



Project Summary

Waste-Soil Treatability Studies for Four Complex Industrial Wastes: Methodologies and Results, Volumes 1 and 2

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The full two-volume report presents information pertaining to quantitative evaluation of the soil treatment potential resulting from waste-soil interaction studies for four specific wastes listed under Section 3001 of the Resource Conservation and Recovery Act (RCRA). Volume 1 contains information from literature assessment, waste-soil characterization, and treatability screening studies for each selected waste. Volume 2 contains results from bench-scale waste-soil interaction studies; degradation, transformation, and immobilization data are presented for four specific wastes: API separator sludge, slop oil emulsion solids, pentachlorophenol wood preserving waste, and creosote wood preserving waste. The scope of the study involved assessment of the potential for treatment of these hazardous wastes using soil as the treatment medium.

The experimental approach used in this study was designed to characterize degradation, transformation, and immobilization potentials for hazardous constituents contained in each candidate waste. For each waste and soil type, treatment was evaluated as a function of waste loading rate, soil moisture, and time. Combinations of selected chemical analyses and bioassays were used as endpoints to characterize treatment.

Methodologies were developed for the measurement of specific soil treatment parameters including "volatilization-corrected" degradation rates and for measurement of partition coefficients among waste, water, and air phases of a

waste-soil matrix. Partitioning between the water soluble extract of the waste-water-air mixture and soil was evaluated by conducting soil isotherm studies using the water soluble extract. These parameters provide input to the proposed U.S. Environmental Protection Agency (EPA) Regulatory and Investigative Treatment Zone (RITZ) model developed to assess treatment potential for potentially hazardous organic constituents in soil.

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

Introduction

Land treatment (LT) is defined in RCRA as the hazardous waste management technology pertaining to application/incorporation of waste into upper layers of the soil for the purpose of degrading, transforming, and/or immobilizing hazardous constituents contained in the applied waste (40 CFR Part 264). Soil systems for treatment of a variety of industrial wastes have been utilized for many years; although, application of hazardous industrial waste to soil utilizing a controlled engineering design and 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 in the soil treatment zone as specifically related

to current regulatory requirements (40 CFR Part 264) concerning treatability, i.e., degradation, transformation, and immobilization of such constituents. Soil treatment systems that are designed and managed based on knowledge of waste-soil interactions may represent a significant technology for simultaneous treatment and ultimate disposal of selected hazardous wastes in an environmentally acceptable manner. This treatment concept also may be useful during remedial activities at certain contaminated soil sites.

In this research project, representative hazardous wastes from two industrial categories, wood preserving and petroleum refining, were evaluated as to the potential for treatment in soil systems. A literature assessment for each waste category was conducted as an aid in the prediction of soil treatment potential. The literature review also was used as a guide for design of an experimental approach for obtaining specific information pertaining to degradation, transformation, and immobilization of hazardous waste constituents in soil.

Standards were promulgated in 40 CFR Part 264.272 for demonstrating treatment of hazardous wastes in soil. These standards require demonstration of degradation, transformation, and/or immobilization of a candidate waste in the treatment zone soil. For the purposes of this research, demonstration of degradation of waste constituents was based on the loss of parent hazardous organic compounds within the waste-soil matrix as opposed to "complete" degradation, which is the term used to describe the process whereby waste constituents are mineralized completely to inorganic end products, i.e., carbon dioxide, water, and inorganic species of nitrogen, phosphorus, and sulfur. Rates of degradation were established by measuring the loss of parent compounds from the waste-soil matrix with time. Transformation refers to partial alteration of hazardous compounds in the soil, thereby converting a problem waste or substances into innocuous or environmentally safe forms. In this context, transformation refers to formation of intermediate products during waste-soil interactions (i.e., physical, chemical, and/or biological mechanisms); some intermediate products may become refractory compounds in the soil matrix. Immobilization refers to the extent of retardation of the downward transport (leaching potential) and upward transport (volatilization potential) of waste constituents. The transport

potential for waste constituents from the waste to water, air, and soil phases is affected by the relative affinity of the waste constituents for each phase, and in this project was characterized in column and batch reactors. Therefore, an acceptable demonstration of soil treatment involves an evaluation/quantification of degradation, transformation, and immobilization processes, in order to obtain an integrated assessment of design and management requirements for successful assimilation of a waste in a soil system.

