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CHARACTERIZATION AND LABORATORY SOIL TREATABILITY STUDIES FOR CREOSOTE AND PENTACHLOROPHENOL SLUDGES AND CONTAMINATED SOIL

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16. ABSTRACT

Information is presented from characterization and laboratory treatability phases of a 3-phase study pertaining to on-site treatability potential of soils containing hazardous constituents from wood-treatment waste (EPA-K001). Specific information contained includes: 1) literature assessment of soil treatability potential for wood treating chemicals; 2) sludge/soil characterization data for 8 wood treating sites; 3) degradation/toxicity data for wood treating chemicals in soils from 4 sites.

Literature data indicated that creosote/PCP waste constituents may be treatable in soil. Each sludge characterized contained the PAH constituents; relative concentrations of individual compounds varied among sludges. PCP sludges contained PCP, OCCD, and traces of hepta/hexa dioxins and corresponding furans.

PAH's with 2 rings generally exhibited half lives < 10 days. Three ring PAH's generally exhibited longer half lives < 100 days. Four or five ring PAH's exhibited half lives > 100 days; in specific cases, some 4 or 5 ring PAH's exhibited half lives < 10 days. PCP half lives varied from 20 to > 1000 days in different soils. PCP was transformed slowly in soils with no prior long term exposure to PCP. Microbial plate counts used in this study did not appear to be closely related to transformation rates.

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ABSTRACT

This 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 underway 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.

This 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 (OCDD), 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.

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SECTION 1

INTRODUCTION

Land Treatment is the hazardous waste management technology pertaining to application/incorporation of waste into the upper layers of soil for the purpose of degrading, transforming, and/or immobilizing of hazardous constituents contained in applied waste (40 CFR Part 264). Land treatment systems have been used for a variety of industrial wastes; however, application of hazardous industrial waste using a controlled engineering design and a management approach has not been widely practiced. This is due, in part, to the lack of a comprehensive technical information base concerning the behavior of hazardous constituents as specifically related to current regulatory requirements (40 CFR Part 264) concerning the treatability in soil, i.e., degradation, transformation, and immobilization, of such constituents. Soil treatment systems that are designed and managed based on a knowledge of soil-waste interactions may represent a significant technology for treatment and ultimate disposal of selected hazardous wastes in an environmentally acceptable manner.

In this research project, representative hazardous waste (K001) from wood-preserving processes was evaluated for potential treatment in soil systems. A literature assessment was conducted as an aid in the prediction of the treatment potential for this type of waste in soil. The literature assessment also was used as a guide to design an experimental approach to obtain specific treatability information pertaining to degradation, transformation, and immobilization of hazardous constituents in soil.

OBJECTIVES

The overall objective of this study is to evaluate the efficacy of land treatment as an on-site management alternative for contaminated soil and sludges containing pentachlorophenol and creosote from wood-treating plants. This project involves three phases: a characterization phase, a treatability screening phase, and a field evaluation phase.

1. Characterization Phase. The characterization phase involved obtaining baseline data on the qualitative and quantitative distribution of wood-treating chemicals contained in representative samples of contaminated soils and sludges collected at eight wood-treating plants located in the southeastern United States. Samples of soil and sludges from each site were collected and characterized using scientifically documented physical and chemical procedures.

2. Treatability Screening Phase. This phase involved laboratory evaluations of the treatment potential of creosote and pentachlorophenol sludges and contaminated soil collected from each selected site.

3. Field Evaluation Phase. The final phase of this project involves a field evaluation study at one of the eight selected sites. This phase is currently in progress.

EVALUATION APPROACH

Standards for demonstrating treatment of hazardous wastes in soil are promulgated in 40 CFR Part 264.272 . The standards require demonstration of degradation, transformation, and/or immobilization of a candidate waste in the treatment soil. Demonstration of degradation/transformation of waste and waste constituents is based on loss of parent compounds within the soil/waste matrix. "Complete

degradation" is the term used to describe the process whereby waste constituents are mineralized to inorganic end products, generally including carbon dioxide, water, and inorganic species of nitrogen, phosphorus, and sulfur. The rate of degradation/transformation may be established by measuring the loss of parent compound from the soil/waste matrix with time. "Transformation" refers to partial degradation in the soil which converts a substance into an innocuous form, or which converts wastes into environmentally safe forms (Huddleston et al., 1986). Ward et al. (1986) also discussed the difference between rates of mineralization (for complete degradation) and rates of biotransformation. "Immobilization" refers to the extent of retardation of the downward transport, or "leaching potential," and upward transport, or "volatilization potential," of waste constituents. The mobility potential for waste constituents to transfer from the waste to water, air, and soil is affected by the relative affinity of the waste constituents for each phase, and can be characterized in column and batch reactors. Therefore, demonstration of soil treatment requires an evaluation of degradation, transformation, and immobilization processes, and the quantification of the processes for obtaining an integrated assessment of the design and management requirements for successful assimilation of a waste in a soil system.

The requirement for demonstrating treatment, i.e., degradation, transformation, and/or immobilization, can be addressed using several approaches. Information can be obtained from several sources, including literature data, field tests, laboratory analyses and studies, theoretical parameter estimation methods, and, in the case of existing land treatment units, operating data. Information presented in the

Literature Review of this report addresses information obtained from the literature. Specific information obtained from literature sources includes quantitative degradation, transformation, and immobilization information for waste-specific hazardous constituents in soil systems. The two organic hazardous waste types from the wood-treating industry--creosote sludge and pentachlorophenol sludge--are considered.

At this time the U.S. EPA (1986b) considers the use of information from the literature only to be insufficient to support demonstration of treatment of hazardous wastes in soil. A laboratory experimental approach used during this project for obtaining additional data concerning soil treatability for the two hazardous wastes selected for study is presented.

The regulations also require that the effect of design and management practices on soil treatment be evaluated. Design and management practices specifically identified in the regulations include waste application rate (loading rate) and frequency of waste application.

The experimental method used in this study compared the rates of degradation of selected components in creosote and pentachlorophenol using eight soil types. Initial studies used a standard mixture of technical grade creosote and pentachlorophenol (standard mixture) in order to compare each site using a common waste. Further studies were done to determine the rate of degradation of sludges from each site in the soil at the site.

For each hazardous waste and soil type selected, treatment was evaluated as a function of waste loading rate and time. Chemical analyses over time were used to characterize treatment effectiveness.

The experimental approach described above was used to determine whether the hazardous waste could be degraded in each selected soil type, to determine how soil type affected the rates and products of degradation, to determine the acute toxicity of the products added to the soil and formed during decomposition in soil using a Microtox® system, and finally, to determine, using intact soil cores, how effective the various soil types are for immobilizing the hazardous constituents using the procedure and methods developed by Battelle-Columbus (EPRI, 1984).

This report documents the characterization of sludges and contaminated soils from eight sites and degradation of wood treating chemicals and sludges in soil from four sites. Subsequent reports will deal with degradation studies from the remaining four sites, and toxicity and immobilization studies of wood treating chemicals and sludges from all eight sites.

WASTE CHARACTERIZATION

Treatment of a hazardous waste refers specifically to treatment of hazardous constituents contained in the waste. Standards identified in 40 CFR Part 264.272(c)(i) refer to Appendix VIII constituents listed in Part 26. Where waste(s) are from an identified process, i.e., wood preserving, EPA may accept analyses performed on a subset of constituents. For creosote sludges, the compounds evaluated for treatment in laboratory studies, based on the literature and laboratory evaluation, included the volatile polycyclic aromatic hydrocarbons PAH's (naphthalene and methyl naphthalenes) and the larger molecular weight

PAH's. For this study, the amounts of pentachlorophenol and octachlorodibenzo-p-dioxin in pentachlorophenol sludges were used as the key parameters.

SOIL CHARACTERIZATION

Eight wood treating sites located in the southeastern United States were selected for study. Sites were selected having a variety of soil types in order to determine how the rates of degradation are affected by factors in the soil, such as the organic carbon and clay content. The eight soil types selected are characterized in detail in Soil Characterization.

WASTE LOADING RATE DETERMINATION

Loading rate (mass/area/application, or mg waste/kg soil) was the first design parameter evaluated. To evaluate the extent and efficacy of treatment, it is necessary to ensure that bacteria capable of utilizing wood treatment chemicals as substrates exist in the soil. The evaluation of the impact of hazardous wastes on indigenous soil microbial populations is important, especially for these wastes, which contain hazardous constituents specifically designed to inhibit biological activity.

The microbial assay used in this study involved plate counting of colony forming units. This was done using a variety of media in order to determine the number of acclimated fungi, actinomycetes, and bacteria in each site soil in the presence of wood-preserving waste.

WASTE TREATMENT IN SOIL

The degradation potential of organic hazardous constituents in waste applied to soil is critical since degradation usually represents the primary removal mechanism for these constituents. The basis for biodegradation coefficient measurements was the determination of soil concentrations of specific constituents as a function of time. In order to compare data using different soil types and concentrations, a first order kinetic rate for the process was used. The first-order reaction-rate constant was used to calculate half-lives for each parameter. The half-lives calculated provided quantitative information for evaluating the extent and rate of treatment, and for comparing treatment effectiveness for each waste/soil combination as a function of design and management factors. Results and discussion concerning degradation of four of the K001 wastes selected for study are presented in the Waste Degradation Evaluation. It should be noted that the use of first-order kinetics was done to compare the rates at various sites and does not necessarily mean that the particular compound was undergoing a first-order reaction at a particular site.

According to current regulations, a hazardous waste cannot be applied to land unless hazardous constituents contained in the waste are reduced in toxicity as a result of treatment. Therefore, conversion of hazardous constituents to less toxic intermediates within the soil treatment medium currently is under evaluation. Information concerning the toxicity reduction in each waste/soil combination is being evaluated using results from an acute toxicity assay (Microtox® assay) as the measurement criteria. Results from the toxicity reduction experiments will be presented in a subsequent report.

Evaluation of treatment also involved an investigation of the extent of migration of each hazardous waste. A loading rate based on biodegradation potential was selected for each soil/waste combination using data generated in an earlier study (Sims et al., 1987). The leaching potentials are being characterized for these loading rates in laboratory soil-column studies. Results from the column experiments also will be presented in a subsequent report.

SECTION 2

CONCLUSIONS

Specific conclusions based on results of this research project to date include:

1. Creosote and PCP wood treating waste contaminants can be transformed in soil systems; however, loading rates and previous exposure of the soil to particular types of waste are important factors in site-specific transformation rates for individual contaminants.
2. Higher molecular weight PAH compounds and PCP usually are transformed more slowly than lower molecular weight PAH's; all of these compounds can be transformed more rapidly under good site management conditions.
3. Populations of PAH and PCP acclimated microorganisms can be expected to increase markedly when these compounds are applied to soil; however, population counts of the type used in this study are not closely related to transformation rates for these compounds.

SECTION 3

LITERATURE REVIEW

INTRODUCTION

Treatment in soil systems may represent a significant engineering method for control/treatment and ultimate disposal of selected hazardous constituents in applied waste. Land application for the assimilation and treatment of hazardous constituents is a potentially significant cost-effective, environmentally safe, low energy technology that has been successfully used for a multitude of domestic and industrial wastes. Soil systems for treatment of a variety of industrial wastes, including food processing, organic chemical manufacturing, coke industries, textiles, and pulp and paper have been utilized for many years (Overcash and Pal, 1979). However, Phung et al. (1978) reported that routine application of industrial hazardous wastes onto the soil surface and incorporation into the soil for treatment is not widely practiced, except for the oil refining industry. There are few definitive data in the literature, quantifying treatment rates in full-scale soil treatment systems (Huddleston et al., 1986).

Land treatment is defined in RCRA as "the hazardous waste management technology pertaining to application and/or incorporation of waste into the upper layers of the soil in order to degrade, transform, or immobilize hazardous constituents contained in the applied waste" (40 CFR Part 264, Subpart M). Land treatment also has been defined as "a controlled application of hazardous wastes onto or into the aerobic surface soil horizon, accompanied by continued monitoring and

management, in order to alter the physical, chemical, and biological state of the waste via biological degradation and chemical reactions in the soil so as to render such waste nonhazardous" (Brown et al., 1980).

The current regulatory requirement for demonstrating treatment, i.e., degradation, transformation, and/or immobilization of hazardous waste constituents in soil systems, can be addressed using several approaches. Information concerning each treatment component can be obtained from several sources including literature data, field tests, laboratory studies, laboratory analyses, theoretical parameters, estimation methods, and, in the case of existing land treatment units, operating data (40 CFR Part 264.272). It is suggested that a combination of data sources be utilized; e.g., literature data, laboratory analyses, laboratory studies and field verification tests; to strengthen confirmation of hazardous constituent treatment efficiency. The availability and completeness of existing literature data influences the need for further collection of performance data. The U.S. EPA considers the use of only literature data to be insufficient to support a demonstration treatment at the present time.

In this project, hazardous waste from eight wood-preserving sites was used to evaluate the land treatment potential of these types of waste in various soil types. A comprehensive assessment of literature available for both waste types, pentachlorophenol and creosote, was conducted as an aid in making these evaluations.

WOOD PRESERVING INDUSTRY

Introduction (Burdell, 1984)

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 1978 volume of wood commodities treated is shown in Table 1 (USDA, 1980).

Table 1. Volume of wood commodities treated in 1978.

Product	Volume treated with		
	Creosote solutions	Penta	Inorganic salts[a]
	1,000 cu. ft.		
Crossties, switch ties, and landscape ties	103,138	449	2,498
Poles	18,237	41,905	4,038
Crossarms	41	1,615	29
Piling	9,993	1,154	943
Lumber and timbers	10,780	21,209	73,317
Fence posts	4,584	10,983	4,461
Other products	7,815	2,681	7,616
Total (1980)	154,587	79,996	92,903

[a]The main inorganic salts are copper, chromium, and arsenic.

About 99% of the creosote solutions, 90% of the penta, and all of the arsenical salts in the preceding tabulation are applied by pressure methods in closed systems. A small amount of creosote and about 3.8

million pounds of penta are applied by commercial thermal and dip treatment methods in open tanks.

Basic Wood-Treating Process

The basic oil-preservative wood-treating cycle begins by placing either seasoned or green wood into a pressure cylinder. If green materials are used, they can be artificially seasoned in the cylinder with steam and either oil preservative or hydrocarbon vapor. Then an initial air pressure (vacuum or positive pressure) is introduced into the system. Next the preservative is pumped into the cylinder and the pressure increased until a predetermined liquid volume is absorbed into the wood. The pressure is released and the preservative is pumped back into the tanks. A final vacuum is applied to remove most of the free liquid on the surface.

The organic preservative most used is coal tar creosote, a by-product from the production of coke from coal. When coal tar is distilled, the 200° to 400°C fractions are creosote. Creosote is mostly aromatic single to multiple ring compounds. Over 200 different components have been identified in creosote.

Pentachlorophenol 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 plus various levels of other chlorinated phenolic compounds.

CHARACTERISTICS OF THE ORGANIC WOOD PRESERVATIVES

The two major organic wood preservatives used in the United States are pentachlorophenol (PCP) and creosote.

Technical-grade PCP used for treating wood contains 85 to 90% PCP. The remaining materials in technical grade PCP are 2,3,4,6-tetrachlorophenol (4 to 8%), "higher chlorophenols" (2 to 6%), and dioxins and furans(0.1%). The tetrachlorophenol is added to PCP to increase the rate of solubilization.

The other contaminants found in technical-grade PCP are formed during manufacture. In the United States PCP is manufactured from phenol by a catalytic chlorination process. During chlorination, the temperature must be maintained above the melting point of the products formed; this, it is felt, contributes to the side reaction that gives rise to contaminants, including traces of trichlorophenol, chlorinated dibenzo-p-dioxins, chlorinated dibenzofurans, chlorophenoxy phenols, chlorodiphenyl ethers, chlorohydroxydiphenyl ethers, and traces of even more complex reaction products of phenol. Chlorodibenzodioxins and furans are the by-products about which there are the greatest concerns. Analyses of PCP have revealed that the principal chlorodibenzodioxin and chlorodibenzofuran contaminants are those containing six to eight 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 (USDA 1980). The composition of a sample of commercial PCP and of a sample of purified PCP is given in Table 2. A representative distribution of isomers is given in Table 3 (U.S. EPA 1978).

The physical properties of a compound play an important role in how the compound behaves under different conditions. These properties influence the mobility of a compound in air or water, its ability to adsorb to surfaces, and its susceptibility to degradation. These

Table 2. Comparison of composition of commercial grade and purified grade pentachlorophenol (U.S. EPA 1978).

Component	Analytical results	
	Commercial[a] (Dowicide 7)	Purified[b] (Dowicide EC-7)
Pentachlorophenol	88.4%	89.8%
Tetrachlorophenol	4.4%	10.1%
Trichlorophenol	0.1%	0.1%
Chlorinated phenoxyphenols	6.2%	--
Octachlorodioxin	2500 ppm	15.0 ppm
Heptachlorodioxins	125 ppm	6.5 ppm
Hexachlorodioxins	4 ppm	1.0 ppm
Octachlorodibenzofuran	80 ppm	1.0 ppm
Heptachlorodibenzofurans	80 ppm	1.8 ppm
Hexachlorodibenzofurans	30 ppm	1.0 ppm

[a]Sample 9522A.
[b]Technical grade PCP purified by distillation.

Table 3. Chlorodioxin isomer distributions in commercial grade PCP (Dowicide 7) and PCP-Na samples (Buser 1975, 1976).

Chlorodioxin	PCP[a] (ppm)	PCP-Na[b] (ppm)
1,2,3,6,7,9-Cl_6D	1	0.5
1,2,3,6,8,9-Cl_6D	3	1.6
1,2,3,6,7,8-Cl_6D	5	1.2
1,2,3,7,8,9-Cl_6D	0	0.1
1,2,3,4,6,7,9-Cl_7D	63	16.0
1,2,3,4,6,7,8-Cl_7D	171	22.0
1,2,3,4,6,7,8,9-Cl_8D	250	110.0

[a]Dowicide 7 (commercial PCP).

[b]Sodium salt of PCP.

factors are important because they relate to the route and rate of exposure by which a compound might be received by man or other organisms. Some of the selected physical properties of pentachlorophenol are given in Table 4.

Pentachlorophenol is quite stable. It does not decompose when heated at temperatures up to its boiling point for extended periods of time. Pure PCP is considered to be rather inert chemically (Bevenue and Beckman, 1967). The chlorinated ring structure tends to increase stability, but the polar hydroxyl group tends to facilitate biological degradation (Renberg, 1974). It is not subject to the easy oxidative coupling or electrophilic substitution reactions common to most phenols. All monovalent alkali metal salts of PCP are very soluble in water, but the protonated (phenolic) form is virtually insoluble. Hence, transport of PCP in water is related to the pH of the environment.

Pentachlorophenol is moderately volatile and a closed system should be used when heating environmental samples or recoveries will be poor (Bevenue and Beckman, 1967). By contrast to other chlorinated organic compounds of low vapor pressure, PCP can be lost from soils by volatilization (Briggs, 1975).

Creosote

The other major organic wood preservative used in the United States is creosote. Creosote, in contrast to PCP, is a very complex mixture of organic compounds produced from coal.

At least 200 chemical compounds have been identified in creosote. Although the chemical composition of this material varies for reasons discussed above, it is generally agreed that creosote contains several

Table 4. Physical properties of PCP (Crosby 1981; Bevenue et al. 1967).

Property	Value
Empirical formula	C_6Cl_5OH
Molecular weight	255.36
Melting point	190°C
Boiling point	293°C
Density	1.85 g/cc
pK_A (25°)	4.70-4.80
Partition coefficient (Kp), 25°	
Octanol-water	1760
Hexane-water	1.03×10^5
Vapor pressure, Torr (mm hg)	
0°C	1.7×10^{-5}
20°C	1.7×10^{-4}
50°C	3.1×10^{-3}
100°C	0.14
200°C	25.6
300°C	758.4
Solubility in water (g/L)	
0°C	0.005
20°C	0.014
30°C	0.020
50°C	0.035
70°C	0.085
Solubility in organic solvents (g/100g solvent)	
in methanol 20°C	57
in methanol 30°C	65
in diethylether 20°C	53
in diethylether 30°C	60
in ethanol 20°C	47
in ethanol 30°C	52
in acetone 20°C	21
in acetone 30°C	33
in xylene 20°C	14
in xylene 30°C	17
in benzene 20°C	11
in benzene 30°C	14
in carbon tetrachloride 20°C	2
in carbon tetrachloride 30°C	3

thousand different compounds which could be identified with GC/MS. Most of these are present in very small amounts. The major components of a typical creosote of U.S. origin and one of German origin are shown in Table 5. There are some rather striking differences between the two types of creosote in the levels of particular polycylic aromatic hydrocarbons and in the overall levels of total PAH's.

The greater part of the composition of creosote consists of neutral fractions. Tar acids, such as phenol and the cresols, as well as such tar bases as pyridenes, quinolines, and acridines, constitute a rather small percentage of the total weight of creosote.

A schematic of the distillation processes is presented in Figure 1. Creosote is a blend of the various distillates designed to impart specific physical characteristics that meet standards of the American Wood-Preservers' Association (AWPA).

Compared to the starting material, the yield of fractions that are blended to make creosote ranges from 25 to 40%, depending upon the point at which distillation is terminated. Both the yield and the chemical and physical properties of the various fractions are influenced by the characteristics of the coal from which the tar originates, the type of equipment used in the distillation process, and the particular process used.

There were 64 producers of coal tar in the United States in 1972 and 24 tar distillation plants producing creosote (U.S. EPA, 1975). Because their chemical composition and properties are not uniform, creosote and blends of creosote and coal-tar are normally described in terms of their physical properties. American Wood-Preservers' Association specifications for creosote for various uses are given in

Table 5. Chemical composition of a United States and a German creosote.

Compound or component	Percent of total	
	U.S. creosote[a]	German creosote[b]
Naphthalene	3.0	7.3
Methyl naphthalene	2.1	4.2
Diphenyl dimethylnaphthalene	--	3.2
Biphenyl	0.8	--
Acenaphthene	9.0	4.1
Dimethylnaphthalene	2.0	--
Diphenyloxide	--	3.4
Dibenzofuran	5.0	--
Fluorene-related compounds	10.0	9.6
Methyl fluorenes	3.0	--
Phenanthrene	21.0	12.6
Anthracene	2.0	--
Carbazole	2.0	--
Methylphenanthrene	3.0	5.4
Methyl anthracenes	4.0	--
Fluoranthene	10.0	6.8
Pyrene	8.5	5.0
Benzofluorene	2.0	4.6
Chrysene	3.0	2.8
Total	90.4	69.0

[a]Lorenz and Gjovik, 1972.
[b]Becker, 1977.

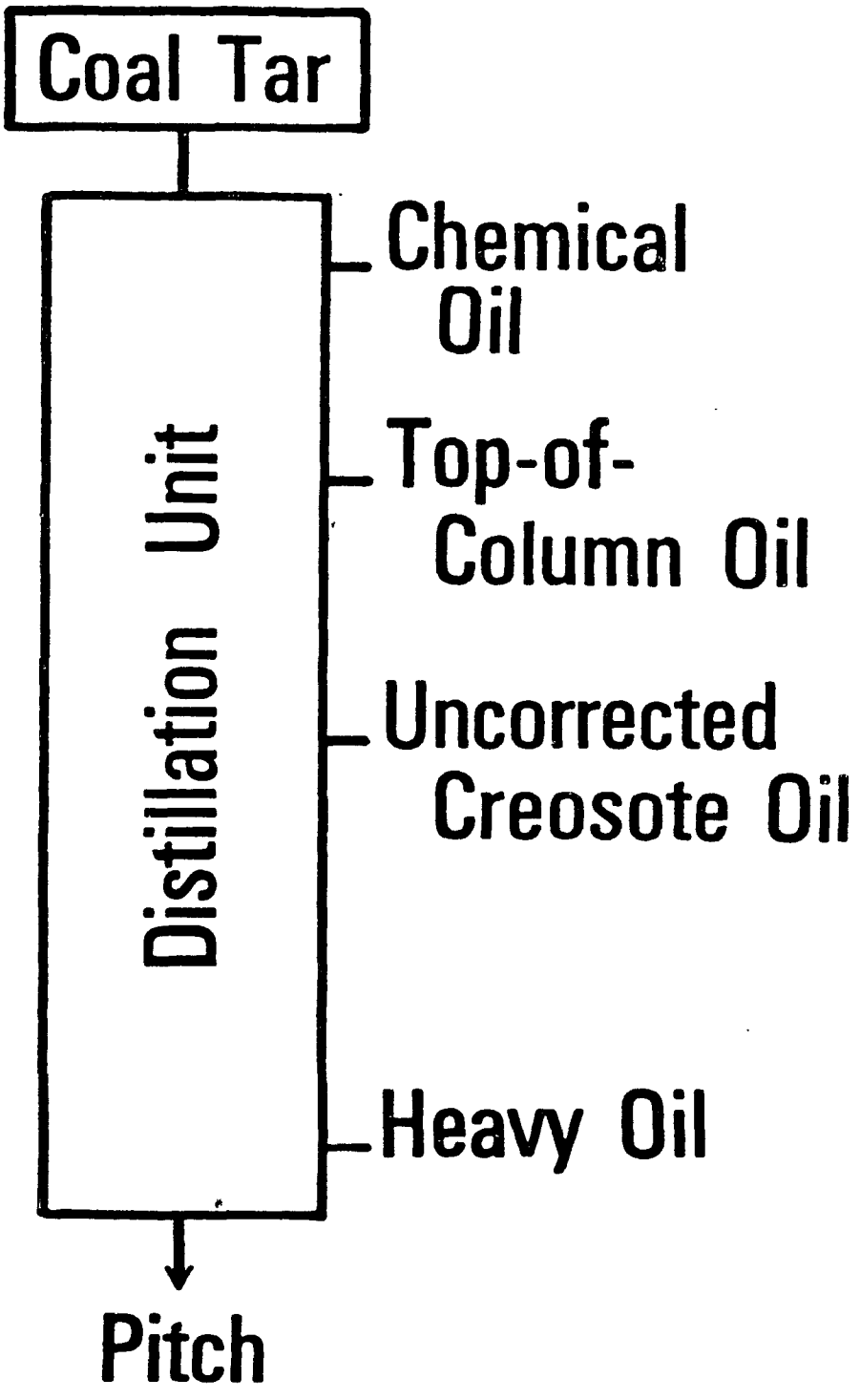


Figure 1. Principal cuts produced in coal-tar distillation.

