United States Environmental Protection Agency
Research and Development
Hazardous Waste Engineering Research Laboratory
Cincinnati OH 45268
EPA-540/S2-84-003 Jan. 1985

EPA

Project Summary

Review of In-Place Treatment Techniques for Contaminated Surface Soils Volumes 1 and 2

R. C. Sims, J. L. Sims, D. L. Sorensen, J. McLean, R. Mahmood, and R. R. Dupont

This two-volume report presents information on in-place treatment technologies applicable to contaminated soils at shallow depths. Volume 1 discusses the selection of the appropriate in-place treatment technology for a particular site and provides specific information on each technology. Volume 2 provides background information and relevant chemical data.

Selection of in-place treatment technologies follows the process outlined in the National Contingency Plan. The type of in-place treatment (extraction, immobilization, degradation, attenuation, or reduction of volatiles) is determined on the basis of information available from the remedial investigation. Selection of a specific technology involves assessment of waste, soil, and site-specific variables. The technology is implemented if it is considered more cost-effective in comparison with the alternatives. Volume 1 provides a guide for selection of in-place treatment technologies, a discussion of each in-place treatment technology, data for estimating the costs of implementing in-place treatment, and an appendix on cost information.

The second volume supports the treatment methodology described in Volume 1. The information presented on monitoring to determine treatment effectiveness, characterization and evaluation of the behavior and fate of hazardous constituents in soil/waste systems, and properties (including adsorption, degradation, and volatilization parameters) for various compounds is intended to help the manual user in making more complex decisions and in selecting analyses concerning site, soil, and waste interactions.

This Project Summary was developed by EPA's Hazardous Waste Engineering Research Laboratory, Cincinnati, OH, 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

Uncontrolled disposal of hazardous wastes frequently produces large quantities of contaminated soils. The cost to excavate, haul, and dispose of these soils in an approved landfill is often prohibitive or impractical. In these situations, an in situ treatment approach may be effective in eliminating or reducing the hazard to acceptable levels In situ treatment of contaminated soils must be based on an understanding of factors and processes that determine the behavior of chemicals in soil systems. Specifically, an evaluation of chemical properties, biochemical processes, and environmental factors influencing the behavior and fate of chemicals is required. The goals of in situ management include treating contaminated soils until acceptable levels of hazardous materials are achieved and so that groundwater and surface water resources are protected without physically removing or isolating the contaminated soil from the contiguous environment. Volume 1 presents a number of physical/chemical and biological techniques, both tried and conceptual, that may be useful in treating hazardous waste contaminated soil in place. Volume 2 provides more fundamental information that will help the site manager select and correctly apply treatments in complex situations.

Scope of the Report

This report has been divided into two volumes. Section 2 of Volume 1 provides a guide for selection of in-place treatment technologies. Section 3 provides a discussion of each in-place treatment technology, including process description, information requirements for application of the technology, wastes *amenable to treatment, current status of* the technology, ease of application, potentially achievable levels of treatment, reliability of the technology over the long term, secondary impacts, and equipment materials required to implement the technology. Section 4 discusses engineering methods for modifying the oxygen content, moisture content, nutrient content, pH, and temperature of the soil to optimize the effectiveness of in-place treatment. In addition, data for estimating the costs of implementing in-place treatment are provided in Section 4 and in an appendix on cost information.

Fundamental soil/waste system processes characterized and evaluated in Volume 2 may serve as a base for selecting and evaluating specific in situ treatment, soil immobilization processes for control of leaching and volatilization, biodegradationprocesses, and transformation processes. Modeling of waste constituents with respect to transport, adsorption, and transport in soil systems are also discussed.

Soil and Site Factors

Before beginning in situ remedial actions to treat hazardous-waste-contaminated soils, the site's characteristics *must be identified.* When the contaminants migrate off site, what are the characteristics of the route? What are the characteristics of the off-site receiver? Route characteristics determine the potential for contamination, and receiver characteristics and the corresponding degree of public health hazard indicate the time frame in which the remedial action must be performed. Site characterization also may serve to explain how site modification or management could help protect human health. Those soil characteristics that affect water movement (i.e., infiltration and permeability) and those factors that affect contaminant mobility are the most important. The specific site and soil characteristics that need to be identified when assessing a site for in situ treatment as well as the site and soil conditions that may be managed to enhance soil treatment are identified in Table 1.

