



Project Summary

Treatability Potential for EPA Listed Hazardous Wastes in Soil

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This study developed comprehensive screening data on the treatability in soil of: (a) specific listed hazardous organic chemicals, and (b) waste sludge from explosives production (KO44) and related chemicals. Laboratory experiments were conducted using two soil types, an acidic soil (Mississippi soil) with less than one percent organic matter, and a slightly basic sandy loam soil (Texas soil) containing 3.25% organic matter. These experiments evaluated the: (a) relative toxicity of the chemicals and waste, (b) degradation of the chemicals and waste in the soils, (c) adsorption characteristics of the chemicals in the two soils, and (d) toxicity reduction that occurred during degradation.

The major conclusions were:

1. The chemical structure of the compounds evaluated affected their relative toxicity. With chlorophenols, the relative toxicity was related to the position of the chlorine group on the phenol ring. The order of relative toxicity was para > meta > ortho. The same order appeared to occur for methylphenols and nitrophenols. The chemical substituted on the phenol ring appeared to have an effect on toxicity. Nitro-substituted phenols appeared to be less toxic than the methyl- or chloro-substituted phenols. Mixing of the chemicals with the soils did not affect the relative toxicity of the chemicals in the two soils.
2. Data characterizing the chemical loss in the soil and in the water soluble fraction (WSF) extracted from the soil as well as the toxicity reduction in the WSF could be represented satisfac-

torily by either first or zero order kinetics. In most cases, the data were represented by either kinetic parameter with high correlation coefficients.

3. The rates of chemical loss were higher in the Texas soil. Chlorophenols with chlorine substituted in the meta position had greater half-lives and lower loss rates. Chemicals with a nitro group substituted in the phenol ring appeared to have a lower loss rate.
4. The Freundlich equation described the adsorption of most of the chemicals with the two soils satisfactorily. The values of the Freundlich constant (K_f) for the chemicals in the two soils were different. For the acid extractables, the K_f values generally were greater in the Mississippi soil. For the amines and alcohols, the K_f values were greater in the Texas soil.
5. The loss of the applied chemical in the soil and in the WSF as well as the reduction of the WSF toxicity were compared for nine of the chemicals. The chemical loss in the WSF was about 1.5 times faster than the chemical loss in the soil. The WSF toxicity decreased at about the same rate as the WSF chemical concentration. No enhanced mobilization of the applied chemical occurred during degradation.

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

Introduction

This study was conducted to provide comprehensive screening data on the treatability in soil of: (a) EPA listed hazardous organic chemicals, and (b) a specific hazardous waste and related chemicals. The results provide data that can be used when permitting decisions are made related to: (a) management of spills, (b) remediation of contaminated soils, and (c) the use of land as a waste management alternative. The degradation and partitioning data can be used as input to predictive models that estimate the movement of chemicals in the unsaturated zone of the soil. The models integrate the processes that affect chemicals in soil (degradation and partitioning) so that an assessment can be made of the extent to which protection of human health and the environment occurs. The understanding that results from the use of such models allows the identification of chemicals and wastes that require control to reduce or eliminate their hazard potential prior to application to soil. Laboratory studies were conducted to determine: (a) degradation kinetics, (b) sorption, (c) toxicity of the chemicals and waste, and (d) the reduction in toxicity that occurred during degradation.

Designated Chemicals and Wastes

The chemicals and specific waste that were part of this study are identified hazardous wastes. These chemicals can be expected to be components of many industrial compounds and wastes that enter the soil from spills and inadequately sealed impoundments (pits, ponds and lagoons) and as part of wastes applied to operating land treatment units. The chemicals that were evaluated are identified in Table 1. The specific hazardous waste, and chemicals related to that waste, that were evaluated are noted in Table 2.

Samples of the explosives waste sludge (KO44) and the chemicals TNT, RDX, and HMX were obtained with the help of the U.S. Army Toxic and Hazardous Materials Agency (USATHAMA). A sample of wastewater treatment sludge resulting from the manufacture and processing of explosives was obtained from the Holston Army Ammunition Plant with the assistance of USATHAMA. This material was stored at 4°C until required for analysis and use.