Table 6. Similar standards have been promulgated by the American Society for Testing and Materials (ASTM) and the General Services Administration (GSA). The principal differences among creosotes for the three uses shown are in specific gravity and the fraction of the oil distilled within various temperature ranges.

A comparison of physical properties of creosote and creosote/coal tar mixtures as shown in Table 7 indicates much higher distillation residue for coal tar. A list of the properties of some of the 16 priority pollutant PAH compounds found in creosote is given in Table 8 (Sims et al., 1987).

Another group of compounds which have been identified in creosote and which are related to the PAH's are the azaarenes which make up approximately 0.13% of creosote (Adams et al., 1984). These compounds are polycyclic hydrocarbons containing nitrogen (e.g., quinoline and acridine).

CHARACTERISTICS OF WOOD-PRESERVING WASTES

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

Prior to the environmental rules on wastewater discharge, the treating plant wastewater effluent generally went directly to surface drainage or a stream. A large number of the plants had sumps or ponds

Table 6. Physical properties of creosote and its fractions. (USDA 1980)

	American Wood-Preservers' Association Standards					
	P1-65[a]		P7-72[b]		P13-65[c]	
Water % volume	< 1.5		< 1.0		< 1.5	
Xylene, insoluble, % by wt.	< 0.5		< 0.5		< 0.5	
Specific gravity 38/15.5°C						
Whole creosote	> 1.050		> 1.060		> 1.080	
Fraction 235-315°C	> 1.027		--		> 1.030	
Fraction 315-355°C	> 1.095		--		> 1.105	
Residue above 355°C	--		--		> 1.160	
Distillation, % by wt.	Min.	Max.	Min.	Max.	Min.	Max.
Up to 210°C	--	2.0	--	1.0	--	2.0
235°C	--	12.0	--	10.0	--	12.0
270°C	20.0	40.0	--	--	20.0	40.0
315°C	45.0	65.0	--	--	45.0	65.0
355°C	65.0	82.0	65.0	--	65.0	75.0

[a] For land and fresh water use.

[b] For brush or spray application.

[c] For marine (coastal water) use.

Table 7. American Wood-Preservers' Association specifications for creosote-coal tar solutions.[a]

		Grade			
		A	B	C	D
Composition					
Creosote	100%	<80	<70	<60	>50
Coal tar	--	--	--	--	--
Water (% by volume)		>3.0	>3.0	>3.0	>3.0
Xylene, insol. (% by weight)		>2.0	>3.0	>3.5	>4.0
Coke residue (% by weight)	0.99	>5.0	>7.0	>9.0	>11.0
Specific gravity 38/15.5°C					
Whole oil	1.102	1.06-1.11	1.07-1.12	1.08-1.13	1.09-1.14
235-315°C	1.054	1.025	1.025	1.025	1.025
315-355°C	1.133	1.085	1.085	1.085	1.085
Residue		--	--	--	--
Distillation					
To 210°C	1.87	5	5	5	5
To 235°C	6.89	25	25	25	25
To 270°C	19.39	--	--	--	--
To 315°C	49.8	36	34	32	30
To 355°C	72.58	60	56	52	48
Residue	26.67	--	--	--	--

[a]Loren and Gjovik, 1972.

Table 8. Properties of 16 priority pollutant PAH compounds. (Sims 1987).

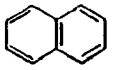
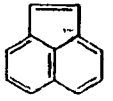
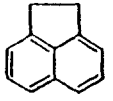
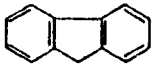
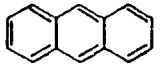
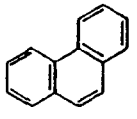
		Molecular Weight	Aqueous Solubility* mg/l	Melting Point* °C	Boiling Point* °C	Vapor pressure @ 20°C torr	Log K_{ow}*	Length of Molecule A^0	K_{oc}
1. Two Rings Naphthalene		128	31,700	80	218	4.92×10^{-2}	3.37	8.0	1,300+
2. Three Rings Acenaphthylene		152	3,470	92	265	2.9×10^{-2}	4.07		
Acenaphthene		154	3,930	96	279	2.0×10^{-2}	4.33		
Fluorene		166	1,980	116	293	1.3×10^{-2}	4.18		
Anthracene		178	73	216	340	1.96×10^{-4}	4.45	10.5	2,600+
Phenanthrene		178	1,290	101	340	6.80×10^{-4}	4.46	9.5	23,000+

Table 8. (continued)

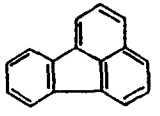
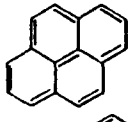
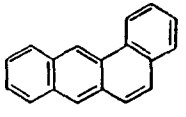
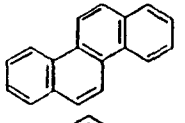
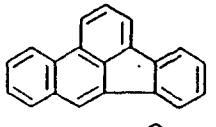
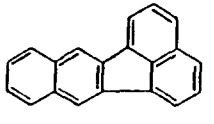
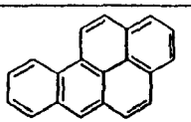
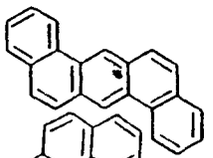
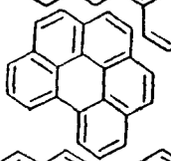
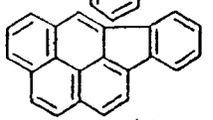
		Molecular Weight	Aqueous Solubility* mg/l	Melting Point* °C	Boiling Point* °C	Vapor pressure @ 20°C torr	Log K_{ow}*	Length of Molecule A°	K_{oc}
3. Four Rings Fluoranthene		202	260	111	--	6.0×10^{-6}	5.33	9.4	
Pyrene		202	135	149	360	6.85×10^{-7}	5.32	9.5	62,700# 84,000+
Benz(a)anthracene		228	14	158	400	5.0×10^{-9}	5.61	11.8	
Chrysene		228	2	255	--	6.3×10^{-7}	5.61	11.8	
4. Five Rings Benzo(b)fluoranthene		252	1.2	167	--	5.0×10^{-7}	6.57		
Benzo(k)fluoranthene		252	0.55	217	480	5.0×10^{-7}	6.84		

Table 8. (continued)

		Molecular Weight	Aqueous Solubility* mg/l	Melting Point* °C	Boiling Point* °C	Vapor pressure @ 20°C torr	Log K_{ow}*	Length of Molecule A°	K_{oc}
Benzo(a)pyrene		252	3.8	179	496	5.0×10^{-7}	6.04		4,510,651
Dibenz(a,h)anthracene		278	2.49	262	--	1.0×10^{-10}	5.97	13.5	2,029,000#
5. Six Rings									
Benzo(g,h,i)perylene		276	0.26	222	--	1.0×10^{-10}	7.23		
Indeno(1,2,3-Cd)pyrene		276	62	163	--	1.0×10^{-10}	7.66		

*Sims and Overcash (1983).
†Karickhoff et al. (1979).
#Means et al. (1980) (mean value is reported).

to trap the heavy oil residuals before discharging to a creek or to the publicly-owned treating works (POTW). Ponds ranged from less than an acre to eight acres. Normally the ponds were lined with the local soils. Typical constituents present in creosote wastewater are given in Table 9.

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

Preservative-contaminated soil is another source of environmental concern. Treated material is withdrawn from the cylinder and moved by rails to storage areas. During transportation the preservative drips from the treated wood onto the soil along the track. The areas around storage, treating, and unloading tanks have had minor preservative spillage from broken pipes, bleeding of treated wood, etc. These areas can be rather large, especially in the older railroad and pole plants.

DECOMPOSITION/IMMOBILIZATION OF PCP AND CREOSOTE COMPONENTS IN SOIL

Pentachlorophenol

A large number of studies on biodegradation of PCP in soil have been done. The sequence of reactions that have been shown to occur is summarized in Figure 2. In soil, PCP undergoes a reversible methylation reaction to form pentachloroanisole, but this reaction apparently is not part of the main decomposition pathway. The main route for decomposition is not through the methyl derivative, but through PCP

Table 9. Daily discharge of creosote wastewater pollutants by the wood-preserving industry (USDA 1980).

Creosote Component	Composition of Whole Creosote	Allowable Discharge[a]	
		1977	1983
	Percent	Pounds/day	
Naphthalene	3.0	5.0	1.4
2-Methylnaphthalene	1.2	2.0	.6
1-Methylnaphthalene	.9	1.5	.4
Biphenyl	.8	1.3	.4
Dimethylnaphthalenes	2.0	3.4	1.0
Acenaphthene	9.0	15.1	4.3
Dibenzofuran	5.0	8.4	2.4
Fluorene	10.0	16.8	4.8
Methylfluorenes	3.0	5.0	1.4
Phenanthrene	21.0	35.3	10.0
Anthracene	2.0	3.4	1.0
Carbazole	2.0	3.4	1.0
Methylphenanthrenes	3.0	5.0	1.4
Methylanthracenes	4.0	6.7	1.9
Fluoranthene	10.0	16.8	4.8
Pyrene	8.5	14.2	4.0
Benzofluorenes	2.0	3.4	1.0
Chrysene	3.0	5.0	1.4

[a] Discharges are based on a flow rate of 5,000 gal/day per plant, 90 plants, and discharge limitations on oil and grease of 45 mg/liter in 1977 and 13 mg/liter in 1983.

discharge limitations on oil and grease of 45 mg/liter in 1977 and 13 mg/liter in 1983.

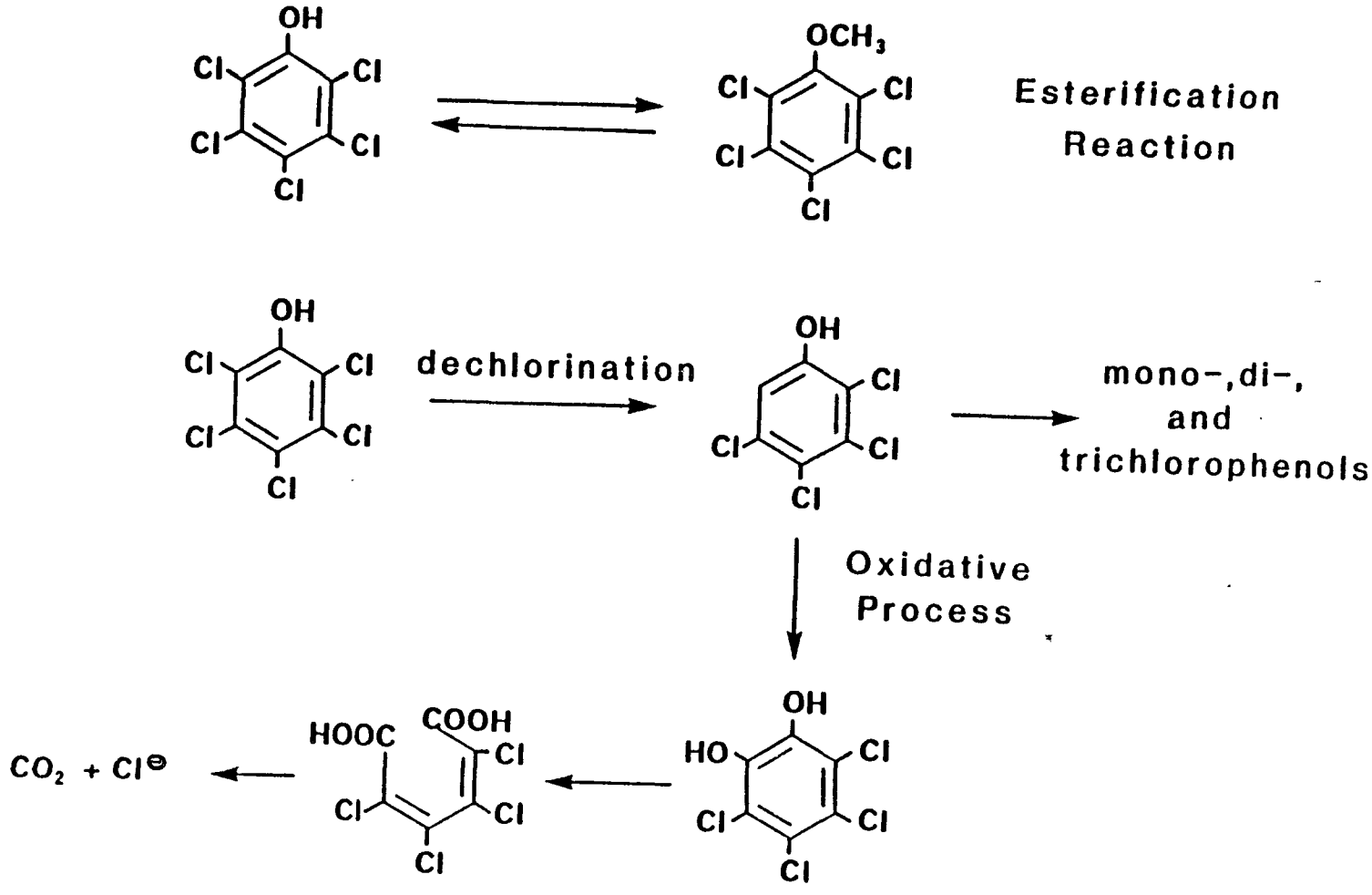


Figure 2. Proposed route for decomposition of pentachlorophenol.

(Kaufman, 1978; Matsunaka and Kuwatsuka, 1975). 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_2 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.

Hilton and Yuen (1963) compared soil adsorption of PCP to the soil adsorption of a number of substituted urea herbicides. They found that the adsorption of PCP was the highest of all compounds studied.

Choi and Aomine (1972, 1974, 1974a) studied the interaction of PCP and soil in detail. Adsorption and/or precipitation of PCP occurred to some extent on all soils tested. Choi and Aomine (1974) concluded in a study of 13 soils that adsorption of PCP depended primarily on the pH of the system. The more acid the soil, the more complete was the "apparent adsorption" of PCP. Different mechanisms of adsorption dominate at different pH values. It should be noted that PCP is an acid which forms a salt at the higher pH's. In the salt form, PCP would be more soluble in water but also more polar. In acid clays "apparent adsorption" involved the adsorption on colloids, and precipitation in the micelle and in the external liquid phase. Organic matter content of soils is important to adsorption of PCP at all pH values. Soil containing humus always adsorbs more PCP than soil treated with H_2O_2 to remove organic

matter. Later investigations led to the conclusion that adsorption of PCP by humus is important when the concentration is low, but at higher concentrations the inorganic fraction increases in importance.

Three of four allophanic soils showed a significant increase in PCP adsorption at higher temperatures, while the fourth soil showed a decrease (Choi and Aomine, 1974a). The difference between the three soils and the fourth soil could be explained by assuming that andosols chiefly adsorb PCP as anions; whereas, the major factor influencing PCP adsorption by the fourth soil, showing a decrease with increasing temperature, is due to Van der Waal's force. Decreasing the concentration of chlorides or sulfate ions also increases the adsorption of PCP to soil. These results indicate the occurrence of competition between inorganic anions and PCP anions for adsorption sites on the soil colloid.

The persistence of PCP in soil depends on a number of environmental factors. Young and Carroll (1951) noted that PCP degradation was optimum when the moisture content of soil was near saturation. Kuwatsuka and Igarashi (1975) reported that the degradation of PCP is faster under flooded conditions than under upland conditions. Loustalot and Ferrer (1950) found that the sodium salt of PCP was relatively stable in air-dried soils, persisted for 2 months in soil of medium moisture content, and for 1 month in water-saturated soil. Although the rates of degradation may be maximized at the higher moisture values, these conditions would not be suitable for land treatment because of the increased potential for migration.

There are several factors in soil which affect the persistence of PCP. PCP is broken down slower in heavy clay than in sandy or sandy clay soils (Loustalot and Ferrer, 1950). This could be due to factors in the soil or to a slower oxygen transfer in the soil. An extensive study of the soil variables affecting the rate of degradation of PCP was carried out by Kuwatsuka and Igarashi (1975). The rate was correlated with clay mineral composition, free iron content, phosphate adsorption coefficients and cation exchange capacity of the soil, while the greatest effect was correlated with organic matter. According to these authors, little or no correlation could be 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 the degradation of PCP in soil. PCP decays more rapidly when the ambient temperature approaches the optimum value for microbiological activity (Young and Carroll, 1951). Ide et al. (1972) found no decay in sterilized soil samples. These factors suggest that microorganisms play an important role in PCP degradation (Kuwatsuka and Igarashi, 1975; Young and Carroll, 1951). Kuwatsuka and Igarashi (1975) studied degradation of PCP in soils collected from flooded and upland areas. Upland soils degraded PCP more rapidly in the laboratory when studied in the aerated condition, while soils obtained from flood conditions degraded PCP more rapidly when tested in the flooded stage. Thus, PCP-degrading microorganisms present in the soil survived the transfer to the laboratory and were most active when placed in an environment to which they were adapted.

A summary of the literature values for the persistence of PCP in soil is presented in Table 10. The persistence ranged between 22 days and 5 years. The 5-year value obtained by Hetrick (1952) was from dry soil sealed in a jar and probably does not represent a realistic evaluation of the environmental half-life. Thus, PCP can be considered moderately persistent under most conditions.

Numerous degradation products have been isolated from PCP-treated soil. Ide et al. (1972) identified 2,3,4,5-, 2,3,5,6-, 2,3,4,6-tetrachlorophenol; 2,4,5- and 2,3,5-trichlorophenol; 3,4- and 3,5-dichlorophenol; and 3-chlorophenol. Similar products were obtained by Kuwatsuka and Igarashi (1975), who also identified pentachloroanisole as a PCP degradation product. This reaction is reversible and pentachloroanisole can subsequently degrade back to PCP. Demethylation and methylation of phenolic groups in biological systems are well known (Williams, 1959). Ide et al. (1972) found 2,3,4,5-, 2,3,5,6- and 2,3,4,6-tetrachloroanisoles; 2,3,5-trichloroanisole; 3,4- and 3,5-dichloroanisoles; and 3-chloroanisole as methylated products of PCP in incubated soil. Based on the results obtained from these investigations, Matsunaka and Kuwatsuka (1975) proposed the soil degradation pathway shown in Figure 2. An excellent review of the parameters important for degradation of pentachlorophenol in soil can be found in a review by Kaufman (1978).

Many types of bacteria and fungi are capable of degrading pentachlorophenol, including Pseudomonas, Aspergillus, Trichoderma, and Flavobacterium. Chu and Kirsch (1972) isolated a bacterial culture by continuous flow enrichment that was capable of metabolizing PCP as a sole source of organic carbon. The morphological and physiological

Table 10. Degradation of pentachlorophenol in soil (USDA 1980).

Degradation parameter	Soil type	Special conditions	Time
90% degradation	Arable layer in rice fields (11 soils)	60% water 25% water	Approx. 50 days Approx. 30 days
	Forest red-yellow soil sublayer	60% water 25% water	No degradation in 50 days
90% degradation	Wooster silt loam	7.5 kg/ha penta, optimum conditions for microbial growth	Approx. 22 days
Complete	Dry soil	Sealed in air-tight container	> 5 years
Effect on growth of corn and cucumbers	Fertile sandy loam	Air-dried Medium water Water saturated	> 2 months 2 months 1 month
90% degradation	Mature paddy soil	Low organic content	1 month

Table 10. (continued)

Degradation parameter	Soil type	Special conditions	Time
Complete degradation	Dunkirk silt loam	Aerated, aqueous soil suspension	Approx. 72 days
Complete degradation	Paddy soil	Soil perfusion	21 days
Complete degradation	Warm, moist soil	--	> 12 months
98% degradation	Permeable soil	Composted with sludge from wood-treating plant	205 days

characteristics of the organisms suggest a relationship to the saprophytic coryneform bacteria. Chu and Kirsch (1973) established that the organism was responsive to enzyme induction with PCP as the inducer. Lesser induction occurred with 2,4,6-trichlorophenol. The degradation products resulting from the metabolism of PCP by this organism were not characterized.

Kirsch and Etzel (1973) derived a microbial population capable of rapid PCP degradation from a soil sample obtained on the grounds of a wood products manufacturer. When fully acclimated, the populations were dosed with 100 mg/liter of PCP and 68% of the PCP was degraded in 24 hours. These cultures were most effective when the PCP was the sole source of carbon.

Watanable (1973) reported penta degradation in soil samples perfused with 40 mg/liter PCP. Bacteria isolates capable of PCP decomposition were derived from a soil perfusion enrichment culture. Degradation and complete dechlorination occurred after 2 to 3 weeks of incubation. The bacterium was characterized as a Pseudomonas sp. or an organism from a closely related genus. Tetrachlorodihydroxyphenols and their monoethyl ethers were tentatively identified as a metabolic product of PCP by Aspergillus sp. (Cserjesi, 1972). A soil bacterium isolated by Suzuki and Nose (1971) was capable of degrading PCP. The major metabolites were pentachloroanisole and dimethyl ether; a minor metabolite was tetrachlorohydroquinone.

More recently Edgehill (Edgehill et al., 1984) isolated a soil bacterium capable of utilizing PCP as a sole source of carbon. The organism was a member of the coryneform group of bacteria, probably the genus Arthrobacter.

It is clear that bacteria and fungi capable of degrading PCP exist in nature. However, the number of species and their population may be limited. In most cases where rapid degradation of PCP by microorganisms has been demonstrated, the source of inoculum was from areas where PCP had been used for a long time.

Creosote Components

The major components of creosote are the polycyclic aromatic hydrocarbons (PAH's) with trace amounts of phenols and azaarenes. A wide range of soil organisms, including bacteria, fungi, cyanobacteria (blue-green algae), and eukaryotic algae, have been shown to have the enzymatic capacity to oxidize PAH's. Prokaryotic organisms, bacteria, and cyanobacteria use different biodegradation pathways than the eukaryotes, fungi, and algae, but all involve molecular oxygen.

Tausson (1950) first demonstrated that several PAH's, including naphthalene, anthracene, and phenanthrene, can serve as substrates for some soil organisms and are "completely" metabolized. Groenewegen and Stolp (1981) isolated microorganisms that can use the compounds mentioned above as their sole C source. However, they could show degradation of some of the less-water-soluble PAH's, such as benz(a)anthracene and benzo(a)pyrene (BaP), only when the PAH's were mixed with soil, water, and a substance to stimulate growth of oxygenase-active organisms. Shabad et al. (1971) discussed a number of experiments that demonstrated bacterial degradation of BaP in soil. They reported 50-80% destruction of BaP over a period of "several" days by bacteria in soil contaminated with shale oil containing high concentrations (up to 20,000 $\mu g/kg$) of BaP. Shabad et al. also found

that the capacity of bacteria to degrade BaP increased with BaP content in the soil and that microflora of soil contaminated with BaP were more active in metabolizing BaP than those in "clean" soil. Cerniglia and Crow (1981) demonstrated the metabolism of naphthalene, biphenyl, and BaP by a number of different species of yeast, some of which were previously reported in high numbers in oil-polluted soils. Cerniglia and Gibson (1979) reported the degradation of BaP by a filamentous fungus, and Dodge and Gibson (1980) demonstrated the degradation of benz(a)anthracene by the same fungal species.

Cerniglia and Gibson (1979) reported that the metabolites formed during the degradation of BaP by a fungus were very similar to those formed during BaP metabolism in mammals. Such metabolites are probably responsible for the carcinogenicity of BaP. However, Shabad et al. (1971) reported that extracts of a medium containing BaP were less carcinogenic to mice (Mus spp.) after microbial degradation than before degradation. A more complete review of earlier research (before 1970) on microbial oxidation of PAH's was presented by Gibson (1972). Biochemical pathways for the degradation of a number of PAH's by soil microorganisms have been proposed by Fernley and Evans (1958), Evans et al. (1965) and Gibson et al. (1975). One proposed mechanism for the reaction is shown in Figure 3.

Generally, rates of degradation for PAH compounds decrease as the molecular weight increases; rates of degradation are faster in soil than water; and overall rates of degradation are faster where there is an acclimated bacteria population (Herbes et al., 1980). These observations had also been made earlier (Sims and Overcash, 1983).