The properties of waste that affect the behavior and fate of chemicals in soil systems *must be characterized because* these properties directly affect how the waste will be treated (or assimilated): (1) degradation, (2) transformation or detoxication, or (3) immobilization of constituents. Factors important in determining the behavior and fate--and therefore the treatment pathways--of waste constituents in soil are listed in Table 2. For each chemical, or chemical class, the information needed can be summarized as characteristics related to:

(1) potential leaching (e.g., water solubility, octanol/water partition coefficients, solid sorption coefficient)

(2) potential volatilization (e.g., vapor pressure, relative volatilization index)

(3) potential decomposition (e.g., half-life, degradation rate, biodegradability index)

(4) chemical reactivity (e.g., oxidation, reduction, hydrolysis potential).

Comparing the properties of the soil at a specific site with the characteristics given above permits the potential for (1)

Table 1. *Site and Soil Characteristics Identified as Important in In Situ Treatment*

Site location/topography and slope

Soil type and extent

Soil profile properties
- *boundary characteristics*
- *depth*
- *texture**
- *amount and type of coarse fragments*
- *structure**
- *color*
- *degree of mottling*
- *bulk density**
- *clay content*
- *type of clay*
- *cation exchange capacity**
- *organic matter content**
- *pH**
- *Eh**
- *aeration status**

Hydraulic properties and conditions
- *soil water characteristic curve*
- *field capacity/permanent wilting point*
- *water holding capacity**
- *permeability* (under saturated and a range of unsaturated conditions)*
- *infiltration rates**
- *depth to impermeable layer or bedrock*
- *depth to groundwater,* including seasonal variations*
- *flooding frequency*
- *runoff potential**

Geological and hydrogeological factors
- *subsurface geological features*
- *groundwater flow patterns and characteristics*

Meteorological and climatological data
- *wind velocity and direction*
- *temperature*
- *precipitation*
- *water budget*

**Factors that may be managed to enhance soil treatment.*

Table 2. Soil-Based Waste Characterization

Chemical class
Acid
Base
Polar neutral
Nonpolar nuetral
Inorganic
Soil Sorption Parameters
Freundlich sorption constants (K, N)
Sorption based on organic carbon content (K_{oc})
Octanol water partition coefficient (K_{ow})
Soil degradation parameters
Half-life ($t_{1/2}$)
Rate constant (first order)
Relative biodegradability
Chemical properties
Molecular weight
Melting point
Specific gravity
Structure
Water solubility
Volatilization parameters
Air: water partition coefficient (K_w)
Vapor pressure
Henry's law constant ($1/K_w$)
Sorption based on organic carbon content (K_{oc})
Water solubility
Chemical reactivity
Oxidation
Reduction
Hydrolysis
Precipitation
Polymerization
Soil contamination parameters
Concentration in soil
Depth of contamination

soil treatment and (2) off-site contamination to be determined.

By determining how toxic, how concentrated, and how extensively inorganic contaminants occurred at a disposal site, a list of hazardous metals was developed: As, Be, Cd, Cr, Cu, Pb, Hg, Ni, Se, Ag, and Zn. As, Se, and Cr are the only metals that can exist as anions in nature, and because of their anionic nature, their behavior in soil will differ from other heavy metals. The behavior and fate of all these metals are discussed in detail in the full report.

The chemistry of heavy metals in soil was divided into two interdependent but separate categories: (1) solution chemistry and (2) interfacial chemistry. Discussions addressing the general principles affecting the dissolution/precipitation of the solid phase are included because solid-phase formation to scavenge metals from soil solution is a primary objective of in situ treatment.

Soil sorption is perhaps the most important soil-waste process affecting the toxic and recalcitrant fractions of the hazardous waste. To effectively use the sorption reaction as a treatment process, the influence of soil sorption on the extent and rate of leaching, and also on biological decomposition of these fractions, must be understood and described. Understanding the effect of different solid surfaces on hazardous waste-constituents provides a mechanism for rationally selecting additional sorbents for use in augmenting the natural ability of a soil system to immobilize hazardous chemicals. Also, understanding the relationship between soil water content and extent of sorption of hazardous chemicals provides the hazardous waste manager with a process for controlling the potential release and migration of constituents through leaching. Volume 2 contains a discussion of the factors involved in soil sorption of chemical constituents and the basic factors influencing the sorption process that may be used in treatment processes to immobilize specific hazardous waste fractions.

Immobilization

The relationship between immobilization of chemical constituents in soil systems (based on soil chemical properties) and chemical class (based on chemical structure) is summarized in Table 3. Generally, nonionic constituents of low water solubility and cationic constituents have low mobilities and leaching potential. Acid constituents at neutral and high pH values are most easily leached from soil systems.

