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# THE ENVIRONMENTAL IMPACT OF SOIL CONTAMINATION:
## BIOAVAILABILITY, RISK ASSESSMENT, AND POLICY IMPLICATIONS

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## EXECUTIVE SUMMARY

Sites which contain contaminated soils are common. While the need to protect human health and the environment at these sites is rarely debated, there are questions about the magnitude of risk posed by the chemicals in such soils and about the cleanup levels that should be achieved. Currently, soil cleanup levels are based on chemical- or media-specific criteria or guidelines, or on limits stemming from risk-based analyses. Chemical availability—the ability of a chemical to reach and adversely affect human health and the environment—is rarely taken into consideration with these approaches.

Recently, however, knowledge about the availability of chemicals in soils—i.e. leachability, mobility, rate of release, and relative toxicity—has increased. There is now considerable weight-of-evidence information from laboratory and field data indicating that for certain common situations—i.e., after chemicals have "weathered" over time, or after bioremediation has been performed—organic chemicals in soils may not be readily available for uptake by organisms, may not have an adverse impact on human health or the environment, and may not require costly remediation.

In this study, the issues associated with chemical bioavailability are presented and discussed, along with a review of current data on the availability of organic chemicals in both treated and untreated soils. The primary conclusions of this study are:

- Increasing experience indicates that measures of chemical concentration alone are insufficient to determine the actual risk posed by the chemicals or concentrations that constitute an environmentally acceptable endpoint.

- Environmentally acceptable endpoints for soils at some sites may be determined using simple approaches such as waste- or material-specific criteria or generic, risk-based state or federal values or standards however, in other circumstances such generic criteria can result in environmentally acceptable endpoints for a specific site that are unnecessarily conservative and that may not be applicable to the conditions at that site.

- Variations in chemical availability, mobility and toxicity are important factors to consider in making decisions about the necessary degree of cleanup or remediation at a given site. Chemical availability differs for fresh and weathered chemicals: chemicals recently released to soils will be more available for leaching, degradation, and bio-uptake than will be weathered chemicals. For some sites where the chemicals have weathered for decades, and where the chemicals are held tightly by the soil and are unavailable for transport, there may be little need for remediation.

- Chemical availability can also change as soil is remediated. Though some of the chemicals originally contaminating the soil might still be detectable, they may have been naturally "stabilized" in the soil matrix. Thus, these remaining chemicals are less mobile and less available, posing a reduced risk to the environment and may require no further remediation.

- Decisions relating to soil cleanup should reflect the fact that many chemicals in soil move slowly, and may be retarded and transformed during such movement. They should also reflect the fact that only a fraction of the chemical associated with a soil is readily available to cause adverse impact. In addition, not every site will have an ultimate use that requires cleanup to background conditions.

- The weight of evidence information on chemical availablity in soils has important implications to research directions as well as to remediation and regulatory policy.

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# I. INTRODUCTION

Management of contaminated soils is a common problem in the United States. Organic chemicals reach soils through spills, leaks, tank and pipeline ruptures, and other disposal pathways. While there is little debate about the need to avoid adverse impacts to human health and the environment from such releases, there are questions about the extent and magnitude of the risk posed by a chemical release, and about the cleanup goals required.

The primary goal in managing contaminated soil sites is to render the soil environmentally acceptable through management or remediation so the site can be used for some acceptable purpose. This goal applies equally to situations where there have been fresh chemical releases, where the releases have occurred over some time, or where the chemicals have been “weathering” at a site for many decades.[1] The latter is the situation at many urban “Brownfield” sites.

The key question in managing contaminated soil is, how clean is clean—what determines an acceptable environmental endpoint? This question is asked at the national level as new laws or changes to existing environmental laws are debated, and at state and local levels every time site cleanup or remediation is considered.

Traditionally, soil cleanup criteria have been set using concentration-based standards that often require remediation to background levels or to other specified levels that are considered administratively acceptable.[2] Recently, however, the focus of soil cleanup criteria has shifted away from a standards-based approach, towards a more risk-based approach. Such an approach recognizes that for a chemical in a soil to pose a risk, it must first be made available to a receptor (such as a human being) through mobilization and transport, and must then elicit an adverse response from the release due to that exposure. Under a risk-based approach, answering “how clean is clean” in a meaningful way requires making a determination of what concentration of a chemical, such as a hydrocarbon, is environmentally acceptable at a specific site.

In determining the relative risk posed by chemicals in soils, it is not enough to simply measure chemical concentration. One must also address the risk-assessment paradigm, the pathways by which human health and the environment can be affected, and the availability of the released chemical for transport and adverse impact. In the general risk-assessment paradigm, environmental risk is defined as the likelihood of injury, disease, death, or adverse impact resulting from human or environmental exposure (real or potential) to chemicals under site-specific circumstances. But while decisions on the suitability of soil-remediation processes commonly focus on chemical-concentration reduction, other parameters important to risk-evaluation decisions—such as the mobility and relative toxicity of the residues from the remediation process—need to be determined and evaluated. Increasing experience indicates that measures of chemical concentration alone are insufficient to determine the actual risk of the chemicals or what constitutes an environmentally acceptable endpoint (EAE).[3]

Site-specific risk assessments require consideration of the pathways by which a chemical may affect human health and the environment as well as a measure of chemical availability that is consistent with the site-specific pathways of concern. Knowledge about chemical availability in soils is an important factor in making site-remediation decisions since it broadens the range of options or tools decision makers can use on a site-specific basis. However, detailed knowledge about chemical availability may not be necessary if other approaches are

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[1] “Weathering” of chemicals and soils covers a number of distinctly different chemical and physical processes. There are different types of chemicals—volatile or non-volatile; reactive or nonreactive with the soil; water soluble or water insoluble; and so on. These different characteristics all affect how “weathering” occurs. Soils also have a wide range of properties that influence actual processes taking place.

[2] "Background levels" are the concentration levels at which a given chemical might be found in a comparable, but uncontaminated soil. For many chemical species, background levels can approach zero, or the limits of detectability.

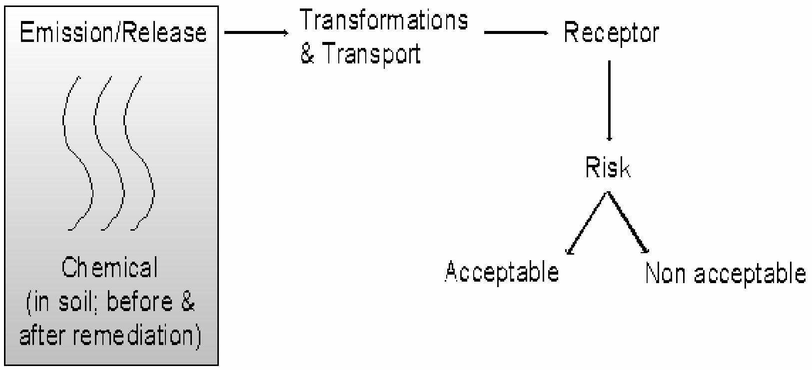
[3] An environmentally acceptable endpoint is a concentration of chemical in a site soil that will not have an adverse affect on human health and the environment, an EAE is determined after considering the mobility and toxicity of a chemical and its expected impact when exposure to humans and ecosystems occurs.

satisfactory. In some cases, environmentally acceptable endpoints for soils at a site may be determined using approaches such as waste- or material-specific criteria or guidelines, or generic, risk-based state or federal values or standards. In many situations, these approaches can be cost-effective and are attractive because they are easily identified and applied by regulators, simple to communicate, and can be imposed at various sites with similar compounds. In other circumstances, however, these "generic" endpoints can yield EAEs for a specific site that are unnecessarily conservative and which may not be applicable to the conditions at that site—not every site will have an ultimate use that requires cleanup to background conditions. In these instances, site-specific measurements of chemical availability will provide a more appropriate EAE that addresses the risk associated with chemicals at that site.

## II. BASIC CONCEPTS IN BIOAVAILABILITY

For a chemical in a soil to pose a risk, it must first be made available to a receptor through mobilization and transport, and then must elicit an adverse response from the receptor due to exposure (Figure 1).

Figure 1: Conceptual Risk Assessment Paradigm



Two points warrant attention when considering the availability of a chemical in soil. The first is the availability of a chemical in the soil under existing conditions. These conditions may include "fresh" chemicals or "weathered" chemicals. Fresh conditions refer to sites where a recent spill or chemical release has occurred. Weathered or aged chemicals are chemicals that have been in soils for many years, even decades. Chemical availability differs for fresh and weathered chemicals: chemicals recently released to soils will be more available for leaching, degradation, and bio-uptake than will weathered chemicals. This difference is an important factor in making decisions about the necessary degree of cleanup or remediation at a given site. For some sites where the chemicals have weathered for decades, and where the chemicals are held tightly by the soil and are unavailable for transport, there may be little need for remediation.

The second point that merits consideration is that chemical availability can change as soil is remediated. The ability of many hydrocarbons to leach and further degrade declines as: a) the chemicals remain in the soil for increasing periods of time, and b) as microorganisms degrade the readily accessible organics.[4] In other words, the remaining chemicals have been naturally "stabilized" in the soil matrix by adsorption or chemical binding. Thus, these remaining chemicals are less mobile and less available, posing a reduced risk to the environment.