Soils

The intent of this study was to provide comprehensive screening data on the treatability of specific chemicals and a hazardous waste in soil. The characteristics of the soil will affect the degradation, sorption, and treatment potential and two soils with different characteristics were used. One was an acid soil with a low organic content and the other was a basic soil with a higher organic content and cation exchange capacity (CEC). The acid soil, obtained from an area near Wiggins, Mississippi, was supplied by researchers at Mississippi State University and was referred to as Mississippi soil. The basic soil was obtained from an area near Austin, Texas, that, to the knowledge of the personnel of this project, had not been exposed to industrial chemicals or wastes. This soil was referred to as Texas soil.

Relative Toxicity and Chemical Loading

The relative toxicity tests that were conducted were not intended to provide information on toxicity from a human health or safety or from an environmental standpoint. Rather, these tests were used as a relative toxicity screening method. Such tests also can be used to identify the relative toxicity reduction that occurs when chemicals and waste are managed by the land treatment process.

Although no single bioassay procedure can provide a comprehensive toxicity evaluation of a chemical, a valid toxicity screening test can provide information about the relative toxicity of a compound and can help predict non-inhibitory chemical application rates. The Microtox® system is a relatively simple, rapid and inexpensive test and was used as the toxicity screening method in this project to determine: (a) the relative toxicity of the chemicals and wastes, (b) the non-inhibitory chemical and waste loadings used in the degradation studies, and (c) the toxicity reduction that occurred in the respective studies. The use of the Microtox® procedure to screen and predict the treatability potential of waste in soil has been evaluated and found to be satisfactory.

Degradation Studies

These experiments were conducted to determine the removal kinetics of the designated chemicals and wastes in soil.

Several of the chemicals could not be evaluated because of chemical reactions in the soils that made analytical determination impossible. These were Diphenylamine, m-Phenylenediamine and Thiophenol.

Biodegradation is believed to be the most important removal mechanism for organic compounds in soil systems. degradation of organics is accomplished in a series of biochemical reactions through which a parent compound is changed or transformed to organic or inorganic end products. Complete degradation is the term used to describe a process whereby constituents are mineralized to inorganic end products, including carbon dioxide, water, and inorganic nitrogen, phosphorus, and sulfur compounds. Aerobic soil bacteria possess the ability to biochemically catalyze the oxidation of organic compounds. For this reason, and because the zone of incorporation at land treatment sites generally is aerobic, the protocol used in this study allowed aerobic conditions and aerobic biodegradation reactions to occur.

The primary goal of biodegradation testing is to obtain an overall estimate of the rate at which a compound will degrade in a soil environment. While many compounds appear in the environment in pure form, a common approach to studying removal rates of organic compounds has been to evaluate individual compounds. Although this approach provides an understanding of the removal rates for specific compounds, it is recognized that during actual land treatment chemicals normally are applied as mixtures. Interactions between compounds in a mixture within the soil matrix may promote or inhibit their removal from soil. The noted chemicals (Tables 1 and 2) were evaluated as individual compounds using standard laboratory microcosm and protocol.

In this study, no distinction was made between specific loss mechanisms. Removal rates can be due to biodegradation, chemical degradation, hydrolysis, photolysis and volatilization. The chemicals that were evaluated did not have high volatilization potential and volatilization was not considered an important removal mechanism in these degradation experiments.

The rate of degradation was experimentally determined by measuring the difference between the amount of compound initially added to a soil and the amount which was recovered after specified time.