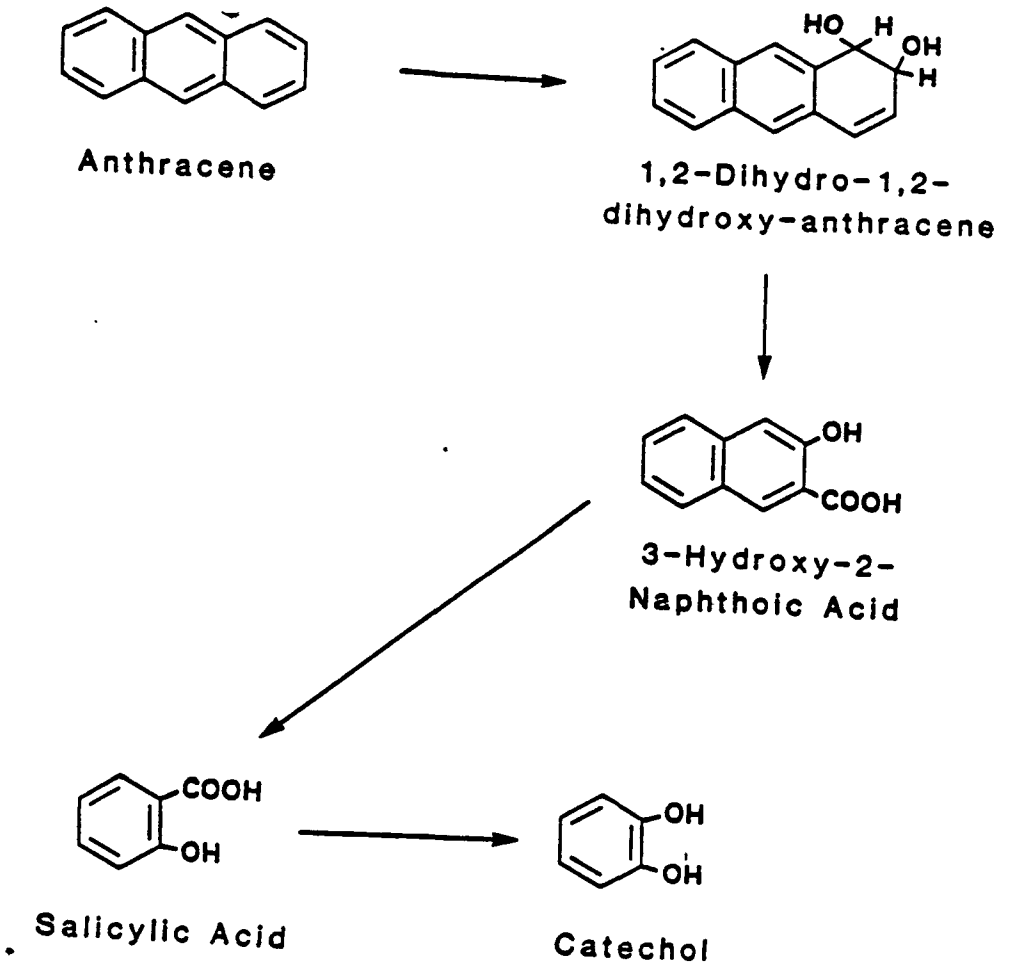


Figure 3. Proposed mechanism for the microbiological degradation of anthracene (Rogoff 1961).

Compounds such as naphthalene, phenanthrene, and anthracene, which are readily metabolized, are relatively water soluble, while persistent PAH's, such as chrysene and benzo(a)pyrene, have a lower water solubility (Table 11). Exceptions exist with pyrene and fluoranthene in that these compounds are more soluble than anthracene and yet have not been found by some researchers (Groenewegen and Stolp, 1981) to be 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 (Overcash and Pal, 1979).

Two sets of studies were recently completed by Bulman et al. (1985) to assess PAH loss from soil. In the first, a mixture containing levels of 5 and 50 mg/kg of eight PAH's [naphthalene, phenanthrene, anthracene, fluoranthene, pyrene, benzo(a)anthracene, chrysene and benzo(a)pyrene] was added to soil and the concentration of each compound was monitored with time. In the second experiment, ^{14}C labeled benzo(a)pyrene and anthracene were added to unacclimated agriculture soil in biometer flasks. The distribution of ^{14}C as volatile, adsorbed, and degraded products was determined in sterilized and biologically active soil. In the first set of studies, naphthalene, phenanthrene, anthracene, pyrene, and fluoranthene disappeared rapidly from soil during an initial period of 200 days or less. A loss of 94 to 98 percent occurred during this period and approximated first-order kinetics, in some cases following a lag period. With the exception of anthracene, the first-order kinetic rate constants were the same for 5 and 50 $mg \cdot kg^{-1}$ additions of PAH. Following the initial period, the remaining 2-6 percent of the added PAH

Table 11. Kinetic parameters describing rates of degradation of PAH and phenolic compounds in soil systems (Sims and Overcash 1983, ERT 1985b).

Substance	Initial Concentration (µg/g soil)	k (day^{-1})	1/2 Life (days)	Reference
Phenol	500	0.693	1.0	Medvedev & Davidov (1972)
Phenol	500	0.315*	2.2*	Medvedev & Davidov (1972)
2,4-dimethylphenol	500	0.35-0.69	1-2	Medvedev & Davidov (1972)
4,6-dinitro-o-cresol	--	0.023	30	Versar, Inc. (1979)
2,4-dinitrophenol	5-50	0.025	28	Overcash et al. (1982)
2,4-dinitrophenol	20-25	0.099-0.23	3-7	Sudharkar-Barik & Sethunathan (1978)
4-nitrophenol	--	0.043	16	Verschuerer (1977)
Pentachlorophenol	--	0.018	28	Murthy et al. (1979)
Naphthalene	7	5.78	0.12	Herbes & Schwall (1978)
Naphthalene	7	0.005*	125*	Herbes & Schwall (1978)
Naphthalene	7	0.173	4+	Herbes & Schwall (1978)
Acenaphthylene	0.57	0.039	18	Sims (1982)
Acenaphthylene	57	0.035	20	Sims (1982)
Anthracene	0.041	0.019	36	Sims (1982)
Anthracene	41	0.017	42	Sims (1982)
Phenanthrene	2.1	0.027	26	Groenewegen and Stolp (1976)
Phenanthrene	25,000	0.277	2.5+	Sisler and Zobell (1947)
Benz(a)anthracene	0.12	0.046*	15.2*	Herbes & Schwall (1978)
Benz(a)anthracene	3.5	0.007	102	Groenewegen & Stolp (1976)
Benz(a)anthracene	20.8	0.003	231	Gardner et al. (1979)
Benz(a)anthracene	25.8	0.005	133	Gardner et al. (1979)
Benz(a)anthracene	17.2	0.008	199	Gardner et al. (1979)
Benz(a)anthracene	22.1	0.006	118	Gardner et al. (1979)
Benz(a)anthracene	42.6	0.003	252	Gardner et al. (1979)

Table 11. (continued)

Substance	Initial Concentration (µg/g soil)	k (day^{-1})	1/2 Life (days)	Reference
Benz(a)anthracene	72.8	0.004	196	Gardner et al. (1979)
Benz(a)anthracene	0.07	0.005	134	Sims (1982)
Benz(a)anthracene	0.10	0.005	142	Sims (1982)
Benz(a)anthracene	0.15	0.005	154	Sims (1982)
Benz(a)anthracene	7	0.016	43	Sims (1982)
Fluoranthene	3.9	0.016	44	Groenewegen and Stolp (1976)
Fluoranthene	18.8	0.004	182	Gardner et al. (1979)
Fluoranthene	23.0	0.007	105	Gardner et al. (1979)
Fluoranthene	16.5	0.005	143	Gardner et al. (1979)
Fluoranthene	20.9	0.006	109	Gardner et al. (1979)
Fluoranthene	44.5	0.004	175	Gardner et al. (1979)
Fluoranthene	72.8	0.005	133	Gardner et al. (1979)
Pyrene	3.1	0.020	35	Groenewegen and Stolp (1976)
Pyrene	500	0.067	10.5	Medvedev and Davidov (1972)
Pyrene	5	0.231	3	Medvedev and Davidov (1972)
Chrysene	4.4	0	-	Groenewegen and Stolp (1976)
Chrysene	500	0.067	10.5	Medvedev and Davidov (1972)
Chrysene	5	0.126	5.5	Medvedev and Davidov (1972)
Benz(a)pyrene	0.048	0.014	50*	Herbes and Schwall (1978)
Benz(a)pyrene	0.01	0.001	694*	Herbes and Schwall (1978)
Benz(a)pyrene	3.4	0.012	57	Groenewegen and Stolp (1976)
Benz(a)pyrene	9.5	0.002	294	Gardner et al. (1979)
Benz(a)pyrene	12.3	0.005	147	Gardner et al. (1979)
Benz(a)pyrene	7.6	0.003	264	Gardner et al. (1979)
Benz(a)pyrene	17.0	0.002	420	Gardner et al. (1979)
Benz(a)pyrene	32.6	0.004	175	Gardner et al. (1979)

Table 11. (continued)

Substance	Initial Concentration (µg/g soil)	k (day^{-1})	1/2 Life (days)	Reference
Benz(a)pyrene	1.0	0.347	2+	Shabad et al. (1971)
Benz(a)pyrene	0.515	0.347	2+	Shabad et al. (1971)
Benz(a)pyrene	0.00135	0.139	5+	Shabad et al. (1971)
Benz(a)pyrene	0.0094	0.002	406*	Shabad et al. (1971)
Benz(a)pyrene	0.545	0.011	66*	Shabad et al. (1971)
Benz(a)pyrene	28.5	0.019	37*	Shabad et al. (1971)
Benz(a)pyrene	29.2	0	--	Shabad et al. (1971)
Benz(a)pyrene	9,100	0.018	39+	Sims et al. (1987)
Benz(a)pyrene	19.5	0.099	7+	Sims et al. (1987)
Benz(a)pyrene	19.5	0.139	5+	Sims et al. (1987)
Benz(a)pyrene	19.5	0.231	3+	Sims et al. (1987)
Benz(a)pyrene	130.6	0.173	4+	Sims et al. (1987)
Benz(a)pyrene	130.6	0.116	6+	Sims et al. (1987)
Dibenz(a,h)anthracene	9,700	0.033	21+	Sims et al. (1987)
Dibenz(a,h)anthracene	25,000	0.039	18+	Sisler and Zobell (1947)

*Low temperature (<15°C)
+High temperature (>25°C)

was lost at a much reduced rate, and the first-order rate constants tended to be higher with the 50 $mg \cdot kg^{-1}$ addition than the 5 $mg \cdot kg^{-1}$ addition of PAH.

Losses of only 22 to 88 percent were observed for benzo(a)anthracene, chrysene, and benzo(a)pyrene, and only one kinetic period was identified within the 400-day incubation period. With chrysene, the first-order kinetic rate constants were the same at the 5 and 50 $mg \cdot kg^{-1}$ levels of addition; however, for benzo(a)anthracene and benzo(a)pyrene the rate constants differed. The disappearance of benzo(a)anthracene approximated first-order kinetics; however, a zero-order kinetics was found for the disappearance of benzo(a)pyrene and chrysene.

The mechanisms of disappearance of anthracene and benzo(a)pyrene were assessed in a second set of studies using ^{14}C labeling. The results indicated that biological activity was responsible for some of the loss of anthracene from soil; however, binding to soil solids and volatilization (either as anthracene or as metabolites) were identified as the major loss mechanisms. Identification of loss mechanisms for benzo(a)pyrene was less successful due to the small amount of benzo(a)pyrene that disappeared during the incubation period. Binding of benzo(a)pyrene to soil solids appeared to be the major mechanism involved, while microbial transformation of the compound was minimal.

Tortensson and Stenstrom (1986) have cautioned, however, that an indirect measurement of mineralization such as liberated $^{14}CO_2$ from a ^{14}C-labeled compound may not always be reliable. They recommend that the rate of transformation of a substance be defined by direct

measurement of its disappearance. Liberation of labeled CO_2 may not be concurrent with transformation because transformed compounds may not be further degraded to labeled CO_2 during the time frame of the study.

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. This process involves the 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. In a study by McKenna and Heath (1976), the co-metabolism of refractory PAH compounds in the presence of two- and three-ring PAH compounds was investigated. The degradation of pyrene, 3,4-benzpyrene, 1,2-benzanthracene, and 1,2,5,6-dibenzanthracene in the presence and in the absence of phenanthrene was measured. Separate cultures of Flavobacterium and Pseudomonas were maintained in the presence of each of the PAH compounds. Both Flavobacterium and Pseudomonas exhibited negligible utilization of the refractory PAH compounds in the absence of phenanthrene. However, Flavobacterium, in the presence of phenanthrene, was able to significantly degrade all four test compounds. Co-metabolism by Pseudomonas was not observed. In a similar experiment PAH compound degradation by a mixed culture was measured. For each PAH compound studied, one container of inoculum received naphthalene as a growth substrate while a second container received phenanthrene as a growth substrate. Cometabolism of pyrene, 1,2-benzanthracene, 3,4-benzpyrene, and 1,2,5,6-dibenzanthracene by the mixed culture was exhibited in the presence of either naphthalene or phenanthrene.

The fate of PAH compounds in terrestrial systems has been reviewed by Sims and Overcash (1983), Edwards (1983), and Cerniglia (1984). These reviews present additional information on PAH degradation.

The types of phenols present in creosote in general are more readily degraded than PAH's or PCP. The effect of phenols on soil microorganisms is dependent on the soil concentration or amount added (Overcash and Pal, 1979). At low doses (0.01-0.1 percent of soil weight), the phenol serves as an available substrate, and there is an increase in microbial numbers. As the dose level is increased (0.1-1.0 percent of soil weight), an increasingly strong inhibitory or sterilizing effect is noted. At these levels, a partial sterilization occurs in which there is a depression in microbial numbers, but not a complete die-off. After a period of time, microbes adapt or phenol is lost through sorptive inactivation or volatilization and a regrowth of population occurs.

BIOACCUMULATION/TOXICITY OF PCP AND CREOSOTE

Plant/Animal Uptake of PCP

Information on the uptake and translocation of PCP by plants is limited, and there is no information on the metabolism of PCP by plants. Jaworski (1955) found less than 0.01 mg/kg PCP in cottonseed oil of field-grown plants sprayed with ^{14}C-PCP. Similarly, Miller and Aboul-Ela (1969) could not detect PCP in cottonseed kernels of open bolls on sprayed plants. However, in contrast to Jaworski (1955), they found some translocation of PCP or a possible metabolite within the plants. PCP residues definitely existed in seed from bolls that were closed at the time of treatment. Miller and Aboul-Ela (1969) also

observed the movement of ^{14}C-labeled PCP in the first two leaves of cotton within 1 hour of treatment. After 8 hours, radioactivity was distributed through all the veins of treated leaves, but there was no movement of radioactivity out of the treated leaves even after 8 days.

Hilton et al. (1970) studied the distribution of radioactivity in sugar cane following either foliage or root application of ^{14}C-PCP. With leaf application, 100% of the radioactivity was found in the treated leaf after 2 weeks. After 8 weeks, 84% of the activity was in the treated leaf with minor amounts in all plant parts except roots. Root application was studied by growing plants in a nutrient solution containing ^{14}C-PCP for 4 weeks. Approximately 90% of the original radioactivity was recovered from the plants after 4 weeks, with over 99% found in the root system.

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. Koss and Koransky (1978) demonstrated the formation of PCP from hexachlorobenzene in rats, mice, hens, and trout. Hexachlorobenzene occurs widely in the environment, and low-level residues are frequently encountered in animal tissues. The rate of PCP formation from hexachlorobenzene is slow compared to the rate of PCP elimination. Thus, the levels of hexachlorobenzene encountered in tissues are not sufficient to account for the levels of PCP generally found.

Many phenols undergo conjugation reactions in animals (Williams, 1959). 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.

Approximately 40% of the ^{14}C-labeled PCP given to mice and rats was excreted unchanged in the urine (Ahlborg et al., 1974). ^{14}C-tetrachlorohydroquinone accounted for 5% of the excreted radioactivity in rats and 24% in mice. Larsen et al. (1972) found that 50% of the radioactivity of orally administered ^{14}C-PCP was excreted in the urine of rats in 24 hours and 68% was excreted in 10 days. Between 9 and 13% was excreted in the feces. Tissue analysis showed small amounts of ^{14}C activity in all tissues, with the highest level in liver, kidneys, and blood. In blood, 99% of the radioactivity was in the serum. A two-compartment urinary excretion pattern was proposed that had a 10-hour half-life for the first 2 days, followed by a 102-day half-life.

Braun et al. (1976) studied the pharmacokinetics and metabolism of PCP in rats and monkeys. Excretion of ^{14}C from the labeled PCP was mainly through the urine in both species. In the monkeys, only PCP was found; while in rats, PCP, tetrachlorohydroquinone, and the glucuronide conjugate of PCP were found. Residues were high in liver, kidneys, and blood, thus agreeing with Larsen et al. (1972). It was suggested that there was reversible binding of PCP to blood proteins. The half-life ranged from 13 to 17 hours in rats and from 72 to 84 hours in monkeys. This work failed to confirm the presence of the long half-life

compartment suggested by Larsen et al. (1972). 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

The widespread use of PCP as an antimicrobial agent and the likelihood of commercial products being contaminated with certain highly toxic polychlorinated dibenzo-p-dioxins and dibenzofurans necessitate a review of the toxicological information currently available. Although this review is primarily concerned with data on PCP per se, available data on commercial samples are included for comparative purposes.

Oral Toxicity--The LD_{50} for PCP in male rats has been reported as 78 mg/kg (Deichmann et al., 1942), 90 mg/kg (Gabrilevskaya and Laskina, 1964), 146 mg/kg and 205 mg/kg, the last being Dowicide EC-7 (USDA, 1980). For the female rat, it was 135 mg/kg (Dow Chemical Co. Summary, 1969) and 175 mg/kg (EC-7) (Gaines, 1969).

The LD_{50} for mice was reported as 130 $\pm$ 9.5 mg/kg (Pleskova and Bencze, 1959); for rabbits, 100-130 mg/kg (Deichmann et al., 1942); for guinea pigs, 250 mg/kg (Gabrilevskaya and Laskina, 1964); and for swine, 120 mg/kg (Harrison, 1959). Dreisbach (1963) has estimated an LD_{50} dose for man to be as low as 29 mg/kg.

These data suggest that PCP has moderate acute oral toxicity, but that the LD_{50} 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.

Skin Absorption--When PCP in an organic solvent was applied to rabbit skin under occlusion for 24 hours, 200 mg/kg was lethal, but 100 mg/kg and 50mg/kg were not (Dow 1969). The LD_{50} for rats has been reported as 96 mg/kg, 105 mg/kg, and 320 mg/kg (Demidenko, 1966; Noakes and Sanderson, 1969; Gaines, 1969) and that for mice as 261 $\pm$ 39 mg/kg (Pleskova and Bencze, 1959).

Subcutaneous Injection--The LD_{50} for rats was 100 mg/kg, for rabbits 70 mg/kg (5% in olive oil) (Deichmann et al., 1942), and for mice 63 $\pm$ 3.2 mg/kg (Pleskova and Bencze, 1959).

Intravenous Injection--The lowest dose of PCP reported to kill rabbits was 22 mg/kg (Kehoe et al., 1939) when it was instilled as a 1% aqueous sodium pentachlorophenate.

Inhalation--Exposure to 5 mg/l dust for one hour did not kill male and female rats (Reichhold Chemicals, 1974). Demidenko (1969) reported the LD_{50} by inhalation to be 225 mg/kg for rats and 355 mg/kg for mice. The exposure concentration and the calculations to arrive at the LD_{50} dose were not given in the abstract. Workers have reported that the dust is irritating to the mucous membrane of the nose and throat.

Irritancy Tests--Rabbit eyes exposed to solid material showed slight conjunctival and slight iritic congestion. Exposure of rabbit skin under occlusion caused minimal irritation on intact skin and slightly more on abraded skin (Dow, 1969).

Commercial samples have produced chloracne in the rabbit ear bioassay; whereas, the purified material has not. Positive reactions have been produced by topical or oral application (Johnson et al., 1973). Allergic contact dermatitis has not been a problem in handling the chemical.

Mutagenic-Cytotoxic Potential--PCP has not shown mutagenic activity in the Ames test (Anderson et al., 1972), the host-mediated assay (Buselmaier et al., 1973), or the sex-linked lethal test on drosophila (Vogel and Chandler, 1974).

Teratogenic and Embryotoxic Potential--PCP did not cause deformities, but it was highly embryolethal and embryotoxic following oral administration to rats of 15, 30, or 50 mg/kg per day on days 6-15 of gestation. No effects were produced at 5 mg/kg (Schwetz and Gehring, 1973; Schwetz et al., 1974). Purified PCP, with its low nonphenolic content, was slightly more toxic than the commercial grade (Schwetz et al., 1974).

Oral administration of PCP to golden Syrian hamsters at levels ranging from 1.25 to 20 mg/kg daily from days 5 to 10 of gestation resulted in fetal deaths and/or resorptions in three of six test groups. PCP was found in the blood and fat of the fetuses (Hinkle, 1973).

Pregnant rats (Charles River-CD Strain) were given 60 mg/kg of labeled PCP on days 8 through 13 of gestation and were sacrificed on the 20th day. Only a small amount of PCP crossed the placental barrier and only slight teratogenic effects were noted (Larsen et al., 1975).

One of the concerns in use of technical grade PCP is the presence of trace contaminants including the chlorinated dioxins and furans. Limited toxicity data on two of the dioxins present in technical grade PCP--hexachlorodibenzo-p-dioxin and octachlorodibenzo-p-dioxin--are given in Table 12.

Table 12. Toxicity of various dioxin isomers to experimental animals.[a]

Compound	LD-50	Teratogenic Effect[b]	Embryo Toxicity[b]	Acnegenic Effect[b]
	mg/kg Body wt.	mg/kg/day	mg/kg/day	mg/liter
2,7-Dichlorodibenzo-p-dioxin	1,000	None	None	None
2,3,7.8-Tetrachlorodibenzo-p-dioxin	0.0006	0.001	0.00003	0.00004
Hexachlorodibenzo-p-dioxin	100	0.1	0.0001	0.01
Octachlorodibenzo-p-dioxin	1,000	None	100	None

[a] Source: Modified from Alliot, 1975.

[b] Values denote the lowest dosage or concentration which gives rise to the corresponding effect.

Plant/Animal Uptake of Creosote

There is very little information on bioaccumulation/toxicity of creosote (Brown et al., 1984). The limited information on plant/animal uptake has recently been reviewed by the USDA (1980). There is considerably more information on the bioaccumulation/toxicity of the individual PAH's found in creosote. Edwards (1983), in a comprehensive review of PAH's in the terrestrial environment, summarizes the sources and fate of these compounds in the environment. His conclusions regarding the uptake, translocation, and metabolism in vegetation were

1) Some terrestrial plants can take up PAH's through their roots and/or leaves and translocate them to various other plant parts.

2) Uptake rates are dependent on PAH concentrations, solubility, phase (vapor or particulate), molecular size, support media anchoring the plants, and plant species.

3) PAH's may concentrate in certain plant parts more than in other parts.

4) Some PAH's can be catabolized by plants.

The health effects of the major PAH constituents in creosote are summarized in Table 13.

Table 13. Health effects of chemical constituents of creosote (U.S. EPA 1984).

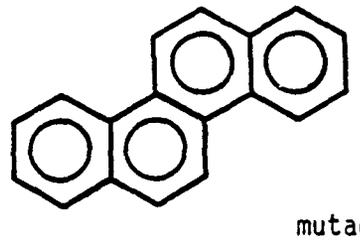
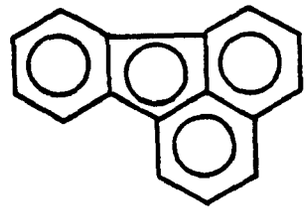
Compound	Effect
1. Unsubstituted 6-membered aromatic ring systems	
	
chrysene	mutagenic initiator, carcinogenic
pyrene	co-carcinogen [with fluoranthene benzo(a)pyrene], mutagenic
benzo(a)pyrene	mutagenic carcinogenic, fetotoxic, teratogenic
benzo(e)pyrene	carcinogenic, mutagenic
benzo(a)anthracene	mutagenic, carcinogenic
benzo(a)phenanthrene	initiator, mutagenic
naphthalene	inhibitor
phenanthrene	initiator, mutagenic
anthracene	mutagenic
dibenzanthracene	mutagenic
acenaphthene	mutagenic
triphenylene	mutagenic
2. Unsubstituted aromatic ring systems containing 5-numbered rings	
	
fluoranthene	co-carcinogenic, initiator, mutagenic
benz(j)fluoranthene	carcinogenic, mutagenic
fluorene	mutagenic

Table 13. (continued)

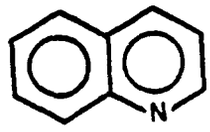
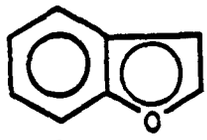
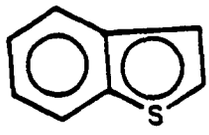
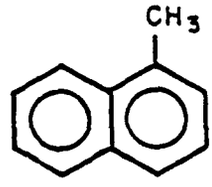
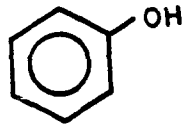
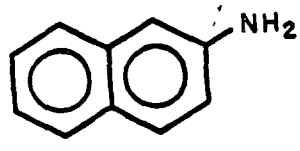
Compound	Effect
3. Heterocyclic nitrogen bases	
	
quinoline	carcinogenic
indole	mutagenic
benzocarbazoles	carcinogenic
isoquinoline	mutagenic
1-methyl isoquinoline	possibly carcinogenic
3-methyl isoquinoline	possibly carcinogenic
5-methyl quinoline	possibly carcinogenic
4-methyl quinoline	possibly carcinogenic, mutagenic
6-methyl quinoline	possibly carcinogenic
5-methyl isoquinoline	possibly carcinogenic
7-methyl isoquinoline	possibly carcinogenic
6-methyl isoquinoline	possibly carcinogenic
1,3-dimethyl isoquinoline	possibly carcinogenic
acridine	mutagenic
carbazole	mutagenic
4. Heterocyclic oxygen and sulfur compounds	
coumarone 	No effects found in the literature for this structural class.
thionaphthene 	
5. Alkyl substituted compounds 	
1-methyl naphthacene	mutagenic
2-methyl anthracene	mutagenic
methyl fluoranthene	possibly carcinogenic
1-methyl naphthalene	inhibitor
2-methyl naphthalene	inhibitor
ethyl naphthalene	inhibitor
2,6-dimethyl naphthalene	inhibitor
1,5-dimethyl naphthalene	inhibitor
2,3-dimethyl naphthalene	accelerator
2,3,5-trimethyl naphthalene	inhibitor
2,3,6-trimethyl naphthalene	accelerator
methyl chrysene	initiator
1,4-dimethyl phenanthrene	initiator, mutagenic
1-methylphenanthrene	mutagenic

Table 13. (continued)

Compound	Effect
6. Hydroxy compounds	
	
phenol	promoter
p-cresol	promoter
o-cresol	promoter
m-cresol	promoter
7. Aromatic amines	
	
2-naphthylamine	carcinogenic
p-toluidine	carcinogenic
o-toluidine	carcinogenic
2,4-xylidine	carcinogenic
2,5-xylidine	carcinogenic
8. Paraffins and naphthenes	
$\left[-CH_2-\right]_n$	(n is large, e.g., greater than 15)
No effects found in the literature for this structural class.	