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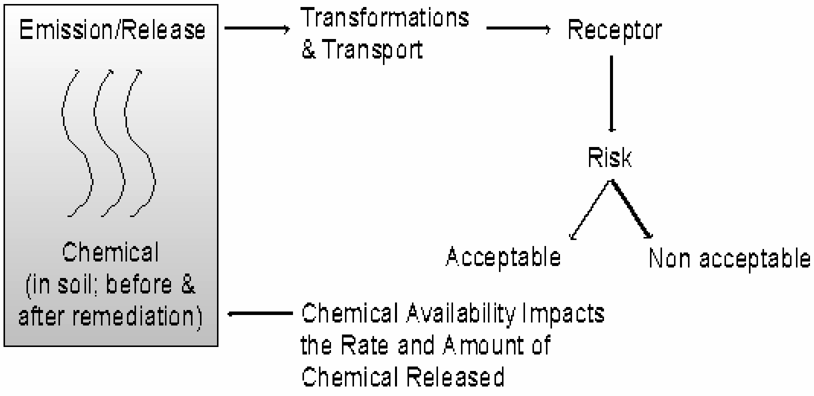
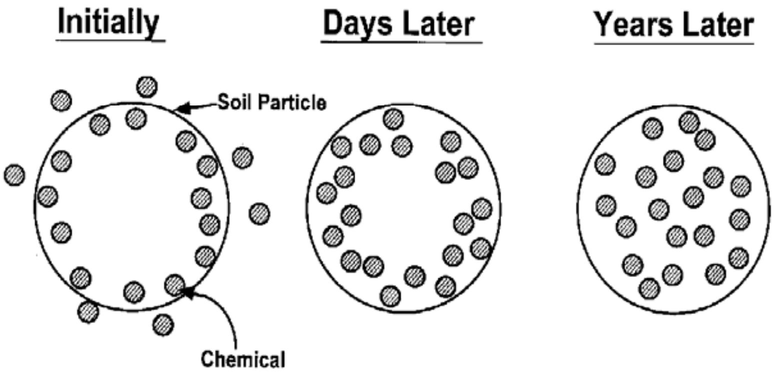
[4] In this context, readily accessible organics are those that are readily soluble and that can be contacted and degraded by microorganisms. Chemicals not readily accessible to microorganisms are chemicals that are tightly held by the soil, that are very insoluble, and that may be in small pores that organisms cannot penetrate.

Figure 2: Impact of Availability on the Risk Paradigm



In terms of the risk-assessment paradigm, chemical availability impacts the rate and amount of chemical released from the soil and the immediate effect (Figure 2). Conceptually, availability can be considered to stem from the way that chemical molecules interact with soil particles. Soils are porous, with many large pores (macropores) and many small pores (micropores). From the moment that a chemical comes into contact with a soil, a series of natural physical and chemical processes occur. These processes result in the diffusion and distribution of the chemical onto the surfaces and into the pores of the individual soil particles as illustrated in Figure 3. As the time of contact increases, the "aging" process results in movement of some of the chemical to the interior of the soil particle surfaces. In addition to the physical interaction, there can be chemical reactions that cause the chemicals in the soil to be more complex and less available for leaching and degradation. This "sequestration" and "complexation" of the chemical over time has an impact on the availability of the contaminants to living organisms. Thus, it is expected that there are differences in the availability between chemicals in weathered soils and chemicals that have been freshly added to soil.

Figure 3: Conceptual Interaction of Chemicals and Soils Over Time



The effect of remediation is considered in Figure 4. As a result of a remediation process, such as bioremediation, soil washing, or vapor extraction, chemicals that are easily released are easily removed. However, not all of the chemicals that have entered the soil are so easily released. Some concentration of the chemicals may still be measurable in the treated soil. The percentage of chemical released is a function of the structure and type of chemical associated with the soil; soil characteristics (particularly the soil organic carbon content); whether the chemical is fresh or weathered; the type of remediation process used; and other factors such as soil type, porosity, pH, and temperature. The hydrocarbons that remain in the treated soil are believed not to be readily available to ecological and human receptors and, therefore, can represent an environmentally acceptable endpoint.

Figure 5 demonstrates what happens to weathered soils and to soils that have received some degree of remediation. Over time, some slow diffusion and release of residual chemical from the soil will occur. These released chemicals are available for potential transport and impact on a human or environmental receptor. If, however, the natural degradation and assimilation processes that exist in soil can treat the released chemicals, none of the slowly released chemical will have an adverse effect. Some evidence indicates that this does occur for weathered chemicals and for chemicals that remain in treated soils.

Figure 4: Effect of Treatment on Chemical Availability

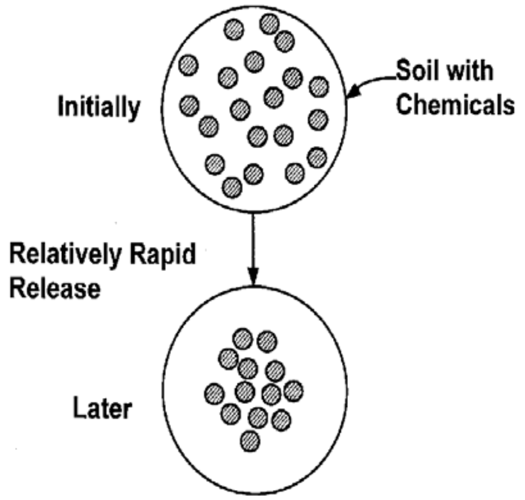
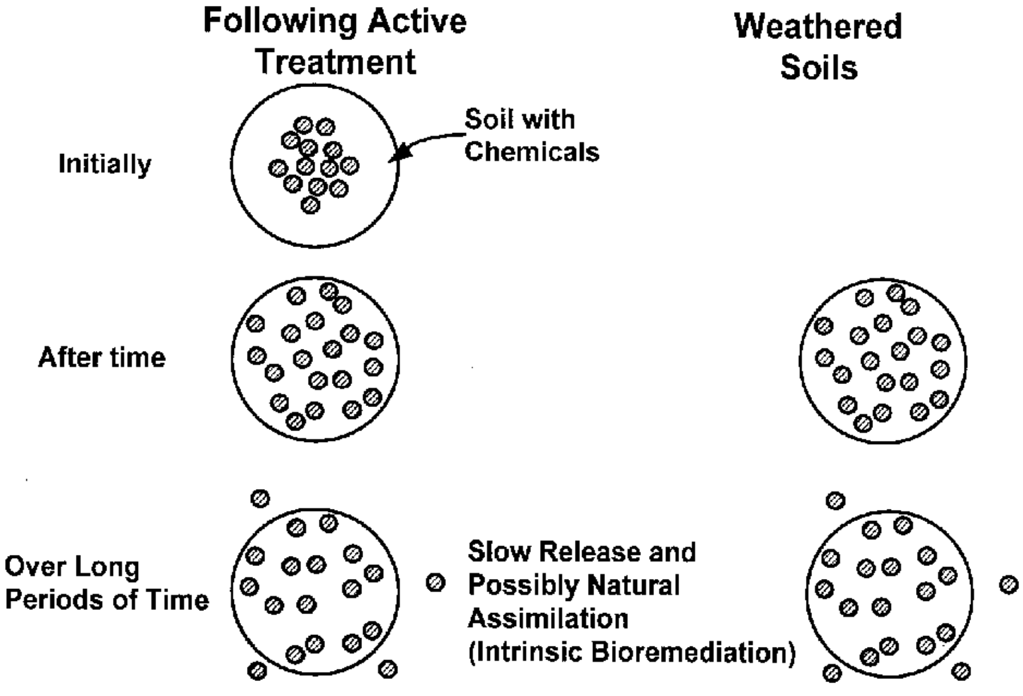
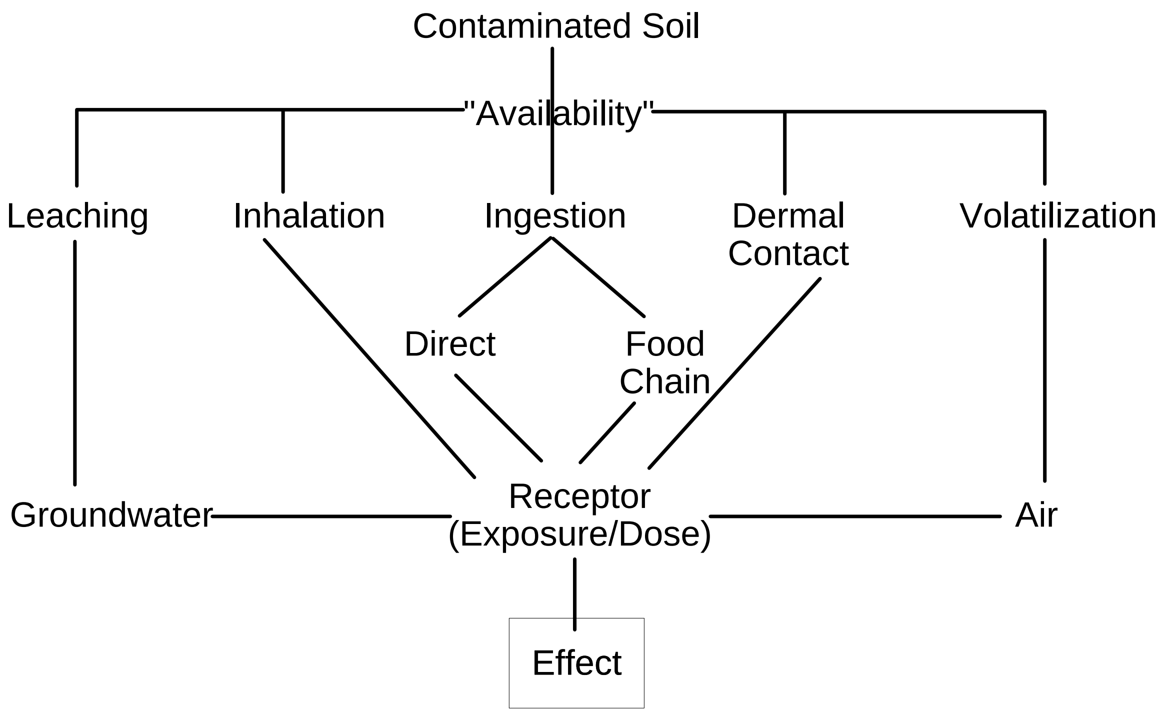


