



## Project Summary

# Characterization and Laboratory Soil Treatability Studies for Creosote and Pentachlorophenol Sludges and Contaminated Soil

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The full report presents information from the first two phases of a three-phase study pertaining to on-site treatability potential of soils containing hazardous constituents from wood-treatment waste (EPA-K001).

Phase I studies involved: (1) developing a soil treatability database from the literature for creosote and pentachlorophenol wood-treating chemicals, and (2) obtaining baseline data on qualitative and quantitative distribution of wood-treating chemicals contained in samples of contaminated soils and sludges collected at eight wood treating sites located in the southeastern United States. Phase II studies involved developing soil transformation, soil transport, and toxicity information for selected wood treating solution constituents identified in these samples. Phase III studies currently under way involve comprehensive field evaluation of soil treatability of creosote and pentachlorophenol waste constituents at one of the eight sites studied in Phases I and II.

The full report contains:

1. A literature assessment of soil treatability potential for wood treating chemicals;
2. Sludge and soil characterization data for eight wood treating sites; and

3. Treatability information pertaining to degradation and toxicity of wood-treating chemicals in soils from four of the sites.

The literature assessment indicated that creosote and pentachlorophenol waste constituents may be treatable in soil. Each of the eight K001 sludges characterized contained the PAH class of semivolatile constituents; however, relative concentrations of individual PAH compounds varied among different sludges. PCP sludges contained pentachlorophenol, octachlorodibenzo-p-dioxin, and traces of hepta and hexa dioxins and the corresponding furans.

PAH's with two rings generally exhibited half lives less than ten days. Three ring PAH's generally exhibited longer half lives in most cases, but less than one hundred days. Four or five ring PAH's exhibited half lives of one hundred days or more; however, in specific cases, particular four or five ring PAH's exhibited half lives less than ten days. PCP half lives varied from twenty days to over a thousand days in different soils. PCP was transformed very slowly in soils with no prior long term exposure to PCP.

Low concentrations of OCDD apparently were transformed slowly

in three of the four soils tested. In the soil that had previous long-term exposure to PCP, OCDD exhibited a half life less than one hundred days even at the highest concentration tested. However, results were variable, and more information must be obtained before a definite conclusion can be made on OCDD transformation rates in soils.

Microorganism population counts of the type used in this study did not appear to be closely related to transformation rates.

*This Project Summary was developed by EPA's Robert S. Kerr Environmental Research Laboratory, Ada, OK, to announce key findings of the research project that is fully documented in a separate report of the same title (see Project Report ordering information at back).*

## Introduction

Treatment of waste containing undesirable organic constituents in a carefully designed and managed soil system is a potentially cost-effective, environmentally safe, low energy technology that has been used successfully for a wide variety of domestic and industrial wastes. Examples of industrial wastes for which soil systems have been used as a waste management alternative include those from the food processing, petroleum refining, organic chemical manufacturing, coke, textiles, and pulp and paper industries. However, there currently are few definitive data in the literature that quantify treatment rates in full-scale soil treatment systems.

This research project is directed toward collecting hazardous waste and soil samples from eight wood-preserving locations in the southeastern United States for use in evaluating and quantifying treatment potential for those types of waste in various soil types. A comprehensive assessment of literature available for two types of wood-preserving wastes, pentachlorophenol and creosote, was conducted to aid in making these evaluations.

This project involves three phases: Phase I - site selection and characterization studies for defining selected soil and sludge characteristics at eight wood-treating sites; Phase II - laboratory treatability studies for determining rates of microbiological degradation or other transformation processes, soil transport properties of creosote and pentachlorophenol waste contaminants, and toxicity of the water-

soluble fraction of waste-soil mixtures; and Phase III - a field evaluation study at one of the eight wood-treating sites. This report presents and discusses results from the characterization phase for each of the eight sites and from the laboratory treatability phase for four of the eight sites.

## Wood-Preserving Industry

Wood preserving in the United States is a hundred-year-old industry. Wood is treated under pressure in cylinders with one of four types of preservatives: (1) creosote, (2) pentachlorophenol in petroleum, (3) water solutions of copper, chromium, and arsenic (CCA), and (4) fire retardants.