SECTION 4

EXPERIMENTAL SECTION

INTRODUCTION

This project was started on February 15, 1985 and consists of 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, 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. The following is a summary of the experimental methods for the characterization phase and the laboratory treatability phase for four of the eight sites. A detailed methodology is presented in Appendix A.

SITE SELECTION CRITERIA

Eight wood-treating sites were selected in the southeastern United States, each having a different soil type. At each plant a site was selected approximately 1/2 to 1 acre in area which could be used for the field evaluation. The sites were selected using the following criteria:

1. Site must have a source of sludges, preferably a separate source for PCP and creosote sludges.
2. Site should have low level exposure to PCP and creosote so that an acclimated bacteria population is available, but there should not be high levels of contamination within or below the treatment zone.

3. There must be a method of collecting and disposing of run-off water from the site.

SITE, SOIL, AND SLUDGE CHARACTERIZATION

During the first visit to each plant site, one or more potential demonstration sites were selected and composite soil samples were collected. Soil samples were collected at 0-6 inches and 6-12 inches and subsequently analyzed for creosote and pentachlorophenol. Based on the chemical analysis, microbial population, and initial observations, one potential field evaluation site was selected at each plant location.

A second visit to each site was made in order to do a thorough site assessment as well as more complete chemical and microbiological characterization of the site soil. Soil samples were collected using a systematic sampling plan. The exact number of samples depended on the size of the area. The samples were then composited and analyzed.

A third visit was made to each site for soil evaluation. Soil profiles were examined at each site in freshly excavated pits and they were described and sampled using standard methods (Soil Survey Staff, 1951). 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. Detailed analytical procedures used at each site are given in Appendix A.

LABORATORY TREATABILITY STUDIES

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

Phase II involved laboratory treatability studies for determining rates of degradation/transformation, soil transport properties of creosote and pentachlorophenol, and toxicity of the water-soluble fraction of waste soil mixtures. As a preliminary experiment to determine possible loading rates, sampling times, refine experimental techniques, and compare results in different soils using a common waste, an initial set of degradation/transformation experiments was conducted by applying, at 1% of the soil dry weight, a mixture of technical-grade pentachlorophenol and creosote at 200 and 2000 ppm, respectively (standard mixture) to a sample of each site's soil. Samples of each soil were taken at 0, 30, 60, and 90 days for chemical and microbiological analysis.

Transformation/Degradation of Site Specific Sludges: Experiment II

The second part of the laboratory degradation studies involved studying the kinetic rates using soil and sludges from the same site. The objective was to assess the feasibility of land treatment of the sludge present at a site in the soil at that site. Three sludge loading rates were tested, and the study was replicated three times. Soil samples were taken at 0, 30, 60, and 90 days for chemical and microbiological analysis.

SECTION 5

RESULTS AND DISCUSSION

SITE AND SOIL CHARACTERIZATION

The eight sites investigated represented very diverse soil, geologic, climatic, and environmental conditions. The 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 as shown in Table 14.

The sites encompassed several geomorphic landforms ranging from fluvial terraces to upland ridges. Soil parent materials varied from sandy Coastal Plain sediments and silty Peoria loess to granite gneiss residuum as shown in Table 15.

A brief discussion of the pertinent characteristics of each site is presented in the following paragraphs.

Grenada, MS--Moderately well-drained Loring soil comprises the site. Silt content exceeded 70% in the surface horizons and increased at deeper depths in the lower sola. Maximum clay content occurred in the Btx1 horizon at depths of 16-26 inches. The fragipan horizons (Btx1, Btx2) had very low hydraulic conductivity and tended to perch water above the fragipan during the wetter winter and spring months. These layers greatly reduced downward leacheate movement. The surface horizon was strongly acid and pH levels increased with depth. Acidity (H) decreased in the deeper horizons as pH increases. Exchangeable Al levels reached a maximum level in the Btx1 horizon at depths of 16-26 inches, comprising 30.7% of the cation exchange capacity. Mg and Ca

Table 14. Site location in Major Land Resource Areas.

Site	MLRA
Grenada, MS	134 - Southern MS Valley Silty Uplands
Gulfport, MS	152A - Eastern Gulf Coast Flatwoods
Wiggins, MS	133A - Southern Coastal Plain
Columbus, MS	133A - Southern Coastal Plain
Atlanta, GA	136 - Southern Piedmont
Wilmington, NC	153A - Atlantic Coast Flatwoods
Meridian, MS	133A - Southern Coastal Plain
Chattanooga, TN	128 - Southern Appalachian Ridges and Valleys

Table 15. Overall field evaluation site soil composition.

Site	Soil	Sand[a]	Silt[a]	Clay[a]
Grenada, MS	Grenada silt loam	16.06	70.17	13.77
Gulfport, MS	Smithton	57.04	28.88	14.08
Wiggins, MS	McLaurin sandy loam	72.55	24.16	3.29
Columbus, MS	Latonia loamy sand	80.03	16.42	3.55
Atlanta, GA	Urban land	--	--	--
Wilmington, NC	Urban land	91.5	6.0	2.5
Meridian, MS	Stough sandy loam	60.2	31.4	8.4
Chattanooga, TN	Urban land complex	13.01	46.77	40.22

[a]These samples were taken from the surface to a depth of 5 inches.

were the dominant metallic cations with levels increasing with depth. Electrical conductivity levels were low indicating no salt toxicity problems. Maximum total S content of 0.018% occurred in the surface horizon. Water holding capacity was high in the surface horizon. The clay fraction of the surface soil was dominated with kaolinite and mica (illite) with illite increasing in the subsoil and kaolinite decreasing.

Gulfport, MS--The site had 7 to 8 inches of mixed fill-soil overlying a poorly drained Smithton sandy loam soil. The site had slow runoff and subsoils that were moderately slow permeable subsoils. Maximum clay content (24.6%) occurred in the fill-soil capping and abruptly decreased to 3% in the subjacent, original surface horizon. Calcareous shells were common in the fill-soil, and were also mixed to the 7- to 12-inch layer. The calcareous materials were part of the fill-soil placed over the natural soil. The water table is near the surface during the wetter months. The added calcareous materials resulted in high levels of exchangeable Ca to depths of 38 inches which produced high base saturation levels and high pH levels (6.3 to 7.7). Low levels of Na were detected. Electrical conductivity values reflected the influence of the calcareous materials. Cation exchange capacity values were less than 6 me/100 g below depths of 12 inches. Total S levels were low with a maximum of 0.018% occurring in the A horizon at depths of 7 to 12 inches. The soil had relatively high available water holding capacity. Kaolinite was the dominant clay mineral in the surface horizon and subsoil. The fill-soil capping contained small amounts of smectite.

Wiggins, MS--Deep, well-drained McLaurin sandy loam soils dominated this site. These soils had slow to medium runoff and moderate permeability. The soil was very strongly to strongly acid throughout the 60-inch solum. The soil was poly-genetic with two distinct clay maxima in the argillic horizon. Maximum clay content of 36.7% occurred at depths of 39 to 60 inches. The soil had low base saturation and cation exchange capacity, and electrical conductivity values reflected the low soluble salt content. The surface horizon had a high saturated conductivity value with variations in the subsoil due to the two clay maxima. The soil had low S contents with a maximum value occurring in the 39- to 60-inch horizon. The subsoil had low water holding capacity. Kaolinite was the dominant clay mineral in the surface and subsoil with lesser amounts of vermiculite-chlorite integrade.

Columbus, MS--A deep, well-drained sandy Latonia soil with moderately rapid permeable subsoil and slow runoff comprised the study area. The soil had loamy sand textures to a depth of 40 inches where gravelly sands occur. A maximum clay content of 7.5% occurred at depths of 17 to 25 inches. The soil was medium to strongly acid throughout the profile. Higher Ca levels were present in the upper horizons due to prolonged additions of leacheate from treated-wood products. The soil had elevated organic matter contents in the surface horizon from cultural additions which resulted in higher cation exchange capacity. Electrical conductivity values reflected the low soluble-salt content, with the highest levels in the surface horizon due to the added leacheate. Low contents of Mg, K, and Na were present throughout the

profile. The highest S content of 0.095 occurred in the surface horizon. Kaolinite was the dominant clay mineral in the surface and subsoil horizons.

Atlanta, GA--The site had been truncated and the soil solum removed by cutting which exposed the subsoil C horizon and weathered saprolite parent material. The surface had accumulated organic carbon from additions of material in the pole yard. The partially weathered saprolite had high bulk density values and was firm in place, but tends to be loose when disturbed. The saprolite had low saturated hydraulic conductivity. The loose upper horizon had sandy loam textures. Clay content was less than 6% in the material sampled. The material was very strongly acid in the lower depths. Calcium is the dominant exchangeable cation. Cation exchange capacities are very low reflecting the low clay content. Kaolinite was the dominant clay mineral.

Wilmington, NC--The site was comprised of made land with 1 to 3 feet of sandy fill material over poorly drained sediments. The water table appeared to be affected by tidal fluctuations of the adjacent Cape Fear River. A water table at 21 inches and saturated sands below limited the depth of sampling. The soil had sand textures throughout the profile with a maximum clay content of 2.5% occurring in the surface horizon. The profile was moderately alkaline to neutral. Organic carbon had accumulated in the surface horizons from added materials. Calcium was the dominant exchangeable cation with low contents of other bases. Cation exchange capacity was essentially due to the added humus material, and value were less than 1 me/100 g at depths below 10 inches. Higher electrical conductivities occur in the upper layers analyzed due to added materials. The soil material had extremely high permeability

with saturated hydraulic values of 34 inches/hr at depths below 10 inches. The material had low water-holding capacity below the surface. A complex mineral suite comprised the small clay fraction with kaolinite the dominant mineral.

Meridian, MS--Somewhat poorly drained Stough soils comprised the study area. These soils had slow runoff, moderately slow permeability, and were formed in thick beds of fluvial sediments. The soil had sandy loam upper horizons and loamy textured subsoils. Maximum clay content of 21.8% occurred at depths of 23 to 35 inches. Slightly firm, brittle horizons occurred at depths below 15 inches which tend to perch water during wet periods. The soil was strongly to very strongly acid throughout the profile. Acidity and calcium dominated the cation exchange complex. Kaolinite dominated the clay fraction of the surface and subsoil.

Chattanooga, TN--The site was located in a soil area mapped as urban land. The surface layer (0-4 inches) was a compacted mixture of limestone gravel and silty clay. The subsoil was a thick argillic horizon of silty clay and silty clay loam textures with slightly firm consistency. The surface horizon was mildly alkaline due to the limestone gravel additions, and the underlying profile was very strongly acid. The site was well-drained with no evidence of free water at depths of 90 inches. The soil had high bulk density and low saturated hydraulic conductivity. Available water-holding capacity was low. Maximum clay content of 49.2% occurred at depths of 38 to 44 inches. Exchangeable Ca, base saturation, and electrical conductivity were influenced by the limestone gravel in the surface horizon. Exchangeable

aluminum comprised a significant proportion of the cation exchange complex in the subsurface horizons. The soil had a complex clay mineral suite dominated by kaolinite.

The general soil type and the amounts of sand, clay, and silt for each location are summarized in Table 15.

Chemical Analysis of Wood-Treating Chemicals in the Soil

One of the main concerns in selecting a field evaluation site for this study was levels of background chemicals in the soil. Chemical analyses of the amount of pentachlorophenol, creosote, and octachlorodibenzo-p-dioxin at various depths are summarized in Tables 16-18. Grenada, Gulfport, and Columbus had no detectable levels of pentachlorophenol below 10 inches. The Wiggins site had pentachlorophenol down to 20 inches, while the other sites had detectable levels down to 60 inches or to ground water. The detection limit for pentachlorophenol in soil was 27 ppb. Soil from Grenada, Gulfport, Atlanta, Meridian, Wiggins, and Chattanooga had no detectable levels of PAH's below 10 inches while those from Columbus and Wilmington had PAH's down to 20 inches or deeper. Octachlorodibenzo-p-dioxin levels at the soil surface (0-6 inches) varied from none detected to 2.38 ppm (Table 18). The soil and sludge detection limits for the individual PAH's, OCDD, and for PCP are given in Appendix A.

Microbial plate counts for soils at each site are presented in Table 19. Counts of bacteria were done on potato dextrose agar (PDA), alone, or with various additives. This data provides an approximate number of total soil bacteria and fungi, as well as the number of soil bacteria that can tolerate or utilize creosote or pentachlorophenol.

Table 16. Soil concentration of PCP at the proposed field evaluation sites.

Depth (inches)	Grenada	Gulfport	Wiggins	Columbus	Atlanta	Wilmington	Meridian	Chattanooga
	Pentachlorophenol concentration (ppm in soil)							
0-10	ND[a]	0.112	0.389	ND	20.64[b]	1.418	0.129[b]	0.288[b]
10-20	ND	ND	0.017	ND	0.088	0.218	0.090	0.099
20-30	ND	ND	ND	ND	0.130	0.209[c]	0.096	0.090
30-40	ND	ND	ND	ND	0.147	--	0.104	0.074
40-50	ND	ND	ND	ND	0.319	--	0.053	0.057
50-60	ND	ND	ND	ND	--	--	--	--

[a]ND = Not Detected.

[b]This value is the average of 4 values, two samples were taken at 0-6 inches, and two were taken from 6-10 inches.

[c]The maximum depth that soil could be collected at this site was 20 to 23 inches due to the high levels of ground water.

Table 17. Soil concentration of PAH's at the proposed field evaluation sites.

Depth (inches)	Grenada	Gulfport	Wiggins	Columbus	Atlanta	Wilmington	Meridian	Chattanooga
	Total polycyclic aromatics in soil[a] (ppm)							
0-10	ND[b]	1.78	0.33	195.9 [c]	110.81[d]	193.3	ND	121.76[g]
10-20	ND	ND	ND	27.45[e]	ND	40.55	ND	ND
20-30	ND	ND	ND	ND[f]	ND	43.94[f]	ND	ND
30-40	ND	ND	ND	ND	ND	--	ND	ND
40-50	ND	ND	ND	ND	ND	--	ND	ND
50-60	ND	ND	ND	ND	ND	--	ND	--

[a]The total concentration of 16 polycyclic aromatic hydrocarbons (naphthalene, 2-methylnaphthalene, 1-methylnaphthalene, biphenyl, acenaphthylene, acenaphthene, dibenzofuran, fluorene, phenanthrene, anthracene, carbazole, fluoranthene, pyrene, 1,2-benzanthracene, chrysene, benzo(a)pyrene, benzo(ghi)perylene.
[b]Normal 16 PAH compounds were detectable in the soil sample.
[c]Sample taken between 0 to 6 inches.
[d]Sample taken between 6 to 16 inches.
[e]Sample taken between 16 to 26 inches.
[f]Analysis done between 20 to 23 inches (ground water was at 23 inches and below).
[g]Average value of 4 samples (2 samples taken from 0 to 6 inches and 2 samples taken from 6 to 10 inches).
[b]ND = Not Detected.

Table 18. Soil concentration of octachlorodibenzo-p-dioxin at the proposed land treatment sites (0 to 6 inches).

	Octachlorodibenzo-p-dioxin (ppm)[a]
Grenada	0.12 ± 0.22
Gulfport	0.37 ± 0.24
Wiggins	0.077 ± 0.19
Columbus	0.034 ± 0.22
Atlanta	2.13 ± 0.34
Wilmington	ND[b]
Meridian	ND
Chattanooga	0.36 ± 0.57

[a]These samples represent soil at 0 to 6 inches and are the average of a minimum of three replicates ± standard deviation.

[b]ND = Not Detected.

Table 19. Microbial plate counts at proposed field evaluation sites.[a]

Site	Soil Depth	Types of media (counts/gram) PDA	PDAA	PDA + creosote	PDA + penta-chlorophenol	PDA + creosote & pentachlorophenol
Atlanta	0-6"	900,000	60,000	700,000	450,000	450,000
Chattanooga	0-6"	473,000	23,000	203,000	30,000	6,000
Columbus	0-6"	290,000	120,000	220,000	20,000	10,000
Grenada	0-6"	1,000,000	180,000	600,000	110,000	125,000
Gulfport	0-6"	1,800,000	100,000	1,000,000	90,000	100,000
Meridian	0-6"	1,683,000	141,000	1,600,000	466,000	250,000
Wiggins	0-6"	1,200,000	80,000	500,000	80,000	80,000
Wilmington	0-6"	763,000	40,000	523,000	166,000	66,000

[a]Each figure represents an average of three replications. The values were obtained by adding 0.1 mg of soil diluted with 9.9 mg of sterile soil to each plate.

Table 20. Nitrogen and phosphorous at the eight selected sites.[a]

	Grenada	Gulfport	Wiggins	Columbus	Atlanta	Wilmington	Meridian	Chattanooga
	ppm							
Total Nitrogen	1709	1999	1150	1598	1501	1231	2990	2000
Total Phosphorous	310	292	255	338	254	597	315	237

[a]Based on dry weight.

The nitrogen and phosphorous contents for the soil at each site are given in Table 20.

Sludge Characterization

Each plant site had different types of sludges. Six of the plants had open lagoons of creosote and/or pentachlorophenol; one site had three lagoons which were segregated into pentachlorophenol, pentachlorophenol in a heavy oil, and creosote; two other plants had no lagoons but had areas of dried sludge and contaminated soil (see Table 21).

The water content, total organic and inorganic materials, pH, and total organic carbon are summarized in Table 22. Water contents of these samples varied from 26.6 to 74.58%. The total organic material ranged from 8.96 to 68.0%. The pH varied from 3.00 to 7.20. The more acidic sites contained large amounts of PCP. The total organic carbon varied from 4.02 to 49.79%. The wide variation in inorganic solids is not surprising since these sludges are stored in large open lagoons. The pH is related to the concentration of PCP in sludge and probably is also affected by the soil pH. The high levels of organic materials are mainly the heavy oils used to dissolve PCP for treating wood and the aliphatic fraction found in creosote.

Total phenolics, oil and grease, nitrogen phosphorus, and chloride content of the sludges are summarized in Table 23. Concentrations of pentachlorophenol and polycyclic aromatic hydrocarbons in the sludges are given in Table 24. A more detailed list of the individual concentration of PAH's in each sludge is given in Table 25.

Table 21. Characteristics of the eight sites used in this study.

Site location	Size & age of plant	Preservative used	Number & type of lagoons
Grenada, MS	100 acres 78 years old	Both pentachloropenol and creosote	Lagoons are closed; contaminated soil and sludge are present
Gulfport, MS	100 acres 80 years old	Both pentachlorophenol (65%) and creosote (35%)	Large lagoon of mixed preservatives and contaminated soil
Wiggins, MS	100 acres 15 years old	Both pentachlorophenol (60%) and creosote (40%)	Individual lagoons of 1) pentachlorophenol, 2) pentachlorophenol in heavy oil, and 3) creosote
Columbus, MS	--	Creosote (100%)	Contaminated soil and lagoon
Atlanta, GA	15 acres 63 years old	Both pentachlorophenol (80%) and creosote (20%)	Contaminated soil and lagoon
Wilmington, NC[a]	--	Both pentachlorophenol and creosote	Lagoons are closed but contaminated soil is available
Meridian, MS	125 acres 61 years old	Both pentachlorophenol (25%) and creosote (75%)	Large lagoon and contaminated soil available
Chattanooga, TN	76 acres 62 years old	Creosote (100%)	Enclosed lagoons and contaminated soil

[a]This site has been an active land farming site for 1 1/2 years.

Table 22. Composition of the sludges.[a]

	Water content (%)	Total organic materials (%)	Inorganic solids (%)	pH	Total organic carbon (%)
Grenada	74.58	24.31	1.11	6.30	7.37
Gulfport	30.62	68.00	1.38	4.80	22.50
Wiggins #1[b]	36.07	40.58	23.35	3.00	37.85
Wiggins #2[c]	31.56	26.02	42.42	3.50	49.45
Wiggins #3[d]	36.52	27.80	35.68	5.70	36.03
Columbus	34.44	61.11	4.45	5.90	49.79
Atlanta	69.10	23.76	7.14	5.00	25.33
Wilmington	26.60	8.96	64.44	7.20	4.02
Meridian	48.27	50.00	1.73	4.00	31.96
Chattanooga	67.35	15.74	16.91	7.10	14.61

Table 23. Chemical composition of the sludges.[a]

Site	Total phenolics (%)	Oil and grease (%)	Nitrogen (ppm)	Phosphorous (ppm)	Inorganic chloride content (ppm)
Grenada	.0041	9.74	7562	236	267
Gulfport	.0097	44.03	2949	506	440
Wiggins #1[b]	.0045	15.86	1119	446	361
Wiggins #2[c]	.0130	22.57	1141	477	753
Wiggins #3[d]	.0171	17.90	640	261	825
Columbus	.0224	44.60	2951	270	49
Atlanta	.0120	14.17	1730	316	278
Wilmington	.0007	0.44	1283	435	1138
Meridian	.0114	35.34	3621	213	220
Chattanooga	.0003	3.68	2090	417	28

[a]All data reported on the starting weight of sludge.
[b]Lagoon contains mainly pentachlorophenol.
[c]Lagoon contains mainly pentachlorophenol in a heavy oil.
[d]Lagoon contains mainly creosote.

Table 24. Concentration of PCP and total PAH's in each sludge sample.[a]

Site	Pentachlorophenol (ppm)	Polycyclic aromatic hydrocarbons[b] (ppm)	Octachloro-dibenzo-p-dioxin (ppm)
Grenada	6,699	96,078	23
Gulfport	5,656	101,023	215
Wiggins #1	29,022	20,463	114
Wiggins #2	30,060	47,075	125
Wiggins #3	1,893	114,127	21
Columbus	ND[c]	475,372	ND
Atlanta	51,974	119,546	160
Wilmington	ND	10,007	ND
Meridian	13,891	119,124	160
Chattanooga	ND	72,346	ND

[a]These values are the means of two replicates and are determined on a dry basis. All were determined by capillary column gas chromatography.

[b]Total of the 17 major polycyclic aromatic hydrocarbons found in creosote.

[c]ND = Not detected. See Appendix A for detection limits.

Table 25. Concentration of creosote and PCP in sludges from the selected sites[a] (μg/g dry weight).

	N	2Mn	1Mn	Bi	Ac	Ace	Di	Fl	Ph	An	Ca	Flu	Py	1,2B	Ch	Bz	Bzg
Grenada	67000	24150	13250	5850	5250	21500	17000	18000	43000	15000	3450	27000	19500	3250	5850	3600	5050
Gulfport	13500	14000	7450	3000	2635	10150	9600	10250	30000	7200	2100	17000	12500	2050	3650	1050	ND[b]
Wiggins #1	3400	2450	1400	535	215	1550	1300	1750	5000	2550	570	2150	1500	185	495	75	ND
Wiggins #2	10200	7450	4000	1900	1050	5550	6050	7450	21000	8150	2650	11500	7500	1300	2400	355	ND
Wiggins #3	17500	12000	6350	3500	2000	13000	11500	14000	34000	14500	4250	22500	19000	3850	6000	580	ND
Columbus	70500	29500	16500	10500	7650	31000	32500	34000	53000	23000	12500	49500	38000	12500	17000	3500	6850
Atlanta	39400	23000	11500	6600	2800	16500	16000	18000	45000	24500	9550	23000	15500	3400	5800	1100	8050
Wilmington	350	330	185	ND	ND	400	425	585	1550	1525	190	840	430	150	150	ND	ND
Meridian	16500	5350	2700	1650	1800	5150	6850	7350	29500	6550	2050	20000	11700	2200	4800	1350	550
Chattanooga	1200	815	585	445	ND	1230	1150	1415	5400	2200	870	3550	2100	200	200	ND	ND

N = Naphthalene
2Mn = 2-Methylnaphthalene
1Mn = 1-Methylnaphthalene
Bi = Biphenyl
Ac = Acenaphthylene
Ace = Acenaphthene
Di = Dibenzofuran
Fl = Fluorene
Ph = Phenanthrene
An = Anthracene
Ca = Carbazole
Flu = Fluoranthene
Py = Pyrene
1,2B = 1,2-Benzanthracene
Ch = Chrysene
Bz = Benzo(a)pyrene
Bzg = Benzo(ghi)perylene
Pentachlorophenol

[a]These values were obtained by GC/MS.