Demonstration of the potential for treatment of a particular hazardous waste in soil 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, or, in the case of existing land treatment units, operating data. In this project, specific information obtained from literature sources included quantitative degradation, transformation, and immobilization data for identified waste-specific hazardous constituents in soil systems. Due to the current lack of a comprehensive technical information base, the U.S. EPA considers the use of literature information only as insufficient to support demonstration of treatment of hazardous wastes in soil at the present time.

Specific objectives of this research project were to:

- (1) Conduct a literature assessment for each candidate hazardous waste (API separator sludge, slop oil emulsion solids, creosote wood preserving waste, and pentachlorophenol (PCP) wood preserving waste) to obtain specific information pertaining to degradation, transformation, and immobilization in soil of hazardous constituents identified in each waste.
- (2) Characterize candidate wastes for identification of specific constituents of concern; and characterize experimental soils for assessment of specific parameters that influence soil treatability potential.
- (3) Conduct laboratory screening experiments using a battery of bioassays to determine waste loading rates (mg waste/kg soil) to be used in subsequent longer term experiments designed to assess potential for treatment of each selected waste in soil.
- (4) Develop degradation, transformation, and immobilization information

for each candidate hazardous waste in the two soils selected for study.

- (5) Develop methodologies for measurement of "volatilization-corrected" degradation rates and partition coefficients; use the methodologies developed to generate degradation kinetics/partition coefficients for a subset of waste-soil combinations and for those constituents common to all wastes.

Objectives 1, 2, and 3 are addressed in Volume 1 of this report; objectives 4 and 5 are addressed in Volume 2.

Research Approach

Four listed hazardous wastes were selected for study (Table 1). The wastes chosen are produced in high volume, contain numerous organic and inorganic constituents, and represent a broad spectrum of physical, chemical, and toxicological characteristics.

API separator sludge—(K051)

This waste is generated from primary settling of wastewaters that enter the oily water sewer and typically consists of water, oil, and solids. Solids are largely sand and coarse silt, but also may contain significant quantities of hazardous metals, i.e., chromium and lead. Heavy oils that settle and become part of the bottom sludge in an API separator are largely composed of heavy tars, large multiple branched aliphatic compounds (paraffins), polyaromatic hydrocarbons, and coke fines. Proportions of oily material which are tar-like, paraffinic or polyaromatic are largely dependent on the crude source.

Slop oil emulsion solids—(K049)

This waste is generated from skimming the API separator and typically consists of approximately 40 percent water, 43 percent oil, and 12 percent solids. Chromium and lead typically are present in significant concentrations in the solid phase.

Table 1. Hazardous Wastes Selected for Evaluation

Waste	EPA Hazardous Waste No.
<i>Petroleum Refinery Wastes</i>	
API Separator Sludge	K051
Slop Oil Emulsion Solids	K049
<i>Wood Preserving Wastes</i>	
Creosote	K001
Pentachlorophenol	K001

Creosote wood preserving waste — (K001)

Creosote is a distillate from coal tar made by high temperature carbonization of bituminous coal. Creosote alone or in combination with coal tar or petroleum is a major preservative used in wood treatment. The principal classes of organic constituents present in creosote wastes are polyaromatic hydrocarbons and phenolics.

Pentachlorophenol (PCP) wood preserving waste — (K001)

Pentachlorophenol is widely used as a wood preservative and also has been used for slime and algae control. The combined PCP-creosote sludge used in this experimental investigation contained polyaromatic hydrocarbons, phenolics, and PCP.

An experimental approach was designed to test the hypothesis that treatment would be achieved for each of four listed hazardous wastes in two soil types and to evaluate the effect of selected design and management factors, i.e., waste loading, on treatment. Therefore, the scope of the study involved addressing the demonstration of treatment of hazardous waste using soil as the treatment medium. The soil treatment potential for each candidate waste was evaluated as a function of waste loading rate, soil moisture, and time. A combination of chemical analyses and bioassays was used to characterize endpoints for degradation, transformation, and immobilization of waste constituents.

