Type B - Technical Information Document:

**Approaches to the Assessment
of Injuries to Soil Arising From
Discharges of Hazardous
Substances and Oil**

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Pacific Northwest Laboratory
Richland, Washington 99352

EXECUTIVE SUMMARY

This report provides useful information for trustees of natural resources who are embarking on a natural resource damage assessment involving potential injury to the soil portion of the geologic resource. Specifically, this document supplies descriptive information on methods to be used for determining the nature and magnitude of injury to the following:

- Soil Chemical Characteristics
 - acidity or pH
 - cation exchange capacity
 - percent base saturation
 - salinity
- Soil Physical Characteristics
 - porosity
 - water holding capacity
 - aggregate stability
- Biological Characteristics
 - microbial activities
 - invertebrate activities
 - vegetation
- Contaminant Transport Potential
 - leaching
 - food chain.

In addition, this document explains how injuries to the soil resource can be translated into a reduction in services provided by that soil in comparison to local baseline (i.e., uninjured) soils. It also provides information important in determining both the ability and time necessary for the soil to recover from the injury.

The information in this document explains that portion of the regulations contained in 43 CFR Part 11 that pertain to the soils portion of the geologic resource. Geologic resources are only one of five groups

into which all resources are placed in the natural resource damage assessment regulations. The other four categories are surface water, ground water, air, and biological resources. Frequently in a natural resource assessment, resources from several of these five groups will be of concern. Biological resources such as earthworms, elements of ground-water resources, and the sediments portion of surface water resources are often studied in conjunction with soil assessments. Information on conducting assessments for these other resources is not included in this document. For these other resources, the appropriate portions of the regulations and referenced documents for those resources should be consulted.

This document is not intended to be a comprehensive listing of all the procedures available to a trustee who would perform an assessment of potential soil impacts. The information in this document supplements the guidance provided in 43 CFR Part 11 but is not required to be followed to obtain the rebuttable presumption provided by those regulations. The regulations in 43 CFR Part 11 should be reviewed prior to applying the information contained in this report. Any discrepancies between information contained within this report and the regulations provided in 43 CFR Part 11 should be decided in favor of the regulations.

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1.0 INTRODUCTION

Section 301(c) of the Comprehensive Environmental Response, Compensation, and Liability Act of 1980 (CERCLA) requires the President to promulgate regulations for the assessment of damages for injury to, destruction of, or loss of natural resources. Executive Order No. 12316 § 8(c), August 14, 1981, delegated this responsibility to the Secretary of the Interior. These regulations may be used to assess damages to natural resources caused by a release of a hazardous substance or a discharge of oil covered by CERCLA or § 311(f)(4) and (5) of the Clean Water Act.

Section 301 mandates two types of regulations be developed, referred to as type A and type B regulations. The type A regulations are for simplified assessments and rely on existing studies and minimum field observations to compute damages. The type B regulations specify "...alternative protocols for conducting assessments in individual cases to determine the type and extent of short- and long-term injury, destruction, or loss [of a trustee's natural resource]. Such regulations shall identify the best available procedures to determine such damages, including both direct and indirect injury, destruction, or loss, and shall take into consideration factors including, but not limited to, replacement value, use value, and the ability of the ecosystem to recover."

The Department of Interior has promulgated these regulations as 43 CFR Part 11. In the final rule, damages are defined as the monetary compensation for injury to natural resources. Injury is considered to be an adverse change in the chemical or physical quality or viability of a natural resource.

1.1 RESIDUALS REQUIRING DAMAGE ASSESSMENT

It is the intent of CERCLA to provide a mechanism to recover costs associated with response, remedial action, and remaining natural resource damages resulting from a release of hazardous substances or oil. The primary impact zone may be the recipient of remedial action. In this case, direct measures are taken to remove or mitigate hazardous substances or

oil. In other areas, the cost of remedial action may far exceed the value of damages. Thus, while remedial action removes or minimizes threats to health and the environment, damages are assigned on those areas where injuries to resources remain after remedial action has been taken. Hence, the natural resource damages are assigned to areas where residual impacts from hazardous substances or oil remain.

1.2 PHASES OF THE ASSESSMENT PROCESS

The natural resource damage assessment process under the CERCLA 301 rule is comprised of three distinct phases:

1. injury determination
2. quantification
3. damage determination.

Initially, the trustee must determine what, if any, injuries have occurred to natural resources. For the purposes of this assessment process, resources have been divided into five categories: surface water, ground water, air, biological, and geologic resources. Each resource category provides services that give the resource economic value. An injury to the resource is a change in its physical, chemical, or biological makeup, which interferes with its ability to perform those services.

Once injuries have been identified, they must be quantified. Quantification involves determining the degree of the injury, the extent of the environment affected, and any loss of services resulting from those effects. After the injury is quantified, the third and final step is 1) to determine the economic value of services lost; that is, damages associated with the injury, and 2) to estimate the cost of restoring or replacing the services provided by the resource.

1.3 SOILS AS A NATURAL RESOURCE

Geologic resources are defined as those materials that would normally comprise the lithosphere (e.g., soil and rock). Of these, soil constitutes the major portion of concern. As a consequence, this discussion addresses

soil. Where relevant, it should be assumed that similar methods can be applied to rock structures as well as ore bodies.

The soil resource is the weathered and fractured outer layer of the earth's surface. It consists of residues from the decomposition of rocks and organic matter, which may reside in layers up to hundreds of feet deep. The chemical and physical properties of soils vary considerably, reflecting the diversity of sources of origin, the nature of the forces that created the soil, and phenomena to which the soils have subsequently been exposed. Wind and water move and mix soil particles, creating an almost infinite array of heterogeneous particulate blends. The degree to which soil will support various activities is therefore a function of the composition and history of the source materials.

Soil plays a vital role in the natural environment. Along with water and air, it is a fundamental resource upon which all terrestrial life forms depend. At the same time, soil fills some roles not so much by virtue of its properties as by its location at the earth's surface. In either case, injury to this resource arising from hazardous substance residuals or oil can affect the soil's ability to fill these roles by altering its physical and chemical properties. Figure 1 shows potential points of injuries to the soil resource that may result from discharge of hazardous substances and oils. The effects may be either direct or indirect, and may influence the services provided by the soil as a medium for vegetation, a habitat for biota, and a reservoir for residuals. Additionally, it may influence the aquatic resource, which is addressed elsewhere in the natural resource damage assessment rule.

Figure 1. Potential Characteristics of the Soil Resource That May Be Injured (those areas in bold outline are covered in this report)

2.0 SOIL PROPERTIES THAT AFFECT INJURY DETERMINATION

As a complex, heterogeneous medium, soil can be characterized by a number of chemical, physical, and biological properties and parameters (see Figure 1). All are meaningful in context, but only a few can be used readily to determine when there has been an injury to the soil resource caused by the release of hazardous substances or oil. The chemical, physical, and biological properties identified in this chapter are of primary interest for establishing when injury has occurred in a type B natural resource damage assessment.

2.1 CHEMICAL CHARACTERISTICS OF SOIL PERTINENT TO INJURY DETERMINATION

The following chemical properties of soil have been identified in 43 CFR Part 11 as injury to geologic resources, or are important factors for the functional use of the soil: acidity or pH, cation exchange capacity, percent base saturation, and salinity.

2.1.1 Acidity or pH

Acidity or pH (negative logarithm of the hydrogen ion concentration) is controlled by many factors in the soil matrix. In natural ecosystems, the source of parent material and extent of weathering have the greatest influence on pH. The pH of a well-aerated calcareous soil often found in arid or semiarid regions is 8.5 and is poised at that pH by calcium carbonate. Soils in more humid regions will generally have pH values ranging from 4.0 to 7.5. In general, the greater the rainfall, the greater the extent of weathering of the soil and the lower the pH. Soils normally do not have pHs below 4.0 unless they contain free acids. The limit (pH of between 4.0 and 7.5) is determined by the pH of an aluminum soil because clays containing replaceable hydrogen ions are unstable and release aluminum ions, which neutralize the negative charges in the soil the hydrogen ions have been neutralizing. Aluminum ions undergo hydrolysis reactions that hold the pH at approximately 4.0 to 4.5. Total soil acidity is different from pH in that it is the quantity of a strong base required to raise the pH to a predetermined level.

2.1.2 Cation Exchange Capacity

One of the most important chemical properties of soils that influences the availability of nutrients is their ability to retain and exchange positively and negatively charged ions on colloidal surfaces. The extent of ion-retaining ability is termed cation exchange capacity (CEC) or anion exchange capacity (AEC). These values are defined as the sum total of exchangeable cations or anions that a soil can absorb. Cation exchange is generally much higher than AEC for most soils because colloids and organic matter are predominantly negatively charged. Many of the essential plant nutrients are mono- and divalent cations; therefore, a high CEC soil will have a greater supply of plant nutrients. Clay mineralogy, level of organic matter, and pH all influence CEC and AEC. Ions show a marked selectivity for cation exchange sites, dependent on their valence and ionic radii.

2.1.3 Percent Base Saturation

The extent to which the ion exchange complex of a soil is saturated with exchangeable cations, other than hydrogen and aluminum, is termed the percent base saturation. It is expressed as a percentage of the total cation-exchange capacity. Typically, arable soils have values greater than 50% base saturation with calcium constituting over 80% of the exchangeable cations, magnesium up to 15%, and sodium and potassium together rarely more than 5%. Highly weathered, infertile soils will generally have percent base saturation values below 50%. Generally, ratios of calcium, magnesium, sodium, and potassium are similar to those in arable soils.

2.1.4 Salinity

Salt-affected soils are common in arid and semiarid regions where annual precipitation is insufficient to meet the evapotranspiration needs of plants. As a result, salts are not leached from the soil. However, salt problems can develop in humid and subhumid regions given the appropriate conditions. A saline, nonsodic soil contains sufficient soluble salts to impair its productivity. The electrical conductivity of the saturation extract is used as a measure of salinity. Generally, if the

concentration of a hazardous substance or oil is sufficient to yield a salt saturation value greater than 2 mmhos/cm in the soil or a sodium absorption value greater than 0.176, then the soil may be considered damaged.