[b]ND = Not detected.

The results in Table 24 are obtained by capillary column gas chromatography while the results in Table 25 are obtained using GC/MS. Gas chromatography/mass spectrometry was also used to identify some of the minor constituents in the sludges. The results are summarized in Table 26.

The trace metal content of the sludges are summarized in Table 27. The most common metals found at most wood-treating plants are mixtures of copper chromium and arsenic salts. None of the sludges had high levels of chromium and arsenic. None of the sites had used fire retardant treatments ($ZnCl_2$).

LABORATORY TRANSFORMATION/DEGRADATION STUDIES

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

The results of Experiment I are shown in Figures 4 and 5 for the microbiological data, and Tables 28 through 36 for transformation/degradation rates.

Gulfport soil was able to transform all the PAH's analyzed, with only two (pyrene and benzo-a-pyrene) having relatively slow breakdown rates. Columbus soil was able to transform all PAH's but anthracene, though at somewhat slower rates than Gulfport for most PAH's. Gulfport and Columbus developed higher levels of acclimated organisms than the other sites, possibly accounting for the better transformation. Soil from the other sites transformed most of the lower molecular weight PAH's readily. 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 were perhaps the most recalcitrant.

Table 26. Minor components present in sludge.

Molecular weight	Possible compounds	Site location and number of isomers									
		Gr	Gp	Wi#1	Wi#2	3Wi#3	Co	At	Wm	Mr	Ch
156	dimethylnaphthalene, ethylnaphthalene	2	3	2	3	2	1	3	--	--	--
168	methyldiphenyl, methylacenaphthene, diphenylmethane	--	--	--	--	--	1	--	--	--	--
170	trimethylnaphthalene	--	1	2	--	--	--	--	--	--	--
182	dimethylbiphenyl, ethylbiphenyl, methyldibenzofuran, dimethylacenaphthene	--	--	--	--	2	2	1	--	--	--
184	dibenzothiopene, tetramethylnaphthalene	1	--	--	--	--	1	1	--	1	--
192	methylphenanthrene, methylanthracene, phenylindene	3	3	--	3	2	3	3	--	3	--
204	phenylnaphthalene, vinylphenanthrene, vinylanthracene	--	--	--	--	1	1	--	--	1	--
216	methylfluoranthene, methylpyrene, benzofluorene	2	2	--	1	1	2	2	--	2	--
218	benzonaphthofuran	1	1	--	1	--	1	1	--	1	--
226	benzo(ghi)fluoranthene, cyclopenta(cd) pyrene	--	--	--	--	--	--	1	--	1	--
252	benzo(k)fluoranthene, perylene, benzo(e) pyrene, benzo(abj)fluoranthene, and others	1	1	--	--	--	2	2	--	--	--
230	tetrachlorophenol	--	--	1	1	1	--	1	--	--	--

At = Atlanta, GA
Ch = Chattanooga, TN
Co = Columbus, MS
Gr = Grenada, MS
Gp = Gulfport, MS
Mr = Meridian, MS
Wi = Wiggins, MS
Wm = Wilmington, NC

Table 27. Concentration of metals in each sludge sample.

Site	Arsenic µg/g	Antimony µg/g	Barium µg/g	Berylium µg/g	Cadmium µg/g	Chromium µg/g	Cobalt µg/g	Lead µg/g	Mercury µg/g	Nickel µg/g	Selenium µg/g	Vanadium µg/g
Atlanta, GA	<.715	<1.50	<0.10	<0.100	<0.200	35.14	0.38	<2.00	0.012	5.82	<0.500	1.78
Chattanooga, TN	<0.500	<1.50	3.32	1.792	<0.200	26.48	<0.30	<2.00	0.008	27.26	0.612	3.64
Columbus, MS	<0.500	<1.50	<0.10	<0.100	0.251	13.11	<0.30	12.43	<0.001	14.97	<0,500	<0.50
Grenada, MS	<0.500	<1.50	<0.10	<0.100	<0.200	5.85	0.35	<2.00	<0.001	7.19	<0.500	<0.50
Gulfport, MS	0.647	<1.50	1.35	0.281	0.143	6.64	<0.30	<2.00	0.003	1.05	<0.500	4.87
Meridian, MS	<0.500	<1.50	<0.10	<0.100	0.160	1.16	<0.30	8.17	0.002	0.30	0.529	1.51
Wilmington, NC	2.491	<1.560	1.83	0.823	<0.200	20.60	<0.30	<2.00	0.003	7.66	<0.500	6.79
Wiggins, MS #1	0.562	<1.50	4.05	0.521	<0.200	6.65	5.84	<2.00	<0.001	4.85	<0.500	1.48
Wiggins, MS #2	<0.500	<1.50	0.14	0.493	<0.200	8.39	0.85	<2.00	<0.001	10.91	<0.500	<0.50
Wiggins, MS #3	<0.500	<1.50	<0.10	0.384	<0.200	25.34	2.32	<2.00	<0.001	17.00	<0.500	2.02

(a) Concentration of metals was determined by digestion method (302E, APHA Standard MTHDS, 16th Edition, pp. 148-149), and Inductively Coupled argon Plasma spectroscopy (ICP).

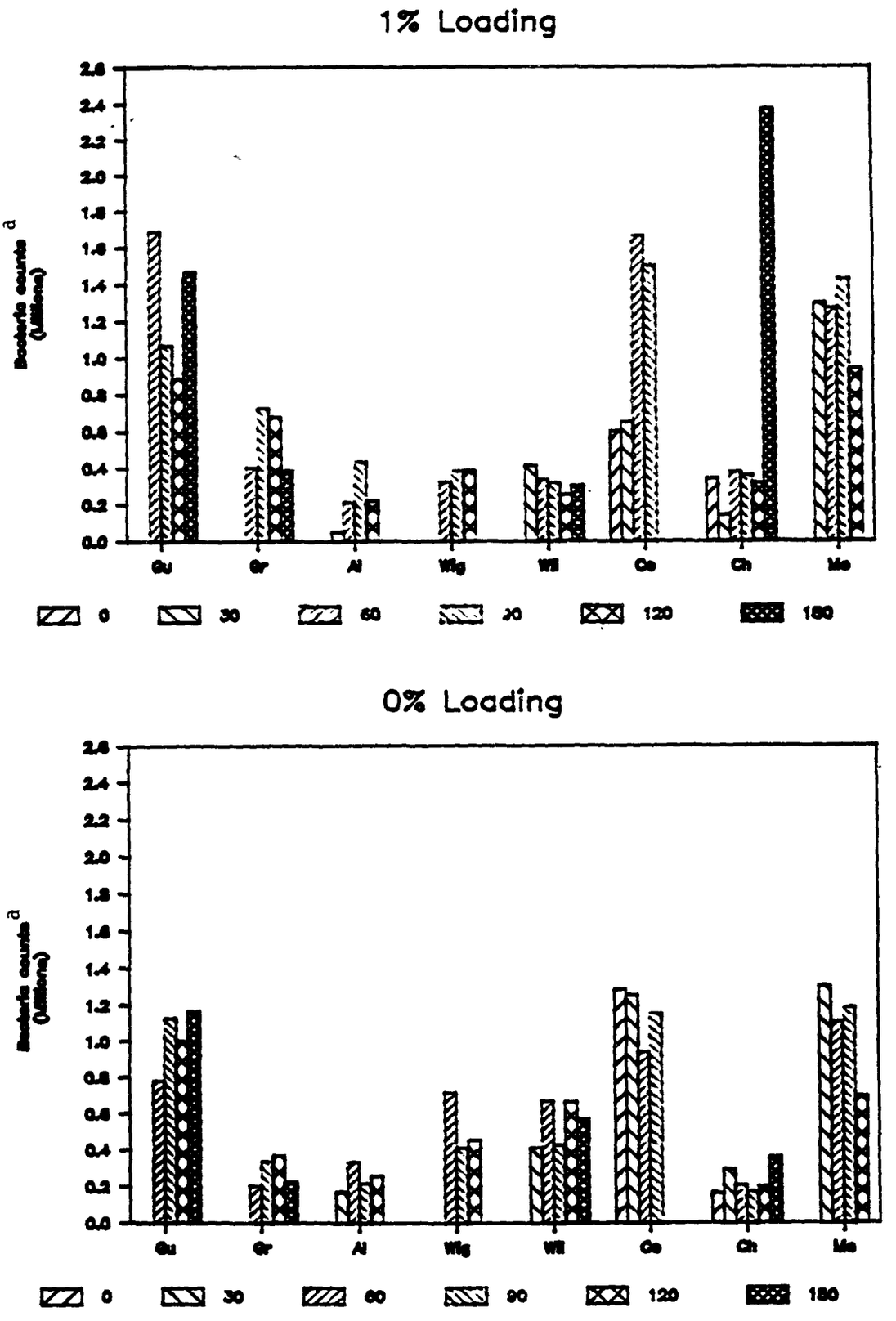


Figure 4. Bacteria counts from all eight sites at 1% and 0% loading rates after the final addition of the standard mixture.

[a]Total bacteria counts on PDA media.

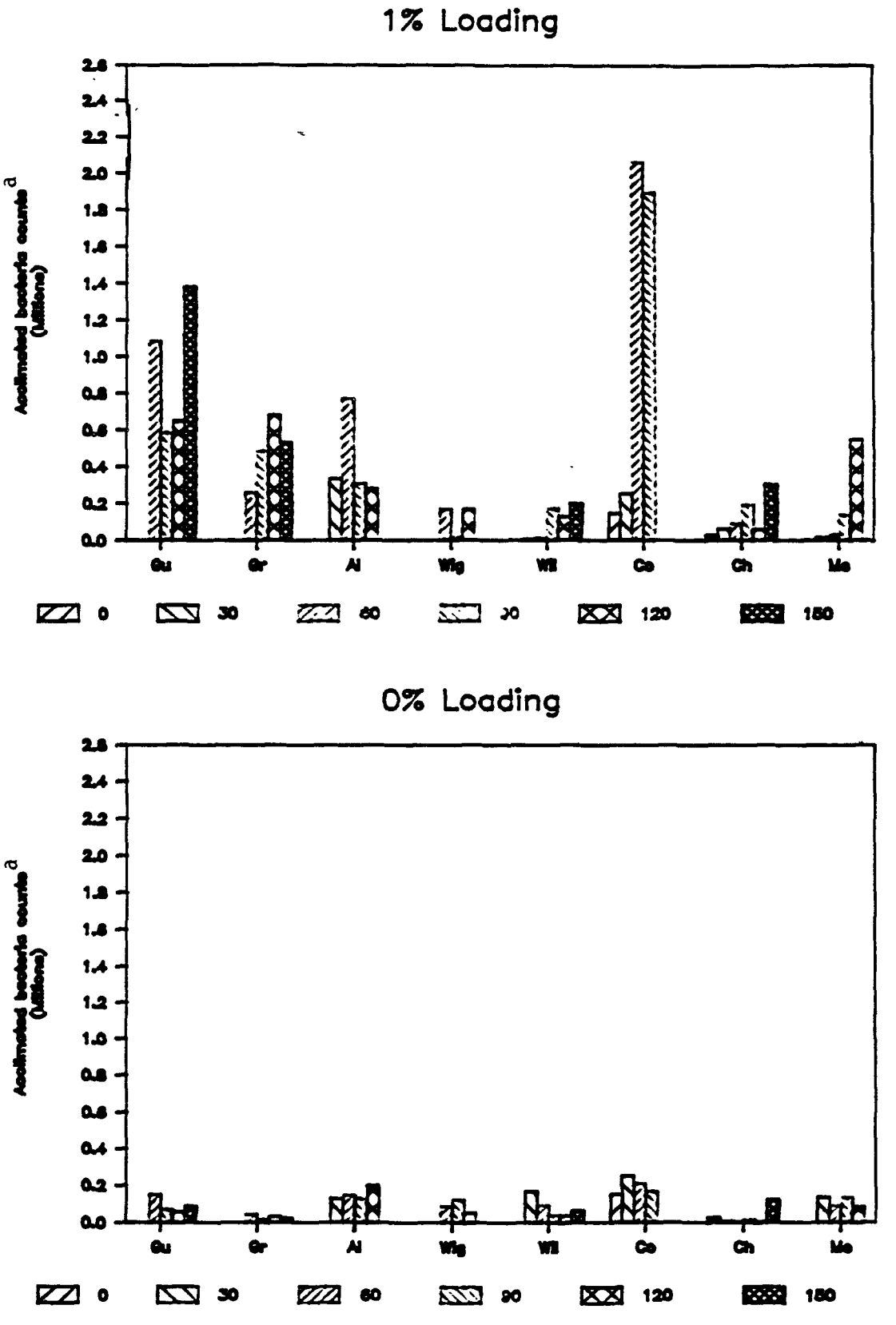


Figure 5. Acclimated bacteria counts from all eight sites at 1% and 0% loading rates after the final addition of the standard mixture.

[a]Bacteria acclimated to both PCP and creosote.

Table 28. Kinetic data for PAH degradation/transformation in Gulfport soils.

Compounds	Loading Dry Wt. (%)	K (day-1)	T 1/2 (days)
Naphthalene	1.0	-0.193	4
2-Methylnaphthalene	1.0	-0.190	4
1-Methylnaphthalene	1.0	-0.183	4
Biphenyl	1.0	-0.179	4
Acenaphthylene	1.0	-0.170	4
Acenaphthene	1.0	-0.200	3
Dibenzofuran	1.0	-0.192	4
Fluorene	1.0	-0.192	4
Phenanthrene	1.0	-0.203	3
Anthracene	1.0	-0.179	4
Carbazole	1.0	-0.184	4
Fluoranthene	1.0	-0.024	29
Pyrene	1.0	-0.001	1155
1,2 Benzanthracene	1.0	-0.194	4
Chrysene	1.0	-0.189	4
Benzo-a-pyrene	1.0	-0.002	365
Benzo-ghi-perylene	1.0	-0.174	4

Table 29. Kinetic data for PAH degradation/transformation in Columbus soils.

Compounds	Loading Dry Wt. (%)	K (day-1)	T 1/2 (days)
Naphthalene	1.0	-0.332	2
2-Methylnaphthalene	1.0	-0.328	2
1-Methylnaphthalene	1.0	-0.316	2
Biphenyl	1.0	-0.025	28
Acenaphthylene	1.0	-0.042	16
Acenaphthene	1.0	-0.014	50
Dibenzofuran	1.0	-0.063	11
Fluorene	1.0	-0.039	18
Phenanthrene	1.0	-0.061	11
Anthracene	1.0	NT[a]	NT
Carbazole	1.0	-0.009	81
Fluoranthene	1.0	-0.012	59
Pyrene	1.0	-0.012	58
1,2 Benzanthracene	1.0	-0.015	47
Chrysene	1.0	-0.014	49
Benzo-a-pyrene	1.0	-0.009	82
Benzo-ghi-perylene	1.0	-0.286	2

[a]NT = no transformation observed.

Table 30. Kinetic data for PAH degradation/transformation in Grenada soils.

Compounds	Loading Dry Wt. (%)	K (day-1)	T 1/2 (days)
Naphthalene	1.0	-0.191	4
2-Methylnaphthalene	1.0	-0.189	4
1-Methylnaphthalene	1.0	-0.181	4
Biphenyl	1.0	-0.178	4
Acenaphthylene	1.0	-0.235	3
Acenaphthene	1.0	-0.202	3
Dibenzofuran	1.0	-0.255	3
Fluorene	1.0	-0.258	3
Phenanthrene	1.0	-0.267	3
Anthracene	1.0	-0.241	3
Carbazole	1.0	-0.056	12
Fluoranthene	1.0	NT[a]	NT
Pyrene	1.0	-0.002	289
1,2 Benzanthracene	1.0	NT	NT
Chrysene	1.0	NT	NT
Benzo-a-pyrene	1.0	-0.006	116
Benzo-ghi-perylene	1.0	-0.166	4

[a]NT = no transformation observed.

Table 31. Kinetic data for PAH degradation/transformation in Chattanooga soils.

Compounds	Loading Dry Wt. (%)	K (day-1)	T 1/2 (days)
Naphthalene	1.0	-0.132	5
2-Methylnaphthalene	1.0	-0.193	4
1-Methylnaphthalene	1.0	-0.187	4
Biphenyl	1.0	-0.181	4
Acenaphthylene	1.0	-0.009	77
Acenaphthene	1.0	-0.010	72
Dibenzofuran	1.0	-0.013	52
Fluorene	1.0	-0.015	47
Phenanthrene	1.0	-0.011	63
Anthracene	1.0	-0.008	91
Carbazole	1.0	NT[a]	NT
Fluoranthene	1.0	-0.001	990
Pyrene	1.0	NT	NT
1,2 Benzanthracene	1.0	-0.002	3655
Chrysene	1.0	NT	NT
Benzo-a-pyrene	1.0	NT	NT
Benzo-ghi-perylene	1.0	-0.008	84

[a]NT = no transformation observed.

Table 32. Kinetic data for PAH degradation/transformation in Wilmington soils.

Compounds	Loading Dry Wt. (%)	K (day-1)	T 1/2 (days)
Naphthalene	1.0	-0.193	4
2-Methylnaphthalene	1.0	-0.196	4
1-Methylnaphthalene	1.0	-0.188	4
Biphenyl	1.0	-0.185	4
Acenaphthylene	1.0	-0.186	4
Acenaphthene	1.0	-0.013	52
Dibenzofuran	1.0	-0.137	5
Fluorene	1.0	-0.009	79
Phenanthrene	1.0	-0.010	68
Anthracene	1.0	NT[a]	NT
Carbazole	1.0	-0.180	4
Fluoranthene	1.0	-0.004	189
Pyrene	1.0	-0.001	1085
1,2 Benzanthracene	1.0	NT	NT
Chrysene	1.0	-0.004	158
Benzo-a-pyrene	1.0	-0.180	4
Benzo-ghi-perylene	1.0	-0.114	6

[a]NT = no transformation observed.

Table 33. Kinetic data for PAH degradation/transformation in Meridian soils.

Compounds	Loading Dry Wt. (%)	K (day-1)	T 1/2 (days)
Naphthalene	1.0	-0.185	4
2-Methylnaphthalene	1.0	-0.186	4
1-Methylnaphthalene	1.0	-0.179	4
Biphenyl	1.0	-0.186	4
Acenaphthylene	1.0	-0.174	4
Acenaphthene	1.0	-0.255	3
Dibenzofuran	1.0	-0.262	3
Fluorene	1.0	-0.258	3
Phenanthrene	1.0	-0.217	3
Anthracene	1.0	ND[a]	ND
Carbazole	1.0	-0.177	4
Fluoranthene	1.0	NT[b]	NT
Pyrene	1.0	NT	NT
1,2 Benzanthracene	1.0	NT	NT
Chrysene	1.0	NT	NT
Benzo-a-pyrene	1.0	NT	NT
Benzo-ghi-perylene	1.0	ND	ND

[a]ND = not detected.

[b]NT = no transformation observed.

Table 34. Kinetic data for PAH degradation/transformation in Atlanta soils.

Compounds	Loading Dry Wt. (%)	K (day-1)	T 1/2 (days)
Naphthalene	1.0	-0.181	4
2-Methylnaphthalene	1.0	-0.181	4
1-Methylnaphthalene	1.0	-0.178	4
Biphenyl	1.0	-0.171	4
Acenaphthylene	1.0	-0.164	4
Acenaphthene	1.0	-0.020	35
Dibenzofuran	1.0	-0.193	4
Fluorene	1.0	-0.254	3
Phenanthrene	1.0	-0.024	29
Anthracene	1.0	-0.175	4
Carbazole	1.0	-0.174	4
Fluoranthene	1.0	NT[a]	NT
Pyrene	1.0	NT	NT
1,2 Benzanthracene	1.0	NT	NT
Chrysene	1.0	NT	NT
Benzo-a-pyrene	1.0	NT	NT
Benzo-ghi-perylene	1.0	-0.167	4

[a]NT = no transformation observed.

Table 35. Kinetic data for PAH degradation/transformation in Wiggins soils.

Compounds	Loading Dry Wt. (%)	K (day-1)	T 1/2 (days)
Naphthalene	1.0	-0.318	2
2-Methylnaphthalene	1.0	-0.313	2
1-Methylnaphthalene	1.0	-0.301	2
Biphenyl	1.0	-0.294	2
Acenaphthylene	1.0	-0.299	2
Acenaphthene	1.0	-0.338	2
Dibenzofuran	1.0	-0.319	2
Fluorene	1.0	-0.329	2
Phenanthrene	1.0	-0.342	2
Anthracene	1.0	-0.309	2
Carbazole	1.0	-0.305	2
Fluoranthene	1.0	NT[a]	NT
Pyrene	1.0	NT	NT
1,2 Benzanthracene	1.0	-0.006	117
Chrysene	1.0	NT	NT
Benzo-a-pyrene	1.0	-0.302	2
Benzo-ghi-perylene	1.0	-0.284	2

[a]NT = no transformation observed.

Table 36. Kinetic data for PCP degradation/transformation in site soils.

Site	Loading Dry Wt. (%)	K (day-1)	T 1/2 (days)
Gulfport	1.0	-0.0107	64
Grenada	1.0	-0.0024	289
Columbus	1.0	NT[a]	NT
Atlanta	1.0	NT	NT
Wiggins	1.0	NT	NT
Chattanooga	1.0	-0.0027	259
Wilmington	1.0	-0.0022	320
Meridian	1.0	-0.0009	815

[a]NT = *no transformation observed.*

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

The results of this preliminary experiment indicate that all of the compounds studied can be transformed in soils at practically useful rates under the appropriate conditions. Microorganism counts of the type used in this experiment do not appear to be extremely accurate indicators of potential breakdown rates for particular compounds. However, there is some tendency for soils with higher populations of acclimated microorganisms to transform more of the different PAH's in creosote sludge at practically useful rates. This might be due to larger numbers of particular microorganisms or to a more diverse array of microbial species.

Since some of the soils exhibited no breakdown of particular PAH's, it would be desirable to test a range of loadings in subsequent experiments to see if lower loading rates might allow enhanced transformation in these soils.

Transformation/Degradation of Site Specific Sludges: Experiment II

The results of Experiment II are shown in Tables 37 through 42 for transformation/degradation kinetic data and Table 43 for microbiological data.

The total PAH breakdown was similar in soils from all four sites for similar loading concentrations. The individual PAH's can be divided into three groups; those with half lives of ten days or less, those with half lives of one hundred days or less, and those with half

Table 37. Kinetic data for PAH degradation/transformation in Columbus soils.

Compounds	Loading Dry Wt. (%)	K (day-1)	T 1/2 (days)	95% Confidence Interval			
				Lower Limit		Upper Limit	
				K (day-1)	T 1/2 (days)	K (day-1)	T 1/2 (days)
Naphthalene	0.33	-0.535	1	-0.573	1	-0.498	1
2-Methylnaphthalene	0.33	-0.536	1	-0.551	1	-0.521	1
1-Methylnaphthalene	0.33	-0.531	1	-0.537	1	-0.524	1
Biphenyl	0.33	-0.513	1	-0.520	1	-0.507	1
Acenaphthylene	0.33	-0.508	1	-0.517	1	-0.498	1
Acenaphthene	0.33	-0.187	4	-0.288	2	-0.086	8
Dibenzofuran	0.33	-0.202	3	-0.242	3	-0.162	4
Fluorene	0.33	-0.204	3	-0.241	3	-0.167	4
Phenanthrene	0.33	-0.039	18	-0.064	11	-0.014	50
Anthracene	0.33	-0.015	46	-0.020	35	-0.010	68
Carbazole	0.33	-0.020	35	-0.024	30	-0.016	43
Fluoranthene	0.33	-0.013	53	-0.024	29	-0.003	248
Pyrene	0.33	-0.003	231	-0.007	100	NT[a]	NT
1,2 Benzanthracene	0.33	-0.002	347	-0.006	122	NT	NT
Chrysene	0.33	-0.007	102	-0.011	61	-0.002	301
Benzo-a-pyrene	0.33	NT	NT	NT	NT	NT	NT
Benzo-ghi-perylene	0.33	ND[b]	ND	ND	ND	ND	ND

[a]NT = no transformation observed.

[b]ND = not detected.

