Bioremediation of Contaminated Soils

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Sources and Practices Contributing to Soil Contamination

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4-1 INTRODUCTION

The term *soil contamination* can have different connotations because anthropogenic sources of contaminants have affected virtually every natural ecosystem in the world; a commonly held view is that contamination occurs when the soil composition deviates from the normal composition (Adriano et al.. 1997). Other specialists have defined soil pollution as the presence of some constituent in the soil. caused by human activity, at such a concentration that there is a significant risk of damage to users of the soil or a restraint of its free use (Finney, 1987). The risk can take many forms: impairment of the health of humans, animals. or plants: damage to buildings or structures on the soil: contamination of ground waters or surface waters in contact with the soil. In their natural state, contaminants may not be classified as pollutants unless they have some detrimental effect to organisms. Pollution occurs when a substance is present in

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greater than natural concentrations as a result of human activities and has a net detrimental effect upon the environment and its components (Adriano et al., 1997). Likewise, groundwater contamination may refer to the degradation of the natural quality of groundwater as a result of human activities (Boulding, 1995). From a plant or animal (including humans) health perspective, soils are not considered polluted unless a threshold concentration exists that begins to affect biological processes. These thresholds can be exceeded by natural concentrations, but generally these are localized occurrences (Freedman & Hutchinson, 1981).

In this chapter we will use the term contamination (or contaminants), since soils are subjected to risk assessment (Fig. 4–1), to determine the severity of contamination (or pollution). Contamination must be characterized to determine the contaminant and/or contaminant-medium interaction at the site (Smith et al., 1995). Information needed to characterize contamination at a given site includes: volume of each contaminant-medium combination, distribution of its contaminants-medium combination, and physical and chemical characterization of each contaminant-media combination.

The pathways by which soil becomes contaminated are varied and can be categorized as both point (direct) and nonpoint (diffuse) sources (Fig. 4-1). Point sources refer to discrete, localized, and often readily measurable discharges of chemicals. Examples of point sources are industrial outfall pipes, untreated storm water discharge pipes. and treated sewage outfalls. A spill of chemicals due to an accident on or near a surface water body also can be regarded as a point source of contamination since the amount and location of the discharge are often well characterized. Nonpoint sources of contamination are more difficult to measure because they often cover large areas or are a composite of numerous point

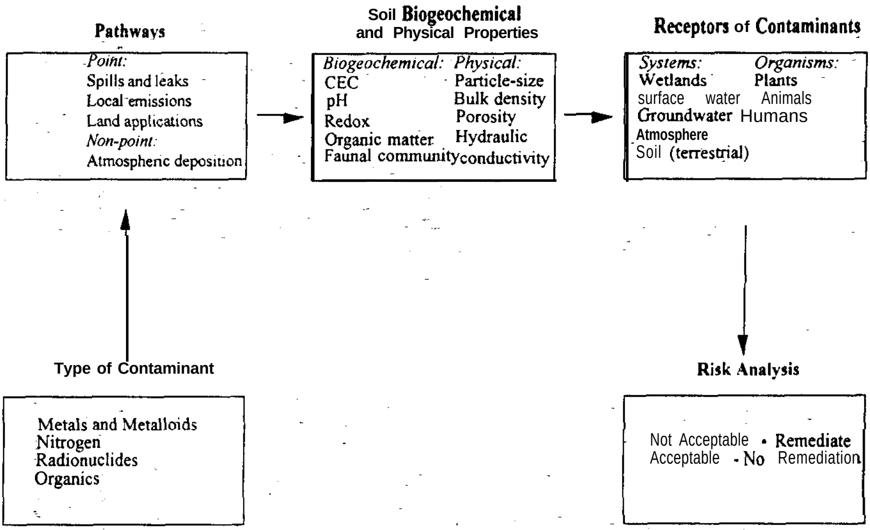


Fig. 4-1. Conceptual model of soil contamination and remediation (modified from Linz & Nakles, 1996).

sources. Examples of nonpoint sources include pesticides and fertilizer runoff from agricultural fields and emissions from automobile exhaust.

Pathways also depend, to a large degree, on the type of contaminant. Heavy metals-originate from both point and nonpoint sources. Soils contaminated by radionuclides are generally from point sources except in extreme circumstances; such as with the Chernobyl accident in 1986 where radionuclide clouds-were transported virtually worldwide (Alexakhin, 1993). Organic compounds (herein referred to as organics) generally result from point sources. A good example is the extensive contamination of aquifers across the USA by a degreasing compound, trichloroethylene (TCE), which has leaked from disposal or containment basins at or beneath the soil surface. Although N is not generally considered a soil contaminant, the effect it has on both surface water and groundwater resources is an environmental concern.

The degree to which soil contaminants become mobile or available depends on soil biogeochemical and physical properties (Fig. 4-I). Generally, as clay minerals, sesquioxides, organic C and the resulting cation-exchange capacity (CEC) increase, the availability of contaminants decrease because of complexation and sequestering (Adriano, 1986); however, processes that lead to greater mobility of dissolved organic carbon (DOC) can lead to greater mobility and availability of those contaminants complexed with DOC (Bergkvist et al., 1989; Borg and Johansson, 1989; McBride, 1994). Soil pH effects on mobility vary with contaminant. For example, As and Se are more mobile in alkaline pH -while Hg, Pb, Cd, and Zn are more mobile in acidic pH soils (Adriano, 1986; Alloway, 1990). The effect of pH on radidnuclides and organic compounds is relatively more specific to the contaminant of concern. Soil redox status has important implications on the oxidation states of contaminants and therefore. their speciation.

The form in which the contaminant occurs greatly influences its behavior in soil, including sorption, methylation, leaching, and others. of metals and radionuclides and sorption, leaching, degradation, and others. of organic chemicals. The combined effects of soil biogeochemical factors partition contaminants between the solid, gas. and soil solution phases. The transport rate of contaminants in the gas and soil solution phases is primarily dependent on soil physical properties, most notably, particle-size and bulk density (Fig. 4-1). Particle-size and bulk density affect water and-air flow characteristics through soils by affecting soil porosity and hydraulic conductivity (Appelo & Postma, 1993).

-This chapter reviews the primary inorganic and organic soil contaminants that may cause environmental risks. Natural and anthropogenic sources are distinguished where appropriate. along with various practices and soil conditions that result in soil contamination. Toxicological concerns are noted for specific compounds when they are well documented. Background levels and elevated concentrations are summarized from the literature. It was not. our intent to document all cases of reported contamination scenarios, rather. we hope to illustrate typical sources and practices that contribute to soil contamination and the observed and potential consequences when available. The chapter is organized to review soil contamination by metals and metalloids, N, radionuclides and representative classes of organic compounds.

4-2 USES AND ENVIRONMENTAL BIOGEOCHEMISTRY OF CONTAMINANTS

4-2.1 inorganic Contaminants

4-2.1.1 Metals and Metalloids

4-2.1.1.1 Arsenic. Arsenic is a labile, semimetallic element or metalloid. present in practically all environmental matrices that exists in several forms and oxidation states. The environmental behavior of As has been recently reviewed by Nriagu (1994). Arsenic commonly exists in one of two oxidation states in soil. The reduced form, arsenite [As (III)] is of greater environmental concern because it is more toxic and mobile than the oxidized form, arsenate [As (V)]. The chemistry of As(V) resembles that of P. Arsenate can be adsorbed by clays, particularly by kaolinite and montmorillonite at low pH, reaching a maximum adsorption near pH 5.0 and becoming desorbed at higher pH (Goldberg & Glaubig, 1988). Anionic arsenic such as arsenate (AsO_4^{3-}) and arsenite (AsO_3^{3-}) behave as chelates and precipitate with many metal cations (Bowell, 1994). As a result, As(V) is less mobile and less toxic than As(III). Arsenic is present in most contaminated sites, either as As_2O_3 or as arsenic compounds derived from As_2O_3. Arsenic also may be present as organometallic forms, such as methylarsinic acid ($H_2AsO_3CH_3$) and dimethylarsinic acid [$(CH_3)_2AsO_2H$], which are active ingredients in many pesticides, as well as arsine (AsH_3) and its methyl derivatives,. including dimethylarsine [$HAs(CH_3)_2$] and trimethylarsine [$As(CH_3)_3$; Smith et al., 1995].

Arsenic is ubiquitous in the environment and has both natural and anthropogenic sources. Natural sources of arsenic include bubble- bursting and gas exchange in oceans, weathering of soils and geologic materials, volcanic eruptions, forest fires and volatilization through methylation in the biosphere (Walsh et al., 1979). Based on analysis of soils from-various parts of the world, Berrow and Reaves (1984) reported a mean As content of 10 mg kg-‘. Voigt et al. (1996) reported that the average As content of uncontaminated soils is about-5 mg kg-‘. The average concentrations of As in igneous, limestone, sandstone.-and shale are 1.5, 2.6, 4.1, and 14.5 mg kg-‘, respectively; however, concentrations in shales can range from 0.3 to 500 mg kg-‘.

Nriagu (1994) reported the following anthropogenic sources of As: burning of fossil fuel, agricultural burning. waste incineration, iron-steel production. copper production, lead-zinc production, mining mineral ore, gold mining and smelting, and arsenic chemicals. The anthropogenic influence on the level of As in soils depends on the intensity of the human activity, the distance from the pollution source, and wind dispersion pattern. In parts of the southeastern USA. where intensive cotton (*Gossypium hirsutum* L.) production (i.e., use of arsenicals as defoliant) was practiced for roughly a century, background levels of As in soils and waters are still quite elevated compared with natural averages (Adriano. 1986).