Figure 5: Chemical Availability of Chemicals in Weathered Soils and Treated Soils Over Time



The issue of chemical availability has many implications for remediation decisions and development of cleanup criteria which are discussed in depth in the following paragraphs. However, two points should be kept in mind when considering these implications. First, the fact that a chemical can be extracted and measured in a soil indicates nothing about its site-specific availability to human health and the environment. That is, chemical concentration data tells one nothing about the risk associated with that chemical. A chemical with low release and toxicity in a soil, i.e., low availability, can result in low relative risk to human health and the environment. Second, chemical concentrations in soil greater than background levels can be safe to human health and the environment.

Figure 6: Importance of "Availability" in Determination of Risk



## III. BIOAVAILABILITY AND RISK DETERMINATION

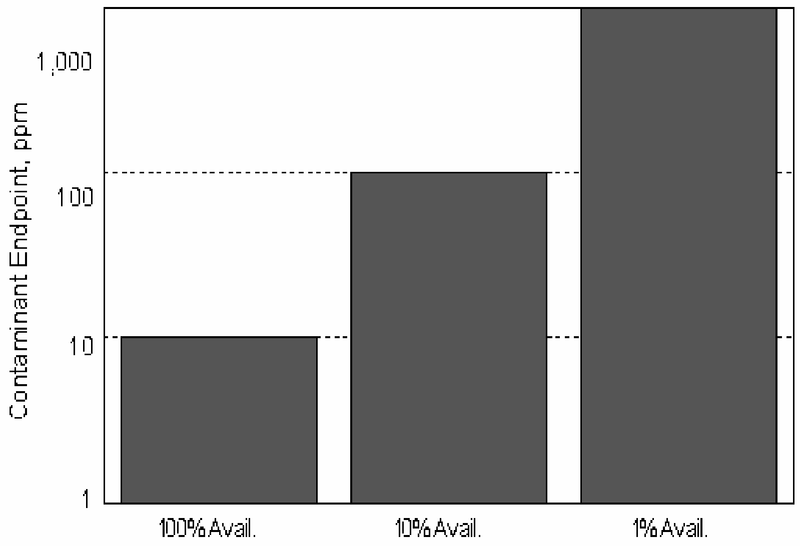
The overall importance of chemical availability to the determination of risk at a given site is shown in Figure 6. This figure depicts the various routes of exposure by which a soil-bound chemical can come into contact with a receptor. These exposure routes include:

- Leaching to groundwater followed by ingestion of the groundwater;
- Direct inhalation;
- Soil ingestion;
- Dermal contact with the soil;
- Volatilization followed by inhalation of the air.

The availability of the chemical governs the degree of exposure that occurs through all of these routes. In the extreme case, if the chemical is completely unavailable, there will be no exposure, no dose, no toxicological effect, and hence, no risk.

Another implication of the importance of chemical availability to acceptable endpoints is shown in Figure 7. Figure 7 indicates that, for a given situation, where a chemical in soil is 100 percent available, an appropriate environmentally acceptable endpoint might be 10 mg/kg (ppm).[5] However, if the chemical were only 10 percent or just 1 percent available in the soil, the appropriate endpoint might be 100 mg/kg or 1000 mg/kg respectively. Such differences are important since they affect the quantity of material that must be remediated or managed and the site-specific risk to human health and the environment.

Figure 7: Impact of Availability on Calculation of Acceptable Contaminant Endpoints in Soil



Chemical availability can also affect the degree of remediation that may be needed. The success of remediation technology has traditionally been measured in terms of reductions in chemical concentrations. A consistent trend in concentration reduction can be observed in all soil batch remediation processes. Initially, there is a relatively rapid decline in chemical concentration. After a period of time, the concentration appears to level. This leveling often is referred to as an apparent concentration plateau. The extent of chemical concentration reduction and the level of the apparent concentration plateau (the residual concentration) vary widely for different soils and other material being remediated.[6]

This pattern is shown in Figure 8 for two soils. Also in the figure is a dashed line which represents a cleanup criterion that has been set by a state or federal agency. In the figure, the approach used for soil remediation at Site 1 would not be able to meet the cleanup criterion and another technology would have to be used. For soil at Site 2, remediation technology could meet the criterion at Point A, but it would take the amount of time equal to $T_A$ to do so. Now assume it could be shown that after accomplishing remediation to point B for Site 1 soil and to point C for Site 2 soil, the remaining chemicals would be unavailable, i.e., immobile, non-toxic, and would not pose a risk to human health and the environment. Under this scenario, the proposed remediation technology could be used for Site 1 soils, and the time to remediate Site 2 soils could be reduced from $T_A$ to $T_c$ and the site-remediation costs could be reduced. Again, knowledge about the availability of chemicals in a soil is relevant to decisions about the degree of cleanup that is needed and the type of remediation that should be used.

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[5] This is an arbitrary value used for illustrative purposes only. A site-specific remediation criterion commonly would be determined using a site-specific risk assessment evaluation.

[6] Available information indicates that the chemical reduction accomplished by remediation processes is related to the type of remediation process used, the length of time the chemical has been in the soil, the structure of the chemical, and soil characteristics such as organic matter and clay content.

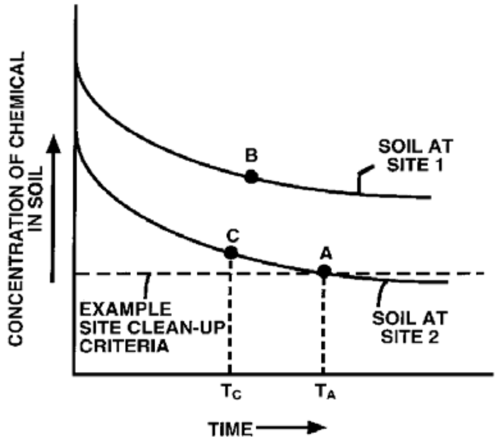

**Figure 8: Achieving Concentrations at Points B and C May Be Environmentally Acceptable**

# IV. ASSESSMENT OF CURRENT KNOWLEDGE

## A. Weight-of-Evidence Information

Over the past decade, many research and field studies have characterized the interaction of hydrocarbons in soils and evaluated the performance of bioremediation processes for these hydrocarbons. With respect to bioremediation, the results have shown that: a) hydrocarbons are biodegraded by indigenous soil microorganisms to a concentration which no longer decreases, or which decreases very slowly with continued treatment; b) reductions below this concentration are limited by the availability of the hydrocarbons to the microorganisms;[7] c) the residual hydrocarbons remaining after biological treatment, regardless of the extent of treatment, are significantly less leachable (in water) and significantly less toxic as measured by simple tests such as earthworm mortality and the Microtox™ test;[8] and d) the aged hydrocarbons in soil are less toxic and less prone to leaching compared to hydrocarbons freshly added to soils.[9]

In addition to research and field studies, information on the transport and fate of chemicals in the soil is available from over forty years of managing chemicals in soils, such as pesticides and fertilizer for agricultural purposes. And there is a growing database on the decrease of chemical availability and toxicity that results from the weathering or aging process.[10]

The available weight-of-evidence on this topic has been summarized in *Environmentally Acceptable Endpoints in Soils*, a report edited by David Linz and David Nakles.[11] The purpose of this report was to: a) present the findings of an evaluation of the state of knowledge on the availability of hydrocarbons and other organic chemicals in soils, and b) incorporate this information into risk-based approaches for defining environmentally acceptable endpoints for soil. In this context, the term “availability” refers to the rate and extent to which the chemical is released from the soil into the environment, i.e., air and water, as well as to ecological and human receptors following direct contact, ingestion, or inhalation. The report’s findings were intended to serve as a basis for a discussion of approaches and research needs to measure chemical “availability” in soil and to incorporate these measurements into a decision framework to define EAEs for soil. This weight-of-evidence summary consists of three discrete but related technical chapters concerned with different aspects of the EAE issue: a) sequestration and bioavailability of organic compounds in soil; b) effect of treatment on contaminant availability, mobility, and toxicity; and c) a framework for biological and chemical testing of soil. The following material draws heav-

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[7] As indicated earlier, microorganisms have difficulty degrading chemicals that are tightly held by the soil or that may be in small pores that the organisms can not penetrate.

[8] The Microtox™ test measures the toxicity of soluble chemicals in a liquid to a specific type of microorganism. It is a rapid, consistent measure of the relative toxicity of chemicals to microorganisms.

[9] Examples of freshly added chemicals are those released by spills, leaks, and overflows that are noticed quickly and for which remediation options are enacted rapidly.