Table 37. Kinetic data for PAH degradation/transformation in Columbus soils. (Continued)

Compounds	Loading Dry Wt. (%)	K (day-1)	T 1/2 (days)	95% Confidence Interval			
				Lower Limit		Upper Limit	
				K (day-1)	T 1/2 (days)	K (day-1)	T 1/2 (days)
Naphthalene	1.0	-0.049	14	-0.072	10	-0.025	28
2-Methylnaphthalene	1.0	-0.096	7	-0.169	4	-0.023	29
1-Methylnaphthalene	1.0	-0.207	3	-0.252	3	-0.162	4
Biphenyl	1.0	-0.149	5	-0.228	3	-0.070	10
Acenaphthylene	1.0	-0.074	9	-0.152	5	NT	NT
Acenaphthene	1.0	-0.028	25	-0.041	17	-0.014	50
Dibenzofuran	1.0	-0.325	2	-0.040	17	-0.025	28
Fluorene	1.0	-0.022	31	-0.031	22	-0.013	52
Phenanthrene	1.0	-0.027	25	-0.041	17	-0.014	50
Anthracene	1.0	NT	NT	NT	NT	NT	NT
Carbazole	1.0	-0.009	75	-0.015	48	-0.004	169
Fluoranthene	1.0	-0.002	289	-0.004	165	-0.001	1155
Pyrene	1.0	-0.002	433	-0.004	187	NT	NT
1,2 Benzanthracene	1.0	-0.001	578	-0.004	173	NT	NT
Chrysene	1.0	-0.002	365	-0.004	173	NT	NT
Benzo-a-pyrene	1.0	NT	NT	NT	NT	NT	NT
Benzo-ghi-perylene	1.0	NT	NT	NT	NT	NT	NT

Table 37. Kinetic data for PAH degradation/transformation in Columbus soils. (continued)

Compounds	Loading Dry Wt. (%)	K (day-1)	T 1/2 (days)	95% Confidence Interval			
				Lower Limit		Upper Limit	
				K (day-1)	T 1/2 (days)	K (day-1)	T 1/2 (days)
Naphthalene	3.0	-0.050	14	-0.066	11	-0.033	21
2-Methylnaphthalene	3.0	-0.029	24	-0.037	19	-0.021	33
1-Methylnaphthalene	3.0	-0.018	39	-0.024	28	-0.011	61
Biphenyl	3.0	-0.012	57	-0.023	30	-0.001	578
Acenaphthylene	3.0	-0.006	112	-0.008	89	-0.005	147
Acenaphthene	3.0	-0.006	124	-0.007	96	-0.004	169
Dibenzofuran	3.0	-0.005	147	-0.007	99	-0.002	301
Fluorene	3.0	-0.003	224	-0.004	169	-0.002	347
Phenanthrene	3.0	-0.001	578	-0.004	173	NT	NT
Anthracene	3.0	-0.004	173	-0.007	96	-0.001	866
Carbazole	3.0	-0.008	90	-0.011	62	-0.004	169
Fluoranthene	3.0	-0.007	107	-0.010	67	-0.003	267
Pyrene	3.0	-0.007	99	-0.011	62	-0.003	248
1,2 Benzanthracene	3.0	-0.002	315	-0.009	82	NT	NT
Chrysene	3.0	-0.007	98	-0.015	47	NT	NT
Benzo-a-pyrene	3.0	NT	NT	NT	NT	NT	NT
Benzo-ghi-perylene	3.0	-0.004	158	-0.011	61	NT	NT

Table 38. Kinetic data for PAH degradation/transformation in Grenada soils.

Compounds	Loading Dry Wt. (%)	K (day-1)	T 1/2 (days)	95% Confidence Interval			
				Lower Limit		Upper Limit	
				K (day-1)	T 1/2 (days)	K (day-1)	T 1/2 (days)
Naphthalene	0.33	-0.531	1	-0.560	1	-0.502	1
2-Methylnaphthalene	0.33	-0.529	1	-0.549	1	-0.508	1
1-Methylnaphthalene	0.33	-0.498	1	-0.519	1	-0.476	1
Biphenyl	0.33	-0.484	1	-0.486	1	-0.482	1
Acenaphthylene	0.33	-0.154	4	-0.279	2	-0.030	23
Acenaphthene	0.33	-0.163	4	-0.251	3	-0.075	9
Dibenzofuran	0.33	-0.160	4	-0.243	3	-0.077	9
Fluorene	0.33	-0.161	4	-0.257	3	-0.065	11
Phenanthrene	0.33	-0.126	5	-0.215	3	-0.038	18
Anthracene	0.33	-0.067	10	-0.142	5	NT[a]	NT
Carbazole	0.33	-0.255	3	-0.378	2	-0.132	5
Fluoranthene	0.33	-0.011	65	-0.014	51	-0.008	91
Pyrene	0.33	-0.010	68	-0.013	53	-0.007	95
1,2 Benzanthracene	0.33	-0.001	3466	-0.004	169	NT	NT
Chrysene	0.33	-0.004	173	-0.007	95	-0.001	866
Benzo-a-pyrene	0.33	-0.001	3466	-0.002	433	NT	NT
Benzo-ghi-perylene	0.33	-0.001	770	-0.006	126	NT	NT

[a]NT = no transformation observed.

[b]ND = not detected.

Table 38. Kinetic data for PAH degradation/transformation in Grenada soils. (continued)

Compounds	Loading Dry Wt. (%)	K (day-1)	T 1/2 (days)	95% Confidence Interval			
				Lower Limit		Upper Limit	
				K (day-1)	T 1/2 (days)	K (day-1)	T 1/2 (days)
Naphthalene	1.0	-0.568	1	-0.596	1	-0.540	1
2-Methylnaphthalene	1.0	-0.562	1	-0.581	1	-0.543	1
1-Methylnaphthalene	1.0	-0.532	1	-0.549	1	-0.515	1
Biphenyl	1.0	-0.510	1	-0.520	1	-0.501	1
Acenaphthylene	1.0	-0.518	1	-0.519	1	-0.516	1
Acenaphthene	1.0	-0.577	1	-0.577	1	-0.577	1
Dibenzofuran	1.0	-0.568	1	-0.573	1	-0.564	1
Fluorene	1.0	-0.579	1	-0.584	1	-0.575	1
Phenanthrene	1.0	-0.058	2	-0.076	9	-0.040	17
Anthracene	1.0	-0.026	27	-0.037	19	-0.016	45
Carbazole	1.0	-0.539	1	-0.555	1	-0.524	1
Fluoranthene	1.0	-0.019	36	-0.027	25	-0.011	65
Pyrene	1.0	-0.016	45	-0.023	30	-0.008	86
1,2 Benzanthracene	1.0	-0.007	107	-0.011	66	-0.002	285
Chrysene	1.0	-0.007	102	-0.011	64	-0.003	248
Benzo-a-pyrene	1.0	NT	NT	NT	NT	NT	NT
Benzo-ghi-perylene	1.0	NT	NT	NT	NT	NT	NT

Table 38. Kinetic data for PAH degradation/transformation in Grenada soils. (continued)

Compounds	Loading Dry Wt. (%)	K (day-1)	T 1/2 (days)	95% Confidence Interval			
				Lower Limit		Upper Limit	
				K (day-1)	T 1/2 (days)	K (day-1)	T 1/2 (days)
Naphthalene	3.0	ND[b]	ND	ND	ND	ND	ND
2-Methylnaphthalene	3.0	ND	ND	ND	ND	ND	ND
1-Methylnaphthalene	3.0	ND	ND	ND	ND	ND	ND
Biphenyl	3.0	-0.523	1	-0.524	1	-0.522	1
Acenaphthylene	3.0	ND	ND	ND	ND	ND	ND
Acenaphthene	3.0	ND	ND	ND	ND	ND	ND
Dibenzofuran	3.0	-0.006	116	-0.009	75	-0.003	248
Fluorene	3.0	ND	ND	ND	ND	ND	ND
Phenanthrene	3.0	-0.095	7	-0.351	2	NT	NT
Anthracene	3.0	-0.087	8	-0.348	2	NT	NT
Carbazole	3.0	ND	ND	ND	ND	ND	ND
Fluoranthene	3.0	-0.033	21	-0.049	14	-0.017	42
Pyrene	3.0	-0.033	21	-0.036	19	-0.029	24
1,2 Benzanthracene	3.0	-0.030	23	-0.038	18	-0.022	31
Chrysene	3.0	-0.010	72	-0.016	43	-0.010	72
Benzo-a-pyrene	3.0	NT	NT	NT	NT	NT	NT
Benzo-ghi-perylene	3.0	ND	ND	ND	ND	ND	ND

Table 39. Kinetic data for PAH degradation/transformation in Meridian soils.

Compounds	Loading Dry Wt. (%)	K (day-1)	T 1/2 (days)	95% Confidence Interval			
				Lower Limit		Upper Limit	
				K (day-1)	T 1/2 (days)	K (day-1)	T 1/2 (days)
Naphthalene	0.33	-0.542	1	-0.551	1	-0.533	1
2-Methylnaphthalene	0.33	-0.490	1	-0.513	1	-0.467	1
1-Methylnaphthalene	0.33	-0.490	1	-0.514	1	-0.466	1
Biphenyl	0.33	-0.166	4	-0.626	1	NT[a]	NT
Acenaphthylene	0.33	-1.551	1	-0.586	1	NT	NT
Acenaphthene	0.33	-0.523	1	-0.532	1	-0.515	1
Dibenzofuran	0.33	-0.544	1	-0.548	1	-0.537	1
Fluorene	0.33	-0.544	1	-0.548	1	-0.539	1
Phenanthrene	0.33	-0.136	5	-0.284	2	NT	NT
Anthracene	0.33	-0.180	4	-0.407	2	NT	NT
Carbazole	0.33	ND[b]	ND	ND	ND	ND	ND
Fluoranthene	0.33	-0.017	41	-0.036	19	NT	NT
Pyrene	0.33	-0.013	53	-0.022	32	-0.003	205
1,2 Benzanthracene	0.33	-0.005	139	-0.012	58	NT	NT
Chrysene	0.33	NT	NT	NT	NT	NT	NT
Benzo-a-pyrene	0.33	ND	ND	ND	ND	ND	ND
Benzo-ghi-perylene	0.33	ND	ND	ND	ND	ND	ND

[a]NT = no transformation observed.

[b]ND = not detected.

Table 39. Kinetic data for PAH degradation/transformation in Meridian soils. (continued)

Compounds	Loading Dry Wt. (%)	K (day-1)	T 1/2 (days)	95% Confidence Interval			
				Lower Limit		Upper Limit	
				K (day-1)	T 1/2 (days)	K (day-1)	T 1/2 (days)
Naphthalene	1.0	-0.108	6	-0.285	2	NT	NT
2-Methylnaphthalene	1.0	-0.096	7	-0.272	3	NT	NT
1-Methylnaphthalene	1.0	-0.091	8	-0.264	3	NT	NT
Biphenyl	1.0	-0.086	8	-0.026	27	NT	NT
Acenaphthylene	1.0	-0.083	8	-0.256	3	NT	NT
Acenaphthene	1.0	-0.101	7	-0.028	25	NT	NT
Dibenzofuran	1.0	-0.109	6	-0.289	2	NT	NT
Fluorene	1.0	-0.107	7	-0.286	2	NT	NT
Phenanthrene	1.0	-0.018	38	-0.044	16	NT	NT
Anthracene	1.0	-0.025	28	-0.161	4	NT	NT
Carbazole	1.0	-0.096	7	-0.273	3	NT	NT
Fluoranthene	1.0	NT	NT	NT	NT	NT	NT
Pyrene	1.0	NT	NT	NT	NT	NT	NT
1,2 Benzanthracene	1.0	-0.048	15	-0.146	5	NT	NT
Chrysene	1.0	-0.043	16	-0.142	5	NT	NT
Benzo-a-pyrene	1.0	NT	NT	NT	NT	NT	NT
Benzo-ghi-perylene	1.0	NT	NT	NT	NT	NT	NT

Table 39. Kinetic data for PAH degradation/transformation in Meridian soils. (continued)

Compounds	Loading Dry Wt. (%)	K (day-1)	T 1/2 (days)	95% Confidence Interval			
				Lower Limit		Upper Limit	
				K (day-1)	T 1/2 (days)	K (day-1)	T 1/2 (days)
Naphthalene	3.0	-0.606	1	-0.637	1	-0.574	1
2-Methylnaphthalene	3.0	-0.577	1	-0.586	1	-0.567	1
1-Methylnaphthalene	3.0	-0.557	1	-0.561	1	-0.553	1
Biphenyl	3.0	-0.516	1	-0.520	1	-0.512	1
Acenaphthylene	3.0	-0.539	1	-0.547	1	-0.531	1
Acenaphthene	3.0	-0.124	6	-0.267	3	NT	NT
Dibenzofuran	3.0	-0.070	10	-0.221	3	NT	NT
Fluorene	3.0	-0.082	8	-0.253	3	NT	NT
Phenanthrene	3.0	-0.086	8	-0.242	3	NT	NT
Anthracene	3.0	-0.124	6	-0.274	3	NT	NT
Carbazole	3.0	-0.585	1	-0.592	1	-0.579	1
Fluoranthene	3.0	-0.008	90	-0.019	37	NT	NT
Pyrene	3.0	NT	NT	NT	NT	NT	NT
1,2 Benzanthracene	3.0	-0.060	12	-0.206	3	NT	NT
Chrysene	3.0	-0.062	11	-0.216	3	NT	NT
Benzo-a-pyrene	3.0	NT	NT	NT	NT	NT	NT
Benzo-ghi-perylene	3.0	ND	ND	ND	ND	ND	ND

Table 40. Kinetic data for PAH degradation/transformation in Wiggins soils.

Compounds	Loading Dry Wt. (%)	K (day-1)	T 1/2 (days)	95% Confidence Interval			
				Lower Limit		Upper Limit	
				K (day-1)	T 1/2 (days)	K (day-1)	T 1/2 (days)
Naphthalene	0.33	-0.523	1	-0.529	1	-0.518	1
2-Methylnaphthalene	0.33	-0.518	1	-0.522	1	-0.514	1
1-Methylnaphthalene	0.33	-0.492	1	-0.505	1	-0.479	1
Biphenyl	0.33	-0.490	1	-0.496	1	-0.485	1
Acenaphthylene	0.33	-0.150	5	-0.565	1	-0.266	3
Acenaphthene	0.33	-0.270	3	-0.422	2	-0.119	6
Dibenzofuran	0.33	-0.271	3	-0.421	2	-0.121	6
Fluorene	0.33	-0.277	3	-0.434	2	-0.120	6
Phenanthrene	0.33	-0.178	4	-0.258	3	-0.097	7
Anthracene	0.33	-0.164	4	-0.248	3	-0.081	9
Carbazole	0.33	-0.174	4	-0.276	3	-0.072	10
Fluoranthene	0.33	-0.024	29	-0.035	20	-0.013	53
Pyrene	0.33	-0.122	6	-0.221	3	-0.023	30
1,2 Benzanthracene	0.33	-0.016	43	-0.106	7	NT[a]	NT
Chrysene	0.33	-0.260	3	-0.391	2	-0.129	5
Benzo-a-pyrene	0.33	ND[b]	ND	ND	ND	ND	ND
Benzo-ghi-perylene	0.33	ND	ND	ND	ND	ND	ND

[a] NT = no transformation observed.

[b] ND = not detected.

Table 40. Kinetic data for PAH degradation/transformation in Wiggins soils. (continued)

Compounds	Loading Dry Wt. (%)	K (day-1)	T 1/2 (days)	95% Confidence Interval			
				Lower Limit		Upper Limit	
				K (day-1)	T 1/2 (days)	K (day-1)	T 1/2 (days)
Naphthalene	1.0	-0.117	6	-0.267	3	NT	NT
2-Methylnaphthalene	1.0	-0.119	6	-0.263	3	NT	NT
1-Methylnaphthalene	1.0	-0.266	3	-0.412	2	-0.119	6
Biphenyl	1.0	-0.258	3	-0.391	2	-0.125	6
Acenaphthylene	1.0	-0.253	3	-0.384	2	-0.123	6
Acenaphthene	1.0	-0.017	41	-0.143	5	NT	NT
Dibenzofuran	1.0	-0.012	58	-0.029	24	NT	NT
Fluorene	1.0	-0.012	58	-0.032	22	NT	NT
Phenanthrene	1.0	-0.012	58	-0.310	2	NT	NT
Anthracene	1.0	NT	NT	NT	NT	NT	NT
Carbazole	1.0	NT	NT	NT	NT	NT	NT
Fluoranthene	1.0	-0.012	58	-0.023	30	-0.001	693
Pyrene	1.0	NT	NT	NT	NT	NT	NT
1,2 Benzanthracene	1.0	-0.001	693	-0.007	99	NT	NT
Chrysene	1.0	NT	NT	NT	NT	NT	NT
Benzo-a-pyrene	1.0	NT	NT	NT	NT	NT	NT
Benzo-ghi-perylene	1.0	-0.525	1	-0.544	1	-0.506	1

Table 40. Kinetic data for PAH degradation/transformation in Wiggins soils. (continued)

Compounds	Loading Dry Wt. (%)	K (day-1)	T 1/2 (days)	95% Confidence Interval			
				Lower Limit		Upper Limit	
				K (day-1)	T 1/2 (days)	K (day-1)	T 1/2 (days)
Naphthalene	3.0	-0.202	3	-0.315	2	-0.089	8
2-Methylnaphthalene	3.0	-0.201	3	-0.311	2	-0.091	8
1-Methylnaphthalene	3.0	-0.155	4	-0.280	2	-0.031	22
Biphenyl	3.0	-0.564	1	-0.565	1	-0.563	1
Acenaphthylene	3.0	-0.542	1	-0.548	1	-0.536	1
Acenaphthene	3.0	-0.040	17	-0.059	12	-0.022	32
Dibenzofuran	3.0	-0.025	28	-0.043	16	-0.007	99
Fluorene	3.0	-0.030	23	-0.048	14	-0.013	53
Phenanthrene	3.0	-0.034	20	-0.052	13	-0.016	43
Anthracene	3.0	-0.014	50	-0.023	30	-0.005	139
Carbazole	3.0	-0.013	53	-0.020	35	-0.006	116
Fluoranthene	3.0	-0.015	46	-0.032	22	NT	NT
Pyrene	3.0	-0.002	347	-0.007	99	NT	NT
1,2 Benzanthracene	3.0	-0.005	139	-0.011	63	NT	NT
Chrysene	3.0	-0.001	7	-0.007	99	NT	NT
Benzo-a-pyrene	3.0	-0.190	4	-0.376	2	-0.004	173
Benzo-ghi-perylene	3.0	ND	ND	ND	ND	ND	ND

Table 41. Kinetic data for PCP degradation/transformation in site soils.

Site	Loading Dry Wt. (%)	K (day-1)	T 1/2 (days)	95% Confidence Interval			
				Lower Limit		Upper Limit	
				K (day-1)	T 1/2 (days)	K (day-1)	T 1/2 (days)
Meridian	3.0	NT[a]	NT	NT	NT	NT	NT
	1.0	-0.0096	72	-0.0176	30	-0.0015	462
	0.3	-0.0152	43	-0.0206	34	-0.0115	60
Grenada	3.0	-0.0335	21	-0.0482	14	-0.0188	37
	1.0	-0.0131	53	-0.0263	26	NT	NT
	0.3	-0.0152	46	-0.0178	39	-0.0125	55
Columbus	3.0	-0.0018	385	-0.0028	248	-0.0009	758
	1.0	NT	NT	NT	NT	NT	NT
	0.3	-0.0006	1087	-0.0021	334	NT	NT
Wiggins	3.0	-0.0066	105	-0.0200	35	NT	NT
	1.0	-0.0076	91	-0.0235	29	NT	NT
	0.3	-0.0060	116	-0.0217	32	NT	NT

[a]NT = no transformation observed.

Table 42. Kinetic data for OCDD degradation/transformation in site soils.

Site	Loading Dry Wt. (%)	K (day-1)	T 1/2 (days)	95% Confidence Interval			
				Lower Limit		Upper Limit	
				K (day-1)	T 1/2 (days)	K (day-1)	T 1/2 (days)
Meridian	3.0	NT[a]	NT	NT	NT	NT	NT
	1.0	NT	NT	NT	NT	NT	NT
	0.3	-0.1251	6	-0.1959	4	-0.0543	13
Grenada	3.0	-0.0152	46	-0.0178	39	-0.0125	55
	1.0	-0.01973	35	-0.03935	18	-0.00011	6301
	0.3	-0.0006	1161	-0.0053	130	NT	NT
Columbus	3.0	NT	NT	NT	NT	NT	NT
	1.0	-0.001	663	-0.004	160	NT	NT
	0.3	NT	NT	NT	NT	NT	NT
Wiggins	3.0	NT	NT	NT	NT	NT	NT
	1.0	NT	NT	NT	NT	NT	NT
	0.3	-0.0009	766	-0.0023	301	NT	NT

[a]NT = no transformation observed.

Table 43. Starting and peak microbe counts.[a]

Media	Loading Dry Wt. (%)	Columbus		Grenada		Meridian		Wiggins	
		Start	Peak	Start	Peak	Start	Peak	Start	Peak
P	0.3	.07A	.15A	.05A	4.40B	.31A	2.10B	.22A	5.10B
	1.0	.02A	.10A	.04A	6.90B	.33A	4.10B	.09A	6.10B
	3.0	.01A	.14B	.05A	4.80B	.24A	5.10B	.05A	4.10B
C	0.3	.50A	.50A	.84A	9.40B	2.70A	3.50A	.40A	4.20B
	1.0	.47A	2.00B	1.20A	7.60B	2.20A	3.80B	.20A	3.00B
	3.0	.50A	2.00B	.70A	7.10B	2.90A	4.60B	.26A	3.90B
C+P	0.3	.09A	.85B	.06A	4.40B	.29A	2.60B	.27A	5.50B
	1.0	.01A	.39B	.04A	8.20B	.30A	4.00B	.10A	6.40B
	3.0	.01A	.11B	.04A	5.80B	.23A	4.60B	.05A	4.70B
NA	0.3	.67A	2.60B	.48A	8.40B	3.20A	3.40A	.42A	5.10B
	1.0	.88A	2.10B	.92A	6.90B	3.00A	4.15A	.39A	5.80B
	3.0	.74A	1.70B	.52A	9.60B	3.60A	4.80B	.05A	4.70B
PDA	0.3	.90A	2.40B	1.10A	10.00B	3.20A	3.20A	.51A	5.70B
	1.0	.91A	2.50B	1.40A	9.10B	2.98A	4.50B	.29A	6.10B
	3.0	.57A	2.90B	1.10A	9.50B	3.30A	6.40B	.27A	5.30B
PDAA	0.3	.05A	.05A	.04A	1.10B	.13A	.17A	.05A	.16A
	1.0	.02A	.04A	.04A	.70B	.13A	.13A	.05A	.11A
	3.0	.01A	.05B	.02A	.30B	.10A	.19B	.07A	.07A

[a]Starting and peak microbe count means within a site, media, and loading rate are not different by Duncan's Multiple Range Test (P = 0.05) if followed by the same letter.

lives of more than one hundred days. Naphthalene, 2-methylnaphthalene, 1-methylnaphthalene, biphenyl, acenaphthalene, acenaphthene, dibenzofuran, and fluorene have half lives of ten days or less in most cases. Phenanthrene, anthracene, carbazole, and fluoranthene have half lives between ten and one hundred days in most cases. Pyrene, 1,2-benzanthracene, chrysene, benzo-a-pyrene, and benzo-ghi-perylene have half lives greater than one hundred days in most cases. In several cases these last five showed essentially no breakdown within the time frame of the experiment.

The breakdown rates of individual PAH's were apparently related to molecular size and structure, as noted in previous studies. The zero to ten day half life group contained compounds with two aromatic rings, the ten to one hundred day half life group contained compounds with three aromatic rings, and the one hundred 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 gives hope that even the most persistent PAH's might yield to biological remediation techniques under the right conditions with appropriate microbial populations.

Carbazole, a compound containing a nitrogen bridge between two aromatic rings, varied greatly in persistence in different soils and loadings. This may be due to the nitrogen atom affecting water solubility and other properties of carbazole under varying local oxidation/reduction potentials and pH.

Acenaphthylene and acenaphthene, differing only in the presence or absence of a double bond (and two hydrogens) show the effect of small changes in structure. Acenaphthene had much longer average half life

than acenaphthylene. Apparently, the double bond is easier to attack, although the single bond in acenapthene also lowers the vapor pressure, possibly affecting the half life by vaporization.

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

PCP transformation occurred in all the soils, but was slow in Columbus soil, which was from a site not exposed to PCP treatment wastes. Grenada soil transformed PCP with half lives ranging from one to two months, a quite practical range for land treatment operations. Meridian soil also exhibited rapid transformation rates except at the highest loading rate. Wiggins soil transformed PCP with half lives of three to four months, still an appropriate range for land treatment 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 land treating PCP at that location. However, it is not known what length of time is 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, at least. It is likely in most soils with chronic exposure to PCP (which is where PCP disposal by landfarming would be needed) that suitable populations could be induced relatively quickly.

OCDD transformation occurred to some degree in all the soils, but only Grenada soil consistently transformed OCDD at all loadings. Since

Grenada soil also consistently transformed PCP, a relationship may exist in the potential for a soil to transform these two compounds. Dioxins are widely regarded as being somewhat recalcitrant to biological transformation, but these data indicate the potential for biological treatment. Concentrated sources of dioxins would probably be incinerated, but biological treatment in soil could be very useful for materials such as wood treating wastes that contain low levels of dioxins.

General Discussion

The results of these experiments indicate that PAH's, PCP, and OCDD 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 clear. Land treatment of creosote and PCP wood treating wastes appears to provide a viable management alternative based on treatability data in the soils tested to date. The data variability does support the need for conducting site-specific treatability studies to discern the appropriate operation and management scenario for a given site.