The toxic effects of As compounds made them attractive for agricultural applications. Until the introduction of DDT and other organic insecticides in the 1940s, inorganic compounds of As were the predominant insecticides available to farmers and fruit producers (Nriagu, 1994). Today, As compounds are used as growth- promoters for chickens (Callus *gallus domesticus),* turkey (*Meleagris gallopavo*), and swine *(Sus scrofa domesticus*) at rates of 10 to 50 mg kg^{-1} of feed (Alloway, 1990; Reilly, 1991) leading to residual As in manure. Arsenic from insecticides and manures may lead to long lasting contamination of soils, groundwater, lakes, and-streams (Francis, 1994).

During coal combustion; As in the coal is volatilized and may condense on the surface of the fly ash particles that enter the atmosphere and are subsequently deposited on terrestrial and aquatic systems (Adriano et al., 1980). Fly ashes contain variable amounts of As (Summers et al., 1983; Ainsworth & Rai. 1987); mean As concentrations in coal ashes have been reported to vary from 56 (Summers et al., 1983) to 156 mg kg^{-1} (Ainsworth & Rai, 1987), to values >200 mg kg^{-1} (Wadge et al., 1986). Water-soluble As in fly ashes ranged from 4 to 17% of total As concentration, which upon deposition, can leach into groundwater and reservoirs (Wadge & Hutton, 1987).

Since most As emissions are associated with industrial operations, it follows that the most contaminated soils occur in their vicinity. Arsenic pollution is frequently reported for Japanese soils; for example, in Nakajo As soil concentrations range from 2.44 to 72.7 mg kg^{-1} (Nakadaira et al., 1995). Studies on As behavior in contaminated soils have shown that paddy soils are more susceptible to As pollution due to their low redox (Asami, 1991). Elevated As soil concentrations (>10 mg kg^{-1}) have been observed near As mineral deposits, copper smelters, mining areas (lead or gold), and in agricultural areas where As pesticides or defoliants were repeatedly used (Bowell, 1994: Sadler et al., 1994; Golow et al., 1996)

Chronic exposure to inorganic forms of As have been shown to cause various forms of cancer. most notably lung cancer (Nriagu, 1994). Drinking water contaminated through natural sources has been shown to cause skin cancer (Williams et al.. 1996). Recently, a most alarming incident is continuous in the Bengali region of India and Bangladesh, where arsenicosis (i.e.. As poisoning) has already claimed human life and millions are potentially at risk from drinking high concentrations of As in groundwater and using these waters for irrigation and cooking (Chakraborti, 1997).

4-2.1.1.2 Chromium. While there are natural sources of Cr in the environment [(mostly Cr(III)] the majority of Cr(VI) originates from industrial activities (Adriano, 1986). World annual production of Cr is approximately 8.2 million Mg with the principal producers being South Africa and the former USSR (Gauglhofer & Bianchi, 1991). Most of the Cr consumed by the USA is in the metallurgical industry (63% of total Cr use in 1979). followed by 20% in the chemical industry, and 17% in the refractory industry (Matthews & Morning. 1980). Chromium used in the metallurgical industry is mainly for the production of wrought-stainless and heat resistant steels. Chromium(VI) chemicals are principally used for metal plating using chromic acid, as dyes. paint pigments. and leather tanning as a mordant.

The natural concentration of Cr in soils and sediment varies greatly because of the influence of the composition of the parent rock from which they are formed (Cary, 1982). As Cr is weathered from minerals. most will initially be present in the trivalent state that may be sorbed on hydroxides. Naturally occurring chromates are rare and found only in highly oxidizing environments (Richard & Bourg, 1991). Thus, the presence of chromates in soils is almost always the result of human activities (World. Health Organization, 1988). Chromium contamination of soils is more commonly due to the dumping of Cr-bearing liquid, sludge, or solid waste from such sources as chromate by-products, i.e., muds, ferrochromium slag, or Cr plating baths (Rosas et al., 1989). Dumping can result in contamination of any combination of Cr(III) or Cr(VI) compounds of various solubilities. Once deposited in soil, Cr can undergo a variety of transformations such as reduction, oxidation, precipitation, dissolution, and sorption. Addition of organic residues to soils containing high levels of manganese will result in the formation of unstable Mn(III) organic complexes that may prevent Cr(III) oxidation and also catalyze the reduction of Cr(VI) (Bartlett & James, 1988). In general, it has been observed that chromates are relatively mobile in soils that are sandy or have low organic matter content (Adriano, 1986).

Chromium is released to the environment primarily from electroplating operations and the disposal of Cr-containing waste. Hexavalent chromium [Cr(VI)] as chromate and dichromate ions (CrO_4^{2-} and $Cr_2O_7^{2-}$), are the major species encountered. The stability of Cr(VI) and Cr(III) is largely dependant on the pH and redox status of soils. Chromate ion predominates above pH 6.0 under oxidizing conditions and Cr(III) predominates at lower pH and redox levels (Smith et al., 1995). Because of its anionic nature, Cr(VI) precipitates with metal cations such as Ba^{2+}, Pb^{2+}, and Ag’. Chromium(VI) is reduced to Cr(III) in the presence of ferrous ions, dissolved sulfides, and organic compounds, particularly those having sulfhydryl groups; Cr(VI) complexes with multiple sites in soil surfaces having positively charged site, the number of which increases with decreasing soil pH. Consequently, sorption of Cr(VI) in these solid phases occurs predominantly at acidic or neutral pH.

The policy decision in some regulatory agencies to regulate the level of Cr(VI) differently from Cr(III) has been based on toxicological, chemical, and epidemiological evidence. Cr(VI) is both a powerful epithelial irritant and a confirmed carcinogen (Adriano, 1986). Additionally, Cr(VI) is toxic to many plants, aquatic animals, and bacteria (National Academy -of Sciences, 1974; U.S. Environmental Protection Agency, 1985). In-contrast, Cr(III) is practically benign and even a known micronutrient in an organic form. Given these considerations. it may be appropriate to develop a policy regulating Cr(III) and Cr(VI) differently.

4–2.1.1.3 Mercury. Mercury is considered one of the most important environmental contaminants because it bioaccumulates in aquatic ecosystems. There are a variety of sources of Hg, both natural and anthropogenic. Weathering of Hg from -geologic materials imparts very little to the local or regional inventory except in areas of elevated concentrations (Barghigiani & Ristori. 199-l). In general, atmospheric deposition is the main source of Hg to terrestrial and aquatic -systems. Natural atmospheric sources of Hg include those where natural gases are expelled into the atmosphere. Cataclysmic events, such as volcanic eruptions and forest fires, emit considerable natural gases and particulates, including Hp. A more-subtle gaseous input is that occurring continually during the decomposition of organic matte? from terrestrial and aquatic systems. Mercury compounds have traditionally been used in fungicides, the paper bleaching process, gold amalgamation, switches in electronic equipment, and in the production of scientific and medical equipment. Point sources include emissions from the production of chlorine and caustic soda, metal production, waste handling and treatment, and coal, pyrite, peat, and wood burning industries (Lindqvist, 1991). Diffuse emission sources include landfill deposits of municipal wastes and slag from metal production, fossil fuel combustion, dental, hospital, and chemical laboratories, electronic equipment production and disposal, and paint applications (Lindqvist, 1991). Global estimates of total emissions (both gaseous and particulate) to the atmosphere have been calculated to be 7500 Mg yr^{-1} (Lindqvist, 1991). The USA contributes approximately 9.5% of the global Hg emissions, although it occupies 7% of the global land area. Europe emits approximately 8% of global emissions, while occupying only 1.5% of the global land area. Fitzgerald (1995) estimates that human activities represent about 70 to 80% of the total annual Hg input to the atmosphere.

The volatilization and subsequent global cycling of Hg leads to elevated concentrations in all surface soils relative to preindustrialization. Some recent background concentrations in soils include 0.002 to 1.53 mg kg-’ in Canada (Richardson et al., 1995), 0.50 mg kg-’ in Tennessee (Lindberg et al., 1995), 0.03 to 0.24 mg kg-’ in Washington (Lindqvist, 1991), 0.10 mg kg-’ in Sweden (Lindberg et al., 1995). and 0.03 to 0.30 mg kg-’ in South America (Roulet & Lucotte, 1995). Significant soil contamination has occurred at a number of sites throughout the world. Soils contaminated by nuclear operations at Oak Ridge, TN, range from 50 to 200 mg kg-’ (Lindberg et al., 1995). Soil Hg concentrations decrease from >100 mg kg-’ near a metal smelter in Flin Flon, Manitoba, Canada to approximately 0.10 mg kg-’ 40 to 80 km from the plant (Henderson & McMartin, 1995). Soils in Bavaria, -Germany. contaminated by organomercurial complexes from pesticides and pharmaceuticals, have a concentration of 65 mg kg-’ (Hempel et al., -1995). Soils contaminated by -gold mining process in the Carson River Drainage Basin in Nevada range from 7 to 12 mg kg-’ (Gustin et al., 1995) while those in Pocone. Brazil. were as high as 5 mg kg-’ Hg (Lacerda et al.. 199 I).