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 261. Where waste(s) are from an identified industry with well defined processes, i.e., petroleum refining, it may be acceptable to perform analyses for a subset of Appendix VIII constituents. The subset of organic constituents selected for evaluation in these waste-soil interaction studies included semivolatile polycyclic aromatic hydrocarbon (PAH) compounds and the volatile organic constituents (VOC) benzene, toluene, xylene, ethylbenzene, and naphthalene for each waste, with the addition of pentachlorophenol for the PCP wood preserving sludge.

Two soil types were selected as treatment media to allow evaluation of the effect of varying soil characteristics on the extent and rate of treatment. Soil types were chosen that (1) represented soils typical of operating land treatment facilities and (2) provided a range of specific characteristics for evaluating treatment as

a function of soil type. Each soil selected was characterized for specific properties considered to be important in influencing soil treatment processes.

The experimental waste loading rate (mass/area/application, or mg waste/kg soil) was the first design parameter determined. In order to evaluate the extent and rate of treatment, sustained soil microbial activity must be maintained. Therefore, the impact of an applied waste on indigenous soil microbial populations must be evaluated, especially for any waste containing hazardous constituents specifically designed to inhibit biological activity, i.e., wood preserving wastes. In this study, a battery of microbial toxicity screening assays was used to estimate acceptable initial waste application rates for use in subsequent bench-scale waste-soil interaction studies.

A comparative study of the sensitivity of five microbial assays: Microtox, soil respiration, soil dehydrogenase, soil nitrification, and viable soil microorganism plate counts, to pentachlorophenol (PCP) and slop oil wastes in Kidman sandy loam soil was performed to evaluate response of these commonly used assays to identical waste-soil mixtures.

The degradation potential of hazardous organic constituents in any waste applied to soil is critical since biodegradation usually represents the primary removal mechanism for such constituents. Degradation coefficient measurements involve determination of soil concentrations of specific organic constituents as a function of time. Degradation was characterized as a first order kinetic rate process for all constituents evaluated; the first order reaction rate constant was then used to calculate half-lives for each constituent. These calculated half-lives 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.

Conversion of hazardous constituents to less toxic intermediates within the soil treatment medium also was evaluated. Information concerning the toxicity reduction of the waste-soil mixture over time was evaluated using an acute toxicity assay (Microtox test), and a mutagenicity assay (Ames *Salmonella typhimurium* test).

Evaluation of treatment also involved investigation of the extent of migration of hazardous constituents contained in each hazardous waste. A loading rate based on degradation potential was selected for

each waste-soil combination; leaching potential was subsequently characterized for these loading rates in laboratory column studies. Partition coefficients among waste (oil), water, and air for a subset of organic constituents also were determined for use as input parameters to the proposed Regulatory and Investigative Treatment Zone (RITZ) model that has been developed by the U.S. EPA Robert S. Kerr Environmental Research Laboratory (RSKRL).

Results and Discussion

Characterization and Loading Rate Selection

Each waste was characterized for polycyclic aromatic hydrocarbons (PAH), volatile organic constituents (VOC), and polychlorinated dibenzo-p-dioxins (PCDD) and polychlorinated dibenzofurans (PCDF) using GC/MS, HPLC, and GC instrumentation. Concentrations of individual PAH compounds in the waste as determined by HPLC are presented in Table 2. Results from VOC analyses for all wastes identified naphthalene as the prominent peak. No TCDD was detected (detection limit 10 ppb) in the PCP waste, although other PCDDs as well as PCDFs were identified.

The highest loading rate for each waste-soil combination was evaluated for mutagenic potential using the Ames test with and without microsomal (S9) activation. With activation all four wastes exhibited a positive mutagenic potential in Durant clay loam soil. Slop oil emulsion solids and creosote wood preserving waste exhibited a positive mutagenic potential in Kidman sandy loam soil; API separator sludge and PCP wood preserving waste did not exhibit a mutagenic potential in Kidman soil.

None of the wastes exhibited a mutagenic potential as measured by the Ames test without microsomal (S9) activation. All wastes exhibited a high degree of water soluble fraction (WSF) toxicity as measured by the Microtox toxicity test.