Further study of treatment of OCDD, PCP, and the higher molecular weight PAH's is needed to determine the most advantageous environmental conditions and management techniques for more rapid transformation of these compounds. Many of these compounds were readily transformed in some cases. Therefore, further study may reveal reliable techniques for enhancing land treatment as a practically useful management alternative for these recalcitrant 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, a reliable, safe, economical remediation technique such as land treatment is very attractive.

REFERENCES

Adams, J. and C. Giam. 1984. Polynuclear Azaarenes in Wood Preservative Wastewater. Environ. Sci. Technol. 18(5):391-394.

Ahlborg, V. G., J. E. Lindgren, and M. Mercier. 1974. Metabolism of Pentachlorophenol. Arch. Toxicol. 32(4):271-281.

Alliot, H. 1975. Chlorodioxins in Pentachlorophenol. British Wood Pres. Assoc. News Sheet. London.

Allison, L. E. 1935. Organic soil carbon by reduction of chromic acid. Soil Sci. 40:311-320.

Anderson, K. J., E. G. Leighty, and M. T. Takahashi. 1972. Evaluation of Herbicides for Possible Mutagenic Properties. J. Agr. Food Chem. 20:649-656.

Barr, A. J., J. H. Goodnight, and J. P. Sall. 1979. SAS Users Guide. SAS Institute, Raleigh, NC, 494 pp.

Becker, G. 1977. Experience and Experiments with Creosote for Crossties. Proc. Am. Wood-Pres. Assoc. 73:16-25.

Bevenue, A. and H. Beckman. 1967. Pentachlorophenol: A Discussion of Its Properties and Its Occurrence as a Residue in Human and Animal Tissues. Residue Rev. 19:83-134.

Blake, G. R. 1965. Bulk density: Core method. In C. A. Black (Ed.) Methods of Soil Analysis, Part I, Agronomy 9:375-377. Amer. Soc. of Agron., Madison, WI.

Braun, W. H. and M. W. Sauerhoff. 1976. The Pharmacokinetic Profile of Pentachlorophenol in Monkeys. Toxicol. Appl. Pharmacol. 38:525-533.

Briggs, G. G. 1975. The Behavior of the Nitrification Inhibitor "N-Serve" in Broadcast and Incorporated Application to Soil. J. Sci. Food Agric. 26:1083-1092.

Brown, K. W. and Associates. 1980. Hazardous Waste Land Treatment. SW-874, U. S. Environmental Protection Agency, Washington, DC.

_____ and K. C. Donnelly. 1984. Mutagenic Activity of Runoff and Leachage Water from Hazardous Waste Land Treatment. Environ. Pollut. (Series A) 35:229-246.

Bulman, T. L., S. Lesage, P. J. A. Fowles, and M. D. Webber. 1985. The Persistence of Polynuclear Aromatic Hydrocarbons in Soil. PACE Report No. 85-2, Petroleum Assoc. for Conservation of the Canadian Environ. Ottawa, Ontario.

Burdell, C. A. 1984. Overview of the Wood Preserving Industry, pp. 7-14. IN: Hazardous Waste Treatment and Disposal in the Wood Preserving Industry, Atlanta, GA.

Buselmaier, W., G. Roehrborn, and P. Propping. 1973. Comparative Investigations on the Mutagenicity of Pesticides in Mammalian Test Systems. Mutat. Research 21(1):25-26.

Buser, H. R. 1975. Polychlorinated Dibenzo-p-dioxins, Separation and Identification of Isomers by Gas Chromatography - Mass Spectrometry. J. Chromatog. 114:95-108.

_____. 1976. High Resolution Gas Chromatography of Polychlorinated Dibenzo-p-dioxins and Dibenzofurans. Anal. Chem. 48:1553.

Butterfield, D. J. and J. D. Devay. 1975. An Improved Soil Assay for Verticillim dahliae. Proc. Am. Phytopathol. Soc. 2:111 (Abstract).

_____ and J. D. Devay. 1977. Reassessment of Soil Assay for Verticillim dahliae. Phytopathology 67:1073-1078.

Carrol, D. 1970. Clay minerals: A guide to their X-ray Identification. The Geological Society of America. Special paper 126. Boulder, CO. 80 p.

Cerniglia, C. E. and D. T. Gibson. 1979. Oxidation of Benzo(a)-pyrene by the Filamentous Fungus Cunninghamelia elegans. J. Biol. Chem. 254(23):12174-12180.

_____ and S. A. Crow. 1981. Metabolism of Aromatic Hydrocarbons by Yeasts. Arch. Microbiol. 129:9-13.

_____. 1984. Microbial Metabolism of Polycyclic Aromatic Hydrocarbons, pp. 30-71. IN: A. I. Laskin, Ed. Adv. in Appl. Microbiol., Vol. 30, Academic Press, New York, NY.

Choi, J. and S. Aomine. 1972. Effects of the Soil on the Activity of Pentachlorophenol. Soil Sci. Plant Nutr. 18(6):255-260.

_____. 1974. Adsorption of Pentachlorophenol by Soils. Soil Sci. Plant Nutr. 20(2):135-144.

_____. 1974a. Mechanisms of Pentachlorophenol Adsorption by Soils. Soil Sci. Plant Nutr. 20(4):371-379.

Chu, J. P. and E. J. Kirsch. 1972. Metabolism of Pentachlorophenol by an Axenic Bacterial Culture. Appl. Microbiol. 23(5):1033-1035.

_____. 1973. Utilization of Halophenols by a Pentachlorophenol Metabolizing Bacterium. Dev. Ind. Microbiol. 14:264-273.

Crosby, D. G. 1981. Environmental Chemistry of Pentachlorophenol. Pure Appl. Chem. 53:1052-1080.

Cserjesi, A. J. 1972. Detoxification of Chlorinated Phenols. Int. Biodeterior. Bull. 8(4):135-138.

Day, P. R. 1965. Particle fractionation and particle size analysis. In C. A. Black (Ed.) Methods of Soil Analysis, Part I. Agronomy 9:552-562. Amer. Soc. of Agron., Madison, WI.

Deichmann, W. B., W. Machle, K. V. Kitzmiller, and G. Thomas. 1942. Acute and Chronic Effects of Pentachlorophenol and Sodium Pentachlorophenate upon Experimental Animals. J. Pharm. Exptl. Therap. 76:104.

_____ and L. J. Schafer. 1942. Spectrophotometric Estimation of Pentachlorophenol in Tissues and Water. Ind. Eng. Chem., Anal. Ed. 14(4):310-312.

Demidenko, N. M. 1966. Toxicological Properties of Pentachlorophenol. Gig. Toksikol. Pestits. Klin. Otravleni. (4):234-239.

_____. 1969. Maximum Permissible Atmospheric Concentration of Pentachlorophenol. Gig. Tr. Prof. Zabol. 13(9):58-60. (CA 72:47095M).

Dixon, J. B. and S. B. Weed. 1978. Minerals in Soil Environments. Soil Sci. Soc. of Amer., Madison, WI.

Dodge, R. H. and D. T. Gibson. 1980. Fungal Metabolism of Benzo(a)anthracene. p. 138. IN: Abstracts of the 1980 American Society for Microbiologists Annual Meeting. ASM, Washington, DC.

Dow Chemical Co. 1969. Toxicity Summary for Dowicide 7.

Dreisbach, R. H. 1963. Handbook of Poisoning: Diagnosis and Treatment. p. 256.

Edgehill, R. U. and R. K. Finn. 1982. Isolation, Characterization and Growth Kinetics of Bacteria Metabolizing Pentachlorophenol. Eur. J. Appl. Microbiol. Biotechnol. 16:179-184.

Edwards, N. T. 1983. Polycyclic Aromatic Hydrocarbons (PAH's) in the Terrestrial Environment--a Review. J. Environ. Qual. 12:427-441.

EPRI. 1984. Development and Validation of a Terrestrial Microcosm Test System for Accessing Ecological Effects of Utility Wastes, Final Report. EA-XXXX-RP1224-5.

ERT, Inc. 1985b. The Land Treatability of Creosote Wastes (second draft). Document No. PD481-400a, Environmental Research and Technology, Concord, MA.

Evans, W. C., H. N. Fernley, and E. Griffiths. 1965. Oxidative Metabolism of Phenanthrene and Anthracene by Soil Pseudomonads. Biochem. J. 95:791-831.

Fed. Proc. 1943. Fed. Am. Soc. Exp. Biol. 2:76.

Fernley, H. N. and W. C. Evans. 1958. Oxidative Metabolism of Polycyclic Hydrocarbons by Soil Pseudomonads. Nature 182:373-375.

Gabrilevskaya, L. M. and V. P. Laskina. 1964. Maximum Permissible Concentrations of PCP and Na-Pentachlorophenolate in Water Reservoirs. Sanit. Okhrana Vodoemov. ot. Zagryazneniya Prom. Stochnymi Vodami. (6):251-272. (CA 62;15304d).

Gaines, T. H. 1969. Acute Toxicity of Pesticides. Toxicol. Appl. Pharmacol. 14(3):515-534.

Gardner, W. S., R. F. Lee, K. R. Tenore, and L. W. Smith. 1979. Degradation of Selected Polycyclic Aromatic Hydrocarbons in Coastal Sediments: Importance of Microbes and Polychaete Worms. Water, Air, Soil Pollution 11, 339.

Gibson, D. T. 1972. The Microbial Oxidation of Aromatic Hydrocarbons. Crit. Rev. Microbiol. 1(2):199-223.

_____, V. Mahadevan, D. M. Jerina, H. Yagi, and H. J. C. Yeh. 1975. Oxidation of the Carcinogens Benzo(a)pyrene and Benzo(a)anthracene to Dihydrodiols by a Bacterium. Science 189:295-297.

Groenewegen, D. and H. Stolp. 1976. Microbial Breakdown of Polycyclic Aromatic Hydrocarbons. Tbl. Bakt. Hyg. I. Abt.: Orig. B162,225.

_____. 1981. Microbial Breakdown of Polycyclic Aromatic Hydrocarbons, pp. 233-240. IN: M. R. Overcash, ed. Decomposition of Toxic and Nontoxic Organic Compounds in Soils. Ann Arbor Science Publishers, Inc., Ann Arbor, MI.

Harrison, D. L. 1959. The Toxicity of Wood Preservatives to Stock, Part I: Pentachlorophenol. New Zealand Vet. J. 7:89-98. (CA 55:23814e).

Herbes, S. E and L. R. Schwall. 1978. Microbial Transformations of Polycyclic Aromatic Hydrocarbons in Pristine and Petroleum-Contaminated Sediments. Appl. Environ. Microbiol. 35, 306.

_____, G. R. Southworth, D. L. Shaeffer, W. H. Griest, and M. P. Masbarinec. 1980. Critical Pathways of Polycyclic Aromatic Hydrocarbons in Aquatic Environments, pp. 113-128. IN: H. Witschi, ed. The Scientific Bases of Toxicity Assessment, Elsevier, Holland.

Hetrick, L. A. 1952. The Comparative Toxicity of Some Organic Insecticides as Termite Scil Poisons. J. Econ. Entomol. 45(2):235-237.

Hilton, H. W. and Q. H. Yuen. 1963. Adsorption of Several Pre-Emergence Herbicides by Hawaiian Sugar Cane Soils. J. Agric. Food Chem. 11(3):230-234.

_____, and N. S. Nomura. 1970. Distribution of Residues from Atrazine, Ametryne, and Pentachlorophenol in Sugarcane. J. Agric. Food Chem. 18(2)217-220.

Hinkle, D. K. 1973. Fetotoxic Effects of Pentachlorophenol in the Golden Syrian Hamster. Tox. and Appl. Pharmacol. 25(3):455 (abstract).

Huddleston, R. L., C. A. Bleckmann, and J. R. Wolfe. 1986. Land Treatment Biological Degradation Processes, pp. 41-61. IN: R. C. Loehr and J. F. Malina, Jr., eds. Land Treatment:A Hazardous Waste Management Alternative. Water Resources Symp. No. 13, Center for Research in Water Resources, Univ. of Texas at Austin, TX.

Ide, A., Y. Niki, F. Sakamoto, I. Watanabe, and H. Watanabe. 1972. Decomposition of Pentachlorophenol in Paddy Soil. Agric. Biol. Chem. 36(11):937-1844.

Jackson, M. L. 1956. Soil Chemical Analysis - advanced course. Publ. by author, Univ. of Wisconsin, Madison.

Jaworski, E. G. 1955. Tracer Studies With 1-^{14}C-Pentachlorophenol in Cotton. Proc. 10th Annu. Cotton Defol. Conf. pp. 36-40.

Johnson, R. L., P. J. Gehring, R. J. Kociba, and B. A. Schwetz. 1973. Chlorinated Dibenzodioxins and Pentachlorophenol. Environ. Health Perspect. 5:171-175.

Karickhoff, S. W., D. S. Brown, and T. A. Scott. 1979. Sorption of Octanol/Water Distribution Coefficients, Water Solubilities, and Sediment/Water Partition Coefficients for Hydrophobic Organic Pollutants. EPA-600/4-79-032. U.S. Environmental Protection Agency.

Kaufman, D. D. 1978. Degradation of Pentachlorophenol in Soil and by Soil Microorganisms. IN: Pentachlorophenol, R. K. Rao, Ed. Plenum Press, New York. pp. 27-40.

Kehoe, R. A., W. Deichmann-Gruebler, and K. V. Kitzmiller. 1939. Toxic Effects upon Rabbits of Pentachlorophenol and Sodium Pentachlorophenate. J. Indust. Hyg. & Toxicol. 21:160-172.

Kirsch, E. J. and J. E. Etzel. 1973. Microbial Decomposition of Pentachlorophenol. J. Water Pollut. Control Fed. 45(2):359-364.

Klute, A. 1965. Laboratory measurement of hydraulic conductivity of saturated soil. In C. A. Black (Ed.) Methods of Soil Analysis, Part I. Agron. 9:214-215. Amer. Soc. of Agron., Madison, WI.

Koss, G. and W. Koransky. 1978. Pentachlorophenol:Chemistry, Pharmacology, and Environmental Toxicology, K. R. Rao, Ed. Plenum Press, New York.

Kuwatsuka, S. and M. Igarashi. 1975. Degradation of Penta in Soils: II. The Relationship Between the Degradation of Penta and the Properties of Soils, and the Identification of the Degradation Products of Penta. Soil Sci. Plant Nutr. 21(4):405-414.

Larsen, R. V., L. E. Kirsh, S. M. Shaw, J. G. Christian, and G. S. Born. 1972. Excretion and Tissue Distribution of Uniformly Labeled ^{14}C-Pentachlorophenol in Rats. J. Pharm. Sci. 61:2004-2006.

_____, G. S. Born, W. V. Kessler, S. M. Shaw, and D. C. Von Sickle. 1975. Placental Transfer and Teratology of Pentachlorophenol in Rats. Environ. Lett. 10(2):121-128.

Lorenz, L. R. and L. R. Gjovik. 1972. Analyzing Creosote by Gas Chromatography:Relationship to Creosote Specifications. Proc. Amer. Wood Pres. Assoc. 68:32-42.

Loustalot, A. J. and R. Ferrer. 1950. The Effect of Some Environmental Factors on the Persistence of Sodium Pentachlorophenate in the Soil. Proc. Am. Assoc. Hortic. Sci. 56:294-298.

Matsunaka, S. and S. Kuwatsuka. 1975. Environmental Problems Related to Herbicidal Use in Japan. Environ. Qual. Safety. 4:149-159.

Means, J. C., G. S. Wood, J. J. Hassett, and W. L. Banwart. 1979. Sorption of Polynuclear Aromatic Hydrocarbons by Sediments and Soils. Environ. Sci. Technol. 14:1524-1528.

Medvedev, V. A. and V. D. Davidov. 1972. Transformation of Individual Organic Products of the Coke Industry in Chemozem Soil. Pochrovedenie. 11:22-28.

Miller, C. S. and M. M. Aboul-Ela. 1969. Fate of Pentachlorophenol in Cotton. J. Agric. Food Chem. 17(6):1244-1246.

Mississippi State University. 1984. Methylene Chloride Soxhlet Recoveries for OCDD and PCP in Soil. Report for MFPUL Environmental Group, Mississippi State, MS.

McKenna, E. J. and R. D. Heath. 1976. Biodegradation of Polynuclear Aromatic Hydrocarbon Pollutants by Soil and Water Microorganisms. Water Resources Center, University of Illinois at Urbana-Champaign. Research Report No. 113, UILU-WRC-76-0113.

Murthy, N. B. K., D. D. Kaufman, and G. F. Fries. 1979. Degradation of Pentachlorophenol in Aerobic and Anaerobic Soil. J. of Environ. Sci. Health, B14:1-14.

Noakes, D. N. and D. M. Sanderson. 1969. A Method for Determining the Dermal Toxicity of Pesticides. British J. of Indust. Med. 26:59-64.

Ochrymowych, J., Western Electric. 1978. Personal communication.

Overcash, M. R. and D. Pal. 1979. Design of Land Treatment Systems for Industrial Wastes - Theory and Practice. Ann Arbor Science Publishers, Inc., Ann Arbor, MI. 684 pp.

_____, J. B. Weber, and M. C. Miles. 1982. Behavior of Organic Priority Pollutants in the Terrestrial System: Di(N-Butyl) Phthalate Ester, Toluene, and 2,4-Dinitrophenol. Office of Water Research and Technology. U. S. Department of the Interior, Washington, DC.

Peech, M. 1965. Exchange acidity. In C. A. Black (Ed.) Methods of Soil Analysis, Part I, Agronomy 9:914-926. Amer. Soc. of Agron., Madison, WI.

Phung, T., L. Barker, D. Ross, and D. Bauer. 1978. Land Cultivation of Industrial Wastes and Municipal Solid Wastes: State-Of-The-Art Study. Volume 1. Technical Summary and Literature Review. EPA-600/2-78-140a, U. S. Environmental Protection Agency, Washington, DC.

Pleskova, A. and K. Bencze. 1959. Toxic Properties of Pentachlorophenol. Pracovni Lekerstvi, 11:348-354.

Reichhold Chemicals. 1974. Report of May 28, 1974.

Renberg, L. 1974. Ion Exchange Technique for the Determination of Chlorinated Phenols and Phenoxy Acids in Organic Tissue, Soil, and Water. Anal. Chem. 46(3):459-461.

Richards, L. A. 1949. Methods of Measuring Soil Moisture. Soil Sci. 68:95-112.

Rogoff, M. H. 1961. Oxidation of Aromatic Compounds by Bacteria. Adv. Appl. Microbial. 3:193-221.

Schwetz, B. A. and P. J. Gehring. 1973. The Effect of Tetrachlorophenol and Pentachlorophenol on Rat Embryonal and Fetal Development. Toxicol. Appl. Pharmacol. 25(3):455. (Abstract).

_____, P. A. Keeler, and P. J. Gehring. 1974. The Effect of Purified and Commercial Grade Pentachlorophenol on Rat Embryonal and Fetal Development. Toxicol. Appl. Pharmacol. 28(1):151-161.

Shabad, L. M., Y. L. Cohan, A. P. Ilnitsky, A. Y. Khesina, N. P. Shcerbak, and G. A. Smirnov. 1971. The Carcinogenic Hydrocarbon Benzo(a)pyrene in the Soil. J. Natl. Cancer Inst. 47(6):1179-1191.

Sims, R. C. 1982. Land Treatment of Polynuclear Aromatic Compounds. Ph.D. Dissertation. Dept. Biol. Agr. Eng., North Carolina State Univ., Raleigh, NC.

_____, and M. R. Overcash. 1983. Fate of Polynuclear Aromatic Compounds (PNAs) in Soil-Plant Systems. Residue Rev. 88:1-68.

_____, J. L. Sims, D. L. Sorensen, and L. L. Hastings. 1987. Waste/Soil Treatability Studies for Four Complex Industrial Wastes: Methodologies and Results. Vol. 1. Project # CR-810979.

Sisler, F. D. and C. E. Zobell. 1947. Microbial Utilization of Carcinogenic Hydrocarbons. Science 106:521-522.

Soil Survey Staff. 1951. Soil Survey Manual. Agric. Handb. No. 18, USDA. U. S. Govt. Printing Office, Washington, D.C.

Sudhakar-Barik and N. Sethunathan. 1978. Metabolism of Nitrophenols in Flooded Soils. J. Environ. Qual. 7:349-352.

Suzuki, T. and K. Nose. 1971. Decomposition of Pentachlorophenol in Farm Soil. (Part 2). Penta Metabolism by a Microorganism Isolated from Soil. Noyaku Seisan Gijutsu, Japan, 26:21-24.

Tausson, V. O. 1950. Basic Principles of Plant Bioenergetics (collected works). p. 73. In: N. A. Maximov, (Ed.), National Academy of Sciences, USSR.

Tortensson, L. and J. Stenstrom. 1986. "Basic" Respiration Rate as a Tool for Prediction of Pesticide Persistence in Soil. Toxicity Assessment 1:57-72.

United States Department of Agriculture. 1972. Soil Survey Laboratory Methods and Procedures for Collecting Soil Samples. Soil Survey Investigations Report No. 1. U. S. Govt. Printing Office, Washington, DC.

_____. 1980. The Biologic and Economic Assessment of Pentachlorophenol Inorganic Arsenicals Creosote. USDA, Number 1658-11. Washington, DC.

U.S. EPA. 1975. Production, Distribution, Use, and Environmental Impact Potential of Selected Pesticides. U. S. Environ. Prot. Agency 540/1-74-001. 439 pp.

_____. 1978. Report of the Ad Hoc Study Group on Pentachlorophenol Contaminant. Environmental Health Advisory Committee. Science Advisory Board, Washington, DC.

_____. 1983. 40CFR Parts 261, 264, 265, and 775. Federal Register. 48(65).

_____. 1984. Creosote - Special Review Position Document 213. U. S. Environmental Protection Agency, Washington, DC.

_____. 1986a. Test Methods for Evaluating Solid Waste. 1B. SW-846. Third Edition.

_____. 1986b. Permit Guidance Manual on Hazardous Waste Land Treatment Demonstrations. Final Draft. EPA-530/SW86-032. Office of Solid Waste and Emergency Response, U.S. Environmental Protection Agency, Washington, DC.

Versar, Inc. 1979. Water-Related Environmental Fate of 129 Priority Pollutants. Vol. 1 and 2, EPA 440/4-79-029. U.S. Environmental Protection Agency, Washington, DC.

Verschueren, D. 1977. Handbook of Environmental Data on Organic Chemicals. Van Nostrand/Reinhold Co., New York. p. 659.

Vogel, E. and J. L. R. Chandler. 1974. Mutagenicity Testing of Cyclamate and Some Pesticides in Drosophila melanogaster. Experientia 30(6):621-623.

Warcup, J. H. 1950. The Soil Plate Method for Isolation of Fungi from Soil. Nature 166:117-118.

Ward, C. H., M. B. Thomson, P. B. Bedient, and M. D. Lee. 1986. Transport and Fate Processes in the Subsurface, pp. 19-39. IN: R. C. Loehr and J. F. Malina, Jr., Eds. Land Treatment:A Hazardous Waste Management Alternative. Water Resources Symp. No. 13, Center for Research in Water Resources, Univ. of Texas at Austin, TX.

Watanabe, I. 1973. Isolation of Pentachlorophenol Decomposing Bacteria from Soil. Soil Sci. Plant Nutr. Tokyo. 19(2):109-116.

Williams, R. T. 1959. Detoxification Mechanisms. 2nd Ed., John Wiley and Sons, Inc., New York, NY. 796 pp.

Young, H. C. and J. C. Carroll. 1951. The Decomposition of Pentachlorophenol When Applied as a Residual Pre-Emergence Herbicide. Agron. J. 43:504-507.

Yuan, T. L. 1959. Determination of Exchangeable Hydrogen in Soils by a Titration Method. Soil Sci. 88:164-167.

APPENDIX A

METHODOLOGY

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Table A-1. Analytical procedures for soil and water (U. S. EPA 1986a).

Process	Method number	Compounds	Comments
Extraction of soil samples	3540	All	Use 10 g of soil
Extraction of water samples	3520	All	Use 1000 ml of water
Clean up	3630	All	Done after methylation of phenols
Analysis	8100	PAH's	For polynuclear aromatic hydrocarbons
Analysis	8040	OCDD+PCP	For chlorinated phenols after methylation and octa-chlorodibenzo-p-dioxin; using an ECD detector
Analysis	8270	All	Check for all compounds
Analysis	8280		Used for low-level dioxins (penta, hexa, and hepta dioxins)

Table A-2. Analytical procedures for sludges.

Process	Procedure
Water content	ASTM D-95-70
Organic content	Heating at 600°C for 2 hours in an oxidative atmosphere
Non-volatile products	Heating at 600°C for 2 hours in an oxidative atmosphere
Organic carbon	Determined by CO_2 evolution
Total phenolics	Method 222E Standard Methods for Examination of Water and Wastewater
Oil and grease	Method 5030 Standard Methods for Examination of Water and Wastewater
Nitrogen	Micro Kjeldahl followed by digestion with 5% hydrogen peroxide and sulfuric acid; nitrogen was determined colorimetrically using nessierization
Phosphorous	Determined after digestion colorimetrically using the Fisbe-Subarrow method
Inorganic chloride	Determined using a chloride specific ion electrode

Extraction of PCP, PAH's, and OCDD from Soil

Soil (10 g) was mixed with dry sodium sulfate (10 g). (The sodium sulfate had been dried at 400°C for four hours and stored in a desiccator.) The sample was placed in an extraction thimble and 1 ml of an internal standard in methylene chloride was added. The internal standard mixture for high levels consisted of 5,000 ppm of diphenylmethane, 1000 ppm of tribromophenol, and 21 ppm of octachloronaphthalene. For low levels, a 1 to 10 dilution of the internal standard was used. The extraction thimble was placed in the Soxhlet unit along with 300 ml of pesticide grade methylene chloride and boiling chips.