Mercury is found in various physical and chemical forms in the environment. In metal-contaminated sites, Hg exists in mercuric form (Hg^{2+}), mercurous form (Hg_2^{2+}). elemental form (Hg^0), or alkylated form (e.g., ethyl and methyl mercury: -Smith et al.. 1995). The type of Hg species present and their associations with complexing ligands or solid matter regulate toxicity. transport pathways, and residence time within compartments of the-ecosystem (Lindqvist, 199 1). Mercury(B) forms relatively strong complexes with Cl^- and CO_3^{2-} (Smith et al., 1995). A small fraction of the total deposition (0–7%) occurs as the methylated form of Hg (MeHg; Fitzgerald et al., 1991; St. Louis et al., 1994). the most biologically toxic and easily bioaccumulated form-of Hg. Once Hg enters the terrestrial or aquatic system. MeHg production is enhanced by low redox (Watras et al., 1995), low pH (Bloom et al.. 1991) and elevated temperature (Matilainen et al., 1991). Recent studies indicate that microbial methylation is the most important origin of MeHg in terrestrial and aquatic systems (Kelly et al.. 1995).

A significant portion of the Hg that reaches the terrestrial system is immobilized in the organic fractions of upper horizons in soils (Nater & Grigal, 1992).

Mercury soil concentrations have been shown to be related to the organic matter in surface horizons, silt plus clay content in subsurface horizons, and distance from point sources of emissions (Nater & Grigal, 1992; Grigal et al., 1994). A small percentage. 0.03 to 0.04%, of Hg in the soil pool is annually transported in runoff from forest soil to surface waters (Aastrup et al., 1991). Others have estimated that ≈4% of-annual atmospheric inputs are transported to surface waters or ground waters (Krabbenhoft et al., 1995; Krabbenhoft & Babiarz, 1992). Although a small fraction, the terrestrial transport of Hg via soil runoff waters has been recognized as an important source of Hg to remote surface waters (Lee & Hultberg, 1990; Lee & Iverfeldt, 1991; Swain et al., 1992). Processes that influence the transport of organic C also influence the transport of Hg (Kolka, 1996).

Plants do not actively uptake Hgthrough the roots and little Hg is translocated to shoots and leaves (Lindqvist, 1991). Passive diffusion of gaseous Hg through the stomata can lead to elevated leaf concentrations in areas where there is considerable soil volatilization (i.e., areas of soil contamination; Hanson et al., 1995). Recent research indicates that Hg volatilization from landscape surfaces is a significant component of the Hg cycle (Lindberg et al., 1995), approaching the magnitude of atmospheric deposition. This implies that soils will continue to be a source of atmospheric Hg even after anthropogenic emissions have been curtailed.

The bioaccumulative nature of MeHg and the number of trophic levels in aquatic systems lead to elevated Hg concentrations in fish, the most important human health risk associated with Hg. Mercury contamination in fish is well known in the Great Lake states, northeast USA, Canada, northern Europe,.and South America. Studies on an outbreak of Hg poisoning in Iraq in 197 1 indicated that prenatal children have a much higher incidence of mental retardation and loss of motor skills with exposure to Hg, while adults have a higher incidence of paresthesia (World Health Organization, 1976; Marsh et al., 1981; Clarkson et al., 1985). Mercury also is implicated in reproductive problems in eagles (*Haliaeetus leucocephalus*), otters (*Lutra canadensis*), mink (*Mustela vison*), and other fish-eating animals in the Great Lakes region, and in panther (*Felis concolor coryi*) deaths in Florida (Douglas, 199 1).

4-2.1.1.4. Selenium. Selenium has gained much attention-in recent years because of its unique properties in the environment. Although Se is considered an essential element for animal nutrition, it is not considered essential to plants. Cases of both animal deficiency and toxicity have been reported (Frankenberger & Benson, 1994). This presents an environmental challenge managing soil Se concentrations to optimize the relatively narrow. range of plant concentrations that are beneficial-to livestock.

Natural inputs of Se to the global cycle -include those from mineral weathering, volatilization from environmental surfaces, and emissions from volcanic activity (Peterson. 1980; Fishbein. 1991). Nriagu (1991) estimated the annual natural input to the global Se cycle as 4500 Mg. The concentration of Se in most soils lies within the range of 0.0 I to. 2.0 mg kg-’ (Mayland, 1994). Selenium concentrations in soils developed from seleniferous. parent materials (Cretaceous shales) in the western USA averaged 4 to 5 mg kg^{-1}, with certain areas having as high as 80 mg kg^{-1} (Combs & Combs, 1986). It is in these areas where natural Se toxicity in livestock has occurred (Mayland, 1994).

Annual anthropogenic inputs are estimated to be 76 000 to 88 000 Mg (Nriagu, 1991), 17 to 19 times those from natural sources. The largest fraction of anthropogenic inputs is from the burning of fossil. fuels, notably coal and oil (Haygarth, 1994). Other anthropogenic sources include by-products from metal production (principally copper and nickel), steel and iron production, municipal sewage sludge incineration, and phosphate fertilizer production (Haygarth, 1994). Although no known natural ore deposits contain sufficient Se to be mined efficiently, Se is commercially available, generally where it is extracted from copper refinery sludge (National Academy of Science-National Research Council, 1983). Selenium is used in the manufacture of batteries, glass and electronic equipment, as a reagent in medical and veterinary medicine, feed additives, and fertilizers (Mayland et al., 1989).

Selenium is a metalloid, with reactivity and chemistry similar-to- sulfur. Studies have found a close relationship between Se and S in soils (Tidball et al., 1989) and an antagonistic relationship between these elements in plant uptake. Generally, the presence of sulfate in soils reduces plant concentrations of Se (Mikkelsen et al., 1989). Selenium soil solution chemistry is controlled by pH and redox conditions (Elrashidi et al., 1987); however, more recent evidence suggests organic C and microbial transformation also influence the availability of Se for plant uptake (Tam et al.. 1995; Zhang & Moore, 1996). Under most soil conditions, inorganic Se in soil solution is found in one of two oxidation states, as selenite (IV, SeO_3^{2-}) and as the more mobile selenate (VI, SeO_4^{2-}). Selenate, the dominant form at high redox and high pH, is more readily taken up by plants and considered to be the most bioaccumulative inorganic-ion (Eisler, 1985); however, organic Se has been shown to be more mobile and bioaccumulative than selenate (Besser et al., 1993; Tam et al.. 1995).

Contamination of soils and surface waters has occurred in areas where Se-rich agricultural drainage waters are concentrated. A case study from- the. San Joaquin Valley in California. an area underlain with seleniferous parent materials. is a prime example of soil and surface water contamination derived from agricultural practices. Seleniferous soils leached by agricultural drainage waters were directed by tile drains and transported to the Kesterson Reservoir. a series of holding and evaporation ponds originally constructed in 1969 to 1975 (Ohlendorf & Santolo, 1994). The impoundment of Se-rich waters led to soil concentrations 100 times higher than those in nearby control sites (Wu & Huang. 1991). Elevated Se concentrations in soil solution led to high concentrations of Se in plants. invertebrates, reptiles, amphibians, fish, mammals, and birds (Ohlendorf & Santolo, 1994). Although no deleterious effects of Se toxicity were found in the terrestrial system, effects were seen in the aquatic system. The most pronounced effects were seen in waterfowl and -shore birds, with common occurrences of embryonic mortality- and deformity, and mortality in adult birds (Ohlendorf. 1989).

Although much of the past research has focused on-areas where Se deficiency is common, problems associated with Se toxicity have been reported since 18.57 in areas of the western USA (Rosenfeld & Beath, 1964). Ranchers in the seleniferous areas continue to experience problems with livestock health and reproduction (Mayland et al., 1989; Ohlendorf, 1989). The development of large-scale surface mining operations- for coal, bentonite, and U has raised additional concerns regarding the potential for Se pollution of soils, surface water, and groundwater in the western USA (Boon, 1989).

4-2.1.1.5 Cadmium, Lead, and Zinc; Cadmium, Pb, and Zn- are often found together in ore deposits, but the metals have different biological effects Zinc is physiologically an essential microelement, whereas Cd and Pb have no known biological functions and may create serious environmental and health hazards (Kabata-Pendias & Pendias, 1992). Cadmium is a relatively rare metal, as shown by its low concentration in the earth’s crust (0.15–0.20 mg kg-‘) and in soils (0.40 mg kg-‘; Berrow & Reaves, 1984). Annual estimated global emissions of Cd to the-atmosphere from anthropogenic (smelting, refining, mining, energy production, manufacturing processes, agricultural uses, and waste incineration) and natural sources is 9000 Mg (Nriagu. 1989). Typical sources of Cd that lead to contamination in soils include plating operations and disposal of Cd-containing wastes, such as Ni-Cd batteries, Cd-plated steel, or electric arc furnace dust. In Cd contaminated sites, Cd may exists as Cd”, Cd-CN-, or $Cd(OH)_2$ sludge. The form depends on the pH and treatments that Ehe Cd waste receives before disposal to pits and/or lagoons.

Lead concentrations range from <l .O mg kg-’ in normal soils to >10 000 mg kg-’ in ore materials. More than 200 Pb bearing minerals have been identified with.galena (PbS), cerussite ($PbCO_3$), and anglesite ($PbSO_4$) as the most economically important. Annual world mining production of Pb in 1994 was 29 000 Mg (Dudka & Adriano, 1997). Estimated global emissions of Pb to the atmosphere is 344.5 x 10^3 Mg yr^{-1} with a global input to soils of 959 x 10^3 Mg yr^{-1} (Nriagu, 1989).