Important differences in soil properties between the two experimental soils included organic carbon content (2.88%, 0.5%), pH (6.6, 7.9), and moisture at -1/3 bar (41.6%, 20%) for the Durant clay loam and Kidman sandy loam, respectively.

Waste loading rates in soil as selected based on results of Microtox and soil respiration assays are presented in Table 3. The wood preserving wastes used in this project exhibited greater levels of toxicity than the petroleum refining wastes used. Loading rates selected were generally higher for the Durant clay loam than

Table 2. Concentration of Individual PAH Compounds in Wastes Determined by HPLC

Compound	Concentration in Waste (mg/kg)*			
	API Separator Sludge	Slop Oil	Creosote	Pentachlorophenol
Naphthalene	580 ± 87 (15%)	2,500 ± 700 (28%)	28,000 ± 1,200 (4%)	42,000 ± 28,000 (67%)
Acenaphthalene	480 ± 100 (21%)	<15	3,600 ± 1,000 (28%)	<2,000
Acenaphthene	<12	<10	180,000 ± 40,000 (22%)	<13,000
Fluorene	29 ± 33 (114%)	440 ± 300 (68%)	23,000 ± 5,900 (26%)	<22,000
Phenanthrene	810 ± 140 (17%)	3,600 ± 2,100 (58%)	76,000 ± 15,000 (20%)	52,000 ± 6,200 (12%)
Anthracene	110 ± 27 (25%)	480 ± 93 (19%)	15,000 ± 6,800 (45%)	11,000 ± 6,800 (62%)
Fluoranthene	5,500 ± 290 (5%)	18,000 ± 5,000 (28%)	72,000 ± 17,000 (24%)	46,000 ± 6,200 (13%)
Pyrene	6,000 ± 440 (7%)	23,000 ± 6,700 (29%)	64,000 ± 12,000 (19%)	56,000 ± 13,000 (23%)
Benzo(a)anthracene	1,400 ± 58 (4%)	2,000 ± 1,100 (55%)	7,400 ± 1,600 (22%)	16,000 ± 2,400 (15%)
Chrysene	570 ± 310 (54%)	1,100 ± 150 (14%)	8,300 ± 2,100 (25%)	6,900 ± 2,200 (32%)
Benzo(b)fluoranthene	<3	340 ± 140 (41%)	3,000 ± 700 (23%)	10,100 ± 5,100 (51%)
Benzo(k)fluoranthene	310 ± 62 (20%)	160 ± 42 (26%)	2,400 ± 460 (19%)	<300
Benzo(a)pyrene	170 ± 73 (43%)	260 ± 200 (77%)	2,700 ± 380 (14%)	<280
Benzo(ghi)pyrene	<10	59 ± 18 (31%)	1,100 ± 280 (25%)	<100
Dibenz(a,h)anthracene	40 ± 11 (28%)	15 ± 1 (7%)	<1,200	<250
Indeno(1,2,3-cd)pyrene	61 ± 25 (41%)	88 ± 19 (22%)	820 ± 76 (9%)	<60

*Average concentration of three replicate analyses ± one standard deviation (coefficient of variation %).

Table 3. Waste-Soil Loading Rates Selected Based on Microtox and Soil Respiration Test Results

Waste	Loading Rates					
	Kidman Sandy Loam			Durant Clay Loam		
	Low	Medium	High	Low	Medium	High
Creosote	0.4	0.7	1.0	0.7	1.0	1.3
Pentachlorophenol	0.075	0.15	0.3	0.3	0.5	0.7
API Separator Sludge	6	9	12	6	9	12
Slop Oil	6	8	12	8	12	14

the Kidman sandy loam, thus indicating a difference with respect to the effect of soil type on waste-soil interactions.

Results from a battery of microbial assays conducted using PCP and slop oil wastes indicated a good correlation between the Microtox, soil nitrification, and soil dehydrogenase assays. Highly variable results were obtained with soil respiration (carbon dioxide evolution) and viable plate count assays. The latter two assays appeared to be much less sensitive to the waste loadings used.