[10] Weathering occurs as a chemical stays in a soil for years or decades. Under such conditions, the chemicals appear to complex to a soil or change form in a manner such that they are less available for microbial degradation.

[11] Linz, D. and D. Nakles, ed., *Environmentally Acceptable Endpoints in Soils,* American Academy of Environmental Engineers, Annapolis, MD, 1996.

ily from the material in the Linz/Nakles report, particularly, the chapter dealing with the effect of treatment on chemical availability.[12]

### 1. Sequestration and Bioavailability

The evaluation of sequestration and bioavailability consisted of an extensive review of approximately 268 technical papers in the areas of environmental chemistry, soil microbiology and physics, environmental engineering, ecotoxicology, and mammalian toxicology.[13] The review revealed numerous data showing that the availability of some chemicals declines as they remain in contact with the soil for increasing periods of time, presumably because the molecules become sequestered in some manner. A corollary to this hypothesis is that chemical concentrations, as determined by current practices of rigorous solvent extraction, are not appropriate predictors of availability and, hence, of toxicity or risk. The evaluation indicated:

- Patterns of disappearance in the field for many persistent chemicals show a rapid initial phase, followed by a period in which little or no loss of chemicals can be detected. Since the chemicals are all known to be biodegradable, the lack of disappearance after the initial phase shows that the chemicals are largely or wholly unavailable to the microorganisms at these field sites.
- Laboratory studies of soils containing naturally aged chemicals show that freshly added chemicals are rapidly biodegraded, whereas aged equivalents are not available to the microorganisms responsible for the transformation.
- The longer many organic chemicals remain in soil, the less readily they are removed by solvents (i.e., they become less readily available to extractants).
- Kinetic analyses suggest that chemical sequestration results from a slow and continuing diffusion of many chemicals to remote sites within soil particles and that subsequent chemical release involves a very slow diffusion of these molecules from the remote internal sites to the surfaces of the soil particles.
- Currently proposed mechanisms of sequestration suggest that molecules of the chemical are present in micropores that are remote from the surfaces of soil particles.

- The longer certain chemicals remain in soil, the lower their toxicity to higher organisms. Such evidence of declining bioavailability of toxicants came from only three studies, none of which involved animals.

A critical review and evaluation of the information cited above is now available.[14]

### 2. The Effect of Treatment

The evaluation of the effect of treatment on contaminant availability, mobility, and toxicity provided a detailed review of laboratory and field studies focused on bioremediation as a treatment process for contaminated soils and sludges.[15] A total of 123 articles and documents were reviewed, including peer-reviewed publications, theses, research reports from the U.S. Environmental Protection Agency, and technical reports from industry and consulting firms concerned with petroleum refining, wood treating, petrochemical manufacture, and gas and electric utilities. The treatability and demonstration data revealed a number of important trends and correlations:

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[12] Loehr, R.C. and M.T. Webster, "Effect of Treatment on Contaminant Availability, Mobility and Toxicity," Chapter 2 in Linz, D. and D. Nakles, ed., *Environmentally Acceptable Endpoints in Soils*, American Academy of Environmental Engineers, Annapolis, MD, 1996.

[13] Alexander, M., "Sequestration and Bioavailability of Organic Compounds in Soil," Chapter 1 in Linz, D. and D. Nakles, ed., *Environmentally Acceptable Endpoints in Soils*, American Academy of Environmental Engineers, Annapolis, MD, 1996.

[14] Alexander, M., "How Toxic are Toxic Chemicals in Soil?" *Environmental Science and Technology*, Vol. 29, 2713-2717, 1995.

[15] Loehr, R.C. and M.T. Webster, "Effect of Treatment on Contaminant Availability, Mobility and Toxicity," Chapter 2 in Linz, D. and D. Nakles, ed., *Environmentally Acceptable Endpoints in Soils*, American Academy of Environmental Engineers, Annapolis, MD, 1996.

- Laboratory and field studies revealed a rapid decline of contaminant concentrations during the initial stages of biological treatment, followed by a rate of contaminant reduction that declined and ultimately approached zero over time.
- The extent of contaminant removal and the final contaminant concentrations achieved differed among the different soils and sludges.
- Biodegradation of freshly added contaminants was more rapid than the same contaminants that had been in the soil for an extended period of time.
- The treatment data indicated that a reduction in contaminant leaching and toxicity also occurs during bioremediation.

### *3. Mobility and Toxicity*

Information from treatability, demonstration, and field studies are particularly relevant to knowledge about the availability of chemicals in soils, since such studies deal with real chemicals in real soils. These studies have been conducted on soils that have weathered chemicals, as well as on soils having fresh releases of chemicals. In addition, chemicals and soils with different characteristics have been part of these studies. Unless noted explicitly, all of the following information and data are parts of the weight-of-evidence identified earlier.[16]

An EAE determination recognizes that for a chemical in a soil to pose a risk, it must be transported to a receptor (mobility) and have an adverse effect on that receptor (toxicity). In this section, the relationships between chemical concentration, toxicity, and mobility are discussed.

**Mobility** - Many procedures exist to assess the mobility of chemicals in soils. The Toxicity Characteristic Leaching Procedure (TCLP) is an acidic extraction designed to simulate the conditions encountered in landfills used for disposal of municipal wastes. A similar test, the Synthetic Precipitation Leaching Procedure (SPLP),[17] simulates the effects acid rain would have on materials. As mobility refers to the ability of chemicals in soil to migrate in the aqueous phase, analysis of the water soluble fraction (WSF)[18] of a soil is another measure of chemical mobility. To analyze the WSF, a liquid/solids separation step is necessary to remove suspended solids from the liquid portion of the soil or slurry system being investigated. This step can be accomplished through processes such as centrifugation and filtration. Water extractions also can be used to assess the WSF of chemicals in soil. The type of water used (tap water, distilled water, actual groundwater) may influence the results. Finally, actual leachate or drainage data provide a direct measure of chemical mobility, as does analysis of the effluent from soil column studies. Table 1 provides a summary of possible chemical mobility measures.

**Toxicity -** Toxicity tests can be divided into two categories: a) those conducted on aqueous samples or extracts of soil or sludge and b) those conducted on bulk soil or sludge samples. Toxicity tests utilize organisms ranging in size and biological complexity from bacteria to fish and rats. Examples of tests that evaluate the potential toxicity of chemicals in a liquid are the Microtox™ test and tests conducted on freshwater organisms such as *Daphnia magna* (water flea), *Selenastrum capricornutum* (alga), and *Pimephales promela* (fathead minnow). These tests are useful in assessing the potential impact chemicals may have on organisms by exposure through aqueous pathways, such as soil water transport to the groundwater or surface waters. Bulk soil tests, or terrestrial tests, allow for the direct exposure of indigenous soil organisms to the soil of concern. This allows for a more direct prediction of the actual effects of soil constituents on parts of the ecosystem. Examples of terrestrial

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[16] Loehr, R.C. and M.T. Webster, “Effect of Treatment on Contaminant Availability, Mobility and Toxicity,” Chapter 2 in Linz, D. and D. Nakles, ed., *Environmentally Acceptable Endpoints in Soils*, American Academy of Environmental Engineers, Annapolis, MD, 1996.

[17] Organic chemicals can be in many types of soils in addition to being disposed of in landfills. The SPLP method approximates the possible leaching that would occur when certain types of precipitation come in contact with the soil containing the organic chemicals.

[18] The WSF represents the potential liquid fraction of a soil that may leach and reach groundwater or a user of the groundwater.

toxicity tests are the earthworm, seed germination, and plant growth and bioaccumulation tests. Table 2 gives a summary of possible toxicity tests.

**Table 1 Measures of Chemical Mobility**

| Type of Measure | Examples |
|---|---|
| Acidic Extractions | Toxicity Characteristic Leaching Procedure (TCLP)<br>Synthetic Precipitation Leaching Procedure (SPLP) |
| Water Soluble Fraction<br>• (WSF) Analysis | Centrifugation<br>Filtration<br>Water Extraction |
| Actual Leachate/Drainage<br>• Data | Land Treatment Unit Leachate<br>Soil Column Effluent |

**Table 2: Assays for Measuring Aqueous and Terrestrial Toxicity**

| Exposure Pathway | Test Method/Organism |
|---|---|
| Aqueous | Microtox<br>Daphnia magna (water flea)<br>Selenastrum capricornutum (alga)<br>Pimephales promela (fathead minnow) |
| Terrestrial | Earthworm<br>Seed Germination<br>Plant Growth and Bioaccumulation |

## B. Research Studies

These studies investigated the relationship between chemical concentration and mobility in soils for both untreated soils and soils that had been bioremediated. The eight examples provided have been adapted from *Effect of Treatment on Contaminant Availability, Mobility, and Toxicity by Ray Loehr* and M.T. Webster.[19]

**Example 1 -** The bioremediation of soils from a specific manufactured gas plant (MGP) site was investigated.[20] The focus was on the degradation of polycyclic aromatic hydrocarbons (PAH) in these soils. Little or no PAH degradation was observed under laboratory conditions, even with the addition of nutrients and acclimated bacteria. Further studies revealed that bacteria were present and were capable of degrading fresh PAHs added to the soil but not those contained in the MGP site soils.

Analysis of the water soluble fraction (WSF) of the MGP soils revealed little or no PAH compounds. Analysis of the WSF using chromatographic and spectrophotometric methods indicated that phenanthrene and anthracene were present at levels close to the method detection limit, and no other PAH compounds were above the detection limits of 5 µg/L. In addition, Microtox™ toxicity results revealed that the WSF of the initial soil samples were nontoxic.