Zinc is the 24th most abundant element in the earth’s crust, with an average concentration of 40 to 70 mg kg^{-1} in soils (Adriano, 1986; Berrow & Reaves, 1984). Most of the Zn produced in the world is from ores containing Zn sulfide minerals. The ores of economic significance are the sulfide-sphhlerite and wurtzite and their weathering products, mainly smithsonite ($ZnCO_3$) and hemimorphite [$Zn_4Si_2O_7(OH)_2.H_2O$]. Annual world production of Zn is 67 x 10^3 Mg yr^{-1} with an estimated global emission of 176.5 x 10” Mg yr^{-1} (Dudka & Adriano. 1997). The main use for Zn is as a corrosion-resistant coating on iron or steel. The Zn coating process, i.e. galvanizing, may be accomplished by several methods, including electroplating (i.e.. electrogalvanizing). Zinc metal also is used in making the casings of Zn-C dry cell batteries, sacrificial anodes,.and a variety of diecast parts. Because it is heavily used in galvanizing and electrogalvaniiing. Zn in waste sites is commonly found with other metals.

The main anthropogenic inputs of Cd, Zn, and Pb to the environment are from mining and smelting processes, sewage sludge applications in agriculture. and burning of fossil fuels. Lead forms stable complexes with both inorganic (e.g., Cl^-, CO_3^{2-}) and organic (e.g.. humic and fulvic acids) compounds present in soils and aquatic systems (Adriano. 1986). Soluble Pb also reacts with carbonates, sulfides, sulfates, and phosphates to form low solubility compounds. It is the low solubility and stable formation of lead phosphate compounds that compelled the use of natural phosphate minerals such-as apatite as a remedial agent at severely lead contaminated sites (Chlopecka & Adriano, 1997). In the vicinity of a Pb-Zn smelter in Trail, British Columbia, Canada, Pb concentrations in soil range from 22 to 4200 mg kg-’ (Schmitt et al., 1979). The soil Pb concentration-and, secondarily, house dust lead concentration, were determined to be the principle avenues that led to elevated blood lead concentration in Trail children (Hertzman et al., 1991).

High soil concentrations of Zn and Cd were found in the vicinity of a Zn smelter at Palmerton, PA. Buchauer (1973) reported Zn in surface soil ranged from 50 000 to 80 000 mg kg-’ and Cd from 900 to 1500 mg kg-‘. Chaney et al. (1988) found that inputs from this Zn smelter led to elevated concentrations of Cd and Zn in nearby garden soils (76 mg Cd kg-’ and 5830 mg Zn kg-‘). In England, the oldest and most extensive sources of Cd, Pb, and Zn pollution are related to areas of historical mining that began in Roman and earlier times and thrived until the end of the 19th century (Thornton & Abrahams, 1984). More than 4000 km^2 of agricultural land in England and Wales have been contaminated with one or more of these metals. For example, in northeast Wales, the Halkyn Mountain mining area is extensively contaminated by Cd and Pb, with the highest Cd concentration >100 mg kg-’ and Pb concentrations ranging from 1000 to 10 000 mg kg-’ (Davies & Roberts, 1978). In Poland, Upper Silesia is reportedly the most polluted area with respect to Cd, Pb, and Zn. The source of these metals includes spoil from black coal and metal ore mines, and inputs from Pb-Zn smelters and coal-fired power plants. Soil contamination is caused mainly by two active Pb-Zn smelters (Gzyl. 1990; Pawlowski, 1990; Marchwinska & Kucharski, 1990). Highest soil contamination occurs near the smelters: houever, other areas of the region are affected by long-range transport of contaminants. The ranges of concentrations of metals in soil are broad: Cd, 0.1 to 143.0 mg kg-‘; Pb, 4 to 8200 mg kg-‘; and Zn, 5 to 13 250 mg kg-’ (Dudka et al., 1995). Japan also has elevated soil concentrations of Pb, Zn, and Cd caused by mining and smelting operations (Asami, 1988). Increased economic development since World War II has led to a large number of metal mines in Japan. According to Asami (1988) and Yamane (1981) mining-smelting industries are the main source of Cd contamination of Japanese soils.

Other major sources of Cd, Pb, and Zn in soil are agricultural applications of sewage sludges, phosphate fertilizers, manure, and pesticides. The greatest concentrations of Cd. Pb. and Zn are in sewage sludges, folldwed by phosphate fertilizers (Kabata-Pendias & Pendias, 1992). Berrow and Webber (1972) analyzed 42 sludges from rural and industrial towns in England and Wales and found Pb concentrations ranged from 120 to 3000 mg kg-‘. In U.S. municipal sewage sludges Pb concentrations range from 2 to 3500 mg kg-’ (Sommers. 1977: Logan & Chaney. 1983). Zinc concentrations in sewage sludges range from 700 to 49 000 mg kg-’ (Kabata-Pendias & Pendias, 1992). Although heavy metals constitute only a small fraction of the sludge solids, usually <1% of the dry weight. the metal concentrations in soils may be significantly raised through long-term applications of sludges (Page & Chang. 1994; Berti & Jacobs, 1996). A number of studies have addressed heavy metal uptake and accumulation by crops grown on sludge-amended soils. mainly focusing on Cd (Berti & Jacobs. 1996; Chang et al., 1996, 1997). Valdares et al. (1983) and Berti and Jacobs (1996) found elevated soil solution concentrations of Cd and Zn even at relatively low loading of sludge. Thus, the addition of relatively small amounts of sludge may lead to elevated metal concentrations in soils.

Impurities in the phosphate rock used for fertilizer manufacture also can lead to elevated Cd concentrations in soils. In Australia, the main -source of Cd -added to agricultural soils is through the use of phosphatic fertilizers. The main rock phosphate sources in Australia, until recently, were from oceanic sedimentary, guano-based deposits with Cd concentrations ranging from 42 to 99 mg kg-’ (McLaughlin et al., 1996). Cadmium inputs to soils from fertilizers for some countries are (g ha-’ yr^{-1}): Australia, 1.5 to 3.0 (McLaughlin et al., 1996); England, 4.3 (Hutton & Symon, 1986); Germany, 3.5 to 4.3 (Kloke et al., 1984): New Zealand, 8.9 (Bramley, 1990); and USA, 0.3 to 1.2 (Morvedt, 1987). The average for European countries is 2.5 g ha” yr^{-1} (Biberacher & Shah, 1990).

Human health problems derived from Cd toxicity have occurred in some Cd polluted areas. For example in Japan, the Itai-itai disease (osteomalacia and concurrent kidney disease), is caused mainly by the intake of Cd in rice (Asami, 1991). Excessive exposure to Pb in the environment may cause Pb poisoning, most commonly afflicting children.

4-2.1.2 Radionuclides

Several natural and synthetic radionuclides have been detected in soils. Many of these radionuclides have long half-lives and can bioaccumulate in organisms. Artificial radionuclide enrichment of soil comes from diverse sources, including nuclear weapons testing, power reactor accidents, nuclear fuel transportation accidents, and as a result of releases from reactor storage basins and cooling effluents (Adriano et al., 1984).

With the onset of nuclear weapons testing in the 1950s, soil contaminated with radionuclides has been a concern. Substantial release of ^{137}Cs and to some extent ^{90}Sr into the environment has occurred. Inparticular, the transfer of ^{137}Cs in the food chain has been a concern in certain ecosystems. For example, ^{137}Cs has been observed to accumulate in edible organs in white tail deer (*Odocoileus virginianus*) at the Savannah River Site, a U.S. Department of Energy facility near Aiken, SC, where soils are sandy, highly leached, and low in indigenous K (Smith et al., 1995). Likewise, ^{137}Cs accumulates in terrestrial plants, including coconut. on the Marshall Islands, where the USA conducted weapons tests (Koranda & Robinson, 1978). Cesium behaves geochemically and physiologically similar to the essential plant nutrient K. and like K, is relatively insensitive to soil pH and organic matter content. The amount and type of clay in the soil influence the bioavailability of ^{137}Cs to plants (Desment & Sinnaeve, 1992). ^{137}Cs accumulates in surface soil, where it is strongly sorbed by vermiculite-type clay minerals and sesquioxides (Adriano et al.. 1981). Of the two radionuclides of strontium. ^{90}Sr has a half-life of 28 yr. Both have been released to the atmosphere from the testing of nuclear weapons and from accidents at nuclear power stations. It has been a cause of great concern because ““Sr behaves like Ca in the food chain. the radionuclide passing into bones from milk and other foods (Wild, 1993).

Today, a great concern is the disposal of nuclear wastes from the production of nuclear weapons and nuclear power plants. These waste products include transuranic radionuclides, which are isotopes produced by the decay of uranium and plutonium. Of these, ^{239}Pu and ^{241}Am are perhaps of most environmental concern. The transuranic nuclides are retained in soils by adsorption, precipitation, and organic matter chelation and are sensitive to pH (Wild, 1993; Adriano et al., 1997).

Radionuclides are a group of contaminants that cause public concern because of radiation exposure. The public's concern about radionuclides was heightened by the 1986 nuclear accident in Chernobyl, Ukraine. This accident, both in terms of released activity and impact area, was one of the worst environmental disasters of our time, where natural and agricultural ecosystems not only in the Ukraine, but also in several countries in Scandinavia, and Eastern and Western Europe were affected (Worely & Lewins, 1988). The accident affected extensive agricultural areas in Russia, Byelorussia, and the Ukraine, where soil contamination levels of 5 to 80 Ci km^{-2} were reported for 1 640 500 ha in the three countries. Consequently, 143 800 ha of agricultural lands have concentrations that are greater than recommended tolerable levels and have been taken out of production.

Other minor sources of radionuclide addition to soils are coal fly ash, cement manufacturing, metal production, fertilizer additions, and other industries (Mattigod & Page, 1983; McBride et al., 1978).