The organic preservative most used is coal tar creosote, a by-product from the production of coke from coal. Creosote is a blend of the various coal tar distillates having specific physical characteristics that meet standards of the American Wood-Preservers' Association (AWPA). Both yield and chemical and physical properties of the various distillate fractions are influenced by: (1) the characteristics of the coal from which the tar originates, (2) the type of equipment used in the distillation process, and (3) the particular distillation process used. Creosote consists mostly of aromatic single to multiple ring compounds. Over 200 different components have been identified in creosote; however, it is generally agreed that creosote contains several thousand different compounds which could be identified with GC/MS. Most of these are present in very small amounts. Pentachlorophenol (PCP) dissolved in No. 2 fuel oil carrier is the second most common organic wood preservative. Technical grade PCP is about 85% to 90% pure PCP. The remaining materials in technical grade PCP are 2,3,4,6-tetrachlorophenol (4 to 8%), "other chlorophenols" (2 to 6%), and dioxins and furans (0.1%). Analyses of samples of technical grade PCP have revealed that the principal chlorodibenzodioxin and chlorodibenzofuran contaminants are those containing 6 to 8 chlorines. The highly toxic 2,3,7,8-tetrachlorodibenzo-p-dioxin (TCDD) has not been identified in any sample of PCP produced in the United States that has been analyzed to date.

Pure PCP is considered to be rather inert chemically. The chlorinated ring structure tends to increase stability, but the polar hydroxyl group tends to facilitate biological degradation. All monovalent alkali metal salts of PCP are

very soluble in water, but the proton (phenolic) form is virtually insoluble. Hence, transport of PCP in water related to the pH of the environment. Pentachlorophenol is moderately volatile; therefore, PCP can be lost from soils by volatilization.

## Wood-Preserving Wastes

There are several sources of contamination at wood-treating sites. During the treatment cycle, wastewater and traces of preservative in water produced from several sources, including: live steaming of the wood, vacuum drying or oil seasoning, vacuum condensate, steam and oil leaks around the system, cleanup, and contaminating rain water. Treatment of this plant wastewater produces sludges that are classified by EPA as K001, Hazardous Waste.

Prior to current environmental regulations pertaining to wastewater discharge, treated wastewater effluent generally went directly to surface drainage or a stream. Most wood-treating plants also had sumps or ponds to trap heavy oil residuals prior to wastewater treatment before discharge to a publicly-owned treating works.

Normal wood-treatment operations create additional waste for disposal. Treating tanks and cylinders have to be cleaned periodically to maintain quality standards. In the past these preservative sludges often were used as fuel, for road paving or were buried at the facility.

Soil contaminated with wood-treating chemicals is another source of environmental concern. Treated wood is withdrawn from the cylinder and moved by rail to storage areas. During transportation, the preservative may drip from the treated wood onto the soil along the track. Contaminated areas are common around storage, treating, and unloading tanks where minor preservative spills from broken pipes, bleeding of treated wood, etc., has occurred. These areas can be rather large, especially in older railroad and pole plants.

## Decomposition/Immobilization of Creosote and PCP in Soil

### Creosote

Major components of creosote are polycyclic aromatic hydrocarbons (PAH's) with trace amounts of phenols and azarenes. A wide range of soil organisms, including bacteria, fungi, cyanobacteria (blue-green algae), and eukaryotic algae, have been shown

have the enzymatic capacity to oxidize PAH's. Generally, rates of degradation for PAH compounds have been found to decrease as the molecular weight increases; rates of degradation have been found to be faster in soil than in water; and, overall rates of degradation have been reported as faster where there is an acclimated bacteria population.

Compounds, such as naphthalene, phenanthrene, and anthracene, that are relatively water soluble have been found to readily metabolize while compounds, such as chrysene and benzo(a)pyrene, that have a lower water solubility have been found to be more persistent. Some researchers have found that pyrene and fluoranthene, although more soluble than anthracene, are less appreciably metabolized by soil microorganisms. Other factors that may affect the persistence of PAH compounds are insufficient bacterial membrane permeability to the compounds, lack of enzyme specificity and lack of aerobic conditions.

Some PAH's with more than four rings are not known to be utilized as a sole carbon source but have been reported to be co-metabolized with other organic compounds. The co-metabolism process involves concurrent metabolism of a compound that a microorganism is unable to use as a sole source of energy along with metabolism of a carbon source capable of sustaining growth.