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[19] R.C. Loehr, and M.T. Webster, "Effect of Treatment on Contaminant Availability, Mobility and Toxicity," Chapter 2 in D. Linz, and D. Nakles, ed., *Environmentally Acceptable Endpoints in Soils*, American Academy of Environmental Engineers, Annapolis, MD, 1996.

[20] These plants used high temperature processes to manufacture gas from coal and oil. The gas was used for homes and industry. These plants are no longer in operation in the U.S. since oil and natural gas have become plentiful.

The results of this study indicated that even though PAHs were present in the MGP site soils, they were not mobile (i.e., were not present in the WSF), and no toxicity was observed in the WSF. Therefore, it was unlikely that these PAHs would leach from the soils and present a risk to organisms via exposure through aqueous pathways.

Figure 9: Percent Mass Leached During TCLP Analyses for Six Individual PAH Compounds: Wood Treating Site Soil Prior to and After Bioremediation

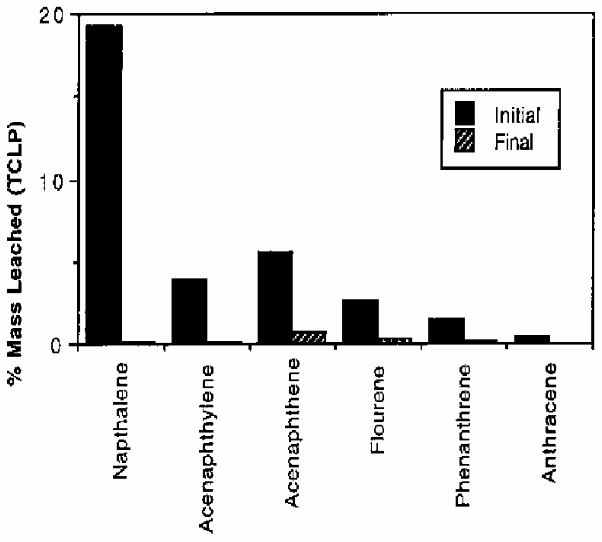
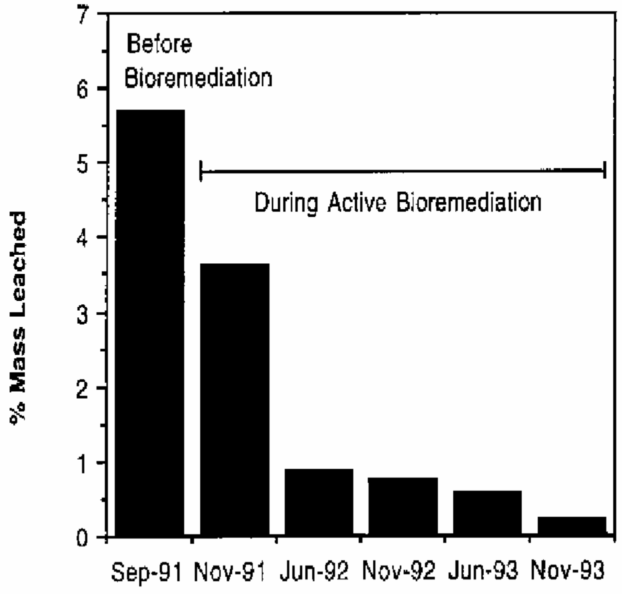


Figure 10: Percent Mass of Total PAHs Leached During TCLP Analyses: Wood Treating Soil Subjected to In-Place Unsaturated Zone Bioremediation



**Example 2 -** Results of in-place, unsaturated-zone, field-scale bioremediation of wood-treating site soils have been obtained. Beside monitoring PAH concentrations (the major chemicals of regulatory concern), TCLP analyses were conducted on the soil before and after bioremediation. Figure 9 shows the percent mass leached for six individual PAH compounds. Leachate (TCLP) concentrations of most of the low solubility, high molecular weight PAH compounds were below detection limits. Roughly 18 percent of the total naphthalene present in the untreated soil leached during the TCLP procedure. Less than one percent of the naphthalene remaining in the soil after bioremediation was leached. Figure 10 shows the percent mass of total PAHs leached using the TCLP over time. Initially, approximately 5.5 percent of the total PAHs present in the soil leached using the TCLP. After the first nine months of bioremediation, less than 1 percent of the total PAHs remaining leached using the TCLP analysis. The percent mass leached remained below 1 percent for the duration of the bioremediation operations. Thus, only a small fraction of the total PAH concentration in the soil was available for transport through aqueous pathways, and the fraction did not increase as a result of the bioremediation. In terms of TCLP concentrations, TCLP extracts of the untreated soil contained 4.38 mg/L total PAHs. After 27 months of bioremediation, total PAH concentrations in TCLP extracts had decreased 93 percent, to

0.32 mg/L. In particular, 99 percent naphthalene reduction was achieved in TCLP extracts between September 1991 (2.73 mg/L) and November 1993 (0.037 mg/L).

**Example 3 -** Column studies were conducted to assess the in-situ treatability of wood-treating site soils. TCLP analyses were conducted on the soil prior to the column study. All PAH compounds and pentachlorophenol (PCP) concentrations in the TCLP extract of the untreated soil were below the detection limit of 0.010 mg/L. Initial total PAH and PCP concentrations in the soil were 1,288 and 150 mg/kg, respectively. Thus, although significant quantities of these chemicals were present in the soil, these compounds were not mobile, as determined by the TCLP. Chemical concentrations in the column effluent also were measured during the study. All 4-, 5- and 6- ring PAHs analyzed were at concentrations below the detection limit of 0.001 mg/L throughout the study. The lower molecular weight PAHs were present in the column effluent at low concentrations (less 0.3 mg/L) early in the study. However, all compounds were below the detection limit of 0.001 mg/L by week 30. At the end of the 37-week test period, total PAH and PCP concentrations in the soil had been reduced to 82 and 1.4 mg/kg, respectively. This corresponded to a 94 percent total PAH reduction, a 74 percent reduction in high molecular weight PAHs, and a 99 percent reduction in PCP concentrations. Thus, this column study of in-situ bioremediation was effective at reducing chemical concentrations, while the chemical mobility was minimal, as evidenced by the TCLP results and the chemical concentrations in the column effluent. Again, the bioremediation that took place in the column did not increase the mobility of the chemicals of concern.

**Example 4 -** In another evaluation, slurry bioremediation studies were conducted on wood treating site soils. PAH analyses were made on the soil from the slurry reactor and on water samples (WSF) collected from the reactor. Water samples were centrifuged to remove suspended solids. WSF and soil chemical concentrations for samples of the untreated soil along with the computed percent mass in the WSF are given in Table 3 for several PAH compounds. Table 3 also gives total PAHs before treatment and after 56 days of bioremediation.

**Table 3: Comparison of Water Phase (WSF) and Soil Chemical Concentrations For PAHs in a Biological Slurry Bioremediation Reactor**

| Compound* | WSF (µg/L) | WSF** (mg/kg - dry weight) | Soil Conc. (mg/kg - dry weight) | % WSF† |
|---|---|---|---|---|
| Time Zero | | | | |
| Naphthalene | 10,000 | 41.8 | 3067 | 1.36 % |
| Fluorene | 270 | 1.13 | 1067 | 0.11 % |
| Anthracene | 63 | 0.26 | 750 | 0.035 % |
| Chrysene | 120 | 0.50 | 2133 | 0.024 % |
| Benzo(a)pyrene | 8.7 | 0.036 | 357 | 0.010 % |
| Total PAHs | | | | |
| Time Zero | 11,838 | 49.5 | 19,043 | 0.26 % |
| 56 Days | 1,244 | 5.20 | 8,633 | 0.06 % |

* Values for the individual PAH compounds represent initial (time zero) values

** Calculated value based on the concentration in µg/L and the liquid/solids ratio in the slurry (19.3% solids)

† % WSF = WSF Conc. (mg/kg)/ Soil Conc. (mg/kg) x 100%

As indicated in Table 3, even when substantial concentrations of PAHs existed in the soil and the soil was subjected to active mixing, only a small fraction of the total mass of PAH compounds was present in the water (WSF) phase. In other words, the percentage of mobile mass of PAH compounds was small to begin with and was reduced as a result of bioremediation, as was the total PAH concentration in the soil. This study indicated that even under the active mixing conditions used in a slurry reactor, only a small fraction of the total mass of chemicals present in the soil was detected in the water phase. Thus, the soil limited the ability of the chemicals to migrate into the water phase. Only this very small fraction of the total mass present in the WSF would be available to be transported to a receptor through aqueous pathways if the chemical were in or on the soil.

### 1. *Summary: Mobility Studies*

The previous examples investigated the relationship between chemical concentration and mobility. Results indicated that only a very small portion of the chemicals present in soils and sludges was readily mobile, as assessed by different measures of leachability and mobility. This was true both for untreated and bioremediated soils and sludges. Thus, soil-chemical interactions limit the ability of chemicals to be transported to a receptor where they may then have an adverse effect. The following information relates to the relationship between chemical concentration and the related toxicity of a soil.

The appropriateness of using chemical concentration to determine cleanup standards for soils relies on the assumption that the relative risk to a receptor is directly proportional to the chemical concentration present in the soil. The next three examples illustrate the difficulty encountered when trying to relate chemical concentrations in soil to measurements of the soil or waste toxicity.