4-2.1.3 Nitrogen

Nitrogen is a plant macroelement that is frequently deficient in cultivated soils..Most N in soil is found in organic forms and therefore is unavailable to plants. Biological processes that influence microbial transformations of N influence the availability of N. The biological transformation of N includes the following processes: (i) assimilation of N in inorganic form, mainly as ammonium and NO_3^- by plants and microorganisms, whereby organic N compounds are formed; (ii) heterotrophic transformation of organic N from one organism to another (e.g., organic N in plants to animal protein); (iii) ammonification, whereby organically bound N is transformed to NH_4^+ or NH_3^-; (iv) nitrification by oxidation of NH_4^+ to NO_2^- and NO_3^-; (v) denitrification by reduction of NH_3^- to N_2O or N_2 gas; and (vi) N fixation, whereby N_2 is reduced to NH_4^+ and organic compounds by microorganisms. Small additional amounts of N_2 are chemically fixed in soils as oxides by lightning.

The main source of N is fertilizers (anhydrous ammonia, ammonium nitrate. urea, and compound fertilizers suppling N and other nutrients). The use of N fertilizer world-wide has increased dramatically since the 1950s and is projected to increase to 100 x 10^6 Mg by the year 2000. In 1994. the total world production of N fertilizers was 92 x 10^6 Mg with the highest production in USA (13 x 10^6 Mg; Minerals Yearbook. 1995). Worldwide, N fertilizers have become a vital part of agricultural production. Without fertilization, yields would fall to uneconomical levels; however, with the increased use of fertilizers, groundwater and surface water contamination has become a serious problem in some areas. Nitrogen applied as NH_4^+ is susceptible to microbial oxidation, first to NO_2^- and then NO_3^-, mobile anions. Excess NO_3^- is either leached from the system or is reduced to N_2 gas and volatilized into the atmosphere. Nitrate lost through soil leaching has the potential to contaminate groundwater and surface water resources. Nitrate lost through reduction and volatilization can exacerbate the problem of greenhouse gas emission. The amount of nitrate leached depends on the following factors: the amount of water percolating through the soil, the amount of NO_3^- in the soil, the soil type, and the cropping system (Kofoed, 1985). In general, greater losses occur from sandy than from clayey soils and normally smaller losses occur under grass than under crops with a shorter growing period.

The direct relationship between N application practices and excessive NO_3^- concentrations in the soil profile is well documented. Nightingale (1972) found a correlation between observed groundwater NO_3^- levels, soil NO_3^- concentration, and N-fertilizer management practices, while Pratt et al. (1972) and Freid et al. (1976) concluded that the amount of NO_3^- available for leaching is strongly related to N application practices.

In addition to manufactured sources, N is available from harvested organic materials, wastes, or crops grown for symbiotic N fixation. Natural N-containing compounds available for fertilization include livestock manures and municipal sewage sludge (Rechcigl, 1996). For farm efficiency, manures have long been used for fertilization, not only as a source-of N but also C and many other plant nutrients. Analyses of animal wastes vary widely depending on the composition of forage, the type of animals involved, and the storage technique used in stockpiling manure prior to its application (Rechcigl, 1996). Generally, poultry manure contains 2 to 4% N (on fresh mass) and cattle manure, cattle slurry, and pig slurry contain about 0.6 % N (Stevenson, 1982). In the initial year of manure application, about one-third of the N becomes available for crop uptake. Sewage sludge contains 20 to 60 g N kg-' or more, much of which is in organic form (Stevenson, 1982). Because there is a potential for NO_3^- build up and eventual leaching, concern has arisen over the effects of high rates of sludge application on the quality of groundwater (Kofoed, 1985).

Health hazards from NO_3^- contamination of grdundwater were first recognized in Iowa in 1945. The illness of two infants was attributed to NO; concentrations of 40 to 140 mg L^{-1} in the water that was used to make their food. The illness, known as methemoglobinemia or blue baby-syndrome, is caused by NO_2, which can be produced from NO_3^- in the gastrointestinal (GI) tract by NO_3^- reducing organisms (Gilliam et al., 1985).

4-2.2 Organic Contaminants

There are hundreds of different types of organic compounds in the environment. Some of these compounds are of anthropogenic origin, whereas many are of natural origin. Irrespective of their origin, they may be toxic to plants and animals if they are available in sufficient concentrations. To further complicate matters, most organic compounds degrade over time, producing an even larger number of compounds. These degradation products are often less. but can be more toxic than their precursors. For example. among the most widespread groundwater contaminants throughout the world is TCE, a solvent and degreasing agent. This compound degrades to various dichloroethylene isomers, which in turn degrade to vinyl chloride. Finally. the vinyl chloride can degrade to either CO_2 (in oxidizing conditions) or methane (in reducing conditions). Vinyl chloride is approximately 100 times more-toxic than trichloroethylene, whereas CO_2 is much less toxic than trichloroethylene. Thus, the organic compound composition and-its relative toxicity in a given system can vary greatly over time. This-dynamic quality introduces additional complexity to assessing the health risks associated with systems contaminated by organic compounds:

It is not possible to discuss the sources and practices contributing to soil contamination of all organic contaminants. The environmental behavior and the properties of a vast majority of organic contaminants can be broadly classified into categories based on their chemical structure (or use, in the case of the pesticide category). Seven major categories of organic contaminants will be discussed in this section:

1. polycyclic aromatic hydrocarbons (PAH) and N-heterocyclic aromatic compounds;
2. nitroaromatics;
3. phenols and anilines;
4. halogenated aromatic;
5. halogenated aliphatic:
6. pesticides; and
7. petroleum products

Of these seven categories, six are based on the chemical structure of the compounds and one category, pesticides, is based on its use. This latter category is quite broad and overlaps with many other categories; however, it is included as such because these compounds are intentionally produced and directly applied to terrestrial systems and they are pervasive in the groundwater in many parts of the world.

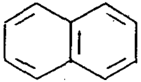
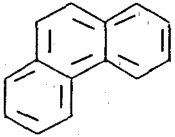
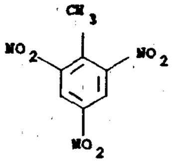
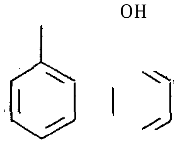
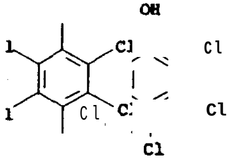
4-2.2.1 Polycyclic Aromatic Hydrocarbons and N-heterocyclic Aromatic Compounds

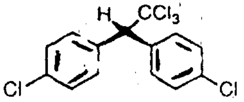
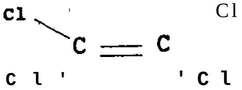
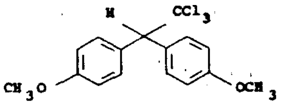
Both polycyclic aromatic hydrocarbons (PAHs) and N-heterocyclic aromatics occur naturally in the environment and form during the combustion of organic material. such as coal. oil, or wood (Table 4-1). PAHs also are constituents in fuels, lubricating oils, and other petroleum products. such as asphalt and creosote. Anthropopenic activities that significantly increase PAH levels in the environment include the combustion of fossil fuels, coal gasification. and asphalt production. PAHs released into the atmosphere return. to the earth's surface by wet and dry deposition. Long-term experiments on agricultural soils indicate that the total PAH burden has increased approximately four-fold or higher since 1880 to 1890 (Jones. 1991). PAHs in aboveground plant tissues are primarily derived from the atmosphere, but PAHs also have been detected in carrots [*Daucus carota sativus* (Hoffm.) Arcang.], with the highest concentrations in the peel, and lower concentrations in the root (Wild & Jones, 1991).

LaGoy and Quirk (1994) summarize data for PAHs in soil, noting low background levels of PAHs in rural areas away from major highways. Concentrations of carcinogenic PAHs range from 0.01-1.30 mg kg^{-1} in forest and natural soils. to 0.06-5.80 mg kg^{-1} in agricultural soils, while concentrations of total PAHs range from 1 to 400 mg kg^{-1} in urban soils. with concentrations in industrial soils exceeding 400 mg kg^{-1}. High concentrations (8-336 mg kg^{-1}) of PAHs also are associated with road dust (LaGoy & Quirk. 1994).

PAH concentrations were measured in household soil and dust to determine whether the track-in of outdoor soil contributes to PAH in house dust. Measured

Table 4-1. Structure and sources for seven categories of organic contaminants.