2.2 PHYSICAL CHARACTERISTICS OF SOIL PERTINENT TO INJURY DETERMINATION

The following physical properties of soil have been identified in 43 CFR Part 11 as injury to the geologic resources, or are important factors for the functional use of the soil: porosity, water holding capacity, and aggregate stability. Of all the physical properties of soil, those involving water are the most important.

2.2.1 Porosity

Porosity is a measure of relative pore volume. Most soils display a porosity in the range 0.3 to 0.6 (30 to 60%), with coarse-textured soils tending to the lower end of the range and fine-textured soils to the high end. Clayey soils have variable porosity as a result of shrinking, swelling, aggregation, dispersion, and cracking under different moisture and pressure conditions. Chemical contamination can similarly affect porosity in clays or may physically occupy pore space and in so doing reduce soil's ability to transmit water.

2.2.2 Water Holding Capacity

Soils may contain water at levels up to complete saturation, wherein water fills all of the pore spaces. The low end is defined as the measurable field capacity, which is the amount of water soil will retain when moist but completely drained. As noted previously, changes in moisture content of clays can affect porosity and the ability of soils to transmit water. Chemical contamination can affect moisture holding capacity either by excluding water (both physically or chemically) or by increasing field capacity through hygroscopicity.

2.2.3 Aggregate Stability

The stability of soil aggregates is indicative of the potential of that soil to erode. The erosional forces can range from wind to slaking by

water. The bonding of soil mineral particles together with plant and microbially derived organic material constitutes the major force involved. The more resistant the soil aggregates are to disruptive forces, the less likely that soil particles will be eroded. Chemical or physical perturbation may lead to a decrease in aggregate stability, resulting in a greater potential for erosion.

2.3 BIOLOGICAL CHARACTERISTICS OF SOIL PERTINENT TO INJURY DETERMINATION

The following biological properties of the soil have been identified in 43 CFR Part 11 as injury to the geologic resources, or are important factors for the functional use of the soil: soil microbial activities, microbial biomass, carbon mineralization, enzyme activity, nitrogen fixation, nitrification, mycorrhizal associations, soil invertebrate activities, and vegetation.

2.3.1 Microbial Activities

Microbiota play a major role in soil with respect to initiation and maintenance of nutrient cycles. Community composition and metabolic processes are specific to the individual nutrient cycles.

Microbial Biomass. A healthy and active soil microbial biomass is required for carbon mineralization. Measurements of the activity and size of the microbial population can include specific enzyme activity (dehydrogenase, catalase, cellulase), size of the soil microbial biomass, soil respiration, and specific microbial populations enumerated by plate count techniques. Further descriptions of these measurements will be summarized in the next chapter.

Carbon Mineralization. The decomposition of plant and animal remains in soil constitutes a basic biological process. Carbon is recirculated to the atmosphere as carbon dioxide (CO_2), nitrogen is made available as ammonium (NH_4^+) and nitrate (NO_3^-), and other associated elements (phosphorus, sulfur, and various micronutrients) appear in forms available to higher plants. In the decomposition process, some of the carbon is assimilated into microbial tissue (the soil biomass) and is partly converted into stable humus.

Enzyme Activity. Enzymes, whether intracellular or extracellular, catalyze all of the biochemical reactions in a soil system. The activity of many of these enzymes play a critical role in nutrient cycling in soil. Phosphatase is a term used to describe a broad group of enzymes that catalyze the hydrolysis of both esters and anhydrides of H_3PO_4 . Phosphatase activity is independent of microbial activity, thus the presence of microbial inhibitors such as toluene during an assay designed to assess phosphatase activity have little effect.

Urease catalyzes the hydrolysis of urea to CO_2 and NH_3 :

Arylsulfatase is the enzyme that catalyzes the hydrolysis of an arylsulfate anion by fission of the O-S bond:

Activity of this enzyme has been found in plants, animals, and microorganisms. Most other enzyme assays developed for soils are for enzymes involved in the catalysis of various carbon compounds (saccharase, cellulase, amylase, etc.) or assay for activity of a general class of enzymes involved in major metabolic pathways (dehydrogenase, catalase).

Nitrogen Fixation. Nitrogen, a major element in living organisms, is required in large quantities by both plants and soil microorganisms. The continuous cycling of nitrogen in the soil is extremely important to the productivity and use of that soil. Soils continuously lose nitrogen by one or more processes and therefore must possess some replacement methods for balancing these losses. On nonfertilized soils, the greatest input is from fixation of atmospheric N_2 by both symbiotic and free-living N_2 -fixing microorganisms.

Symbiotic nitrogen fixation in agriculture is confined to microsymbiotic leguminous plants, but in natural ecosystems a number of trees and shrubs carry root nodules containing microbes that have been proven to fix N_2 . Rhizobium sp. is the microbial symbiont for most legume species; however, less is known about the symbionts forming root nodules on plants outside the legume family. Some of these microorganisms are thought

to be actinomycetes or bacteria such as Beijerinckia and Klebsiella. One property these organisms share is that in their free-living state they exist as heterotrophic soil microorganisms.

Soils also contain a number of free-living nitrogen-fixing organisms that have been identified as bacteria and include the genera Azotobacter, Azospirillum, Beijerinckia, Xanthobacter, and Thiobacillus, as well as methylotrophic bacteria, the facultatively anaerobic enterobacteriaceae, and the photosynthetic bacteria. A number of blue-green algae and a few fungi also share this capability.

Nitrification. Another crucial aspect of the nitrogen cycle is nitrification, the biological oxidation of ammonium (NH_4^+ to nitrate NO_3^-). Decomposition of organic matter releases NH_4^+ , which is relatively immobile in the predominantly positively charged soil matrix. NO_3^- is mobile and can readily move to and into plant roots in the transpiration stream. The microorganisms involved in this oxidation are obligate autotrophs, deriving energy from the oxidation process and fixing carbon as CO_2 for cellular synthesis. Two groups of bacteria catalyze the two-step nitrification process: Nitrosomonas oxidizes NH_4^+ to NO_2^- (nitrite) and Nitrobacter oxidizes NO_2^- to NO_3^- . Temperature, soil water, and pH all influence the activity of these bacteria in soil.

Mycorrhizal Associations. Fungi living symbiotically with the roots of higher plants are known as mycorrhizae. There are two distinct types of mycorrhizal associations with plants. Ectotrophic mycorrhizae cause the formation of short, many-branched structures on sublateral tree roots that take the place of root hairs. These structures are composed of both a mantle and sheath of fungal mycelium enclosing the roots whose cortical cells are enlarged, and also of fungal hyphae filling the intercellular spaces. Endotrophic mycorrhizal hyphae are predominantly intracellular, growing within the cells and forming inclusions. These inclusions are termed either vesicles or arbuscules. Endotrophic mycorrhizae are much more widespread among plants than are ectotrophic mycorrhizae, and the roots of almost every plant species growing on some soil may appear to be mycorrhizal. Mycorrhiza have been shown to benefit plant growth through

increased nutrition and soil water relations. A number of plant nutrients are present in elevated concentration in mycorrhizal plants, but phosphorous uptake is most often improved.

2.3.2 Invertebrates

Soil invertebrates are involved in the breakdown and decomposition of a wide variety of both plant and animal materials as part of the natural cycling of materials in the environment. Invertebrates, therefore, may be critical in the breakdown of organic materials and the resultant release of minerals and stored energy. The importance of soil biota in carrying out these activities has long been recognized, but until recently little was known about their functional roles. Soil animals aid in the breakdown of plant organic matter in several ways: 1) they physically disintegrate tissues and thereby increase surface area; 2) they selectively decompose some materials such as sugars, cellulose and lignin, often through their symbiotic microbes; 3) they transform residue into humic materials; 4) they mix decomposed organic matter within the upper soil profile; and 5) they help in the formation of complex aggregates between organic matter and the mineral fractions of the soil (Edwards 1974).

Nematodes. Nematodes occupy phytophagous, predaceous, and saprophagous trophic levels. These extremely abundant organisms feed mostly on the primary producers, and include plant parasites and algae feeders. Others feed on fungi or bacteria, or function as facultative bacterivores (Twinn 1974). The taxa that feed on fungal hyphae and bacteria are of special interest in terms of the role of nematodes in decomposition processes.

Most descriptions of soil dwelling nematode populations have been based on some estimate of relative abundance, although in some instances density estimates (number of nematodes per unit area) have been obtained. Estimates of nematode population densities of 2.1 million per square meter have been made for the upper 30-cm layer of dune sands. Half of the nematodes were classed as bacterivores, and a few fungivores were present (Twinn 1974). The highest reported nematode densities have come from the soils of deciduous forests where totals of 29 million nematodes per square

meter (to a depth of 20 cm) have been reported from a *Quercus-Fraxinus* forest (Twinn 1974). The reported population levels for grasslands have been variable. Estimates as high as 20 million per square meter have been obtained for some grasslands, but in other studies the densities have been much lower. Smolik and Rogers (1976) reported a peak density of over 5 million nematodes per square meter (to a 30-cm depth) for a sagebrush-bunchgrass grassland. Sixty-two percent of the taxa were found to be phytophagous, 32% were saprophagous, and 8% were predaceous. Data on nematodes from cultivated land are usually limited to the important economic (parasitic) species. Where estimates of free-living taxa have been made, abundance has been low (Twinn 1974). It is clear that nematodes represent some of the most abundant of soil animals in a variety of soils.

Oligochaetes. Earthworms have long been known to contribute significantly to the fertility of soil (Darwin 1881). The most important group of oligochaetes in terms of litter breakdown and turnover for temperate soils are the lumbricid earthworms. These organisms may process up to 78% of the litter in temperate soils (Heath et al. 1966). Lumbricus terrestris is the most important species of the group.