A series of experiments were conducted to evaluate the PAH extraction procedure using the Tekmar Tissumizer. Results for spiked recoveries of 16 PAH compounds from Durant clay loam and Kidman sandy loam soils are presented in Table 4. Four concentration levels were used to bracket the range of PAH concentrations in waste-soil mixtures from the beginning (high concentration) to the termination (low concentration) of the degradation experiments.

Information presented in Table 4 indicates consistent and generally high re-

coveries for all 16 PAH compounds from both soil types. Also, recoveries did not vary greatly and were relatively high through a three-log change in soil PAH concentrations. Thus, the soil extraction procedure used in this project appeared to provide consistent and relatively high extraction efficiencies for both soils over the range of concentrations of concern.

Treatment Results

Results of degradation studies for all four wastes in both soils generally indicated an increase in PAH half-life with increasing molecular weight or compound size. This observation is generally consistent with results obtained in other studies for the PAH class of compounds in soil systems. However, soil half-lives for some higher molecular weight PAH compounds in these complex wastes were observed to be lower than half-lives reported in the literature for PAH compounds only, i.e., without the waste matrix. The observed variation in degradation rates and half-lives obtained for PAH constituents in these studies may be due, in part, to the diffi-

culty in accurately analyzing individual constituents in soil mixed with complex environmental mixtures. These degradation rates and half-lives observed in these studies may be lower, however, as a result of cooxidation/cometabolism or other matrix-induced phenomena.

An increase in soil moisture content from -2 to -4 bars to -1/3 to -1 bars generally was associated with a decrease in PAH compound half-life for waste-soil mixtures.

Results also indicate that half-life values for constituents in each petroleum waste were similar for some compounds even though waste loading rates were different. These results would be expected if degradation followed first order kinetics.

Half-life values for waste constituents in each wood preserving waste also were similar even though loading rates were different. These results are similar to those observed for the petroleum wastes, and are expected if degradation processes follow first order kinetics.

After the first experimental period of approximately 280 days, wastes were reapplied to the soil according to the following schedule: 1) waste originally loaded at the medium rate was reloaded at the medium rate (M/M); 2) waste originally loaded at the low rate was reloaded at the high rate (L/H); 3) nonacclimated soil was loaded at the high rate of waste application (N/H); and 4) waste-soil mixtures originally loaded at the high loading rate, but not reloaded (H/NR). Results from reapplication experiments were converted to first order reaction rate constants and half-life values. A subset of waste-soil mixtures for each soil and waste type was

Table 4. Tissue Extraction Recovery Results for PAH Compounds in Kidman and Durant Soils*

Compound	Kidman Sandy Loam Soil concentration in mg/kg				Durant Clay Loam Soil concentration in mg/kg			
	1000	100	10	1	1000	100	10	1
Napthalene	92.3 (3.8)	96.0 (0.0)	86.3 (14.6)	-	99.0 (3.0)	111.7 (5.0)	158.3 (8.1)	-
Acenaphthalene	89.7 (4.7)	82.0 (4.4)	41.7 (25.5)	-	87.3 (7.2)	89.3 (8.1)	78.5 (5.0)	-
Acenaphthene	82.3 (3.2)	80.0 (1.7)	68.7 (3.2)	-	86.7 (3.1)	86.3 (11.2)	77.5 (5.0)	-
Fluorene	98.0 (1.0)	96.7 (0.6)	96.0 (1.7)	103.5 (5.0)	98.7 (0.6)	97.7 (1.5)	94.3 (4.0)	94.5 (7.8)
Phenanthrene	98.7 (1.5)	99.3 (0.6)	99.3 (2.1)	110.0 (0.0)	99.0 (1.0)	99.0 (1.0)	98.7 (2.5)	115.3 (7.2)
Anthracene	98.7 (1.5)	89.3 (1.5)	82.0 (3.0)	57.7 (2.5)	94.3 (7.2)	93.0 (2.7)	86.7 (3.5)	65.0 (5.3)
Fluoranthene	95.0 (2.7)	99.3 (1.2)	97.0 (0.0)	85.3 (2.1)	96.0 (0.0)	100.3 (2.3)	98.7 (1.5)	88.0 (16.5)
Pyrene	106.3 (3.1)	107.7 (0.6)	103.0 (1.0)	73.7 (4.0)	107.0 (2.7)	108.0 (3.6)	105.0 (5.3)	80.0 (24.3)
Benzo(a)anthracene	97.0 (2.0)	97.3 (1.2)	97.3 (2.3)	96.3 (5.1)	97.3 (1.2)	98.7 (1.2)	99.0 (1.7)	100.0 (1.4)
Chrysene	95.6 (1.5)	97.0 (1.0)	96.7 (2.1)	94.7 (3.1)	96.7 (0.6)	86.3 (0.6)	98.0 (1.0)	97.0 (1.7)
Benzo(b)fluoranthene	-	61.0 (0.0)	64.0 (1.0)	87.7 (1.5)	-	61.3 (0.6)	63.3 (1.2)	86.7 (2.1)
Benzo(k)fluoranthene	-	104.0 (1.0)	103.7 (1.5)	105.0 (2.7)	-	104.3 (1.5)	105.0 (2.0)	99.7 (2.5)
Benzo(a)pyrene	-	75.3 (2.5)	66.3 (4.7)	61.7 (3.1)	-	79.3 (0.6)	61.7 (2.1)	68.3 (10.0)
Dibenz(ah)anthracene	-	101.7 (2.1)	103.3 (6.4)	78.0 (8.5)	-	103.3 (3.2)	101.3 (4.0)	86.3 (2.3)
Benzo(ghi)pyrene	-	91.0 (0.0)	90.7 (0.6)	102.0 (2.7)	-	92.7 (1.2)	90.3 (2.5)	111.0 (4.6)
Indeno(1,2,3-cd)pyrene	-	97.0 (1.0)	98.3 (1.5)	100.0 (2.0)	-	98.3 (0.6)	98.3 (1.2)	108.0 (0.0)