**Example 5 -** In one study, earthworm and Microtox™ toxicity tests were conducted on four manufactured gas plant (MGP) site soils. Total PAH concentrations, the chemicals requiring reduction in remediation of these soils, were compared to the results of the two toxicity tests. No clear-cut relationship between total PAH concentration and toxicity existed, although the two soils with the highest total PAH concentrations did exhibit the highest toxicity to earthworms. Microtox™ toxicity analysis provided different results than the earthworm tests. Microtox™ EC50 values for the four soils indicated that the soil with the largest PAH concentration did not have the largest toxicity.

**Example 6 -** Microtox™ toxicity testing was conducted on two wood-treating wastes (a creosote sludge and a pentachlorophenol (PCP)-creosote mixed sludge) and on two petroleum refinery wastes (API separator sludge and slop oil emulsion solids) prior to bioremediation studies. PAH were the major chemical group of human and environmental concern in these wastes. There was no apparent relationship between Microtox™ toxicity and total PAH concentration. In fact, the waste with the highest total PAH concentration exhibited the least Microtox™ toxicity.

**Example 7 -** In addition to the above are studies in which both chemical leachability and the toxicity of the material being treated were evaluated. One such evaluation examined the composting of explosives-contaminated soils. Figure 11 shows the changes in Ames mutagenicity and leachate toxicity as a function of composting time. After an initial increase, the mutagenicity decreased continually over the 90-day test period. The toxicity of the aqueous leachates to *Ceriodaphnia dubia* decreased continuously throughout the study.

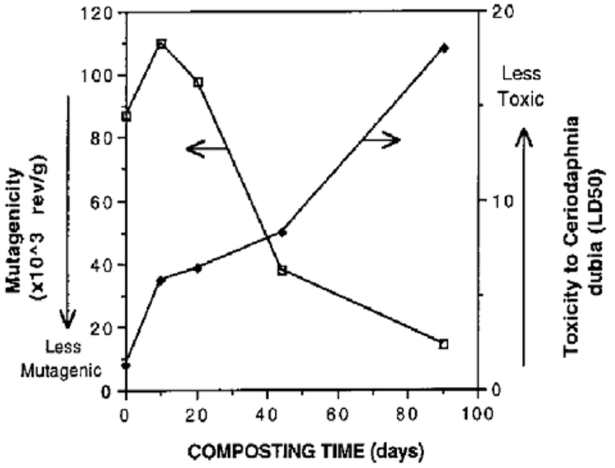
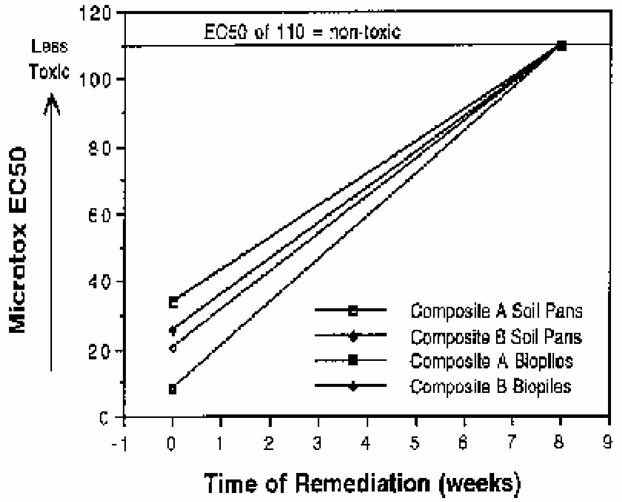


Figure 11: Ames Mutagenicity and Toxicity to Ceriodaphnia dubia of Explosives-Containing Soils Subjected to Static Pile Composting Bioremediation

**Example 8 -** A biotreatability study of two composites of soils from a petroleum-products plant also provides such data. Composite A was prepared from soils containing mostly gasoline-range ($C_6$-$C_{12}$) and diesel-range ($C_{12}$-$C_{24}$) hydrocarbons, and composite B was prepared from soils containing mostly oil-range ($C_{24}$-$C_{32}$) hydrocarbons. Laboratory bioremediation treatability studies were used to investigate the performance of biological treatment. Microtox™ and *Ceriodaphnia* bioassays were conducted on soil samples before and after treatment. Initial Microtox™ EC50 values ranged from 8.5 to 33.7 percent and indicated that the initial soils had moderate toxicity. Following eight weeks of bioremediation, the toxicity of both composites A and B in each treatment method had been reduced to nontoxic levels (EC50 > 100%), as shown in Figure 12.

The *Ceriodaphnia* assay was conducted on water extracts of composite A and B soil samples before and after the laboratory treatability studies. Before treatment, water extracts of both soil composites caused 100 percent mortality of the test organisms. After twelve weeks of the laboratory studies, the toxicity of composite A was reduced, and a slight reduction in the toxicity of composite B was observed. The mortality of the *Ceriodaphnia* after twelve weeks of treatment was 55 percent, whereas it had been 100 percent before treatment. Thus, bioremediation decreased the toxicity of the soils as measured by both the Microtox™ and *Ceriodaphnia* assays.

Figure 12: Microtox™ EC50 Changes in a Bioremediation Treatability Study Conducted on Petroleum Industry Site Soils



## C. Field Evaluations

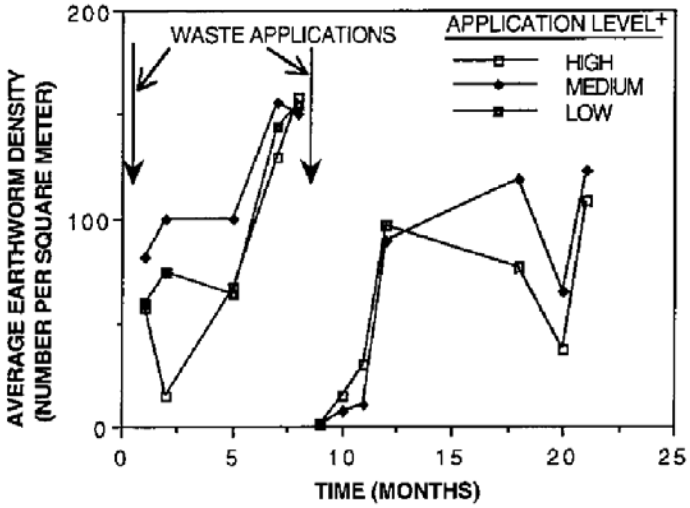
In this section, three examples are presented to indicate the changes in chemical concentration, toxicity, and chemical mobility that can occur in field bioremediation systems.

**Example 9 -** The land treatment of an industrial oily waste of unknown origin was investigated at a site in New York using four waste loadings. The potential impact of the oily waste on soil biota was assessed using earthworms. Figure 13 shows the response of earthworms to oily waste applications. The general trend was one of earthworm population recovery as the applied waste was remediated by the land treatment process. The flat part of the curves, around months two through five and fourteen through seventeen correspond to samples taken during the winter months, when less earthworm activity could be expected.

Two extensive field evaluations of the leachability and toxicity of contaminated soils have been conducted. Both studies focused on bioremediation used for soils containing chemicals used to treat and preserve wood.

**Example 10 -** An engineered land treatment system was operated at a creosote wood-treating site in the northeastern part of the United States, from May 1986 through December 1987. Remediation to achieve specific losses of PAH was required. Four soil lifts were applied to the unit: one in 1986 and three in 1987 (May, July and September). During this period, active bioremediation occurred, and the PAH concentrations decreased until the desired reduction occurred and the required endpoint (1000 mg/kg total PAHs) was reached. Since the performance goals had been achieved, no further soil was added to the site and the site was left untouched until

Figure 13: Average Earthworm Density in a Bioremediation Land Treatment Unit Treating an Industrial Oily Waste



(high=4.6 kg/m2, medium=2.7 kg/m2, and low=1.5 kg/m2 application, respectively, of the oily waste

1993. At that time, a sampling program was initiated to characterize the treated soils and determine the extent of further degradation and potential migration of the residual organic constituents contained in the soil. Figure 14 shows the total PAH concentrations in samples taken before bioremediation, after two months of active bioremediation, and six years after the termination of active bioremediation. The data indicated that chemical concentrations continued to decline over time, even after active bioremediation had been discontinued. A similar pattern was observed for PCP concentrations as well. TCLP analyses also were conducted on soil samples before bioremediation, after two months of active bioremediation, and six years after the termination of active bioremediation (Figure 14). A sharp decrease in total PAH and PCP concentrations in TCLP extracts resulted from the two months of active bioremediation. Chemical concentrations in TCLP extracts declined even further (approaching zero) during the six years of passive remediation. Site subsurface soil samples and stormwater retention pond samples indicated that there was no migration of chemical constituents away from the treatment unit. Thus, the waste constituents that remained following the active bioremediation continued to decrease over time. Analysis of the site data indicated that the long-term intrinsic biodegradation was capable of treating the slow release of residual chemicals from the treated soils. In other words, treatment continued to occur without the migration of chemicals from the site. The authors described the soil as "biostabilized".[21] Without significant migration of the chemicals from the site, the risk associated with the site had been reduced, even though significant quantities of PAHs (1000 mg/kg) had been left after active remediation.