Most of the food material for lumbricid earthworms is taken from the surface litter, although some nourishment may be obtained while burrowing through the soil. Many species move material to the soil surface, which facilitates the burial of litter and thereby assists in bringing the material into contact with other decomposer groups. When feeding, earthworms help fragment the material and thereby help make it available for other decomposer groups. Earthworms also help incorporate the fragmented and decomposed parts of plant material into the soil system.

Earthworm populations vary in numbers depending on the particular soil systems. In general they tend to be highest in fertile soils, lowest in fallow and arid soils, and somewhat variable in arable lands. The highest estimate in terms of population density have occurred for orchard and pasture habitats where the densities were over 500 earthworms per square meter (van Rhee and Nathans 1961; Svendsen 1957).

Microarthropods. The term "microarthropod" is generally taken to include the Collembola (springtails); Acari (mites); Diplura, Thysanura, and Protura (apterygotes); Symphyla; and Pauropods. The Collembola and Acari are usually the most abundant and are thought to have the greatest influence on litter breakdown.

Collembolan density estimates range from about 100 per square meter for deserts (Wallwork 1972) to over 200,000 per square meter for temperate grasslands and antarctic habitats (Harding and Stuttard 1974). The abundance of Acari are also highly variable. For oribatid mite populations, density estimates can range from 6,000 to over 100,000 per square meter (Berthet 1963).

Large numbers of microarthropods are presumed to be associated in some way with the decomposition process, but the extent to which decomposition is dependent on microarthropods has not been well documented (Harding and Stuttard 1974). The feeding habits of most of these animals remain uncertain. The diet of many of the Acari (Prostigmata and Cryptostigmatid mites) and the Collembola for example is almost completely unknown. Consequently any attempt to assess the true role of the microarthropods in litter decomposition will need to depend on additional site-specific information.

Macroarthropods. The main groups of macroarthropods involved in litter breakdown include the Isopoda (woodlice), Symphyla (symphylids), Oiplopoda (millipedes), Isoptera (termites), Diptera larvae (flies), and Coleoptera larvae and adults (beetles). The Psocoptera (booklice), Thysanoptera (thrips) and Hemiptera (coccids and aphids) may also play a contributing role.

Woodlice generally only occur in sheltered moist habitats. They are omnivorous but generally feed on dead and decaying plant material (Edwards 1974). Woodlice densities as high as 7900 per square meter have been reported from scrub grasslands in Great Britain (Sutton 1972). In general, woodlice seem to be more populous in alkaline rather than acidic soils. In general, isopods are considered to be less important than millipedes in litter breakdown.

Millipedes tend to be very aggregated in their distributions. They seem to be much more abundant in calcareous soils than in acid ones. Population densities of millipedes differ considerably, but in woodlands, about 100 individuals per square meter can be considered a reasonable average. Millipedes consume large amounts of litter and, in temperate woodlands, are one of the most important groups involved in litter breakdown. They are less abundant in grassland and desert soils.

Termites occur in temperate areas but are mostly considered to be tropical or subtropical animals. All are social and live in nests or colonies. They feed almost exclusively on decaying vegetation. Termites mix the disintegrated plant organic matter into the soil in much the same way that earthworms do. Few attempts have been made to estimate the actual number of termites per unit area. Most estimates are in terms of the number of mounds per unit area. No estimates have been made of the total termite population for any given habitat (Lee and Wood 1971).

A variety of fly and beetle species are found in soil. The populations, habits, and foods of these animals vary so much that no one really knows their contribution to the breakdown of plant litter. They tend to be more abundant in mesic regions, although one family of beetles, the tenebrionidae, are important detritivores in arid regions.

Mollusca. The majority of molluscs are marine or freshwater creatures, but one class, the gastropods (snails), are found on land. From the limited data available it appears that the greatest population densities and diversity of terrestrial molluscs occur in woodlands. Their population densities are highly variable. Densities generally range from 1 to 20 snails in relatively open grassland and shrubland sites. Snails are, broadly speaking, generalized feeders, taking anything that comes their way. They have been observed to eat green herbaceous material, soil, lichens, soil algae, and fungi (Mason 1974).

2.3.3 Vegetation

Vegetation is an important component of the soil resource. It functions: 1) to stabilize the soil surface, thereby minimizing erosion or

movement of contaminated soil off site or into surface waters; 2) to provide organic matter that is critical for both soil microbial and invertebrate activities; and 3) to assist in the long-term weathering process of the soil, which ultimately enhances the soil's value and the services it can provide.

Vegetation growing on contaminated soils can be affected directly or indirectly by hazardous substance or oil residues that remain in the soil. Direct phytotoxicity (i.e., plant toxification) can result from exposure of the plant to inorganic (nondegradable) or organic (degradable) chemical species, disruption of ion balances caused by the presence of an excessively high concentration of a nondegradable species, or inhibition of root zone gas exchange. These types of impacts are usually observed within days of exposure and are considered harmful to vegetation and, thus, constitute an injury to the geologic resource.

Indirect effects are more protracted, taking months or years to manifest, and result from disruption of biotic processes within the rooting zone. These biotic processes are important to long-term plant growth and survival. Indirect effects include the adverse effects of a hazardous substance or oil on the soil organisms that make the basic nutrients available to the plant root system.

Thus, three key characteristics--root growth, shoot growth, and seed productivity--must be considered when adverse effects on vegetation are used as an indicator of injury to the soil resource.

Root Growth. Roots have a structure that actively exploits the soil in a way that can optimize plant growth. Roots anchor the plant to the soil, absorb water and nutrients, and play an important role in weathering of soils and rock substrates. The growth of roots is controlled by plant hormones, which direct root growth in a downward direction. Thus, disruption of the osmotic potential in the root system will affect hormonal activity and can directly or indirectly affect the ability of the roots to elongate and provide water and nutrients to the shoot and leaves of the plant. Poorly developed root systems that are the result of phytotoxification will keep the plant from reaching its maximum size, and

thus may adversely influence the plant's ability to mature and produce seed. Roots also play a critical role as an interface for microbial activity. Root exudates have been found to be critical to survival and growth of certain microorganisms (Russell 1977).

Shoot Growth/Plant Productivity. Shoots are important in transporting nutrients and water to the leaves of the plant, where most photosynthetic activity takes place. If shoot growth is adversely affected, then the ability of the plant to transport the nutrients and water necessary to carry out the photosynthetic function has been damaged and reduced productivity and seed production may result.

Seed Productivity/Plant Reproduction. The primary plant functions are directed toward growth of both roots and shoots; however, these activities all culminate in production of seed or in the development of viable shoots that will allow for new growth in other areas of soil. A large amount of energy is focused on reproduction and, therefore, one of the potential characteristics that can be adversely affected is seed production. Without a large annual production of seeds, it is unlikely that most species could survive in the local environment.

2.4 CONTAMINANT TRANSPORT POTENTIAL

In addition to the discrete services provided by soil, its value as a resource is also affected by its ability to act as a source for contaminant transport in pathways to other resources. Oil or hazardous substance residuals in soil may be leached or physically transported to surface and ground-water resources. They may volatilize into the air resource, or they may be taken up by plants or soil organisms and, thus, introduced into the food chain. Since all of these media (water, air, and food) are consumed directly by man and other animals, this transfer may lead to more significant injuries than those posed by residuals remaining with the soil.

2.4.1 Leaching and Runoff

As the medium on the surface of the earth, soil serves to transfer and store precipitation. Soil properties can greatly affect both the

quantity and quality of runoff and infiltrate. To the extent that hazardous substance or oil residuals change porosity and related hydraulic properties, these substances will affect the distribution of precipitation between runoff and infiltrate. This type of effect may be considered injurious or beneficial depending on a given site. At the same time, hazardous substance or oil residuals in the soil can be solubilized or carried with particulate matter, thereby affecting the quality of surface and ground-water resources. This mode of contaminant transport transfers the damage from the soil to the water environment. The degree to which contaminant transport occurs and the mode of transport are largely determined by geochemical factors. A chemical's affinity for soil solid surfaces may result from adsorption or exchange phenomena and will compete with its solubility. The pH, Eh, ionic strength, and presence of other chemicals will alter both solubility and surface attraction mechanisms. Guidance in 43 CFR Part 11 for injuries to ground-water or surface-water resources should be consulted for further information on contaminant impacts to water.

Soil physical properties with the most influence on the mobility of a particular contaminant are those relating to the flow of water through soil and the soil's erodability. Included in this list are texture and organic matter content, soil porosity, soil structure, and stability of aggregates. Soil chemical properties, such as composition of the exchangeable ion complex and concentration of electrolytic solutes, can also influence the movement of water through the soil and the detachment of soil particles.

2.4.2. Volatilization

Volatile hazardous substance residuals in soil can be slowly released into the atmosphere through vaporization. The rate of release will depend on the affinity the chemical has for the soil and its vapor pressure. For the most part, chemicals capable of being released at rates that will produce harmful concentrations in the atmosphere will pose short-term hazards. Materials that volatilize over long time frames are subject to atmospheric dispersion, which reduces levels below injury thresholds. Short-term hazards will be considered in the atmospheric resources damage

assessment. Exceptions may result from materials which are transformed to volatile by-products over time. Guidance in 43 CFR Part 11 for injuries to the air resource should be consulted for further information on contaminant impacts to air.

2.4.3 Food Chain

Hazardous substances can be taken up directly by plants and soil organisms and thus enter the food chain. Subsequent bioconcentrations can ultimately produce concentrations injurious to higher levels in the food chain. Thus, soil is also a reservoir for the biological pathway. Many times the chemical forms of these hazardous substances, once metabolized by plants, are more biologically available (to organisms) than their parent forms. This presents a potential near-term risk to wildlife inhabiting a contaminated area. Guidance in 43 CFR Part 11 for injuries to biological resources should be consulted for further information on contaminant impacts to biological resources.