*Table values represent average recoveries of triplicate extractions at each loading level with standard deviations in parentheses.

selected for detailed characterization of degradation. The subset was evaluated for approximately an additional 100 days.

For the petroleum wastes, reapplication did not appear to alter the half-life values for PAH constituents. Neither an inhibiting nor stimulating effect was observed. For the wood preserving wastes, there is no trend that would suggest a change in half-life with one reapplication.

PAH degradation results for wastes incubated in Kidman sandy loam soil generally followed the trend observed for waste treatment in Durant clay loam soil. PAH degradation generally appeared to be influenced by molecular weight or compound ring size. Variation in the data obtained for degradation increased when waste was reloaded.

Pentachlorophenol degradation also was evaluated for the PCP wood preserving waste. Kinetic information is presented in Tables 5 and 6 for PCP waste in Durant clay loam soil and Kidman sandy loam soil, respectively. Half-life values are similar (257 days and 204 days) for PCP initially loaded at the high rate in both soils and not reapplied. Acclimation of Kidman sandy loam soil to PCP may have occurred as indicated by comparing results in Table 6 for experiments N/H and H/NR in Kidman soils. Both sets of experiments received PCP waste at the high loading rate (0.3%). However, PCP in mixtures incubated for 400 days (H/NR) had a half-life of 204 days, while PCP in mixtures incubated for 164 days (N/H) had a half-life of 330 days. Evidence for acclimation is also indicated in the experimental set (L/H) initially receiving the low loading rate (0.075%) and reloaded at the high rate

Table 5. Degradation Kinetic Information for Pentachlorophenol in Pentachlorophenol Wood Preserving Waste Reapplied to Durant Clay Loam Soil at -1 Bar Soil Moisture

Loading Rate	C ₀ * (mg/kg)	k (day ⁻¹)	t _{1/2} (days)
M/M ⁺	4.0E2	0.0016	433
H/NR [#]	2.3E2	0.0027	257

*C₀ = initial soil concentration immediately after waste incorporation into soil.

⁺M/M = originally loaded at medium rate (0.5%), reloaded at medium rate.

[#]H/NR = originally loaded at high rate (0.7%), not reloaded.

