384.3	ARAR
DDT	1,620	1330.8	78.3	Eco
DDD	287	559.8	223.3	Eco
DDE	554	84.6	47.3	Eco
Dieldrin	68.4	69.6	46.7	Eco
Endrin	40	63.8	8.7	Eco
Heptachlor Epoxide	21	10.0	7.0	HH

COC – Constituent of Concern

ARAR – Applicable or Relevant and Appropriate Requirements

Eco – Ecological

HH – Human Health