3.0 METHODOLOGIES FOR DETERMINING INJURY TO SOIL

The site-specific, quantitative assessments required by the type B regulations necessitate soil sampling and analysis to identify and later quantify environmental injuries when injury to soil is suspected. Sampling and analysis methods appropriate for characterizing injuries from hazardous substances and oil are the same as methods used for contamination assessments during CERCLA remedial investigations.

Trustees are encouraged to identify as early as possible the need for sampling as part of a soil injury assessment. Early recognition of the need for injury assessment can allow collection and analysis of samples that serve dual purposes, thereby ensuring uniformity of methods and conservation of resources. Suggestions for sampling and analysis are provided in the Appendix.

Because site characterization analyses for Superfund studies are conducted through the remedial investigation and feasibility study (RI/FS) process conducted by the U.S. EPA Contractor Laboratory Program (CLP), some contamination characterization for soil injury studies will probably also be conducted by a CLP laboratory. The CLP methods for routine analyses are based on gas chromatography/mass spectrometry for organics and either atomic absorption or inductively coupled plasma-emission spectroscopy for inorganics. When a CLP is not used, analytical methods and QC procedures consistent with the CLP are preferable.

3.1 CHEMICAL PROPERTIES

The following test methods can be used to quantify injury to the chemical properties of soil that are essential for the functional use of the soil. Some useful references for soil sampling and chemical analysis are provided by U.S. EPA (1983, 1984a,b,c).

3.1.1 Acidity or pH

Soil pH is one of the most indicative measurements of the chemical properties of a soil. Some of the factors that should be taken into

consideration when measuring pH of the soil are the nature and type of organic and inorganic constituents that contribute to soil acidity, the soil/solution ratio, and errors associated with equipment standardization and liquid junction potentials. A pH-sensing electrode attached to a meter for measuring electromotive force (emf) is normally used to measure the liquid-junction potential created by the concentration difference of hydrogen ions across a membrane. The pH is usually measured on a 1:1 soil to water suspension, although 0.01 M calcium chloride solution may be substituted for the water (McLean 1982). The use of a 0.01 M calcium chloride as a solution masks small differences in salt content without displacing a large fraction of the aluminum or hydrogen ions.

3.1.2 Cation Exchange Capacity

Cation exchange capacity (CEC) is usually expressed in milliequivalents per 100 g of soil. In general, it is the sum of the negative charges in soil constituents. A measure of these negative charges determines the quantity of cations that can be held to soil particles. Many different methods are available for determining CEC. The methods use various combinations of soil pretreatment, saturation, washing, and extraction procedures, and different saturation and replacing cations, washing solvents, and pH control. The main steps for determining CEC include: 1) saturating exchange sites with a specific cation (K^+ or NH_4^+), 2) washing or equilibrating with the same solution, 3) extracting with another cation solution, and 4) determining the amount of the replacement cation. Methods for determining CEC in arid land soils are different than for soils of more humid climates (i.e., soils with a lower pH) (Rhoades 1982a).

3.1.3 Percent Base Saturation

The exchangeable cations Ca^{+2} , Mg^{+2} , K^+ , and Na^+ , often called exchangeable bases, commonly occur in soils in the order listed. The sum of these bases relative to the total CEC is termed percent base saturation. In a procedure very similar to that for CEC determination, the basic cations are replaced on the soil exchange sites by NH_4^+ (Thomas 1982). The cations Ca^{+2} , Mg^{+2} , K^+ , and Na^+ are then quantified in the extracting

solution using flame photometry, atomic absorption, or chemical methods (Knudsen et al. 1982; Lanyon and Heald 1982).

3.1.4 Salinity

Soil salinity is most often measured as the electrical conductivity (EC) of the saturation extraction of a soil. Electrical conductivity measurement is quick and sufficiently accurate for most purposes. When an electrical potential is imposed, the amount of current varies directly with the total concentration of dissolved salts. At constant potential the current is inversely proportional to the solution's resistance and can be measured with a resistance bridge. Conductance is the reciprocal of resistance and has the units of reciprocal ohms or mhos. A conductivity or Wheatstone bridge is used to make this measurement (Rhoades 1982b) (see section 2.1.4 for clarification of critical salinity values for damage assessment).

3.2 PHYSICAL PROPERTIES

The following test methods can be used to determine injury to the physical properties of soil that are essential for the functional use of the soil.

3.2.1 Porosity

Characterizations of the soil pore system are important to the storage and movement of water and gases. Total porosity provides information of little utility. It is usually preferable to measure pore-size distribution or the volume occupied by the larger pores. The measurement of pore size distribution is based on the theory that soil pores behave as capillaries of different radii. The smaller the pore radii, the more tightly held the water. A suction force is applied to the soil and the subsequent volume of water removed is determined. The results are calculated on a soil dry weight basis (Vomocil 1965).

3.2.2 Water Holding Capacity

Water capacity of a soil can be determined either through solving the differential equations for water flow through unsaturated soil (Klute 1965)

or obtained as a by-product of other soil physical measurements (Klute 1965). In the latter of these two procedures, a known volume and weight of soil is saturated with water, and then positive, constant air pressure is applied. After a constant weight is obtained, an oven-dry weight determination of the sample is made, from which the volumetric water content can be determined for the particular pressure used.

3.2.3 Aggregate Stability

The forces involved in aggregate stability generally include impact and shearing forces administered while taking and preparing samples, abrasive and impact forces during sieving, and/or forces involved in the entry of water into the aggregate. In determining aggregate stability, known amounts of some size fraction (or fractions) are obtained. The aggregates are subjected to a disintegrated force designed to simulate some important field phenomenon. The amount of disintegration is measured by determining the portion (by weight) of the aggregates that are broken down into primary particles smaller than some selected size. In general, the wet-sieving method obtains the most consistent results (Kemper 1965).

3.3 BIOLOGICAL PROPERTIES

The following test methods can be used to determine injury to the biological properties of soil that are essential for the functional use of the soil.

3.3.1 Microbial Activities

Injuries to soil microbial activities are measured in terms of effects on microbial biomass, carbon mineralization, enzyme activity, nitrogen fixation, nitrification, and mycorrhizal associations. Some useful references for verifying an injury to microbial populations are provided by Jenkinson and Powlson (1976) and Anderson and Oomsch (1978).

Microbial Biomass. Methods used to measure the total soil microbial biomass include microscopic counting, soil fumigation, glucose-response, and adenylyate energy charge. There are advantages and disadvantages to each; however, soil fumigation and glucose-response are methods used most

often. If a soil is fumigated, the respiration rate of the soil immediately after removal of the fumigant will be less than that of a nonfumigated soil. After a time, the respiration rate of the fumigated soil will sharply increase to a value exceeding that of the nonfumigated soil. This flush in carbon dioxide is largely due to the decomposition of microbial cells killed by the fumigant. The size of this flush has been shown to be proportional to the initial size of the microbial biomass. Carbon dioxide released after fumigation is trapped in sodium hydroxide and measured by titration. A more rapid method, after initial standardization, is the glucose-addition method. It has been demonstrated that solids differ in their initial respiratory response to optimum concentrations of glucose. This initial respiratory response to glucose has been used as an index of the existing total microbial biomass. The carbon dioxide released is determined by gas chromatography (Jenkinson and Powlson 1976; Anderson and Domsch 1978).

Carbon Mineralization. Both soil respiration and dehydrogenase activity measure carbon mineralizing activity of the soil microbial biomass. Microbial respiration is defined as the uptake of oxygen or release of carbon dioxide by bacterial, fungal, algal, and protozoan cells in the soil. Both laboratory and field methods have been used to measure soil respiration. The rate of oxygen disappearance, carbon dioxide appearance, or both, can be employed. The biological oxidation of organic compounds is generally a dehydrogenase process, whereby enzymes in this class catalyze the transfer of hydrogen (electrons) to acceptors. The dehydrogenase activity associated with soil is intracellular only as these enzymes are not active outside the cell. Briefly, one method used to measure carbon mineralization activity involves adding triphenyltetrazolium chloride (water soluble) to the soil and allowing it to incubate, during which time it is reduced to methanol soluble triphenyl formazan by dehydrogenase. After 24 hours, the triphenyl formazan is extracted from the soil with methanol and measured colorimetrically (Anderson 1982; Tabatabai 1982).

Enzyme Activity. The assay for phosphatase in soil is rapid, accurate, and precise. The procedure works with either fresh samples or air-dried soil. It involves the colorimetric estimation of the p-nitrophenol released when soil is incubated with buffered sodium p-nitrophenol phosphate solution and toluene. The procedure used to extract the p-nitrophenol from the soil released as a result of phosphatase activity develops a stable color and gives quantitative recovery of p-nitrophenol added to soil. Toluene is used to inhibit microbial activity, since phosphatase is active as an extracellular enzyme (Tabatabai 1982; Tabatabai and Bremner 1969).

Urease activity in soil is also extracellular in nature. Soil amended with a THAM buffer, urea solution, and toluene is incubated for 2 hours at 38°C. The ammonium released is determined in the incubated soil by treatment with 2 N KCL containing silver sulfate (to stop urease activity). Alternatively, the amount of urease remaining after incubation can be determined (Tabatabai and Bremner 1969; Tabatabai 1982).

Nitrogen Fixation. The microbial catalyzed reactions involving nitrogen fixation and nitrification are normally considered separate from soil enzyme activities. Nitrogenase is the enzyme present in microorganisms that allows them to fix atmospheric nitrogen to ammonium. The enzyme has a strong affinity for acetylene (much stronger than for nitrogen) and catalyzes its reduction to ethylene. Soil cores can be placed in air-tight containers which are then filled with acetylene gas. After incubation under appropriate light and temperature conditions, a gas sample is removed and analyzed for ethylene using a gas chromatograph. This procedure will estimate the nitrogen-fixing potential to the free-living microorganisms in the soil. A similar system can be used to assay the nitrogen fixing capacity of rhizobium in legume root nodules (Knowles 1982).