Compound class	Example of structure	Examples of compounds	Sources
Polycyclic aromatic hydrocarbons (PAHs)	 (Naphthalene)  (Phenanthrene)	• Naphthalene • Phenanthrene	• Combustion of coal, oil, and wood, • Asphalt, creosote • Automobile emissions, fuels, lubricating oils • Coal tar†
Nitroaromatic	 (TNT)	• 2,4,6-Trinitrotoleune (TNT) • octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX) • trifluralin, benefin, ethalfluralin, methyl parathion • pyroxylin	• Military installations • Bombing ranges • Bactericides • Pesticides
Phenols, anilines	 (phenol)  (Pentachlorophenol)	• Pentachlorophenol (PCP) • Phenylamideherbicides: phenylureas, phenylcarbamates, and acylanilides,	• Wood preservative • Biocide • Dyestuff wastewater • Phenylamide herbicides

Halogenated aromatic	 (DDT)	• Polychlorinated biphenyls (PCBs) • Chlorinated pesticides (aldrin, BHC, dieldrin, endosulfan, endrin, endosulfan) • Dioxins[‡] • DDT (DDD, DDE)	• Pestiiide application • Incineration of medical and municipal waste • Forest fires and volcanic eruptions • Cement kilns and boilers • Petroleum, coal, and tire combustion • Hazardous waste and sewage sludge incineration • Draft black liquor boilers • Secondary lead smelting
Halogenated aliphatic	 (Tetrachlorethylene, PCE)	• Methylchloride, chloroform, bromomethane, formaldehyde, carbon tetrachloride • Vinyl chloride, 1,1-dichloroethylene, trichloroethylene (TCE), tetrachloroethylene (PCE)	• Degreasing solvents • Former dry-cleaning facilities • Plastics manufacturing
Pesticides	Pesticides have a large structural diversity, including compound classes hiscussed in this table: chlorinated aliphatics, phenols, halogenated aromatics, nitroaromatic compounds  (Methoxychlor)	• Alachlor, aldicarb, atrazine, carbofuran, chlordane, cyanazine, 2,4-D, diazinon, dicamba, diquat, diuron, endrin, lindane, malathion, methoxychlor, paraquat, picloram, 2,4,5-T, 2,4,5-TP (Silvex), trifluralin	• Agriculture • Residential and industrial pest control
Petroleum	A highly complex mixture of paraffinic, cycloparaffinic (naphthenic), and aromatic hydrocarbons containing a tow percentage of sulfur and trace amounts of nitrogen and oxygen coumpounds.[§]	• Crude oil, refined oil, crankcase oil	• Oil recovery and refining industry • Automobiles and other forms of transportation • Oil tankers, pipe lines, and other modes of transporting oil • Industry

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Coal tar is a liquid byproduct of the coal gasification process that was commonly disposed of in burial pits at gaswork sites.

Dioxins is a common term used to collectively refer to the congeners of polychlorinated dibenzodioxins and dibenzofurans.

Sax and Lewis, 1987.

PAH concentrations ranged from 16 to 580 mg kg^{-1}, consistent with the above finding for road dust (Chuang et al., 1995). The general concentration trend was reported as: entryway soil > house dust > pathway soil > foundation soil (Chuang et al., 1995).

Because of the variety of natural and anthropogenic sources of PAHs in the environment, there is considerable interest in determining the primary sources that contribute to contaminated soil and sediment. Stationary sources (e.g., coal -combustion) accounted for 80 to 90% of PAH emissions prior to 1980 (Harrison et al., 1996). More recent research has identified vehicular emissions (Harrison et al., 1996; O'Malley et al., 1996) and crankcase oil (Latimer et al., 1990; O'Malley et al., 1996) as primary sources of PAHs in urban sediments. PAH concentrations in soil have been found to decrease exponentially with distance from the source (Munch, 1993; Van Brummelen et al., 1996).

PAHs are the primary constituents of concern in coal tar, a liquid-byproduct of the coal gasification process that was commonly disposed of in pits or on the ground surface at gas work sites. These practices have resulted in highly contaminated soils with. PAH concentrations exceeding parts per thousand (Yu et al., 1990). One concern with coal tar contaminated soils is the potential emission of these volatile organic compounds back to the atmosphere on sites that have been developed or are under consideration for future development. Groundwater contamination is another concern. Although gasification operations were discontinued for >30 yr, soils and residual nonaqueous phase liquids in the soil of a former coal and oil gasification plant are a source of groundwater contamination at a city park that was developed on the site (Tumey & Goerlitz, 1990).

Use of PAH-containing wood preservatives has resulted in the direct contamination of soils in utility and railway right-of-ways. Mean PAH concentration8 of soils at the base of utility poles treated with creosote were 3076 mg kg^{-1} (Wan, 1994). For comparison, concentrations were 213.5 mg kg^{-1} in railway right-of-way ditch sediments, and 0.79 to 1 mg kg^{-1} in agricultural drainage ditches on farmland (Wan, 1991, 1994).

4-2.2.2 Nitroaromatics

Nitroaromatic compounds are used in chemical manufacturing, oil refining, and as pesticides, bactericides, explosives (Windholz, 1983; Boopathy et al., 1994), and intermediates in the synthesis of dyes and other high volume chemicals (Haderlein et al., 1996; Table 4-l). Trifluralin [2,6-dinitro-N, N-dipropyl-4-(triflurormethyl)benzenamine], benefin [N-butyl-N-ethyl-2,6-dinitro-4-(triflurormethyl)benzenamine], ethalfluralin [N-ethyl-N-(2-methyl-2-propenyl)-2,6-dinitro-4(tifluoromethyl)benzenamine], and isopropalin [4-(1-methylethyl)-2,6-dinitro-N.N-dipropylbenzenamine] are dinitroaniline herbicides that are used on a variety of crops: extractable residues of trifluralin in field soils were on the order of 10 to 30 mg kg^{-1} (West et al., 1988). The herbicide methyl parathion is another nitroaromatic compound that is now used instead of the highly toxic parathion, however, paranitrophenol. a hydrolysis product of both parathion and methyl parathion, also is toxic (Out & Sharma, 1989; Megharaj et al., 199-I). In addition to the agricultural use of pesticides. various industrial practices contribute to soil and sediment contamination with nitroaromatic compounds.

A large number of military installations are contaminated with nitroaromatic residues from the manufacture, distribution, destruction, or testing of munitions (Bauer et al., 1990). Disposal of waste-water from munitions packing and loading operations at the Louisiana Army Ammunition Plant (Doyline. LA) resulted in highly contaminated lagoon sediments (Williams et al., 1992). Some reported concentrations of explosives in these lagoons were 56 800 mg kg^{-1} of 2,4,6-trinitrotoluene (TNT), 17 900 mg kg^{-1} of hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX), 2390 mg kg^{-1} of octahydro-1,3,5,7-tetranitro-1,3,5,7-tetraazocine (HMX), and 650 mg kg^{-1} of N-methyl-N,2,4,6-tetranitroaniline (tetryl; Williams et al., 1992). Also caused by the disposal of waste water, the concentration of the propellant nitrocellulose (pyroxylin) in soil at the Badger Army Ammunition Plant in Baraboo, WI, was 18 800 mg kg^{-1} (Williams et al., 1992). Analysis of HMX, RDX, TNT and other nitroaromatics in soils from. military sites in five states gave similar concentrations, which ranged from <1 to 15 000 mg kg^{-1} (Jenkins et al., 1989; Bauer et al., 1990).

4-2.2.3 Phenols and Anilines

Phenols and anilines are toxic constituents of dyestuff waste water. which is routinely released to the environment (Kanekar et al., 1993; Table 4-1). Mean concentrations of phenols and ammoniacal nitrogen (a measure of aniline) in waste water from a dye factory in India (Pune, India) were 761 and 341 mg L^{-1}, respectively, prior to soil application (Kanekar et al., 1993). Aniline and its chlorinated derivatives in soil also result from biotransformation of numerous phenylamide herbicides, including phenylureas, phenylcarbamates, and acylanilides (Moreale & Van Bladel. 1979). In microbially or enzymatically active systems, phenolic and anilinic residues can bind to soil humic materials (Bollag. 1992), subsequently decreasing their bioavailability.

Pentachlorophenol (PCP) is produced primarily for use as a wood preservative,. but also is used as a general biocide. Detection of PCP at part per million levels in human. urine from nonoccupationally exposed individuals (Hattemer-Frey & Travis, 1989) indicates PCP ubiquity in the environment. Background concentrations of PCP were reported at 33.3 mg kg^{-1} in soil and < 0.01 mg kg^{-1} in water, which agree with predictions based on equilibrium partition coefficients (Hattemer-Frey &Travis, 1989). Fort et al. (1995) report levels ranging from 500 to 6000 mg kg^{-1} in Washington soils. PCP sorption is dependent upon pH (Lee et al., 1990); the relative abundance of neutral versus anionic PCP should be considered when estimating its environmental fate.

4-2.2.4 Halogenated Aromatics

Polychlorinated biphenyls (PCBs) and many-of the chlorinated pesticides. first manufactured in the 1920 to 1930s, are ubiquitous, stable. lipophilic compounds that persist in surface soils and sediments (Table 4-1). Atmospheric deposition is the primary source of PCBs and chlorinated compounds to the terrestrial environment (Jones. 1991). Analysis of archived agricultural soil samples from England indicates a sharp rise in PCB concentration between 1940 and the early 1960s. with a maximum of 140 to 560 mg kg^{-1} total PCB during the late 1960s to early 1970s (Alcock et al., 1993). World PCB production peaked in the

1960s and the industrial use of PCBs in Europe and the USA has been restricted since the mid 1970s (Alcock et al., 1993).

Dioxins are similar with respect to their persistence, chemical, and transport properties, but are not intentionally produced and occur as trace contaminants in many industrial and thermal processes (Fiedler, 1996). The term dioxin is often used to collectively refer to the congeners of polychlorinated dibenzodioxins and dibenzofurans that are emitted following combustion. Like PAHs, dioxins are a natural product of forest fires and volcanic eruptions, but historical records indicate human activity as the primary source of dioxin in the environment (Thomas & Spiro, 1996). Incineration of medical and municipal wastes along with cement kilns and boilers are the top three anthropogenic sources of dioxin. Industrial wood burning, secondary copper smelting, and forest fires are the next most common sources of dioxin emissions. Petroleum, coal, and tire combustion; hazardous waste and sewage sludge incineration; residential wood burning; kraft black liquor boilers; drum reclamation; and secondary lead smelting also contribute to dioxin emissions (Thomas & Spiro, 1996). Fiedler (1996) notes that dioxins can concentrate in sewage sludge, compost, and other municipal and hazardous wastes, and reenter the environment when applied to agricultural soils.