Table 1. Chemicals that were Evaluated in this Study

Compound	Formula	EPA Hazardous Waste Number
Acid Extractables		
Phenol	C_6H_6O	U188
o-Cresol	C_7H_8O	U052
p-Cresol	C_7H_8O	U052
m-Cresol	C_7H_8O	U052
2-Chlorophenol	C_6H_5ClO	U048
3-Chlorophenol	C_6H_5ClO	NOS
4-Chlorophenol	C_6H_5ClO	NOS
2,3-Dichlorophenol	$C_6H_4Cl_2O$	NOS
2,4-Dichlorophenol	$C_6H_4Cl_2O$	U081
2,5-Dichlorophenol	$C_6H_4Cl_2O$	NOS
2,6-Dichlorophenol	$C_6H_4Cl_2O$	U082
3,4-Dichlorophenol	$C_6H_4Cl_2O$	NOS
2,4,5-Trichlorophenol	$C_6H_3Cl_3O$	U230
2,4,6-Trichlorophenol	$C_6H_3Cl_3O$	U231
Pentachlorophenol	C_6HCl_5O	U242
2,4-Dimethylphenol	$C_8H_{10}O$	U101
2-Methyl-4-Chlorophenol	C_7H_7ClO	NOS
3-Methyl-4-Chlorophenol	C_7H_7ClO	U039
3-Methyl-6-Chlorophenol	C_7H_7ClO	NOS
p-Nitrophenol	$C_6H_5NO_3$	U170
2,4-Dinitrophenol	$C_6H_4N_2O_5$	P048
4,6-Dinitro-o-Cresol	$C_7H_6N_2O_5$	P048
Thiophenol	C_6H_6S	U014
Amines		
Diphenylamine	$C_{12}H_{11}N$	X016
m-Phenylenediamine	$C_6H_8N_2$	X017
Toluenediamine	$C_7H_8(NH_2)_2$	U221
Brucine	$C_{23}H_{26}N_2O_4$	P018
Alcohols		
Isobutyl alcohol	$C_4H_{10}O$	U140
Allyl alcohol	C_3H_6O	P005
Propargyl alcohol	C_3H_4O	P102
1-Butanol	$C_4H_{10}O$	U031
2,3-Dichloropropanol	$C_3H_6Cl_2$	X006
Methanol	CH_4O	U154
Other		
Carbon disulfide	CS_2	P022
2-Nitropropane	$C_3H_7NO_2$	U171
Thiourea	CH_4N_2S	U219

Table 2. The Hazardous Waste and Related Chemicals that were Evaluated

Specific Hazardous Waste		
KO44 -- Wastewater treatment sludge from the manufacturing and processing of explosives		
Explosive and Munitions Manufacturing Chemicals		
Compound	Formula	EPA Hazardous Waste Number
2,4-Dinitrotoluene	$C_7H_6N_2O_4$	U105
2,6-Dinitrotoluene	$C_7H_6N_2O_4$	U106
TNT (2,4,6-Trinitrotoluene)	$C_7H_5N_3O_6$	—
RDX +	$C_3H_6N_6O_6$	—
HMX + +	$C_4H_8N_8O_8$	—

+ RDX = Hexahydrotrinitrotriazine
 + + HMX = Cyclotetramethylenetetranitramine

intervals. A plot of the disappearance of a constituent originally present in the chemical/soil mixture versus treatment time provided the following: (a) the type of reaction (generally zero or first order), (b) the reaction rate constants for the zero or first order reactions, and (c) the half-life ($t_{1/2}$) time of each constituent of concern. The soil used: (a) had not had previous exposure to industrial chemicals or wastes, and (b) did not receive any pretreatment such as soil amendments or specially acclimated biological cultures prior to these experiments. The naturally occurring soil microbial consortium was responsible for the bioremediated removal of the chemicals.

Chemical mass loadings were determined as part of the toxicity screening evaluations and ensured that the loadings at which the chemicals were applied did not inhibit soil microbial activity. Soil pH was not adjusted nor were supplementary organic substrates used.

Adsorption Experiments

The persistence of hazardous organic compounds in soils is related to reactions that affect the transport and fate of such chemicals. One of the most important reactions is adsorption. Adsorption is the process by which ions or molecules present in one phase tend to concentrate at a surface or interface. The tendency of organic molecules to adsorb on soil is

determined by the physical and chemical characteristics of the chemical compound and the soil to which it is added. The two driving forces for adsorption are the lyophobic (solvent-disliking) character of a solute relative to a particular solvent, and the affinity of the solute for the solid, such as electrical attraction.