Nitrification. A standard most probable number (MPN) procedure is used to enumerate the nitrifier populations of Nitrosomonas and Nitrobacter (Alexander and Clark 1965). Serial dilutions of soil containing Nitrosomonas (which oxidizes ammonium to nitrite) are inoculated into an

inorganic medium containing ammonium as the source of nitrogen. If the bacterium is present, growth will occur and nitrite will be produced. Hence, a positive test for nitrate in the inoculated medium, but not in the controls, indicates the presence of Nitrosomonas. A negative test for nitrite, however, does not prove the absence of Nitrosomonas because nitrite-oxidizing microorganisms may also be present. This would cause the nitrite to be oxidized to nitrate. A positive test for either nitrite or nitrate in the medium and a negative test in the uninoculated controls indicate the presence of Nitrosomonas. Nitrobacter is also enumerated in a mineral medium, but contains nitrite as the only source of energy. The presence of Nitrobacter is indicated by a negative test for nitrite in the medium.

The nitrifying potential of a soil can be used to indicate the maximum activity of an unenriched indigenous nitrifying population. The procedure is relatively simple and can be used as an alternative to MPN estimates of nitrifier populations. Soil is amended with ammonium sulfate and the appearance of nitrate and nitrite is measured over time (Schmidt and Belser 1982).

Mycorrhizal Associations. Estimation of the amount of mycorrhizal (VA) infection in plant roots is normally estimated via microscopic analysis. Root segments whole or fresh are fixed in FAA (13 mL formalin, 5 mL glacial acetic acid, 200 mL 50% ethanol) and heated to 90°C for 1 hour in 10% KOH. This procedure removes the host cytoplasm and most of the nuclei. The roots are then stained by simmering for 5 minutes in 0.05% trypan blue in lactophenol and the excess stain removed in clear lactophenol. The fungal hyphae and structures stain deep blue against the outline of root cells. The procedures for staining and estimating percent infection are rather laborious (Phillips and Hayman 1970).

3.3.2 Invertebrates

Injuries to soil invertebrates are measured in terms of effects on nematodes, oligochaetes, microarthropods, macroarthropods, and mollusca.

Nematodes. Detection of injury to nematode populations involves collecting samples of nematodes from the soil system. One commonly used method for separating nematodes from soil involves wet screening of the soil samples followed by Baermann funnel extraction. The efficiency of the screening can be determined by re-extracting the soil samples. Efficiency of the Baerman funnel can be established by examination of residue to determine the number that failed to pass through the screen. Additional details can be found in Christie and Perry (1951).

Oligochaetes. Of the numerous methods used to sample earthworm populations, none are adequate for all species and habitats. Three methodologies are generally used to extract worms from the soil: those that use irritant solutions, those that use an electric current, and those that extract worms from soil samples taken from the field and trapping methods. Satchell (1971) reviews the various sampling methodologies for oligochaetes.

The need to assess the toxocity of various hazardous materials to soil invertebrates has resulted in the development of various bioassay techniques. A terrestrial bioassay for earthworms is described by Karnak and Hamelink (1982).

Microarthropods. The density of soil-dwelling mites and other small arthropods is most often determined by means of sampling with a cylindrical corer of constant volume and area. Individual mites are then extracted from the soil sample. A review of all of the methods available for extracting edaphic mites has been provided by Phillipson (1971).

Macroarthropods. A variety of larger arthropods spend at least a portion of their time developing or living within the soil. For example, many of the beetles deposit their eggs, and the larvae develop within the soil. Unfortunately, little is known about the quantitative aspects of the ecology of some of these groups; therefore, it is not always possible to determine the best method of sampling their populations for injury. Clearly, no one extracting method is equally efficient for all soil-dwelling macroarthropod groups or for a particular group occupying a variety of soil and habitat types. Phillipson (1971) has reviewed this subject and

provides insight into the selection of particular sampling methods. Bioassays for assessing the toxicity of hazardous substances to crickets are described by Walton (1980) and Burkhardt and Fairchild (1967). A bioassay for ants is described by Gano et al. (1985).

Mollusca. Terrestrial molluscs comprise those animals known as slugs and snails. They live either on the surface or in the top 20 to 30 cm of the soil. Traditionally, the abundance of soil-dwelling molluscs has been determined by washing and hand sorting soil samples.

3.3.3 Vegetation

The following test protocols can be used to assess either the potential toxicity of a mixed or unknown hazardous substance or oil to soil, or the extent of restoration measures required to reduce plant and associated impacts to acceptable levels. The following tests are basically EPA standard test guidelines provided in U.S. EPA 1982a.

Root Growth. The Seed Germination/Root Elongation Toxicity Test (U.S. EPA 1982a, Section EG-12) is a standard EPA test protocol for rapidly evaluating the extent of injury to plants in the germination and early phases of growth. The test can be used both to assess injury and subsequently to evaluate the effectiveness of remedial actions.

Shoot Growth. The Early Seedling Growth Toxicity Test (U.S. EPA 1982a, Section EG-13) is a second-tier evaluation of the extent of plant injury from contaminants associated with the soils collected from affected sites. In this test, plants are allowed to grow beyond the seedling stage on contaminated soils, and are then examined to assess any adverse metabolic or developmental problems induced by a hazardous substance or oil.

Seed Productivity. The Experimental Terrestrial Soil-Core Microcosm Test Protocol (Van Voris 1985) is a test designed to evaluate chemical effects on both plant productivity and seed productivity. It employs an intact soil profile from the suspect site and control sites to allow for testing injury to plants, microorganisms, soil invertebrates, and soils.

Each of these tests uses agronomic plant species to assess toxicity and/or absorption of hazardous substances or oil. While the use of agronomic species is acceptable, the test results may represent unacceptably high toxicity ratings for native plants normally associated with relatively harsh, natural environments. Therefore, these test results may not indicate natural resource injury.

3.4 CONTAMINANT TRANSPORT POTENTIAL

The determination of injuries associated with soil-related pathways to other resources is made by direct testing of the propensity for residuals to be transferred to other media. Only leaching and biological uptake are considered here, since volatilization is evaluated along with injuries to the air resource.

3.4.1 Leaching and Runoff

Because of the surface properties of particles, dissolved chemicals often move through soils at a much slower velocity than the water by which they are carried. These attenuation properties are specific both to the soil and the chemical. They are often characterized very generally in the form of a retardation factor, which is defined as the ratio of the velocity of water in a soil to that of the chemical. For chemicals with a retardation factor >1.0 , the soil acts as a continuing source from which hazardous substances or oil can be leached and transported to surface waters in runoff or ground water in infiltrate. The degree to which the soil's role as a storage medium can be measured directly as the propensity for the soil to release the hazardous substances or oil in leachate. The more tightly bound the substance is to the soil, the less likely it will produce toxic leachate.

A variety of procedures have been developed to measure the leachability of solids. Batch tests mix the solid in a suitable leaching solution for a prescribed contact period. The solids are then separated out and the solution tested for contaminants. Column tests use a glass column packed with the solid of interest. Leaching solution is then pumped or allowed to drain through the solid and analyzed as it exits the column. Batch tests are more commonly employed because they take less time and are

less expensive. Column tests more closely approximate conditions associated with percolation of water through soils.

In addition to differences in contact mode (batch versus column), candidate procedures prescribe alternate contact times and alternate formulas for the makeup of the leaching solution. In the latter case, choice of the solution is dictated by the scenario the leaching test is intended to simulate. The EPA Toxicity Characteristics Leaching Procedure (TCLP), by which wastes are designated as hazardous, is designed to simulate leaching in a mixed waste landfill. As a consequence, acetic acid at pH 5.0 is employed as a buffer representative of organic acids, which may arise from the decomposition of organic wastes. Similarly, the State of California Waste Extraction Test (WET) employs citric acid at pH 5 to simulate organic chelates and other solubilizing agents that may be present as degradation by-products. Other test procedures require use of distilled or deionized water to simulate rainwater or snowmelt. The latter solutions are most relevant to assessing contamination potential of soils. Therefore, if a given method such as the EP is applied for in a natural resource damage assessment, the procedure should replace the leaching solution with distilled or deionized water. Relevant batch extraction methods are described in U.S. EPA (1982b) and in Garrett et al. (1981), and methods for sample preservation are described in U.S. EPA (1982c). Additional tests for both solubility of the compound (CG-1500), transport (CG-1700), and transformation (CG-2000) are available in U.S. EPA (1982d).

As noted previously, soil contaminants may also affect the quantity of infiltrate produced at a site by changing the permeability of the soil. Changes in the quantity of infiltrate may or may not constitute an injury (some changes may be beneficial); therefore, no standard assessment method can be specified. Furthermore, phytotoxicity and biota habitat considerations will come into play long before permeability changes occur at a significant level.

3.4.2 Food Chain

Two EPA Test Protocols are suggested for assessing the potential for contaminant transport into the food chain. These include the Plant Uptake and Translocation Test, and the Soil-Core Microcosm Test.

The Plant Uptake and Translocation Test (U.S. EPA 1982a, Section EG-14) is designed to assess the extent of uptake of specific hazardous materials by plant roots and the translocation and accumulation of those materials in shoot tissues. The test provides a basis for determining the concentrations of a substance accumulated in aboveground tissues, which may be ingested by fauna, and for determining subsequent injury to the food chain.

The Soil-Core Microcosm Test (Van Voris 1985, Section 4 Test Guidelines) is preferred to the plant uptake and translocation test. The microcosm test can use site-specific soils and local vegetation types, and is much more useful in assessing near-term transport and transformation of a given hazardous substance or oil. If properly conducted, the microcosm test may be suitable for evaluating injury to either the soil's plant species within the microcosm, or to the soil's microflora and invertebrates.