Perhaps the most widely known incident of contamination in the USA with 2,3,7,8-tetrachlorodibenzodioxin (2,3,7,8-TCDD), considered the most toxic species, occurred in Times Beach and other areas of Missouri in the early 1970s when mixtures of used oil and chemical waste were used to spray horse arenas, roads, and parking lots. Levels of 2,3,7,8-TCDD in soil ranged from <100 to >1000 μg kg^{-1} in soil (Tiernan et al., 1985). In Germany, slag residues from copper ore smelting were applied as a cover material for recreational and other areas (Theisen et al., 1993). Slag residues and soils were analyzed for levels of dioxin and related compounds that are produced in the smelting process (PCBs, chlorinated benzenes, chlorinated naphthalenes); concentrations in the slag were in the low milligram per kilogram range, whereas soil concentrations were in the low microgram per kilogram range (Theisen et al., 1993).

Terrestrial runoff and sewage discharges have resulted in the contamination of marine sediments with organochlorine pesticides. Total DDT (includes DDD and DDE) and chlordane residues in Casco Bay, ME, sediments range from below detection limit (0.25 μg kg^{-1}) to 21 μg kg^{-1} for DDT and 4.9 μg kg^{-1} chlordane (dry weight); other organochlorines, including aldrin, BHC, dieldrin. endosulfan, endrin, heptachlor. toxaphene, and hexachlorobenzene were near or below the detection limit (Kennicut et al., 1994). Levels. were similar in coastal sediments of West India. where residues of DDT and metabolites also were the highest, and greater than other chlorinated pesticides (HCH > aldrin > dieldrin); highs ranged from 30-40 μg kg^{-1} to 0.5–3 μg kg^{-1} in an area that was considered to be free of industrial discharge (Sarkar & Gupta, 1991).

4-2.2.5 Halogenated Aliphatic

Halogenated aliphatic compounds are a subset of volatile organic compounds (VOCs) that have been widely used as solvents and degreasers. for dry cleaning, and in plastics manufacturing (Table 4-I). They are ubiquitous soil and groundwater contaminants. with TCE being the most frequently reported contaminant at hazardous waste- sites on the U.S. Environmental Protection Agency National Priority List (Tursman & Cork, 1992). Contamination of soil and groundwater with chlorinated hydrocarbons, such as tetrachloroethylene (perchloroethylene, PCE), TCE, and carbon tetrachloride are well documented at U.S. Department of Energy (DOE) facilities (Riley et al., 1992; McNab & Narasimhan, 1994). Multiple activities at large DOE facilities (e.g., Hanford, Oak Ridge National Laboratory, Savannah River Site) were chemically intensive; chlorinated hydrocarbons were used as solvents and degreasing agents in nuclear fuels reprocessing and fabrication (Riley et al., 1992). Much of the waste was disposed on the ground surface, or in ponds, cribs, basins, pits, injection wells, and landfills, which has resulted in subsurface contamination (Riley et al., 1992; McNab & Narasimhan, 1994). Fifteen chlorinated hydrocarbon constituents were identified in soils-sediments at DOE sites, with TCE; 1,1,1-trichloroethane; PCE; dichloromethane and carbon tetrachloride among the most commonly reported (Riley et al., 1992). It is important to note that some of the constituents are abiotic degradation products of the original reagents.

TCE was the major contaminant in soil from a hazarhous waste disposal. site in New York state that was tested for volatile and extractable organic compounds; levels ranging from 1.6 to 10.0 mg kg-’ were reported (Pavlostathis & Jaglal, 1991; Hewitt et al., 1992). Levels of TCE in a contaminated soil from the Cold Regions Research and Engineering Laboratory in New Hampshire were highly variable and ranged from 0.2 to 26.9 mg kg-’ for samples that were designated low-level and high-level, respectively (Hewitt et al., 1992).

4–2.2.6 Pesticides

Organic compounds representing a variety of chemical classifications are used as pesticides (Table 4–1). Where appropriate, comments on specific classes (e.g., organochlorine) are included above. Pesticide residues in soil are primarily of concern due to the potential for plant uptake and residues in food and feedstuffs, and more recently because of the impact on surface and groundwater quality. Pesticides are intentionally produced for release in the environment: even when applied on the foliage. residues are ultimately distributed in soils and sediments. A recent study on the occurrence and distribution of pesticides in streams indicated that both urban and agricultural areas were probable sources of pesticides in streams. with 30 and 22 pesticides detected in the agricultural and urban areas, respectively (Kimbrough & Litke, 1996). The importance of point sources, such as locations where pesticides are mixed and/or loaded also is noted (Miles et al., 1990).

Several studies indicate that residues of-moderately soluble pesticides and herbicides, which are expected to be less persistent than the organochlorine compounds noted above. can persist long after they are applied to soil (Capriel et al.. 1985; Raju et al.. 1993). Pseudo first-order herbicide disappearance was observed during a 174-d period after field application: concentrations on Day 174 in the upper 2.5 cm were approximately 80 and 30 μg kg^{-1} for atrazine [6-chloro-N-ethyl-N’-(1-methylethyl)-1,3,5-trizine-2,4-diamine] and metolachlor [2-chloro-N-(20 ethyl-6-methylphenyl)-N-(2-methoxy-1-methylethyl)acetamide], respectively (Southwick et al.. 1990). Soils from a corn (*Zea mays* L.) field treated with atrazine (1985–1987), cyanazine [1-[[4-chloro-6-(ethylamine)- 1,3,5-triazin-2-yl]amino]-2-methylpropanenitrile; 1987; 1988], and metolachlor (1987, 1988) were analyzed for parent compound and selected metabolites 4 yr after the last application (Raju et al., 1993). Mean residue concentrations in soil ranged from 103.4 μg kg-’ for metolachlor to 15.65 and 9.61 for atrazine and cyanazine, respectively. Mean levels for de-alkylated atrazine and hydroxyatrazine were <6 mg kg-’ (Raju et al., 1993). Although it is clear that decreases are observed following -application, long-term monitoring indicates that residues of moderately soluble compounds persist. Additional field studies addressing pesticide transport in soils are summarized in a recent review by Flury (1996).

4-2.2.7 Petroleum Products

Due to their widespread industrial, commercial, and domestic use, accidental. releases or spills of petroleum products in the environment are common (Table 4-l). Any site where petroleum products are processed, transported, transferred, stored, or used generally results in contaminated soil (National Academy of Science, 1985).

Hydrocarbons typically associated with crankcase oil were found in street dust, roadside soil, roadside vegetation, and atmospheric deposition in residential, commercial, highway, and industrial areas in Rhode Island (Latimer et al., 1990). Concentration in atmospheric deposition was highest in all areas tested (1940-I 25 000 mg kg-‘), followed by street dust in industrial and highway areas (3490 and 1680 mg kg-‘, respectively), suggesting that dust and particulates are important transport vectors. Concentrations in roadside soil ranged from 39 (residential) to 265 (highway); with a high of 856 mg kg-’ at the industrial site. Concentrations in vegetation were 40 to 46 mg kg-‘, with a high of 290 mg kg^{-1} at the industrial site (Latimer et al., 1990).

Hazardous waste disposal areas present unique remediation challenges due to the presence of complex mixtures of chemicals from a-variety of sources. Analyses of soil cores from two areas in Spain that received wastes from diverse sources indicated that petroleum tar residues and lubricating oils constituted the two major types of organic wastes present in the dumps (Navarro et al., 1991).

4-3 SOURCES OF CONTAMINANTS AT WASTE SITES

The various sources of contaminants at waste sites are presented in Table 4-2. Category 1 includes sources that are intentionally designed to discharge substances; such systems are designed primarily to use the capacity of the soil to treat wastewaters (Table 4-2). Septic- tanks and cess pools have been reported to discharge the largest volume of wastewater into the ground and are-commonly reported as sources of. groundwater contamination-(U.S. Environmental Protection Agency, 1977). A common and inexpensive method of disposing of wastewater and sludge is through land application. It has been estimated that upwards of 50% of the municipal sludge generated annually is applied to the land (U.S. Environmental Protection Agency. 1983). Contaminants of concern include organics, nitrate, phosphate. and other inorganics, including metals.

‘fable 4-2. Sources of contaminants at hazardous sites (from Boulding, 1995).

1. Sources from disposal-discharges of substances
   - Land application: waste water (via irrigation), sewage sludge, hazardous waste, nonhazardous waste
   - Subsurface percolation: septic tank and cess pools
2. Sources from storage, treatment, and/or disposal of substances; discharge via unplanned release
   - Landfills: industrial hazardous waste, industrial nonhazardous waste, municipal refuse
   - Open dumps
   - Residential disposal
   - Surface impoundments
   - Waste piles and tailings
   - Above ground storage tanks’
   - Underground storage tanks
   - Containers
   - Radioactive burial sites
3. Sources from transport or delivery of substances
   - Pipelines
   - Materials transport and transfer operations
4. Sources from discharging substances as a result of planned activities
   - Pesticide and fertilizer application
   - Livestock feeding operation
   - Urban runoff
   - Mining and mining drainage
   - Irrigation practices
5. Natural sources or release of substances enhanced by human activities
   - Areas near metalliferous sites

Category 2 includes sources designed to store, treat, or dispose of substances, not release contaminants to the subsurface. This includes landfills. local-residential disposal areas. open dumps, surface impoundments, and others. In category 3 (Table 4-2). contaminants are released through accident or neglect: for example, as a consequence of pipeline breakage or a traffic accident. Usually substances that are released are not considered waste, but are raw materials or products to be used for some beneficial purpose. Category 4 (Table 4-2) includes agriculturally related sources such as irrigation return flows, livestock operations. and agrochemical applications including fertilizers. Also, urban runoff and atmospheric deposition from industrial emissions are examples in this category. Category 5 includes naturally occurring sources whose release is induced or exacerbated by human activity. Presented in Table 4-3 are the occurrence of contaminants from various sources that include both organics and metals. It is to be noted that the majority of the si-tes surveyed had mostly organic contaminants. such as aromatic hydrocarbons; halogenated hydrocarbons, alkyl-benzenes, and pesticides. Similarly. organics appear to have dominated the contaminants at the U.S. Superfund sites (Fig. 4-2).