The soil in the Soxhlet unit was extracted for 16 hours with a minimum recycle rate of 5/hour. The extraction units were cooled and transferred to a Kuderna-Danish unit and condensed to a volume of approximately 3 ml.

The condensed extract was diluted to exactly 5 ml and aliquots were taken for OCDD and PCP and PAH analyses. The remaining solution was stored in a freezer at -27°C in a teflon-lined, screw-cap vial.

Clean-up and Determination of PAH's and PCP in Soil Extracts

Silica gel was activated at 130°C for 16 hours (100-120 mesh Davison Chemical Grade 923 or equivalent) in a beaker covered with foil. The silica gel was stored in an air-tight desiccator and redried every two weeks. The columns (10 mm i.d.) were packed using 9 grams of activated silica gel. The silica gel was packed into the column with gentle tapping. The column was pre-eluted with 20 ml of pentane

(pesticide grade or HPLC grade). The pentane was allowed to elute until the solvent was just above the silica gel. The silica gel was not allowed to dry before sample addition.

An aliquot of the methylene chloride extract was put in a sample tube. The exact amount depended on the loading amount of creosote or the analysis of previous sample. Three ml of sample was added if the loading rate was less than 0.632% (wt/wt) of creosote on soil or if the previous sample contained less than 6,000 ppm total PAH's.

Diazomethane solution (0.1 ml) was added to the sample tube and mixed with a vortex mixer. An aliquot was added to the column. If a 1-ml aliquot on column was used, 2 ml of methylene chloride was added to the column. A 1 to 3 ml aliqot of 40% methylene chloride/60% pentane was added three times to ensure that all the sample is absorbed on the column. Columns were eluted with 50 ml of the 40/60 mixture and the eluant was collected. The eluant was concentrated to 5 ml by evaporation using a gentle stream of dry air or nitrogen and analyzed using gas chromatography conditions shown below for PAH's.

A 1-ml sample was removed for PCP analysis and stored in a glass teflon-lined crimp-top vial. This sample had to be diluted for GC/ECD analysis. The exact dilution depended on the anticipated concentration of PCP.

Tracor 540 Gas Chromatograph Parameters for PAH Analysis

Column: J and W DB-5 fused silica capillary
Length: 30 meters
Film thickness: 1.00 µm
Inside diameter: 0.32 mm
Injector temperature: 325°C
Oven temperature program: 4 minutes to 40°C, then 6°C per minute for 15 minutes to 325°C
Carrier gas: Helium; Pressure: 12 psi
FID temperature: 325°C
Hydrogen flow: 60 cc/min

Air flow: 400 cc/min
Nitrogen makeup: 40 cc/min
Injection: 2 μl splitless, vent after 1.5 min.
Amplifier range: xl

Tracor 540 GC Parameter for PCP Analysis

Column: 6 ft x 2 mm i.d. glass packed with 3% SP-2250 on 100/120 mesh supelcoport
Carrier gas: Ar/CH_4 at 10 cc/min
Injector: 250°C
Oven: 220°C
Detector: 350°C
ECD detector makeup gas: 95% argon/5% methane at 60 cc/min.

Clean-up and Determination of Octachlorodibenzo-p-dioxin in Soil (MSU 1984)

The analysis of OCDD in soil presented two significant problems which had to be dealt with in order to obtain reliable results. First, an extraction procedure had to be used which would be highly efficient in removing OCDD from the sample matrix. This was especially important, since the anticipated concentration of OCDD in the soil was in the parts-per-billion range. Secondly, the majority of the compounds which co-extracted with OCDD were likely to be several orders of magnitude higher in concentration than OCDD. A clean-up technique had to be used which allowed the concentration of OCDD with minimal chemical interference.

Method Summary--Methylene chloride Soxhlet extraction was found to be very efficient in the removal of OCDD from a soil matrix (U. S. EPA 1983). Thus, an aliquot of soil extract from the PAH analysis, which uses the same extraction procedure, was considered to be adequate and also would save analysis time. For our purposes, the removal of the majority of chemical interferences could be accomplished by a modification of two column clean-up techniques recommended by EPA for

2,3,7,8-TCDD analysis (U. S. EPA 1983). An elution profile and recovery were determined for this modified column clean-up and were found to be quite adequate (Mississippi State 1984).

Materials and Supplies--

Basic alumina, type WB-5, Activity Grade I, Sigma Chemical Co. or equivalent.

Silica gel, 100/200 mesh, Fisher Scientific Co. or equivalent.

5 ml disposable pipet, Scientific Products Co.

Silane treated glass wool, Supelco, Inc.

9" disposable Pasteur pipets, Scientific Products Co.

10 ml graduated cylinder, Pyrex.

Small funnel with a cut latex bulb attachment.

Disposable 1 ml serological pipet, Scientific Products Co.

Compressed air with regulator and manifold.

Water bath.

Benzene (Burdick and Jackson distilled in glass).

OCDD for standards, Analabs.

Gas chromatograph equipped with ECD and a 6-ft x 2-mm i.d. glass column packed with 3% SP-2250 on 100/120 mesh supelcoport.

Procedure--

Before use, the silica gel and basic alumina were activated for 16-24 hours at 130^{o}C in a foil-covered glass container.

A small plug of glass wool was placed in the bottom of a 5-ml pipet.

A funnel with a cut latex bulb attached was placed on the pipet and 2 ml of basic alumina (bottom) and 2 ml of silica gel (top) were added to the pipet.

The column was pre-rinsed with two 4-ml portions of Benzene which was then discarded.

A 10-ml volumetric flask was placed under the column. Before clean-up, the methylene chloride extract was exchanged with benzene by blowing down the methylene chloride to dryness with dry air in a 50°C water bath and adding 1 ml of benzene.

The benzene extract was placed on the column.

After the sample extract had flowed into the silica gel layer, 4 ml of benzene was added to the column.

All of the eluate was collected until the column stopped dripping.

The eluate was diluted to 10 ml with benzene and a 1 µl sample was injected on the Tracor 540 GC/ECD using the following conditions:

Oven: 280°C; Injector: 330°C; Detector: 350°C

Quality Assurance Program for Soil Extraction and Analysis

Four types of internal checks were used to monitor the accuracy of the soil extraction and analytical procedures.

Blanks--This control was used to monitor the glassware, solvents, and the solid supports (silica gel and alumina) background levels. The blank was processed exactly the same way as the samples except no soil was used during the Soxhlet extraction. Diphenylmethane, 2,4,6-tribromophenol, and octachloronaphthalene were added to the extracts as an internal standard.

Spike Samples--Standard solutions of PAH's, PCP, and OCDD were prepared using the best standards available (purity = 99% or better) in methylene chloride. A sample of the standard solution was added to the soil before Soxhlet extraction. The sample was extracted and cleaned up using the normal procedures. The values of the spiked sample were used to determine the recovery values for the individual compounds. Diphenylmethane, 2,4,6-tribromophenol, octachloronaphthalene were used as internal standards. All standards were prepared using a Mettler

5-place analytical balance. Each time a standard was prepared, the weight, date, and standard number were recorded, and the balance was checked with standard weights (Class S - National Bureau Standards).

Standard Solutions for Gas Chromatography Calibration--A standard solution of PAH's containing the 16 compounds of interest was prepared. It contained an internal standard (diphenylmethane). Standard solutions were also made for the PCP and octachlorodibenzo-p-dioxin and analysis with the corresponding internal standards 2,4,6-tribromophenol and octachloronaphthalene. A minimum of three concentration levels was used for each compound.

Blind Samples--Blind samples containing EPA standard reference materials (Quality Assurance Branch EMSL-Cincinnati, U. S. EPA) were diluted by the Quality Control Officer (Dr. Hamid Borazjani) and analyzed.

GC/MS Analysis--A part of each sludge sample after homogenizing (approximately 1 gram) was weighed to three significant figures, mixed with an equal weight of anhydrous sodium sulfate and extracted for 16 hours with 300 ml of methylene chloride in a Soxhlet extractor. The volume of methylene chloride from each sample was adjusted to 100 ml with a volumetric flask. A 1.00 ml aliquot of each extract was transferred to a screw cap test tube and stored at approximately $4^{o}C$ prior to GC/MS analysis. The sample weight range and dilution volume were based on prior knowledge of concentrations determined by GC/FID analysis.

The GC was a Carlo Erba fitted with a J and W DB-5 capillary column [0.25 μm film thickness and 30 m (1) by 0.25 mm (i.d.)]. After sample injection the GC was operated at $70^{o}C$ for 2 minutes and

then programmed to 280°C at 6 deg/min and from 280° to 320°C at 12 deg/min. The GC oven temperature was kept at 320°C for 20 minutes. The injector and transfer line temperatures were 320° and 280°C, respectively.

The mass spectrometer (Kratos MS80RFA) was operated in the electron impact mode (70 eV) with a source temperature of 250°C. After a 6.0-minute delay for elution of the solvent peak, mass spectral data were acquired with a scan rate of 1 sec/dec for 54.0 minutes. Two standard solutions (10 μg/ml and 200 μg/ml) containing known concentrations of selected analytes were used to establish instrument response factors. The concentration of each compound in solution was reported by the DS-90 data system and the concentration in sludge was calculated as follows:

$$C\ \mu g/g = \frac{100\ ml \times c\ \mu g/ml}{W}$$

Here, C = concentration of each compound in sludge (μg/g); 100 = dilution volume, c = concentration of each compound in the sample extract, and W = dry weight of the sludge sample in grams.

Site and Soil Characterization

Soil profiles were examined at each site in freshly excavated pits and they were described and sampled using standard methods (Soil Survey Staff, 1951). 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. Bulk density was determined on major horizons using the non-disturbed core method (Blake, 1965). Saturated hydraulic conductivity was determined on non-disturbed

cores using the constant heat method (Klute, 1965). Soil moisture retention was determined on non-disturbed cores using a pressure membrane apparatus (Richards, 1949).

Soil samples were air-dried in the laboratory, crushed with a wooden rolling pin, and sieved through a 10-mesh sieve to remove fragments larger than 2 mm (USDA, 1972). Particle size distribution was determined by the hydrometer method and sieving (Day, 1965). Organic matter was determined by a wet combustion procedure (Allison, 1935). Extractable acidity was determined by the barium chloride-triethanolamine method (Peech, 1965). Exchangeable aluminum was determined in KCl extractions following the procedure of Yuan (1959). Exchangeable cations were extracted with neutral 1 N NH_4OAc and determined by atomic absorption spectrophotometry (USDA 1972). Soil pH was measured in water and 1 N KCl using a 1:1 soil-to-liquid ratio. Electrical conductivity was determined in saturated paste extracts using a Wheatstone conductivity cell. Total sulfur was determined on soil samples ground to pass a 60-mesh sieve in a LECO Sulfur Analyzer using an induction furnace and I.R. detection.

The clay fraction (<2 mm) was separated by centrifugal sedimentation using Calgon as a dispersing agent. Clays were K-saturated, Mg-saturated, and glycerol-solvated for x-ray diffraction analysis. The clay fraction was analyzed with a Norelco Geiger counter spectrophotometer using Cu K radiation and a Ni filter. Minerals were identified based on comparison of diffraction spacings and frequencies to standard minerals as indicated by Jackson (1956), Carrol (1970), and

Dixon and Weed (1978). Relative estimates of the amounts of clay minerals present were based on peak area measurements with corrections for Lorentz polarization at peaks greater or equal to 14 Å.

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

Wet soil was spread upon a new sheet of plastic and air-dried for 24 hours or longer until the moisture content was reduced. The dried soil was stored in clean glass containers that had been labeled with the soil source, the collection day, and a number. A sample of each new soil was sent to Delta Labs, Inc., for analysis of soil parameters, nitrogen, phosphorus, organic carbon, and inorganic metals; pH and chloride ion was determined in-house. The soil was sieved just before use to remove coarse plant materials from the soil, and the moisture content was determined. Spiked soil samples were prepared using the following procedure: Soil samples (50.0 g/beaker) were accurately weighed into 10 beakers. Known amounts of creosote and/or technical grade pentachlorophenol were added into each beaker. Technical grade PCP was dissolved thoroughly in methylene chloride or methanol before being added to the soil in the beaker. Then contents of all ten beakers were combined and mixed for 2 hours in a clean glass jar using a sample rotator with a minimum of 50 revolutions/minute. The dual procedure for mixing was found to give more uniformly mixed material. Soil moisture was adjusted to 70% of water-holding capacity by adding deionized H_2O into the soil when mixing was finished. The same mixing procedure was repeated for controls.

Two test units were set up for each site. One unit was a control (0%), and one was loaded at 1% with the standard creosote/PCP mixture. Each unit consisted of a brown glass container with a lid (baking dish) containing 500 g of soil (dry weight). Soil moisture content was adjusted to 70% of water-holding capacity, and the container's weight was determined. The accurate weight of the unit was important since this value was used to maintain a proper moisture content during the study. The test units were put into a constant temperature room maintained at $22^{o} \pm 2^{o}C$ for the duration of the study.

Each test was begun by hand stirring the samples and removing two separate 20 g samples of soil (air-dry weight) from each of the units. One sample was used to analyze for PAH's, PCP, and octachlorodibenzo-p-dioxin using the procedure described in a later section of this report. The second sample was used for bacterial counts, pH and chloride ion analysis.

The moisture content of each unit was adjusted weekly to 70% by adding deionized water. The soil was aerated by thoroughly mixing the total contents of each unit every 7 days.

The first samples were taken after 30 days (20 g dry weight) and analyzed for PAH's, PCP, and OCDD. Further samples were taken every 30 days until the experiment was complete.

Soil from sites at Gulfport, Grenada, and Wiggins were loaded initially and at 30 and 60 days. Soil from sites at Atlanta, Meridian, and Wilmington were loaded intially and at 30 days, while the soil from sites at Columbus and Chattanooga were loaded only at day 0. A change was made in loading frequency because data for several sites indicated that the bacteria at the sites were readily acclimated with one loading.

Kinetic data needed to calculate the half lives, assuming first order kinetics, were taken after the final loading and over a 60-120 day period.

No organic or inorganic additions were made to the soil during the initial set of experiments. The parameters measured were:

- microbial plate counts
- pentachlorophenol
- major PAH's contained in creosote

The soil microflora were measured using five different media. The total amounts of bacteria, acclimated bacteria, and fungi were determined using various media. The same media that were used to count bacteria (PDA) were amended with creosote (PDA-C), pentachlorophenol (PDA-P), a combination of creosote and PCP (PDA-PC), and PDA with antibiotics to count fungi (PDA-AA). Because of the very low counts of fungi and because their population counts did not change appreciably during the studies, only the results from the bacteria and acclimated bacteria are reported.

Transformation/Degradation of Site Specific Sludges: Experiment II

In this phase of the study, three different loading rates in soil were studied--0.3%, 1.0%, and 3.0%--based on the total dry weight of solids. A single loading was used instead of multiple loading, and three replications of each soil and loading rate combination were used. Chicken manure was added to all soil at 4% by weight. Sludges from Columbus did not contain PCP, so in order to get information on the rates of degradation of PCP with this soil type, 128-3000 ppm of PCP were added to the Columbus soils. The parameters measured were

bacteria, fungi, actinomycetes, acclimated bacteria, pentachlorophenol, major PAH's in creosote, and octachlorodibenzo-p-dioxin. A control sample of soil from eachsite which contained no added sludges or PCP was used as a control for the plate counting procedures and to determine the background levels of PCP, PAH's, and OCDD. Although technical grade PCP contains traces of two other series of dioxins, their levels are extremely low (less than 5% of the octachlorodibenzo-p-dioxin levels). Because of time and resource restraints, it was not possible to monitor trace level dioxins as part of this study.

All other experimental methods, with the exception of the addition of chicken manure to the soil (discussed below) were the same as in Experiment I.

Rationale for the Addition of Chicken Manure to Soil in the Degradation/Transformation Studies

During the course of this series of experiments, the data generated reemphasized the importance of soil organic matter in facilitating the microbial transformation of applied organic wastes. Since the ultimate goal of these studies was to establish an operating landtreatment test facility, the decision was made to maximize the operating effectiveness and efficiency of the facility by amending the experimental soils with an animal manure. This amendment accomplished several objectives. The manure furnished: (1) a carbon source for potential cometabolism, which has been found in at least some instances to be an important component of the transformation process; (2) both major and minor nutrients; and (3) a wide variety of microbes that were potentially important biodegraders. Also, added organic matter should markedly decrease mobility of hazardous constituents in organic applied wastes, which is highly desirable in a landtreatment operation. Although other animal

manures might serve as well, chicken manure was chosen for study because it is readily available in many parts of the United States. A typical analysis of the chicken manure used in this study is given below:

Total organic carbon = 8.97%

Total nitrogen = 1.35%

Total phosphorous = 0.12%

A comparison between bacteria counts of four of the soils used in this study was done before and after manure addition. No PCP or creosote was added to the soil (0% controls) and the bacteria counts were determined in soil 30 days after manure loading. The results (Table A-3) indicate a large increase in both the total bacteria and the acclimated bacteria in the soil with added chicken manure.

Microbiological Procedures

The media used for this study were potato dextrose agar, PDA (Difco Laboratories, Detroit, Michigan), 39 g in one liter of deionized water, PDA amended with 5 mg/L of technical-grade pentachlorophenol [PDA-P] (Vulcan Materials Company, Wichita, Kansas), PDA amended with 10 mg/L of whole creosote [PDA-C], PDA amended with a combination of 5 mg/L of pentachlorophenol and 10 mg/L of whole creosote [PDA-CP], PDA amended with antibiotics--120 mg/L of streptomycin sulfate (Nutritional Biochemical, Cleveland, Ohio) and 30 mg/L of chlorotetracycline hydrochloride (Nutritional Biochemical, Cleveland, Ohio) [PDAA], and actinomyces broth (Difco Laboratories, Detroit, Michigan) [ACA], 57 g in one liter of deionized water amended with 15 g of Difco agar and 30 mg/L of Pimaricin. The PDA was autoclaved for 20 minutes at 15 psi and 121^{o}C and then cooled to 55^{o}C. Both creosote and pentachlorophenol were

Table A-3. Bacteria levels in four soils at 0% loading before and after addition of chicken manure[a].

Site	Total bacteria counts (million counts/gram of soil)		Acclimated bacteria counts[b] (million counts/gram of soil)	
	Before addition	After addition	Before addition	After addition
Gulfport	1.13	4.50-7.20	0.07	0.50-0.61
Wiggins	0.41	3.10-4.50	0.12	0.64-2.30
Columbus	1.25	2.80-3.10	0.25	0.14-0.35
Meridian	1.10	3.10-4.20	0.09	0.48-0.92

[a]These soils were 0%-loaded, and counts were taken 30 days after addition of chicken manure.

[b]Bacteria acclimated to PCP and PAH's.

dissolved thoroughly in methyl alcohol and added to cooled PDA. The antibiotics were added to the cooled liquid medium before pouring into petri dishes. The pH of the media was adjusted to 6.9 to 7.1 before autoclaving. Twenty-five ml of PDA, PDA-C, PDA-P, PDA-CP, PDAA, and ACA were poured into disposable petri plates and were allowed to solidify.

For colony counts, triplicate samples of loaded and non-loaded soils were air-dried for 24 to 28 hours under a sterilized transfer hood. The air-dried soil was then screened with a 400 mesh sieve. Serial dilutions were made by using sterilized screened soil. Three 20-mg soil samples were weighed out from treated and non-treated soil for each medium at each sampling date. A modified Anderson sampler (Butterfield et al., 1975, 1977; Warcup, 1950) was used to distribute the soil on the agar. Three 20-mg samples were distributed over each medium for each treatment. Colonies were counted after 24 to 48 hours of incubation at 28°C. A Darkfield Quebec Colony Counter (AO Scientific Instrument, Keene, New Hampshire) was used to count the number of colonies on each plate.

The number of counts recovered on PDA plates provided an estimate of the total number of bacteria per gram of dry soil. On creosote-containing plates, it represented the approximate number of bacteria per gram of dry soil that were acclimated to creosote; on PCP-containing plates, it represented the approximate number of bacteria per gram of dry soil that was acclimated to pentachlorophenol; on PDA-CP plates, it represented the approximate number of bacteria per gram of dry soil that was acclimated to both creosote and pentachlorophenol; on PDAA plates, it represented the approximate number of fungi per gram of dry soil; and on ACA plates, it represented the approximate number of actinomycetes per gram of dry soil.

Statistical Procedures

Statistical methods were used to help determine estimates of compound half-lives and confidence intervals for individual compounds. Differences in concentration of PCP, PAH, and OCDD between sampling times were evaluated by calculating a linear regression based on first-order kinetics. The slope of the regression line was used to calculate the first-order degradation rates in the soil/sludge mixtures. The half-life of each compound was calculated from the first-order degradation rate. The half-life values for the lower and upper 95 percent confidence intervals were also calculated for PCP, PAH, and OCDD compounds, when waste was applied to soil, to indicate the range of values about the half-life.

If the slope of the first-order regression was non-negative, indicating that no treatment by degradation was observed, or if degradation could not be quantified due to initial low concentration (near or below detection limit), no degradation information was reported in the tables.

The microbiological results for the sludges were analyzed using a complete random design using days as treatments with three replications and three samples for each replication. Duncan's multiple range test was used to compare treatment mean differences at ($P = 0.05$). Data was processed using the Statistical Analysis System (SAS) of prepackaged programs at VIVC (Barr et al., 1979).

Table A-4. Detection limits for soil and sludge.

	Sludge (ppm)	Soil (ppb)
Naphthalene	17	220
2-Methylnaphthalene	23	290
1-Methylnaphthalene	17	220
Biphenyl	18	240
Acenaphthylene	22	280
Acenaphthene	18	240
Dibenzofuran	21	270
Fluorene	18	230
Phenanthrene	27	340
Anthracene	26	330
Carbazole	36	460
Fluoranthene	35	450
Pyrene	37	480
1,2-Benzanthracene	43	560
Chrysene	46	590
Benzo(a)pyrene	47	610
Benzo(ghi)perylene	48	620
Pentachlorophenol	0.27	27
Octachlorodibenzo-p-dioxin	0.54	54

FOREWORD

EPA is charged by Congress to protect the nation's land, air, and water systems. Under a mandate of national environmental laws focused on air and water quality, solid waste management and the control of toxic substances, pesticides, noise and radiation, the Agency strives to formulate and implement actions which lead to a compatible balance between human activities and the ability of natural systems to support and nurture life.

The Robert S. Kerr Environmental Research Laboratory is the Agency's center of expertise for investigation of the soil and subsurface environment. Personnel at the laboratory are responsible for management of research programs to (a) determine the fate, transport, and transformation rates of pollutants in the soil, the unsaturated and saturated zones of the subsurface environment; (b) define the processes to be used in characterizing the soil and subsurface environment as a receptor of pollutants; (c) develop techniques for predicting the effect of pollutants on ground water, soil, and indigenous organisms; and (d) define and demonstrate the applicability and limitations of using natural processes, indigenous to the soil and subsurface environment, for the protection of this resource.

Environmentally acceptable management of process sludges and contaminated soils from wood treating facilities presents a widespread problem that must be addressed under both RCRA and CERCLA regulations and guidelines. On-site management of these wastes may be the most desirable alternative currently available from both an environmental and economic viewpoint. Treatment of these wastes in well designed and operated soil systems is one of the on-site management technologies proposed. There currently is a lack of readily available information relative to the treatability potential of wood preservative waste contaminants in complex waste-soil matrices. This report adds to this information base by presenting and discussing data from the characterization and treatability screening phases of a three-phase study directed toward quantitative evaluation of treatment potential for pentachlorophenol and creosote waste contaminants in the site soil at wood treating facilities. Characterization data are presented for soils and sludges from eight wood treating locations in the southeastern U.S. Degradation kinetic data are presented for four of these locations. Additional results from the screening phase plus results for the field evaluation phase will be presented in subsequent reports.

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SUMMARY

Eight wood treating plant sites were chosen to study the effectiveness of land treatment for remediation of wood treating wastes. The morphological, chemical, and microbiological parameters of the soil at each site were characterized. Typical wood treating waste sludges from each site were chemically analyzed. Soil samples were taken from each site to study the rate of microbiological breakdown of wood treating waste components. In a preliminary experiment, a synthetic waste was mixed with each soil at 1% of the dry weight of the soil in order to ascertain waste breakdown rates using the same waste for all soils. In a second experiment, waste sludge from each site was mixed with soil from each site at three different loading rates (0.33, 1.0, and 3.0% by weight). Chicken manure was added to the soils at 4% weight. The soils were tested at thirty day intervals to determine microbe populations and amounts of waste compounds remaining. Degradation rates were calculated for PCP, OCDD, and seventeen PAH's.

The general conclusions from this study are that PAH's and PCP are readily degraded in soil systems. PAH's were transformed easily in all the soils tested, but PCP was transformed much more quickly in soils with long term exposure to PCP. Lower molecular weight PAH's and PCP were usually transformed more quickly than higher molecular weight PAH's and PCP. Application of PAH and PCP containing wastes to soil greatly increases the population of PAH and PCP adapted microorganisms in the soil. The results of this study indicate that land treatment is an effective alternative for remediation of PAH and PCP containing wood treating wastes.