4.0 QUANTIFICATION

Injury to chemical, physical, or biological characteristics of soil can be translated into loss of services provided by soil. Quantifying the services that are lost is best achieved by evaluating individual soil characteristics, because no single test addresses all the potential services. Moreover, relationships among soil properties may in some cases mask, mediate, or exacerbate injuries; therefore, testing individual soil properties is the easiest way to identify potential injuries.

4.1 STATEMENT OF SERVICES PROVIDED BY SOIL

For purposes of a natural resource damage assessment, soils can be viewed as providing three major services:

- soil as a growth medium for vegetation
- soil as a habitat for biota other than vegetation
- soil as a reservoir affecting the quantity and quality of runoff and leachate (i.e., precipitation transfer) and edible biota (i.e., food chain transport).

4.1.1 Soil as a Growth Medium for Vegetation

Soil acts as both the support structure within which vegetation grows and as a reservoir of essential nutrients for plant growth. These functions can be impaired by hazardous substances and oil as a result of several interactions:

- Phytotoxic chemicals can render the soil unsuitable for vegetative growth via direct toxic action.
- Oils or other organic chemicals can alter the water transmissivity properties of soils, thus leading to plant dehydration.
- Chemicals may reduce the availability of nutrients in soil which, in turn, would reduce productivity.

Although a high soil concentration of any hazardous substance or oil can cause immediate plant death, it is the continuous, low-level insult that affects plant performance and survival and is of long-term concern. The

latter plant response results from the accumulation of oils or hazardous substances; moreover, this general deterioration of metabolic and reproductive performance may occur without obvious visual symptoms.

4.1.2 Soil as a Habitat for Biota

The soil environment harbors a diverse population of microorganisms and macroinvertebrates that form a discrete link in the ecosystem. As in the case with vegetation, these life forms may be threatened by the presence of toxic chemicals in soil or by physical barriers to the interchange of air or water. The specific concern posed by a given hazardous substance will differ between vegetation and biota because of the biochemical differences between the two types of organisms.

Soil microbes and microbial-mediated processes are sensitive to soil pH and, in general, are deleteriously affected by extremes in pH or by sudden marked changes in pH. Bacteria and actinomycetes favor pH values near neutral. Their populations decline as the H^+ ion concentration increases (i.e., as pH decreases). Fungi also favor pH values of around 7.0, but in general are more tolerant of acid conditions than are bacteria and actinomycetes. Decomposition typically proceeds faster in near neutral soil than in acid soils, and the nitrification rate falls off markedly below pH 6.0. Certain trace metals become more available as soil pH decreases and, in some cases, can reach inhibitory concentrations. In addition, cation, anion exchange capacity, and soil salinity as well as percent base saturation, influence productivity and soil microbial populations. The effects of these properties on the microflora are mainly indirect, such as sorption of heavy metals to exchange sites.

Soil aeration status, as measured by soil porosity, can strongly influence the composition of the microbial community and the biochemical processes that occur. Most surface soils are normally aerobic and contain predominantly aerobic microbial populations. Facultative microorganisms also comprise a segment of the microbial population and anaerobes can survive in some anoxic microsites in the soil. Most of the important microbially mediated processes are favored by aerobic conditions; however, some are favored under O_2 -limited conditions.

The primary ecological role of the soil-dwelling macroarthropods occurs in the breakdown of plant organic matter. Soil animals assist in this breakdown by physically disintegrating plant tissues and thereby increasing the surface area available for microbial action. Any reduction in the rate of litter breakdown will result in a corresponding reduction in the rate of nutrient return to the soil system. While the effects of any reduction in the rate of litter breakdown and nutrient return is highly dependent on conditions within specific habitats, nutrient-poor soils would be expected to show a reduction in plant growth (productivity) and perhaps species diversity within a single season. For those habitats containing higher concentrations of soil nutrients, the effect would likely be postponed for some period of time.

4.1.3 Soil as a Pathways Reservoir

Soil's service as a reservoir for infiltrate and nutrients for ground water and vegetation, respectively, are affected when hazardous substance or oil residuals are present at levels that will adversely alter the quality of those receiving resources. Such service reduction can be measured directly with pathway testing or can be surmised from chemical characterization. For inorganic substances, CEC and base saturation measures may also provide data indicative of injury. In particular, if exchange capacity is exhausted, it is likely that contaminant levels will be high enough to be transferred in leachate, in the food chain, or in both pathways.

4.2 IDENTIFICATION OF BASELINE FOR SOIL

Identification of spatial or temporal trends, as well as linkage of measured concentrations to specific sources, requires that background, reference, or control samples be taken. These samples characterize an area that is unaffected by the specific source being studied. Because soil materials consist of weathered and fragmented minerals and organic materials, there is no generic definition of a "clean" soil; baseline soil conditions must be established for each site. This is done by selecting a control area from which background samples can be taken.

For the selection and sampling of control areas, a combination of judgmental and random sampling is recommended (Barth and Mason 1984). Based on available information and the assumed transport model, a control region should be selected that is similar to the study area in every important aspect, excepting the expected absence of hazardous substances. Hence, the area should be upwind and upflow of known source sites. Soil type should be the main factor in selecting the control, but other differences, such as depth to ground water, vegetation type, topography, and spatial relation to source(s), should be minimized.

Frequently, the selection of a control region is complicated by the presence of contaminants from multiple sources or mixing of contaminants of recent origin with those of past origin. The purpose of the study will dictate the importance of these complicating factors and guide selection of the control region. Barth and Mason (1984) and Mason (1983) recommend that the same degree of effort be directed toward selecting and sampling the control area as is directed toward selecting and sampling the study area. The control area should be designated in the Sampling Plan before any field work begins in the study area (see Appendix).

4.3 ABILITY, AND TIME REQUIRED, FOR THE RESOURCE TO RECOVER

The recovery of the soil resource will depend on various factors such as the specific chemical nature of the hazardous substance, its solubility (if inorganic) or half-life in soil (if organic), the physical extent of the affected area, and projected land uses. Physical, chemical, and biological phenomena will all have a role in determining how long recovery will take. It is important to determine the recovery period in order to estimate the temporal extent of loss of services; i.e., how long will services be lost as a result of a given injury. In general, these phenomena can be divided between those which transport the chemical residuals from the geologic resource to another matrix (e.g., water, air, or biota) and those that transform the residuals to less injurious products.

4.3.1 Transformation Mechanisms

Many hazardous substances and oils are subject to biochemical and/or chemical degradation. In general, chemical degradation can result from a number of processes, including oxidation-reduction, hydrolysis, depolymerization, or isomerization. Many of the tests available to determine recovery periods require time frames on the order of the recovery period. As a consequence, whenever possible, it is desirable to employ the results of previous laboratory and field studies on a given hazardous substance to estimate probable recovery times. Caution is necessary, however, since degradation can be site specific. If data are not available, standard biochemical oxygen demand (BOD) tests or structural activity relations can be applied to estimate environmental half-life. Residuals will biologically degrade if enzymes for degradation have been acquired by microorganisms during the course of evolution. Because environmental conditions differ from site to site, however, some hazardous substances that are readily biodegradable in one environment may persist in another. Ideally then, the potential success of chemical and biological recovery mechanisms is assessed at each site.

The potential of a soil to biodegrade a particular hazardous substance or oil, which will affect the time required for recovery, can be influenced by several of the soil microbiological characteristics discussed earlier. These properties are soil microbial biomass and carbon mineralization potential (see Section 2.3.1).

Biological degradation is influenced by the microbial population and by soil conditions that affect their activity. These conditions include pH, moisture, temperature, exposure to air and sunlight, and presence of organic matter. The chemical nature of a waste and its structure can also influence degradation by influencing the composition and abundance of microbial and invertebrate communities.

4.3.2 Transport Mechanisms

Soil is a relatively immobile medium in the environment. As such, it is subject to cleansing when contaminants move into the more highly mobile

atmosphere and hydrosphere. Thus, soil may be restored naturally by contaminant transport mechanisms in addition to degradation processes. The former include:

- volatilization and dispersion in the atmosphere
- atmospheric resuspension of contaminants attached to particulate matter
- suspension of contaminated particulate matter in runoff
- dissolution in runoff and/or infiltrate.

The predominance of any mechanism or mechanisms is a function of the contaminant's properties and site features; for example, transport of particulate matter is more important for strongly sorbed materials, while runoff considerations increase with slope. In general, volatilization and dissolution in infiltrate are the most active transport mechanisms. A recent review of dioxin movement near contaminated sites revealed that particulate transport mechanisms were active only during severe storm events, and then rarely accounted for removal of a significant fraction of the contaminant.

It is difficult to accurately predict contaminant transport with a simple test. Microcosm studies are often used to observe degradation rates, but they are too small to provide for climatological conditions representative of actual sites, and they do not involve accelerated time frames. Tests which offer the latter are typically focused on a single transport mechanism. For instance, column leaching tests can be used to predict the leaching action of infiltrate. Pressurizing the leach solution accelerates flow rates so that high total rainfall levels can be simulated in a short period of time. For volatilization, elevated temperatures may be employed. Alternately, transport and hence persistence can be predicted by applying models or algorithms. The latter approach is less accurate because of the state of the art in modeling, but much less expensive and can be a very effective screening tool. As a consequence, a tiered approach is best for determining how effective transport processes will be in restoring contaminated sites. Volatilization and leaching are the two pathways of concern. The tiered approach would be implemented as follows:

Volatilization. A number of models are available to predict volatilization from soil. Each is described, and guidelines are provided for selection of the most appropriate approach, in Lyman et al. (1982). If application of these approaches indicates that volatilization losses may significantly affect contaminant levels and, hence, resource damage valuations, a more accurate estimate should be obtained from a laboratory study.