Table 6. Degradation Kinetic Information for Pentachlorophenol in Pentachlorophenol Wood Preserving Waste Reapplied to Kidman Sandy Loam Soil at -1/3 Bar Soil Moisture

Loading Rate	C ₀ * (mg/kg)	k (day ⁻¹)	t _{1/2} (days)
M/M ⁺	2.7E2	0.0024	289
L/H [#]	1.6E2	0.0046	151
N/H ^{**}	- ⁺⁺	0.0021	330
H/NR ^{##}	1.8E2	0.0034	204

*C₀ = initial soil concentration immediately after waste incorporation into soil.

⁺M/M = originally loaded at medium rate (0.15%), reloaded at medium rate.

[#]L/H = originally loaded at low rate (0.075%), reloaded at high rate (0.3%).

^{**}N/H = nonacclimated soil loaded at high rate (0.3%).

⁺⁺ = not analyzed.

^{##}H/NR = originally loaded at high rate (0.3%), not reloaded.

(0.3%). The half-life for PCP in this soil was 151 days. Acclimation of soil microorganisms to PCP would be expected to result in lower half-life values when waste is reapplied.

Transformation of hazardous wastes in all waste-soil combinations was evaluated by measuring changes in the toxicity of the water soluble fraction (WSF) of waste-soil mixtures as indicated by the Microtox test. An increase in WSF toxicity was observed for all waste-soil mixtures evaluated during the first experimental period, and a decrease in WSF toxicity was generally observed during the second experimental period. These results were considered to be indicative of the formation and subsequent degradation of toxic intermediate constituents.

The Microtox assay proved to be an extremely sensitive assay that did not correlate with gross degradation indicators such as soil respiration studies, and therefore could not be used to positively identify the level at which soil biodegradation was inhibited. The WSF toxicity results did indicate, however, that transformation of the waste occurred for all waste-soil combinations. Since the WSF may contain hazardous intermediates, it may be concluded that lower loading rates will be required if the treatment evaluation criterion is complete detoxification of the waste-soil mixture.

Results of mutagenicity evaluations for soil detoxification of petroleum refinery wastes indicated a reduction from mutagenic to nonmutagenic activity with treatment time for API separator sludge in Durant clay loam soil and for slop oil emulsion solids incubated in Durant clay loam

and in Kidman sandy loam soils. Wood preserving wastes, however, were not rendered nonmutagenic after 400 days of soil incubation in Durant clay loam soil at waste loading rates of 1.3 percent and 0.7 percent for creosote and PCP wastes, respectively. However, no mutagenicity was detected at a loading rate of 0.3 percent PCP waste in Kidman sandy loam soil, and the initial positive mutagenic potential for a loading rate of 1.0 percent creosote waste was reduced to a nonmutagenic level with a treatment time of 400 days.

Immobilization of hazardous waste was measured using one bioassay, the Microtox test, of laboratory column leachates. Microtox test results indicated the presence of little toxicity in leachates from petroleum wastes incubated at the high loading rates in both Durant clay loam and in Kidman sandy loam soils. Leachates produced from creosote and PCP loaded columns exhibited definite toxicity to Microtox, thus indicating the potential for leaching of water soluble toxicants that should be considered when defining waste loading rates for these experimental soils. The absence of Microtox test toxicity of some leachates did not conclusively demonstrate that leachates were free of toxic constituents.

Partition coefficients that were determined for PAH and volatile constituents of all four wastes indicated highest partitioning of constituents into the oil (waste) phase. Relative concentrations between water and oil (waste) phases for PAH constituents were generally 1:1000 to 1:100,000, with the higher ratios observed for the petroleum wastes. Relative concentrations among air:water:oil (waste) phases for volatile constituents were generally 1:100:100,000.

Conclusions

Specific conclusions based on objectives and results of this research project include:

- (1) Literature assessment of specific hazardous constituents experimentally identified in each candidate waste indicated a potential for treatment in soil systems.
- (2) Characterization of all candidate wastes by GC/MS, GC, and HPLC identified the PAH class of semivolatile constituents as common to each waste. In addition, the PCP wood preserving waste contained pentachlorophenol and some dibenzo-p-dioxins and dibenzofurans; however, no tetrachlorodibenzodioxins were detected at a detection limit of 10 ppb.
- (3) A comparative study of the sensitivity of five microbial assays for selection of initial waste loading rates indicated that Microtox, soil dehydrogenase, and soil nitrification assays were the most sensitive to the presence of hazardous wastes, and would result in selecting lower loading rates. Soil respiration and viable soil microorganism plate counts were much less sensitive to hazardous waste application, and would result in selecting higher loading rates.
- (4) Based on screening assay results, initial loading rates for petroleum refinery wastes were indicated to be an order of magnitude higher than for wood preserving wastes.
- (5) A methodology was developed for measurement of "volatilization-corrected" degradation rates in soils in order to more accurately evaluate degradation as a treatment mechanism. For the semivolatile PAH compounds studied, volatilization was important only for naphthalene.
- (6) A methodology was developed for measurement of partition coefficients for hazardous constituents among waste (oil), water, and air phases. It was not possible to measure the partitioning between the water soluble extract and soil because the very low water solubilities of the aromatic hydrocarbons and the very high affinity of these constituents for soil resulted in reduction of constituent concentrations in the water soluble extract to below detection limits. The methodology proved useful for obtaining partition coefficients for waste (oil)/water (K_o), air/water (K_h), and air/waste (oil) (K_{oa}), for volatile constituents and for waste (oil)/water for semivolatile constituents.
- (7) PAH constituents contained in each of the four wastes investigated were degraded under conditions of initial waste application to nonacclimated soils as well as when wastes were reapplied to soils. In general, PAH degradation did not appear to be influenced by variations in soil type or loading rates used in this study; however, PAH degradation in petroleum refinery wastes generally exhibited higher rates than in wood preserving wastes.
- (8) All waste-soil mixtures tested exhibited an initial increase in WSF

toxicity followed by a decrease in toxicity with incubation time. The pattern of WSF toxicity with time was considered to be an indication of formation and degradation of toxic intermediates.

- (9) Partition coefficients determined for PAH and volatile constituents contained in each of the wastes evaluated demonstrated highest partitioning of constituents into the oil (waste) phase. Relative concentrations between water and oil (waste) phases for PAH constituents were generally 1:1000 to 1:100,000, with the higher ratios observed for the petroleum wastes. Relative concentrations among air:water:oil (waste) phases for VOCs were generally 1:100:100,000.

Recommendations

The following recommendations are made in regards to conducting future soil treatability studies for hazardous wastes:

- (1) The use of chemical analyses alone appears to be insufficient to characterize treatability potential of a hazardous waste in soil. Use of chemical analyses alone fails to account for interactions of components in a waste and the production of toxic/mutagenic metabolites. Use of bioassays to characterize the degradation, transformation and immobilization processes should be used to complement chemical analyses information.
- (2) Careful attention in future soil treatability studies should be given to potential fate, transport and effects of intermediate products formed during waste-soil interactions. Information obtained concerning degradation, transformation, and immobilization of hazardous constituents should be used to aid in selecting waste loading rates to be used in field evaluation study.
- (3) When determining partition coefficients (K_o , K_h , K_D , K_{ao}) for evaluation of immobilization processes in waste-soil mixtures, several different ratios of waste:water volumes and several water soluble fraction volumes:soil weights should be used to generate partition isotherms with several points in order to evaluate the ranges of linearity for the isotherm and partition coefficient values. Determination of partition coefficients between soil and

water soluble extract of the waste (K_D) will require larger amounts of waste and water than used in this investigation to generate larger amounts of water soluble fractions.

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The complete report consists of two volumes, entitled "Waste/Soil Treatability Studies for Four Complex Industrial Wastes: Methodologies and Results,"

"Volume 1. Literature Assessment, Waste/Soil Characterization, Loading Rate Selection," (Order No. PB 87-111 738/AS; Cost: \$18.95)

"Volume 2. Waste Loading Impacts on Soil Degradation, Transformation, and Immobilization," (Order No. PB 87-111 746/AS; Cost: \$24.95)

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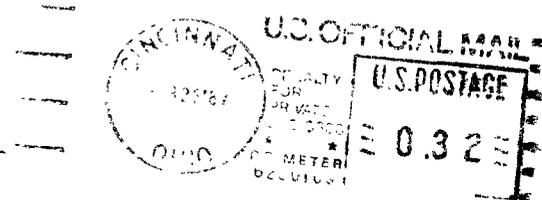
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