Understanding the relationship between soil water content and extent of sorption of hazardous chemicals provides the hazardous waste manager with a tool for controlling potential release and migration of constituents through the control of the leaching process. One commonly used isotherm that is useful in describing the immobilization of organic constituents in soil is the Freundlich isotherm:

$$S = KC^{1/n}$$

where

K and n are constants,

S = **amount of chemical associated with solid phase, or the solid phase concentration,**

C = **amount of chemical associated with the solution phase, or the solution phase concentration.**

The Freundlich isotherm related the solid phase concentration to the solution phase concentration at equilibrium conditions.

An important linear isotherm can be obtained from the Freundlich isotherm when n=1, i.e.,

$$S = K_dC$$

where K_d = the distribution coefficient.

The relationship between K_d1, soil moisture content Θ, and percent adsorption of an organic chemical can be used to manage a soil system:

$$\text{percent adsorbed} = K_d/(K_d + \Theta)$$

Table 3. Leaching Potential of Chemicals in Soil Systems

	Chemical Class							
	Nonionic			*Ionic*				
	Water Solubility			*Basic*		*Cationic*	*Acidic*	
Leaching Potential	*high*	*med*	*low*	*Low pH*	*neutral pH*		*low pH*	*neutral pH*
Low			*X*	*X*		*X*		
Medium		*X*			*X*		*X*	
High	*X*							*X*

The extent of sorption as a function of soil moisture content for different values of the distribution coefficient is illustrated in Figure 1. Thus careful control of soil moisture content will determine, to a large extent, the relative immobilization of a given set of chemical constituents identified at a remedial site. Optimization of cost effective and efficient treatment may require a compromise between optimum soil moisture content for biodegradation versus sorption.

The full report includes discussions of soil microbiological factors related to in situ treatment: the soil microbial environment, soil microorganisms, biogeochemistry of toxic metals, microbial decomposition of xenobiotic compounds, genetic engineering, co-metabolism, and degradation of specific classes of organic compounds

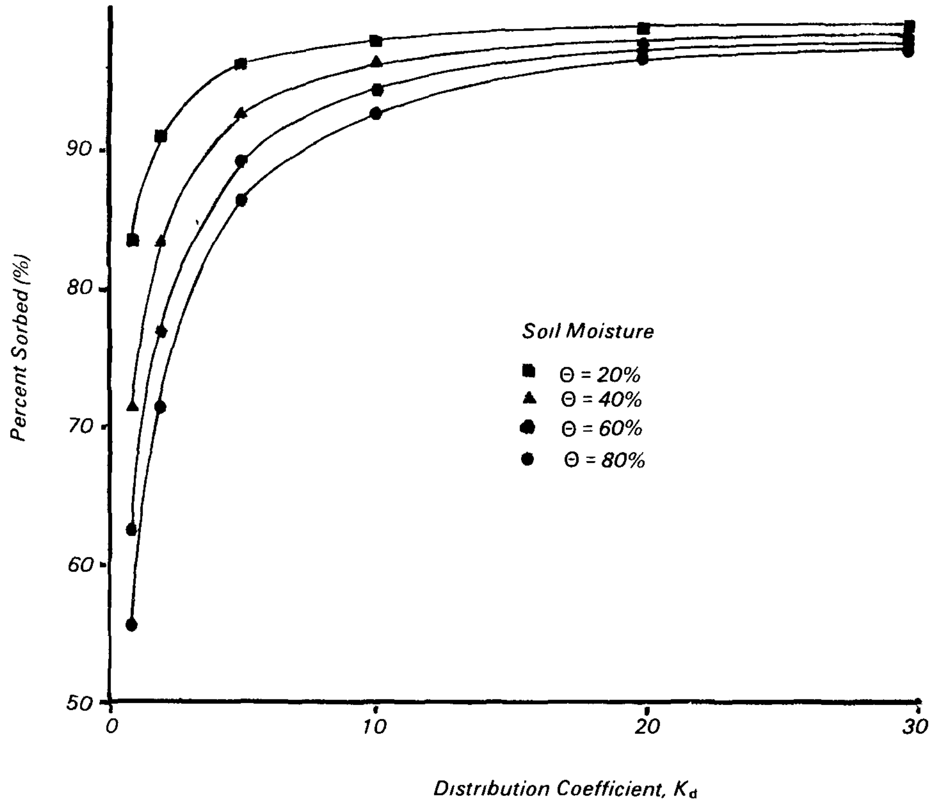

Figure 1. *Extent of sorption as a function of soil moisture Θ and K_d.*

Biodegradation

The quantitative aspects of microbial decomposition of organic constituents are also discussed. Mathematically, the rate of decomposition represents a sink term in organic transport models--models needed to predict potential groundwater contamination with respect to magnitude and type of contamination and the time factor for contamination (rate of transport). The power rate model, the hyperbolic rate model, and the effect of sorption on the rate of degradation are considered. Results for degradation are tabulated from the literature. Degradation rate as a function of soil concentration and chemical structure for the polynuclear aromatic class of priority pollutants is discussed.