Example 11 - In the second evaluation, land treatment was one component of the remedial actions at a former wood-treating site that had operated at the site until 1982. During the operation of the facility, wastewater was piped into an unlined surface impoundment, used as a sedimentation basin, for the recovery of creosote. Creosote contamination resulted in the soil and groundwater, requiring remediation. As part of the site remediation efforts, creosote sludge and creosote-impacted soils were excavated from the impoundment, placed in a storage pile, and subsequently bioremediated on-site using the land treatment process. Soil samples from the land treatment unit (LTU) were analyzed for PAHs, the chemicals of regulatory concern, over a five-year period (Figure 15). An initial rapid PAH concentration reduction resulted, followed by a decreasing rate of reduction to a point of little or very slow reduction. Total PAH concentrations were reduced 98 percent, from 8340 mg/kg on September 9, 1989 to 159 mg/kg on March 21, 1994. Figure 15 also shows Microtox™ EC50 values over time, giving an assessment of the relative toxicity of the soil samples over time. The soils initially exhibited substantial relative toxicity,

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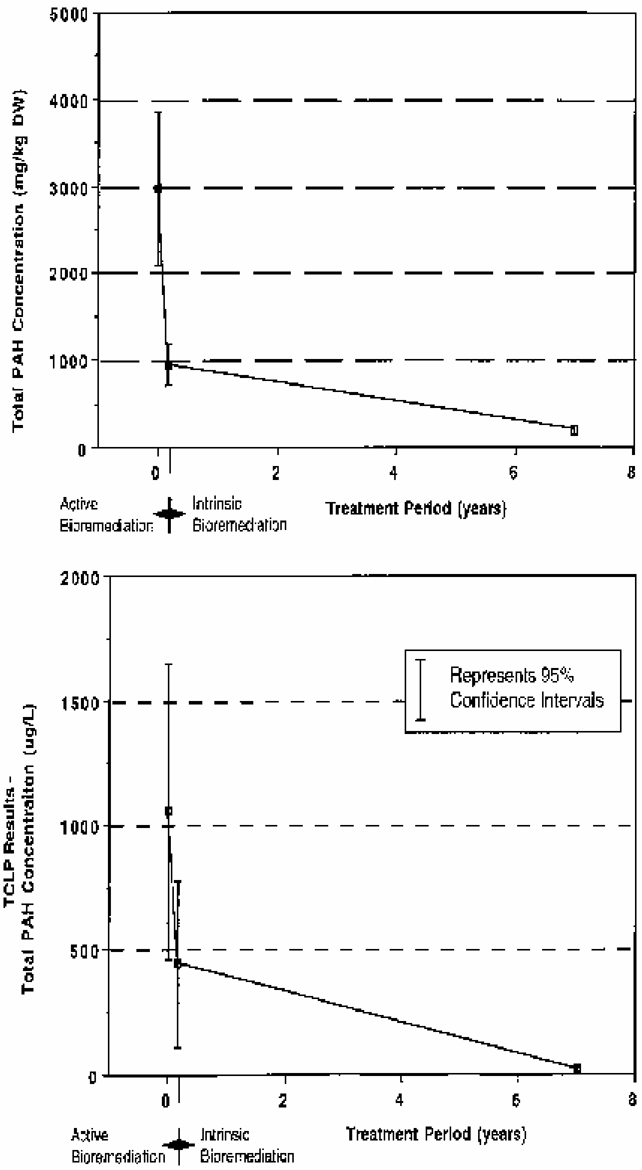
[21] Smith, J.R., R.M. Tomicek, P.V. Swallow, R.L. Weightman, D.V. Nakles, and M. Helbling, "Definition of Biodegradation Endpoints for PAH Contaminated Soils Using a Risk-Based Approach," Presented at the Ninth Annual Conference on Contaminated Soils, University of Massachusetts at Amherst, October 18-20, 1994.

decreasing steadily over the first two years (increasing EC50 values). By the end of the third year of this batch land treatment operation, EC50 values <100 (non-toxic) were reported. No toxicity, as measured by the Microtox™ method, has been measured in the LTU remediated solids since the spring of 1992. Soil samples collected in October 1991, April 1992, and September 1992 were analyzed for Ames mutagenicity. Samples were collected from the surface of the soil to twelve inches deep, and from twelve to thirty-six inches deep. None of the soil samples tested showed any mutagenic activity. No mutagenicity data were available for initial soil and sludge samples. Thus, it cannot be determined whether the mutagenic activity was reduced through land treatment, or whether there was any mutagenic activity to begin with. However, the lack of mutagenic activity, as well as decreasing Microtox toxicity, indicate that no nonsorbed toxic by-products were generated as a result of this form of bioremediation. The potential mobility of PAHs from this land treatment unit has been assessed through monitoring of groundwater, subsurface soil samples and lysimeter samples. Subsurface soils were sampled at depths of thirty-six and sixty inches below the bottom of the land treatment unit. Samples were collected semiannually at two locations per treatment cell (fourteen samples overall). While the thirty-six inch samples contained PAHs at low levels (parts per million, or ppm), none of the sixty inch samples had such constituents. No detection of PAH compounds has been detected in groundwater samples collected semi-annually around the perimeter of the LTU. No PAHs have been detected in tests performed on soil-pore water samples collected after each application. In Spring 1995, two of the treatment cells were closed. The treatment goal of 100 mg/kg total PAHs was reached in both of these cells as of September 1994. Closure consisted of seeding with grass and continued monitoring of Zone of Infiltration (ZOI) soil.

Figure 14: Total PAH and TCLP Concentration Reduction Achieved During Active and Intrinsic Bioremediation (Adapted from Reference 6)

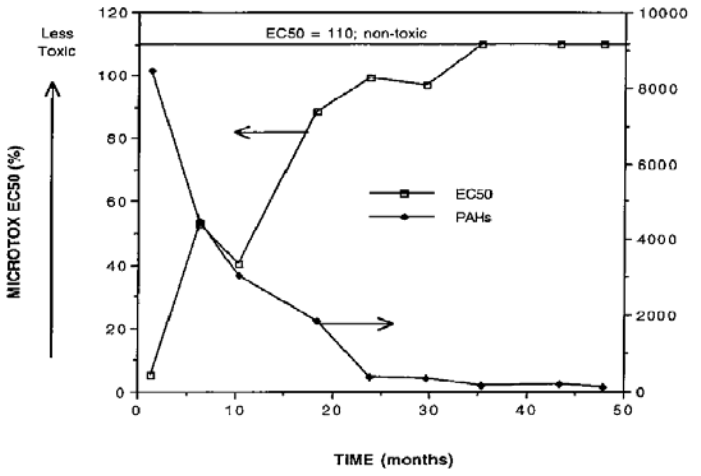


Both extensive field studies noted above demonstrated the effectiveness of land treatment bioremediation in reducing chemical concentrations and relative toxicity in creosote sludges and creosote impacted soil.

## D. Summary of Research and Field Study Findings

The available weight-of-evidence from research and field studies indicates that soil bioremediation processes can be effective at reducing both chemical concentration and toxicity in soils and sludges. In addition, while chemical mobility is limited in soils, bioremediation can reduce that mobility further. In addition, several extensive field studies have shown that:

Figure 15: Total PAH Concentrations and Microtox™ Toxicity Over Time: Land Treatment Bioremediation of Wood Treating Site Soils



- The concentrations and mobility of contaminants in a soil from a wood-treating site decreased during periods of both active bioremediation or land treatment as well as during passive or intrinsic bioremediation.
- Land treatment of another wood-treating site soil resulted in a gradual, but continual, decrease in the concentration of contaminants during a five-year period. The toxicity of the surface soils disappeared in the first three years of operation, and no migration of the contaminants was detected beyond the treatment zone.
- The concentration of organic contaminants in an oily waste from a petroleum refinery was reduced by bioremediation (land treatment), the remaining contaminants were immobilized in the soil, and earthworms repopulated the soil containing the bioremediated oily waste.

# V. POLICY IMPLICATIONS

The available scientific and technical information makes it clear that the ability of an organic chemical in soil to produce an adverse effect on human health and the environment is not simply a function of its measured concentration. Rather, that possibility depends on the properties of the chemical and soil, the time of contact between the chemical and the soil, i.e., weathering, and the type and extent of treatment to which the contaminated soil has been subjected. Thus, the chemical availability—i.e. ability to be released from a soil, migrate to a human or ecological receptor, and have an impact—is a critical factor in determining the environmental acceptability of chemicals in soils.

A weight-of-evidence review of a large amount of data from a broad range of studies on chemicals released into soils clearly indicates that bioremediation reduces the concentration, mobility, and toxicity of the chemicals in the untreated soil and sludges. The information on mobility and toxicity sheds light on the availability of these chemicals to be transported to and have an effect on human or environmental receptors. As Figure 16 illustrates, remaining chemicals in bioremediated soils are less available to be transported in the environment and, therefore, represent a reduced risk.