### **Pentachlorophenol**

A large number of studies on biodegradation of PCP in soil have been conducted. The route of decomposition involves dechlorination leading to a series of partial dechlorinated products, such as 2,3,5,6-tetrachlorophenol. The second step in the decomposition reaction involves an oxidation step to form substituted hydroquinones or catechols, such as 2,3,4,5-tetrachlorocatechol. The oxidation product then undergoes ring cleavage, ultimately forming CO<sub>2</sub> and an inorganic chloride ion.

Mobility, persistence, and fate of PCP in soils depend on physical and chemical characteristics of the soil as well as the prevailing microbial population. Adsorption of PCP depends primarily on the pH of the system. The more acid the soil, the more complete is the "apparent adsorption" of PCP. Organic matter content of soils is important to adsorption of PCP at all pH values. Soil containing humus always adsorbs more PCP than soil in which organic matter has been removed by treatment with hydrogen

peroxide. Adsorption of PCP by humus is more important when the concentration is low, but the inorganic fraction increases in importance at higher concentrations.

Persistence of PCP in soil depends on a number of environmental factors. For example, the sodium salt of PCP has been found to be relatively stable in air-dried soils, to persist for 2 months in soil of medium moisture content, and to persist for 1 month in water-saturated soil. Although the rates of degradation in soil may be maximized at the higher moisture values, these high moisture conditions may not be environmentally acceptable because of the increased potential for migration.

PCP also has been found to break down more slowly in heavy clay than in sandy or sandy clay soils. The rate of degradation of PCP has been found to correlate with clay mineral composition, free iron content, phosphate adsorption coefficients and cation exchange capacity of the soil, although the greatest effect was found to correlate with organic matter. Little or no correlation has been found with soil texture, clay content, degree of base saturation, soil pH, and available phosphorus.

The preponderance of information indicates that microbial activity plays an important part in degradation of PCP in soil. Many types of bacteria and fungi are capable of degrading pentachlorophenol, including *Pseudomonas*, *Aspergillus*, *Trichoderma*, and *Flavobacterium*. However, the number of species and their population may be limited. In most cases where rapid soil degradation of PCP by microorganisms has been demonstrated, the source of the soil and/or inoculum was from areas where PCP had been used for a long time.

### **Bioaccumulation/Toxicity of Creosote and PCP**

#### **Plant/Animal Uptake of Creosote**

Little information was found on bioaccumulation/toxicity of creosote; however, considerably more information was found on the bioaccumulation/toxicity of individual PAH's contained in creosote. Higher plants can take up PAH's and translocate them throughout the plant, although the PAH's may concentrate in certain plant parts. Some PAH's can be catabolized by plants.

#### **Toxic Effects of Creosote**

Many of the components of creosote, especially the higher weight PAH's, are

considered to be mutagenic, carcinogenic, fetotoxic, or teratogenic. The heterocyclic oxygen and sulfur compounds, paraffins, and naphthenes are not known to be toxic.

### **Plant/Animal Uptake of PCP**

Limited information was found on the uptake and translocation of PCP by plants, and no information was found on the metabolism of PCP by plants. Uptake of PCP by animals can occur by inhalation, oral ingestion (including consumption of PCP-contaminated food and licking or chewing treated wood) and dermal absorption by direct contact with treated wood. There is some evidence that PCP may be a metabolic product of other environmental contaminants, but the significance of this source is not known.

Many phenols undergo conjugation reactions in animals. These reactions include the formation of glucuronides, ethereal sulphates, and monoesters of sulfuric acid. Some PCP is excreted unchanged, and the amount that is metabolized or conjugated depends on the species. The short half-lives of PCP suggest that there will be no buildup of residues to a toxic level with continuing intake of PCP.

### **Toxic Effects of PCP**

Available data suggest that PCP has moderately acute oral toxicity, but that the LD<sub>50</sub> value may vary with the quality and quantity of contaminants. Man appears to be more susceptible than the rodent and the female to be more susceptible than the male. Commercial samples have produced chloracne in the rabbit ear bioassay, but the purified material has not. Positive reactions have been produced by topical or oral application, but allergic contact dermatitis has not been a problem in handling PCP. Workers have reported that the dust is irritating to the mucous membrane of the nose and throat.

### **Study Sites**

#### **Site Selection Criteria**

The eight wood-treating sites selected were located in the southeastern United States, each having a different soil type. The wood-treating sites were selected using the following criteria:

1. Site had to have a source of sludges, preferably a separate source for PCP and creosote sludges.

2. Site demonstration area soil should have had low level exposure to PCP and creosote so that an acclimated bacteria population would be available; however, high levels of contamination should not be contained within or below the proposed treatment zone (1 meter).
3. Site had to have an available method for collecting and disposing of runoff water.