Adsorption is the major retention mechanism for most organic and inorganic compounds in soils. As a result, the leaching potential of a chemical in soil is, in general, proportional to the magnitude of the adsorption (partitioning) coefficient of that chemical in a soil. The adsorption potential of a chemical is governed by the properties of both the soil and the chemical. Important properties of the chemical that affect adsorption include: (a) chemical structure, (b) acidity or basicity of the molecule (pK_a or pK_b), (c) water solubility, (d) permanent charge, (e) polarity, and (f) molecule size.

At equilibrium, the solute remaining in solution is in dynamic equilibrium with that of the soil surface. At this point, there is a defined distribution of solute between the liquid and solid phases. The preferred form for depicting this distribution is to express the quantity q_e (amount of solute sorbed per unit weight of solid sorbent) as a function of the equilibrium solution concentration (C_e) at a fixed temperature. An expression of this type is an adsorption isotherm.

An adsorption equation that has been used widely for solid-liquid systems is the Freundlich equation:

$$q_e = K_f C_e^{1/n}$$

where q_e is the equilibrium distribution coefficient (mg of chemical/gm of adsorbent), C_e is the equilibrium chemical concentration (mg/liter of solvent), and K_f and $1/n$ are constants. The constant, K_f , is related to the capacity or affinity of the adsorbent and the exponential term, $1/n$, is an indicator of the intensity, or how the capacity of the adsorbent varies with the equilibrium solute concentration. The Freundlich isotherm has had success describing sorption behavior of organic chemicals, and the adsorption data generated in this study were evaluated by this equation.

Toxicity Reduction

A major objective of this study was to provide comprehensive screening data on the treatability of specific organic chemicals in soil. Hazardous constituents that enter the soil are to be detoxified, immobilized. When a chemical is added to the soil, it is transformed into other products through chemical and biological reactions with or without complete detoxification and immobilization. Measuring the loss of the parent compound does not assure that complete detoxification and immobilization occurs. Intermediate degradation products, which may be more

mobile and/or toxic than the parent compound, may be generated as the parent compound degrades. Additional information on the transformation and/or detoxification of a chemical is necessary to establish that the loss of the parent compound leads to the complete detoxification of the chemical or waste. Such information can be obtained using either chemical or bioassay analyses.

The reduction of toxicity that occurred in selected degradation studies was evaluated by determining the toxicity of the water soluble fraction (WSF) of the chemical/soil mixture at the same sampling intervals used to obtain the degradation data. The chemical compounds that can be extracted with water represent the potentially leachable fraction of the chemical or any intermediate chemical detoxification products. The WSF of the chemical poses the greatest threat to groundwater contamination. Hence, evaluating the loss of the potentially leachable fraction of a chemical is important. The concentration of the parent chemical in the WSF also was determined. This concentration was expressed in terms of quantity of chemical that was water extractable per kg of the soil. To put the toxicity reduction data in perspective, the WSF toxicity reductions, the WSF chemical concentration reductions and the soil chemical concentration reductions were compared.

Conclusions

Specific conclusions based on the results of the project include:

1. The Microtox® biological assay represents an appropriate method with which to evaluate the EC₅₀ toxicity of a chemical or waste.
2. Comparison of the EC₅₀ data indicated that: (a) the alcohols were less toxic than the acid extractable compounds, and (b) within chemical categories, there were considerable differences in relative toxicity.
3. The chemical structure of the compounds evaluated affected the relative toxicity of a compound. With chlorophenols, the relative toxicity was related to the substitution position of the chlorine group on the phenol ring. The order of relative toxicity was para > meta > ortho. The EC₅₀ data suggested that the same order occurred for methylphenols and nitrophenols.
4. The chemical that was substituted on the phenol ring appeared to have an effect on toxicity. Nitro-substituted phenols, even when substituted in the para position, appeared to less toxic than the methyl- or chloro-substituted phenols.
5. When the chemicals were mixed with two different soils, and the EC₅₀ value of the water soluble fraction (WSF) of the soil mixtures was measured, the values also indicated that chemicals with the chlorine in the para position had the greater toxicity. Mixing of the chemicals with the soils did not affect the relative toxicity of the chemicals in the two soils.
6. In general, the acceptable non-inhibitory chemical loading rates for the Mississippi soil were lower than those for the Texas soil. There was no consistent pattern for the differences.
7. The chemical or waste loading procedure (described in Table 9, Section 4 of the full report) resulted in chemical loadings that did not inhibit the non-acclimated organisms in the laboratory microcosms, except in one case (4,6-Dinitro-o-Cresol). This procedure provided a good estimate of initial, acceptable chemical loadings that can be used in laboratory degradation studies.
8. Both zero and first order kinetics provided adequate representation of the data. For most of the chemicals, the data could be fit to either kinetics with high correlation coefficients.
9. The rates of chemical loss were higher in the Texas soil than in the Mississippi soil. There did not appear to be any pattern to the differences in rates in the two soils.
10. Chlorophenols with the chlorine substituted in the meta position had greater half-lives and therefore lower chemical loss rates. This was particularly evident with the mono-, di-, and trichlorophenols in the Texas soil.
11. Chemicals that had a nitro group substituted on the phenol ring appeared to have a lower loss rate.
12. The Freundlich equation described the adsorption of the chemicals on the two soils satisfactorily, with high correlative coefficients, except for a few chemicals.
13. The range of chemical concentrations evaluated ranged from the low mg/l concentrations to near or at saturation concentrations, and for most chemicals covered two to three orders of magnitude. For these concentration ranges, a linear adsorption relationship, i.e., $n = 1$, did not occur.
14. The values of the Freundlich constant (K_f) for the chemicals in the two soils were different. For the acid extractables, the K_f values generally were greater in the Texas soil which had the higher pH and the greater organic carbon content. For the amines and alcohols, the K_f values were greater in the Mississippi soil, which had the lower pH and the lower organic carbon content.
15. Two loading rates, the Texas soil, and nine chemicals (phenol and eight chlorinated phenols) were used in this study. Both first and zero order kinetics satisfactorily fit the water soluble fraction (WSF) chemical loss data and the toxicity reduction data.
16. The higher chemical loading rates resulted in higher chemical concentrations in the WSF and higher WSF toxicities at the beginning of the experiments.
17. The higher chemical loading rates generally resulted in slower chemical losses (higher half lives) and slower toxicity reduction. However, at both loading rates for each chemical, the chemicals were degraded and the toxicity was reduced. No differences due to the loading rates were apparent in zero order kinetics.
18. The loss of the chemicals in the WSF was about 1.5 times faster than the loss of the chemical in the soil.
19. The WSF toxicity for each chemical decreased as the soil chemical and the WSF chemical concentrations decreased.
20. The WSF toxicity decreased at about the same rate as the WSF chemical concentration when the data for all nine chemicals were compared.
21. No enhanced mobilization of the applied chemicals occurred as the degradation and detoxification occurred.
22. No water soluble toxic products appeared to be formed as the chemicals were degraded in the soil.
23. The Freundlich equation described the sorption of 2,4- and 2,6-Dinitrotoluene in the two soils satisfactorily. It did not do so for TNT, RDX, or HMX.

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24. No loss of 2,4-Dinitrotoluene occurred over a 47-day study even though the loading rate used was determined to be acceptable using procedures discussed in Section 4 of the full report. Degradation loss rates were obtained for 2,6-Dinitrotoluene and TNT. First order kinetics were a better representation for TNT than were zero order kinetics.
 25. The half life of TNT in the Mississippi soil was shorter, and the loss faster, than in the Texas soil. No difference in the loss rates in the two soils for 2,6-Dinitrotoluene was apparent.
 26. The sludge resulting from the manufacture and processing of explosives contained: (a) high concentrations of nitrogen and COD, (b) concentrations generally less than 10 mg/l for heavy metals, and (c) no TNT, RDX or HMX.
 27. The munitions sludge had a high toxicity as measured by the Microtox® procedure. The constituents causing the relative toxicity were in the soluble phase of the sludge.

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Scott G. Huling is the EPA Project Officer (see below).

The complete report, entitled "Treatability Potential for EPA Listed Hazardous Wastes in Soil," (Order No. PB 89-166 581/AS; Cost: \$21.95, subject to change) will be available only from:

National Technical Information Service
5285 Port Royal Road
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Telephone: 703-487-4650

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