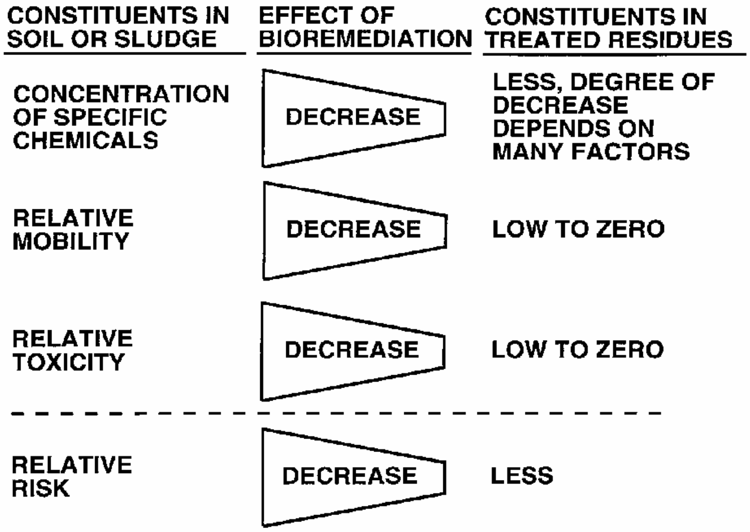
## A. Research Policy

The existing information on the availability of chemicals in soils overwhelmingly is weight-of-evidence information. Such information was obtained as an incidental part of investigations of soil characteristics or evaluations of what happened to chemicals added to soils, through spills or tank leakage.[22] The toxicity, mobility, and leachability data also were obtained from evaluations of the effectiveness of bioremediation processes. In such investigations, a limited number of chemicals have been evaluated. These may have been studied due to intellectual curiosity, interest in chemicals that possibly could have an impact, or as a result of regulatory requirements.

To date, no comprehensive laboratory or field experiments or studies have carefully and critically evaluated the question of chemical availability in soils. The current information is useful, directional, and of a weight-of-evidence nature, but not comprehensive or conclusive. For instance, the measures of leachability, chemical release, mobility, and toxicity have been those that are convenient and available for use for other purposes.

Tests exist for measuring availability of chemicals in soils for most groups of ecological receptors and for most of the toxicological endpoints of interest. However, similar tests for human receptors have either not been validated with soil or have not received regulatory acceptance. A common shortcoming is the lack of correlation of the commonly used short-term chemical and toxicological tests with toxicological endpoints of long-term significance. Existing tests for availability appear to be useful for screening and ranking sites, assisting in the identification of areas of high-contaminant concentration, monitoring changes as a result of treatment, supporting ecological risk assessments, and judging the acceptability of treated soil. At present, these tests do not seem adequate for risk assessments of human health.

Figure 16: Effect of Bioremediation on the Concentration of Specific Chemicals, and on the Relative Mobility and Toxicity of Soils and Sludges Being Bioremediated



As indicated in the beginning of this study, the issue of chemical availability in

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[22] R.C. Loehr and M.T. Webster, "Effect of Treatment on Contaminant Availability, Mobility and Toxicity," Chp. 2 in D. Linz, and D. Nakles, ed., *Environmentally Acceptable Endpoints in Soils*, American Academy of Environmental Engineers (Annapolis, MD, 1996).

soils has many implications regarding the need for and degree of site remediation; long-term protection of human health and the environment; and the use of natural resources such as time, human energy, and available funds. Therefore, these issues point to the need for increased focus on acquiring the knowledge needed for sound decisions. Using scarce resources for clean-up activities that may result in few additional reductions in risk may not be sound policy.

Increased knowledge can come from small-scale research as well as from field studies. Examples of the types of studies and knowledge needed to better aid site clean-up decisions include:

- Determination of the mechanisms of chemical sequestration and contaminant aging in soils and the resulting effects on chemical availability;
- Determination of whether changes in chemical availability, toxicity, biodegradability, and extractability are correlated;
- Identification of the rate of release of chemicals from untreated and bioremediated soils and sludges;
- Acquisition of data from long-term field studies of contaminated sites, with and without active bioremediation, to evaluate the reductions in contaminant concentrations that are achieved over time and to correlate these reductions, if possible, to reductions in availability, mobility, and/or toxicity;
- Development of simple, rapid, inexpensive tests to measure chemical availability in soils to different receptors;
- Identification and/or development of physical, chemical, and biological assays to assess the availability and ecological/toxicological effects of contaminants in the soil;
- Development and validation of extraction techniques that mimic the physiological processes that determine the availability of an organic chemical through the skin (i.e., dermal) or following ingestion (i.e., oral) by human or ecological receptors;
- Identification and verification of appropriate surrogate tests to minimize the number of analytical tests related to chemical availability that are needed for site-remediation decisions.

These evaluations should be done with a specific emphasis on the question of chemical availability in soils. The focus should be on evaluation of hypotheses and scenarios that increase knowledge on this subject. The evaluations should build upon the existing weight-of-evidence information but should include a broader array of specific chemicals as well as of measures of leachability, mobility and toxicity. Some research of this nature is underway. However, the talents from many disciplines as well as more focused efforts are needed.

Without a more focused research effort to obtain this kind of knowledge, the public and the regulatory community will have only the current weight-of-evidence type of information for subsequent decisions.

## B. Remediation Policy

The need to remediate a site is a risk-management decision. These decisions are made based on various factors related to the site, the chemicals present at the site, and possible impact of those chemicals on humans or the environment. The decisions are implicitly based on generic approaches or explicitly based on site-specific information. All parties involved in the management of a site have a strong desire to develop investigative and management methods that insure the protection of humans and ecological receptors and that are straightforward, easy to understand, and cost-effective.

Individually and/or collectively, many considerations enter into remediation decisions for soil at a given site. The more important of these are:

- extent and nature of contamination;

- current and future potential land use;
- state and/or federal standards or guidelines;
- risk to human or ecological receptors;
- availability of site- and contaminant-specific data; and
- feasibility and economics.

The relative importance of these considerations vary from state to state, site to site, and chemical to chemical, and to the practical aspects of remediating sites and restoring land for a particular use.

Until recently, the concept of chemical availability rarely was used in arriving at soil-remediation decisions. As indicated in this report, knowledge about the availability of chemicals in soils is important in making sound decisions about: a) the need for remediation of specific soils, b) the degree of remediation that should be accomplished, and c) the type of remediation process appropriate for a particular site and soil. Increasing weight-of-evidence information from field data indicate that, particularly in weathered soils, chemicals may not be readily available, i.e. rapidly leached and able to be transported to a human or ecological receptor. This lack of availability of chemicals in soils is further supported by studies showing that the biodegradation of chemicals freshly added to a soil is more rapid than the same chemicals that had been in the soil for an extended period of time.

Typically, the data available for a given site include the concentration of chemicals in the soil and information on the toxicity of the pure chemicals. The additional site-specific information needed to understand chemical availability is rarely obtained, such as the fraction of the chemical that is available for leaching or for uptake directly by an organism, the chemical dose that is received by the receptors, and the toxicity of the chemical dose to the receptor.

The implications of chemical availability for the management of contaminated sites are significant. Thus, in terms of remediation decisions, decision makers should understand that:

- the need for and type of remediation necessary at a site should be based on the availability (leachability, mobility, toxicity) of a chemical in the site soil;
- knowledge about chemical availability should be included in decisions about the degree of remediation needed to protect human health and the environment at a site since such knowledge affects decisions regarding when it is appropriate to conclude a remediation action, and what residual chemical concentrations can remain in soils at a site;
- when obtaining site characterization data about soils and chemicals at a site, information about chemical availability should be obtained; such information should be used in site-remediation decisions;
- In making site-specific remediation decisions, it should be recognized that the fact that a chemical can be extracted and measured in a soil indicates nothing about the site-specific availability of that chemical to have an adverse impact on human health and the environment; that chemicals with low release, toxicity, and transport potential in a soil, i.e., low availability, can have a low relative risk to human health and the environment; and that chemical availability appears to decrease as a soil weathers and as remediation occurs.

## C. Regulatory Policy

Many approaches have been used to assure protection of human health and the environment. These include use of: a) local, regional, or state background concentrations; b) chemical- or media-specific criteria or guidelines; c) generic state or federal limits that have been developed using risk-based analyses; or d) target concentrations developed using site-specific and chemical-specific information and risk-based analyses. However, as indicated elsewhere in this document, chemical availability in a soil is rarely a component of these approaches.

Risk-based regulatory decisions are being recommended and considered, such as the ASTM Standard Guide for Risk-Based Corrective Action.[23] Chemical availability in a soil should be a component of risk-based analyses and other approaches used for regulatory decisions. The types of chemical availability that are of interest in risk assessments are a function of the specific exposure route and receptor and include availability to: groundwater by aqueous leaching; plants, soil invertebrates, wildlife, aquatic biota via groundwater discharge or surface run-off, and humans via skin contact, ingestion, and inhalation.

Thus, in terms of state or national regulations, it is appropriate that:

- the regulations include statements that data on chemical availability in soils be obtained and used in arriving at site-specific remediation decisions;
- risk assessments used to determine the nature and magnitude of risks to human health and the environment utilize existing data on chemical availability in soils;
- risk-based analyses should consider only the available portion of the chemical in soil, not the total amount that may be determined by existing extractive analytical procedures;
- such regulations require the acquisition of data identifying the chemical availability in soils as part of collecting site-characterization data;
- such regulations encourage the acquisition of data identifying chemical availability as part of research related to soil-remediation evaluations as well as part of the field evaluations of soil-remediation technologies; and
- the regulations recognize that there are many approaches to achieve site-specific decisions that protect human health and the environment. Thus, a flexible, tiered approach should be allowed that will use chemical availability data as appropriate. Such an approach is needed to allow site-management decisions to be made any time sufficient data have been collected to support a risk-based decision. The tiered strategy must be sufficiently flexible to address a range of issues at diverse sites.

## ACKNOWLEDGMENTS

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[23] American Society for Testing and Materials, *Emergency Standard Guide for Risk-Based Corrective Action Applied at Petroleum Release Sites*, ASTM Document ES 38-94 (Philadelphia, PA, July 1994).