### **Site, Soil, and Sludge Characterization**

An initial visit was made to each plant site to select one or more potential field demonstration areas. Composite soil samples were collected for analyses of creosote and pentachlorophenol and for determination of soil microbial populations. Based on results from the chemical analyses, microbial populations found, and initial observations, one potential demonstration area approximately 1/2 to 1 acre in size was selected at each plant location. A second visit to each site was made in order to do a thorough site assessment including a more complete chemical and microbiological characterization of the field demonstration area soil.

A third visit was made to each site to conduct soil evaluation tests. Soil profiles were examined at each site in freshly excavated pits, and they were described and sampled using standard soil survey methods. Soil morphological descriptions included horizonation, Munsell color, texture, horizon boundaries, consistency, coarse fragments, root distribution, concretions and pedological features. Each horizon was sampled for laboratory analyses.

### **Laboratory Treatability Studies**

#### **Transformation/Degradation Using a Standard Creosote/PCP Mixture: Experiment I**

Laboratory treatability studies were conducted for each soil to determine rates of degradation/transformation, soil transport properties of creosote and PCP, and toxicity of the water-soluble fraction of waste-soil mixtures. An initial set of degradation/transformation experiments for each site was conducted by applying, at 1% of the soil dry weight, a standard mixture containing 200 ppm technical-grade PCP and 2000 ppm technical-grade creosote to a sample of the site soil. Sample aliquots from test units set up for each soil-waste mixture

prepared were taken at 0, 30, 60, and 90 day time intervals. These aliquots were subjected to chemical and microbiological analyses.

#### **Transformation/Degradation of Site Specific Sludges:**

##### **Experiment II**

The second part of the laboratory degradation studies involved studying the kinetic rates of degradation using samples of the soil and sludge collected from each site. The objective was to assess the potential for treatment of the sludge present at a site in the soil at that site. Three sludge loading rates were tested for each site, and each set of experiments was replicated three times. Sample aliquots were taken at 0, 30, 60 and 90 day time intervals. These aliquots were subjected to chemical and microbiological analyses.

### **Results and Discussion**

#### **Site and Soil Characterization**

The eight sites investigated represented diverse soil, geologic, climatic, and environmental conditions. These sites ranged from near sea level in Gulfport, Mississippi, and Wilmington, North Carolina to elevations above 1000 feet at Atlanta, Georgia. The study areas were located in six Major Land Resource Areas (MLRA) of the United States. The sites encompassed several geomorphic landforms ranging from fluvial terraces to upland ridges. Soil parent materials varied from sandy Coastal Plain sediments to silty Peoria loess to granite gneiss residuum.

#### **Sludge Characterization**

Each plant site had different types and sources of waste. Six of the plants had open lagoons of creosote and/or PCP; one site had three lagoons which were segregated into PCP, PCP in a heavy oil, and creosote; two other plants had no lagoons but had areas of dried sludge and contaminated soil.

#### **Transformation/Degradation with the Standard Mixture: Experiment I**

All PAH compounds selected for analyses were transformed in the Gulfport soil; however, pyrene and benzo(a)pyrene exhibited relatively slow breakdown rates. All PAH's but anthracene were transformed in the Columbus soil, though at somewhat slower rates than the Gulfport soil for

most compounds. Gulfport and Columbus soils developed higher levels of acclimated organisms than the other sites, possibly accounting for the better transformation. Soil from the other sites transformed more of the low molecular weight PAH's readily; however, many of the higher molecular weight PAH's (fluoranthene, pyrene, 1,2-benzanthracene, chrysene, and benzo(a)pyrene) tended to transform slowly, if at all. Pyrene and fluoranthene appeared to be the most recalcitrant at all locations.

Technical grade PCP transformation occurred in Gulfport, Grenada, Clinton, Tanoga, Wilmington, and Meridian soils. The PCP half life was 64 days in Gulfport soil, but well over 100 days for the other soils. Columbus, Atlanta, and Wiggins soils exhibited no transformation of technical grade PCP.

The results of this preliminary experiment indicated that all of the compounds studied potentially could be transformed in soils under appropriate conditions. Microorganism counts of the type used in this experiment were not found to be extremely accurate indicators of potential breakdown rates for particular compounds; however, there appeared to be some tendency for soils with high populations of acclimated microorganisms to transform more of the different PAH's found in creosote and somewhat faster rates. This may have been due to larger numbers of particular microorganisms or to a more diverse array of microbial species.