No standard methods are prescribed for evaluating the volatilization loss mechanism. However, volatile losses will occur in microcosm and other methods designed to measure biochemical degradation. Therefore, this parameter can best be measured in a combined form.

Leaching. Data from the extract test to predict the threat to ground-water can be used to assess leaching potential. The degree to which contamination threatens ground-water quality is proportional to its propensity to be cleansed by leaching. The results of the extraction test provide an estimate of partitioning between the soil and precipitation. An optimistic estimate of soil residence time can be made by taking the product of leachate levels in the extract test and the annual infiltration levels. If the mass of contaminant leached is significant, then a more accurate column test is in order. To date, the American Society for Testing and Materials (ASTM) has not published a standard procedure. Most researchers design their own for studies of interest. A typical column procedure can be found in Relyea (1982) or Relyea et al. 1980. These methods are designed to measure adsorption of contaminants, but with minor modifications are also appropriate for desorption. Results must be interpreted, since some sorption may be irreversible.

4.4 RESTORATION MEASURES

In 43 CFR Part 11 restoration is defined as replacement of services previously provided by the resource. When a trustee has decided to restore the soil resource, the natural resource damage assessment process requires the development of a site-specific "Restoration Methodology Plan." To

develop this plan, injury must be quantified such that the plan allows for restoration of the services previously provided by the resource.

This section described the nature of alternatives that are available as restoration measures for soil. For the soil resource, the primary services provided are presented in terms of the ability of the soil to provide a growth medium for vegetation, habitat for other biota, and as a transport reservoir affecting the quantity and quality of runoff and leachate.

The type and extent of restoration measures for type B injuries to vegetation are tempered by the chemical nature of the hazardous substance. Restoration measures may vary depending on the type of hazardous substance or oil present. In general, restoration may encompass activities to modify soil properties (as in the case on nondegradable substances) or accelerate recovery times (as in the case of degradable substances).

Nondegradable Hazardous Substances. In the case of an inorganic hazardous substance that is nontoxic, except at high concentration, and soluble in soil with little soil holdup, as in the case of fertilizers (nitrate, ammonia, phosphate, sulfate, carbonates, etc.), simple treatments can reduce the immediate and near-term impacts to vegetation. In this instance, corrective action can range from flushing the plant root zone with water to reduce the salt load, with or without tillage to accelerate natural water infiltration and weathering, to liming or sulfating to reduce any adverse pH effects. In this instance, any injury to vegetation would be transient, and little injury to fauna ingesting the vegetation would be projected. Furthermore, no change in land use would need to be imposed.

If the hazardous substance is chemically toxic (containing such elements as cadmium, lead, chromium), not only can vegetation be injured, but also wildlife that graze on the vegetation. In the case of chemically toxic material, the measures used will depend on the concentration, extent, and chemical nature of the hazardous substance. In the event of a spill or release, surface soil may be removed to limit further dispersion of toxic material and to reduce the soil concentration of the hazardous substance available for plant uptake.

If the hazardous substance is relatively soil insoluble, and of only moderate toxicity, contaminated surface soils could be impounded and covered or otherwise isolated from the environment. In the case of highly toxic material, contaminated soils may have to be removed from the site. Subsurface soils containing elevated but substantially reduced concentrations of contaminant could be treated to reduce near- and long-term injury to both vegetation and wildlife. This secondary treatment could include liming (increased pH) to reduced the soil solubility of hydrolytic cations, sulfating (decreased pH) to insolubilize certain anions, and/or amendment of soils with ion exchange type materials such as clay or organic matter to bind soluble species. Depending on the nature of the contaminant, its concentration in soil, its bioaccumulation factor, and its relative animal toxicity, wildlife access to the contaminated site may have to be restricted, seasonally or totally, until concentrations available to plants are reduced by natural weathering processes.

Degradable Hazardous Substances. Injury associated with the environmental release of a hazardous organic substance will depend on several factors, such as the toxicity of the substance to plants and animals, its bioavailability and ability to be transferred through the food chain, its soil solubility and ability to migrate to subsurface and surface waters, and its environmental half-life.

In addressing restoration measures for a given release or spill, a number of factors should be kept in mind. If the compound is biologically available and/or toxic, then the concentration of the hazardous material must be reduced to avoid toxicity response in plants and furthermore, to concentrations that produce little or no injury to fauna ingesting the vegetation. In this instance, removal and disposal of highly contaminated soil would be appropriate. Should the contamination event involve a relatively nontoxic organic or oil product with a finite half-life in soil, where only indirect plant effects would be anticipated, then restoration efforts may require a less stringent approach.

Several factors can affect the half-life of an organic residue in soil. These include chemical hydrolysis, biotic decomposition (soil

invertebrates and soil microbes), and photodecomposition. These processes rapidly decompose organic compounds residing in soils. Half-lives can range from a few days for many pesticides and phenols, to a few months for anilines and heterocycles, to a year for oil related hydrocarbons. Depending on half-life and the extent of contamination, restoration measures for nontoxic organics could involve simple periodic tillage of affected soils; this would have the effect of maximizing photodecomposition and biotic turnover of residuals.

4.5 MONITORING DEGRADATION OF HAZARDOUS SUBSTANCES

A number of methods can be used to monitor the disappearance (i.e., biological and chemical degradation) of hazardous substances or oil released into the environment. The most direct method involves sampling over time and extracting the compound from the soil for subsequent chromatographic analysis. The particular methods used for extraction and analysis will be dependent on the chemical nature of the compound. The decrease in concentration of a particular compound in the soil may not only be due to biological transformation but to adsorption or incorporation into biological and soil material. The accuracy of these measurements will be dependent on the efficiency of extraction of the compound from the soil.

The carbon-14 (C-14) method may also be used to follow the rate of degradation of a particular chemical in the soil. If a C-14 labeled form of the contaminant is available, or at least a model compound similar in structure, the extent of its degradation can be estimated by the amount of C-14 carbon dioxide evolved. This is strictly a laboratory method and requires trapping the carbon dioxide evolved from an amended soil sample in a respirometer flask in KOH and determination of the C-14 by liquid scintillation counting (Albertsson and Ranby 1976). One problem with this method is that it may be difficult to simulate the exact environmental conditions and concentrations of the xenobiotic at the field site where the release of the contaminant occurred, thus providing an inaccurate rate of degradation. Also, the release of C-14 carbon dioxide will not be stoichiometric with the mineralization of the toxicant. Some of the carbon

may be incorporated into microbial cells, or released as a breakdown by-product of decomposition.

An alternative to the C-14 method is simply to monitor the rate of carbon dioxide evolved; this may be particularly applicable in the case of oil. The basis for this method is that during the microbially mediated biodegradation of carbonaceous substrates, carbon dioxide is liberated and oxygen is consumed. The amount of carbon dioxide evolved from an amended sample minus that from an unamended soil is assumed to be due to the degradation of the added compound. As with the C-14 method, this analysis is done in the laboratory and requires the use of a biometer flask (Bartha and Pramer 1965; Dibble and Bartha 1979). Alternatively, an electrolytic respirometer may be used to measure both carbon dioxide evolved and oxygen consumed (Knapp et al. 1983).

Assessment of toxicants in the soil has also been done with computer models. The processes that control the fate of a chemical in the environment are separated into two groups: one which occurs relatively fast and can be treated as an equilibrium of thermodynamic properties and another which is a slower group of processes that require kinetic treatment. One particular model, exposure analysis modeling system (EXAMS), predicts environmental concentrations of chemicals by assuming the dynamics of a xenobiotic in the environment can be represented as a sum of contributing processes (Lassiter et al. 1979). These processes include: quantity or concentration of a compound, volatilization, photolysis, hydrolysis, microbial degradation, exchanges with sediments, dilution, and loading of substance into a system.

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APPENDIX A
SAMPLING AND ANALYSIS TECHNIQUES

APPENDIX

SAMPLING AND ANALYSIS TECHNIQUES

The objectives of sampling are to collect portions of the environment that are representative of the material of interest and to maintain the chemical integrity of the samples until analysis.

Soil is by nature extremely variable. Superimposed on this variability is the potential variation in contaminant distribution, which may be regular or irregular. Sampling activities must be designed and conducted to adequately account for these expected variations while minimizing variation caused by the sampling process itself. Differences in soil type and properties, contaminant type, and depth of contamination will require different sampling strategies and techniques. Thus, the sampling procedure should be selected on a site-specific basis. The sampling guidance described in this Appendix includes elements of 40 CFR 136, 40 CFR 141, and U.S. EPA QA requirements (U.S. EPA 1979), which apply to sampling activities and are routinely applied in implementing requirements of the U.S. EPA.

SAMPLING PLAN

A sampling plan is a complete written description of the purposes for, and procedures to be used during, a field investigation. Information helpful for preparing a sampling plan is described in the Remedial Investigation Guidance Document (U.S. EPA 1984). The plan may be used as guidance for specifying the number, type, and locations of sampling points, analytes of interest, methods and procedures, and sample preservation techniques. Soil sampling points will frequently be selected on the basis of statistical design. Statistical design ensures that the natural variability of the soil system, the expected contaminant distribution variability, sampling precision and bias, and analytical precision and bias are considered. Each of these factors may be important in linking the potential injury to the discharge or release of the hazardous substance or oil. Therefore, these issues must be addressed during planning activities.

SAMPLING TECHNIQUES

Two portions of the soil are important: the surface layer and the subsurface zone. The surface layer (0 to 15 cm) reflects the deposition of airborne pollutants, especially those recently deposited pollutants. The subsurface zone may contain pollutants that have been deposited by liquid spills, or by long-term deposition of water soluble materials. The methods of sampling each of these are slightly different, but all make use of one or two basic techniques. Samples can either be collected with some form of core sampling or auger device, or they may be collected by use of excavations or trenches. In the latter case, the samples are cut from the soil mass with spades or short punches. The American Society for Testing and Materials (ASTM) has developed a number of methods that have direct application to soil sampling. These may need to be modified slightly to meet the needs of the environmental scientist who requires samples for chemical analyses, since the ASTM methods are designed primarily for engineering tests. The techniques used should be closely coordinated with the analytical laboratory to meet the specific requirements of the analytical methods used.