To describe the behavior of waste constituents in soil systems, Volume 2 considers one-dimensional transport models, including a water flow model and a solute transport model. The models represent a first-cut approach to ranking chemicals and chemical classes with respect to potential mobility and, therefore, an approach to ranking chemicals with highest priority for immobilization treatment.

Volatilization and Photodegradation

The factors affecting volatilization of organics in soil systems include: (1) contaminant vapor pressure, (2) contaminant concentration, (3) soil/chemical adsorption reactions, (4) contaminant solubility in soil water, (5) contaminant solubility in soil organic matter, and (6) soil temperature, water content, organic content, porosity, and bulk density.

The major contaminant property affecting volatilization is its vapor pressure, and the major environmental factors affecting the contaminant's vapor pressure are the soil/water and air/water partition coefficients that exist for the soil/water/air environments within a soil system. Additional complexity results if the contaminant is added along with an additional adsorbing fluid such as oil in refinery waste, where partitioning of the contaminant between the oil/soil, oil/water, and oil/air phases would also be expected to affect the volatilization of vapor pressure of the volatile compounds.

Photodegradation of organic compounds may occur by two processes (1) direct photodegradation and (2) sensitized photooxidation. The relative importance of photodegradation of chemicals on or within a soil will depend to a large extent upon its partitioning between the air/water/soil media within the soil system. Using photochemical reactions to enhance compound biodegradation is an area of interest for hazard mitigation from hazardous waste sites.

Monitoring

To ensure that the objectives of in situ treatment are attained, a monitoring program must be established to: (1) ensure that the hazardous or toxic constituents of the waste are being degraded, detoxicated, or inactivated as planned, (2) monitor degradation rates of degradable constituents, (3) ensure that waste constituents are not entering runoff or leachate water and leaving the area in unacceptable concentrations, and (4) determine whether adjustments in treatment management are needed to maintain the treatment process.

A complete program would monitor soil core and soil-pore liquid in the treatment zone and outside the treatment zone, groundwater, runoff water, and atmosphere. Constituents that should be monitored include those determined to be hazardous in the initial site/waste characterization study as well as expected, important degradation or transformation products. The monitoring program may also include substances needed for treatment, whether these substance are native to the soil or added as a treatment agent. Volume 2 includes specific monitoring information for each medium (soil, water, and atmosphere) and cost estimates for various monitoring techniques.

An appendix to Volume 2 of the full report contains a data base for assessing the soil/waste interactions of individual chemicals. Specific quantitative information for each chemical includes: (1) compound/chemical properties, (2) adsorption parameters, (3) degradation parameters, and (4) volatilization parameters. Thus qualitative and quantitative analyses can be conducted for the site/soil/waste information presented in the main section of the report with the use of this data base.

Conclusions

In situ treatment of hazardous waste contaminated soils requires considerable information and understanding about site/soil/waste interactions. Available treatment techniques need to be carefully evaluated and selected based on this information and understanding. In addition, evaluating the success of any treatment or combination of treatments requires an effective monitoring program. This two-volume report provides a basis for meeting these needs.

The full report was submitted in fulfillment of Contract No. 68-03-3113, Task 41-1 by JRB Associates under subcontract to Utah State University under sponsorship of the U.S. Environmental Protection Agency.

R. C. Sims, J. L. Sims, D. L. Sorensen, J. McLean, R. Mahmood, and R. R. Dupont are with Utah State University, Logan, UT 84322.

***Naomi P. Barkley** is the EPA Project Officer (see below).*

The complete report consists of two volumes, entitled "Review of In-Place Treatment Techniques for Contaminated Surface Soils:"

"Volume 1. Technical Evaluation," (Order No. PB 85-124 881; Cost: $17.50)

"Volume 2. Background Information for In Situ Treatment," (Order No. PB 85-124 899; Cost: $29.50)

The above reports will be available only from: (cost subject to change)

National Technical Information Service
5285 Port Royal Road
Springfield, VA 22161
Telephone: 703-487-4650

The EPA Project Officer can be contacted at:

Hazardous Waste Engineering Research Laboratory
U.S. Environmental Protection Agency
Cincinnati, OH 45268

☆ U S GOVERNMENT PRINTING OFFICE: 1985 - 559-111/10776