#### **Transformation/Degradation of Site Specific Sludges: Experiment II**

Breakdown of total PAH's for simulated waste loading concentrations was similar in soils from each of the four sites. Based on breakdown rates, individual PAH's could be divided into three groups: those with half lives of 10 days or less, those with half lives of 100 days or less, and those with half lives of more than 100 days. Naphthalene, 2-methylnaphthalene, methylnaphthalene, biphenyl, acenaphthalene, acenaphthene, dibenzofuran, and fluorene exhibited half lives of ten days or less in most cases. Phenanthrene, anthracene, carbazole, and fluoranthene exhibited half lives between 10 and 100 days in most cases. Pyrene, 1-benzanthracene, chrysene, benzo(a)pyrene, and benzo-(g,h,i)-perylene exhibited half lives greater than 100 days in some cases. In several cases, however, essentially no breakdown was

observed for these last five compounds within the time frame of the experiment.

Breakdown rates of individual PAH's apparently were related to molecular size and structure, as noted in previous studies. The 0 to 10 day half life group contained compounds with two aromatic rings; the 10 to 100 day half life group contained compounds with three aromatic rings; and, the 100 plus day half life group contained compounds with four or more aromatic rings. However, some of the larger, most recalcitrant compounds apparently were broken down readily in some situations. This indicates that even the most persistent PAH compounds may yield to biological remediation techniques under the right set of management conditions.

The microbial populations found in the plate counts were not closely related to PAH breakdown; PAH breakdown was similar at similar concentrations over the four sites, while microbe counts were highly variable.

PCP transformation occurred in all the soils, but was slow in Columbus soil, a site not previously exposed to PCP type wastes. Grenada soil transformed PCP with half lives ranging from one to two months, a range which should be practical for soil treatment system operations. Meridian soil also exhibited rapid transformation rates of PCP except at the highest loading rate. Wiggins soil transformed PCP with half lives of three to four months, a range which still should be appropriate for soil treatment system

operations especially considering its deep south location where soil temperatures are high enough for good microbiological activity most of the year. Although the Columbus soil did exhibit some transformation of PCP, the low rates would bring into question the practicality of treating PCP in a soil system at that location without additional studies. It is not known what length of time would be required to build up a population of microorganisms suitable for rapid degradation of PCP in hitherto unexposed soil. Evidently, the relatively short time frame of these experiments was insufficient for the Columbus soil. It is likely in most soils with chronic exposure to PCP (which is where PCP treatment in soil systems would be used) that suitable microbial populations exist and that these populations could be enhanced relatively quickly with proper management.

Transformation of OCDD occurred to some degree in soils from all sites, but only in the Grenada soil was consistent OCDD transformation indicated at all loadings. Since PCP also was consistently transformed in the Grenada soil, the potential for transformation of these two compounds in a soil may be interrelated. Dioxins are widely regarded as being highly recalcitrant to biological transformation in soils, but these data, while variable, indicate that this may not be the case for all soils. Further study is needed to investigate this possibility.

## **General Discussion**

Results from these experiments indicated that PCP and PAH compounds in wood-preserving wastes potentially can be transformed at practically useful rates in soil. Although the variability of the data is relatively large in some cases, the general trend is apparent. Treatment of creosote and PCP wood-treating wastes in soil systems appears to provide one viable management alternative at some locations. The data variability, however, supports the need for conducting site-specific treatability studies for a given site to discern the appropriate operation and management scenario.

Further study of treatability of PCP and higher molecular weight PAH compounds in soils is needed to determine the most advantageous environmental conditions and management techniques for more rapid transformation of these compounds at a given site. Further study may reveal reliable techniques for enhancing soil systems for treatment of even the more recalcitrant wood-preserving compounds. Since the environmental problems that the wood-treating industry has to deal with are almost unlimited, and the resources available to solve these problems are quite limited, reliable, safe, economical bioremediation techniques using soil systems are very attractive and warrant thorough study and evaluation.

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John E. Matthews, is the EPA Project Officer (see below).

The complete report, entitled "Characterization and Laboratory Soil Treatability Studies for Creosote and Pentachlorophenol Sludges and Contaminated Soil," (Order No. PB 89-109 920/AS; Cost: \$28.95, subject to change) will be available only from:

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