Soil samples from both the vadose and saturated zones can be obtained using the same technique. In many locations, subsoil samples to depths of about 10 ft can be obtained by hand corers. Deeper than 10 ft or in locations where "hardpan" or cobble occur, a hollow-stem auger drill rig is used. Samples are obtained by driving split-spoon samplers or Shelby tubes at prescribed intervals. The samples are immediately placed in appropriate containers. Subsoil samples are frequently obtained during monitor well installations to make optimal use of the equipment and to provide vertical contaminant distribution. Either hand or drill-rig techniques provide samples for any contaminant of interest.

Discussions of sampling techniques and site-specific characteristics requiring special consideration are provided in Preparation of Soil Sampling Protocol: Techniques and Strategies (Mason 1983), Remedial

Investigation Guidance Document (U.S. EPA 1984), and Characterization of Hazardous Waste Sites -- A Methods Manual: Volume II. Available Sampling Methods (Ford et al. 1983).

Any of the appropriate sampling techniques provides a grab sample. Frequently, grab samples are composited to reduce analytical costs and to estimate average concentrations over an area. For the purpose of natural resource damage assessments, compositing is not recommended because it masks variations in contaminant concentrations. Statistical descriptions of the variation of fluid samples, such as kriging, are not possible when composite samples are taken.

If compositing is deemed necessary, the procedure is best performed in the laboratory rather than in the field. Laboratory equipment such as a stainless steel mixer ensure thorough mixing and can be cleaned to prevent cross contamination. Discussions of sample compositing are provided in Preparation of Soil Sampling Protocol: Techniques and Strategies (Mason 1983) and Soil Sampling Quality Assurance User's Guide (Barth and Mason 1984).

All sample containers should be cleaned before field use according to the procedures in EPA-600/4-82-029 (U.S. EPA 1982). In general, wide-mouth, amber-glass bottles are suitable as containers for soil samples. Other container materials may be suitable if they are compatible with the analytes of interest. Currently, there is no standard method for sampling soils containing volatile constituents. Depending on the analytical technique, samples may be sent to the laboratory in sealed core tubes or in septum-top vials. Regardless of the container, sample handling and container head space should be minimized to avoid analyte loss. If several contaminant classes are of concern, a separate sample must be taken for volatiles; analysis of sample aliquots from a wide-mouth bottle indicated 50-90% volatile analyte loss compared to samples taken in 40-ml, septum-top vials.

Soil samples are preserved by cooling to 4°C. Chemical preservatives are not appropriate for soil samples.

SPLIT SAMPLES, SPIKED, AND BLANKS

Split samples, spiked samples, and blanks are used to provide a measure of the internal consistency of the samples and to provide an estimate of the components of variance and the bias in the analytical process.

Samples can be split to achieve several purposes:

- to provide samples to both parties in a litigation or potential litigation situation
- to provide a measure of the within sample variability (this is needed to determine the influence of other factors that may be confounded with sample splitting)
- to provide materials for spiking in order to test recovery
- to provide a measure of the sample bank and extraction error.

The location of the sample splitting determines the component of variation that is measured by the split. A split made in the sample bank measures error introduced at that level. A split made in the field measures field handling along with the within sample variation. A split or series of subsamples made in the laboratory for extraction purposes measures the extraction error.

Spike samples are prepared by adding a known amount of reference chemical to one of a pair of split samples. The results of the analysis of a spiked-split compared with the nonspiked member of the split measures the recovery of the analytical process and also provides a measure of the analytical bias.

Blanks provide a measure of various cross-contamination sources, background levels in the reagents, decontamination efficiency, and any other potential error that can be introduced from sources other than the sample. For example, a trip blank measures any contamination that may be introduced into the sample during shipment of containers from the laboratory to the field and back to the laboratory. A field blank measures input from contaminated dust or air into the sample. A decontamination blank measures any chemical that may have been in the sample container or on the tools after decontamination is completed.

The exact types of splits, spikes, and blanks will depend on the analytes of interest, statistical design of the sample program, and analytical methods used. As a rule of thumb, at least 1 out of every 20 samples is assigned to each of these categories.

QUALITY ASSURANCE (QA)

The purpose of QA for environmental sampling is to ensure that the samples sent to the laboratory are obtained in a manner that does not compromise sample integrity and that all data generated during sampling are accurate, complete, documented, and maintained in a legally defensible manner.

A sampling plan, written as part of the assessment plan, would identify sampling locations, sample type, sample frequency, number of samples, duration of sampling, sample volume, sample collection methods and holding times, equipment to be used for the sample collection, sample containers, pretreatment of containers, sample preservation, blanks, duplicates/triplicates, spiked samples, replicates, chain-of-custody procedures, and other pertinent matter that will have a bearing on the QA in sample collection and handling. Required documentation and levels of approval are usually identified in the sampling plan.

All field measurement equipment should be calibrated according to documented procedures. These procedures establish routine maintenance, testing, and calibration intervals; list the required National Bureau of Standards reference calibration standards; detail the step-by step maintenance, testing, and calibration activities, and specify the documentation system for audit purposes. All equipment should be labeled showing date of last calibration, due date of next calibration, and the signature of who performed the last calibration.

Random control checks should be conducted by program QA personnel by making unannounced trips to a site to audit the sampling effort. Each major type of sampling should be inspected at least once during these trips. The purpose of these inspections is to ensure that appropriate sampling guidelines on sample collection, handling, and chain-of-custody

are followed by the field personnel; deviations, if any, must be rectified. If program QA personnel determine that significant deviations from approved protocols have occurred, resulting in a compromise of sample integrity, all samples acquired since the previous audit should be discarded and replaced with new samples. All such corrective actions must be thoroughly documented.

RECORDKEEPING

It may be helpful to keep a record of all sampling activities in a bound logbook. Entries could be made with waterproof ink by the field staff member(s) and could then be certified by the sampling team leader. Recording of the following information is suggested:

1. date
2. time of day
3. location
4. samples obtained/containers filled
5. preservation
6. analyte(s)
7. field measurements (including sample depth)
8. sample number
9. observations of unusual or interesting conditions and sample appearance
10. sampling technique employed
11. name of sampler.

Each page of the sample log should be signed by the sampler and reviewed and signed by the team leader.

Sample tags ensure that each sample is unambiguously identified and can be referenced to the sample logbook. Recording the following information on the tag is suggested:

- site identification
- sample number
- date and time

- site location
- sampler's initials
- preservation
- analyte(s)

Labels should be covered completely with polyethylene tape to protect readability. The tape should be overlapped around the container in such a manner that the label would be destroyed if removed.

At the termination of the sampling trip, all logs should be forwarded to Project Document Control for maintenance. Upon completion of an episode, a Sampling Technical Memorandum should be prepared that includes the scope, procedures used, personnel involved, activity log, samples obtained, and chemical analysis results obtained during the sampling effort.

CHAIN-OF-CUSTODY

Chain-of-custody procedures are specific recordkeeping methods used to ensure that sample custody is traceable from the time of collection until data presentation.

Chain-of-custody procedures are quite rigorous. A summary of the EPA procedure (EPA 1983) states that a sample is under custody if:

- it is in your possession,
- it is in your view after being in your possession,
- it was in your possession and then you locked it up to prevent tampering, or
- it is in a designated secure area.

A number of chain-of-custody procedures will affect field activities. Nine of these are described in the following paragraphs.

1. In collecting samples for evidence, collect only that number which provides a good representation of the media being sampled. To the extent possible, the quantity and types of samples and sample locations are determined before the actual fieldwork. As few people as possible should handle samples.

2. Both the field staff member and the team leader are personally responsible for the care and custody of the samples collected until the samples are transferred or dispatched according to the protocols.
3. The QA coordinator determines whether proper custody procedures were followed during the fieldwork and decides if additional or new samples are required.
4. Samples are accompanied by a Chain-of-Custody Record. When transferring the possession of samples, the individuals relinquishing and receiving will sign, date, and note the time on the record. This record documents sample custody transfer from the field staff, through other persons, to the analyst in the laboratory.
5. Samples will be packaged properly for shipment and dispatched immediately to the appropriate laboratory for analysis, with a separate custody record accompanying each shipment container. Shipping containers will be padlocked and sealed for shipment to the laboratory. The method of shipment, courier name(s), and other pertinent information are entered in the "Remarks" box, and become part of the chain-of-custody record.
6. Whenever samples are split for shipment to different parties, such occurrences are noted in the "Remarks" section. The note indicates with whom the samples are being split and is signed by both the field staff member and recipient. If either party refuses a split sample, this will be noted and signed by both parties. The person relinquishing the samples to the party or agency should request the signature of a representative of the appropriate party, acknowledging receipt and custody of the samples. If a representative is unavailable or refuses to sign, this is noted in the "Remarks" space.
7. All shipments must be accompanied by the Chain-of-Custody Record identifying its contents. The original record should accompany the shipment, and a copy should be retained by the QA coordinator.
8. If sent by mail, the package will be registered with return receipt requested. If sent by common carrier, a Bill of Lading or Shippers

Certificate should be used. Air freight shipments are usually sent collect. Freight bills, Post Office receipts, and Bill of Lading should be retained as part of the permanent documentation.

9. A bound field notebook must be maintained by the sampling team leader to provide a daily record of significant events. All members of the survey party must use this notebook. The notebook is kept as a permanent record. In a legal proceeding, notes, if referred to, are subject to cross-examination and are admissible as evidence.

APPENDIX REFERENCES

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- U.S. EPA. 1984. Remedial Investigation Guidance Document. Office of Emergency and Remedial Response, Washington, D.C.

* Available for purchase from the National Technical Information Service, Springfield, VA 22161

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