Contamination sources also can be classified into incidental and accidental (Finney, 1987). Incidental contamination arises as a consequence of deliberate

Table 4-3. Classification of types and sources of soil contamination in the Netherlands based on a sample of 100 cases (Boulding, 1995).

Source of contamination	Type of contamination	Frequency (%)
Gasworks	Aromatic hydrocarbons, phenols, CN^-	45
Waste dumps and landfills	Halogenated hydrocarbons, alkyl-benzenes; Metals like As, Pb, Cd, Ni, CN^-; pesticides	26
Chemical production and handling sites (including painting industries and tanneries	Halogenated hydrocarbons, alkyl-benzenes;metals like Pb, Cr, Zn, As	13
Metal plating and cleaning industries	Tri- and tetrachloroethylene, benzene, Toluene, Cr, Cd, Zn, CN^-	9
Pesticide manufacturing sites	Pesticides, Hg, As, Cu	4
Automobile service facilities (including gasoline storage tanks)	Hydrocarbons, Pb	3

activity. Examples include emissions from a stack that may result in particulate deposition on the soil. Accidental contamination is essentially the consequence of an unplanned event such as sudden failure of a storage vessel, a transport accident, or others. Usually accidental contamination can be followed promptly by efforts to clean and restore the affected soils.

Industrial processes may result in a variety of metal-bearing solid waste materials. This includes slags, fumes, fly ash, mold, sand, abrasive waste, spent catalysts, spent activated C, and refractory bricks (Zimmerman & Coles, 1992). These processed wastes may be deposited above the ground as w&e piles or below ground in landfills. Sludge is a thick, water-based suspension of solid

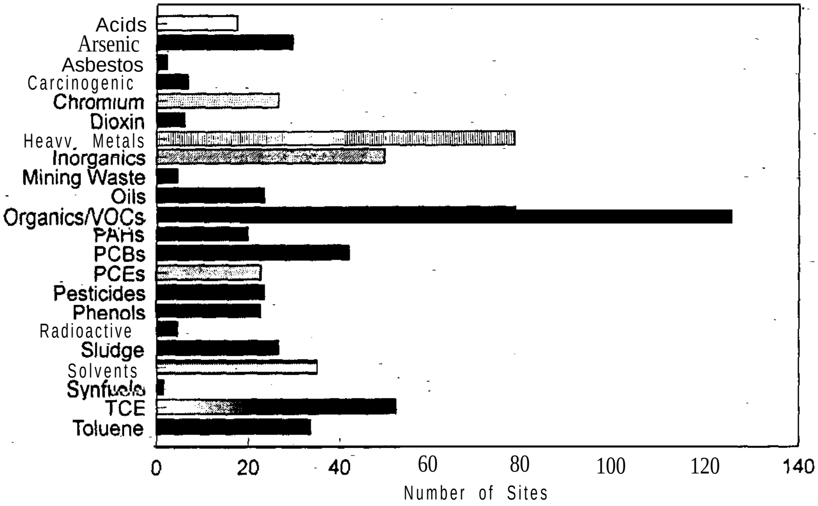

Fig. 4-2. Major contaminants at USA superfund sites (Boulding. 1995).

materials, and may include metal hydroxides, carbonaceous materials, silicates, organics, including pesticides, and other industrial by-products formed into a semisolid form. Many industrial metal-laden sludges are hydroxide or sulfide precipitates from treatment of wastewater (Smith et al., 1995). In addition to the chemicals added to cause precipitation, the sludge may contain flocculants and filter aid. Depending on the source and the age of the sludge, the waste matrix composition is usually heterogenous.

Wastes may be regulated for exhibiting one of the four characteristics of a hazardous waste as determined by the USEPA (Grasso, 1993): ignitability, corrosivity, reactivity, and toxicity, using approved methods such as the toxicity characteristic leaching procedure (TCLP). When the extract from a waste contains any of the contaminants having concentrations equal to or greater than the published values it is considered hazardous (Grasso, 1993).

4-4 DISCUSSION

Bioremediation may be defined as the use of living organisms to reduce or eliminate environmental hazards resulting from the accumulation of toxic chemicals and other hazardous wastes (Gibson & Sayler, 1992). Other options to remediate contaminated soils include physical and chemical methods, or a combination of both. The remedial choice usually will depend on the nature and concentration of the contaminants, hydrogeological environment, and the extent of contamination. Currently, bioremediation is often the method of choice for treating petroleum hydrocarbons because it is cost effective and it converts the petroleum hydrocarbons into harmless by-products, such as CO_2 and H_2O.

Indigenous and genetically-altered organisms have been shown to degrade industrial solvents, PCBs, explosives, and many different agrochemicals. Furthermore, microorganisms that transform and sequester metals and radionuclides have been identified and employed, although to a limited extent for in situ bioremediation.

An emerging form of bioremediation is the use of terrestrial plants, i.e., phytoremediation (Wenzel et al.. 1998). This group of technologies include phytostabilization, phytoimmobilization. phytoextraction, phytodegradation, phytovolatilization, and rhizofiltration. Phytoremediatidn could play a dual role in simultaneously treating inorganic and organic chemicals, such as those that may occur in mixed wastes. Through microbial activity in the rhizosphere, biodegradation has been shown to substantially transform and eventually degrade organic contaminants (Schnoor et al., 1995; Cunningham & Ow, 1996). Through phytoextraction, metals and organics can be taken up by the plant and recycled by harvesting in the case of stable metals or, in the case of organics. degraded through enzymatic action within the plants. Recently. special enzymes made possible through genetic engineering have been shown to phytovolatilize mercury and selenium (Meagher & Rugh. 1996: Terry, 1996).

Chromium is redox sensitive and can be transformed from the more mobile and toxic form [Cr(VI)] to the less mobile and toxic form [Cr(III)] through microbial action (DeFilieti, 199-l). This may bc accomplished using anaerobic bacteria that use sulfate as the terminal electron acceptor or aerobic bacteria that use Fe (III) as the terminal electron acceptor. The bacterially-produced H_2S

reacts with the Cr(VI) thereby reducing it to Cr(III), with the final product of reduction as chromic hydroxide [$Cr(OH)_3$].

Classes of chemical-contaminants present in soils and groundwaters of more than one-half of all DOE facilities include fuel hydrocarbons. chlorinated hydrocarbons, metals, and radionuclides. Organic acids, phthalates, explosives, alkyl-phosphates, complexing agents (i.e., EDTA, DTPA, NTA), and pesticides also are significant contaminants at individual sites. Also, more than one-half of the DOE sites were contaminated with mixtures of two or more compound classes (Riley et al., 1992). The most-common mixtures reported were metals and radionuclides. Codisposed mixtures of compounds have resulted in modified transport and toxicity properties that can increase environmental risk. For example, complexation of metals with ligands enhances their mobility, altering behavior at mineral surfaces and affecting their availability to microorganisms. At military installations in the USA, the goal is for the bioremediation of petroleum hydrocarbons, explosives, propellants, and organophosphates. In agricultural-ecosystems, the effort has been to focus on bioremediation to degrade toxic pesticides, and for other sites such as mining sites, the emphasis is on the bioremediation of metals and ground waters; thus, there are at least four agencies in the USA concerned with environmental cleanup using bioremediation, i.e., the DOE, the Department of Agriculture, the Department of Defense, and the Department of Interior.

The common sources of metals in agriculture are municipal sewage sludge, manure, and phosphate fertilizers (Kabata-Pendias & Adriano, 1995). The mobilization of metals from smelters and mine spoil by transfer with runoff, seepage water, or airborne dust also may be important sources of soil metals. The form and species of anthropogenical metals. in soils may be influenced by their chemical form at the time of deposition. Atmospheric particulates are commonly in the form of oxides, silicates, carbonates, sulfates, and/or sulfides. Similarly, metals. entering the' soil with mineral fertilizers have rather defined structural forms while those added with plant residues and livestock waste may be mostly organically bound or chelated. Likewise, metals entering the soil with the addition of municipal sewage sludge will differ according to the source and treatment of the waste. Anthropogenic metals in soils are in most cases more mobile than metals of indigenous origin and are therefore more bioavailable to plants.

Although many organics undergo biodegradation, it is clear that organic contaminant residues can persist in soils for long periods of time. Persistence is generally dependent on sorption, which is governed by chemical hydrophobicity and soil organic matter content. Sorption is a key determinant of bioavailability and therefore toxicity. There is a growing body of evidence demonstrating decreased extractability or desorption of organic compounds from soil with time, and recent evidence for decreasing bioavailability. The implication for bioremediation, site assessment. and restoration are suggested, but such issues have only-recently become the focus of scientific research.

The availability (bioavailnbility) of chemicals depends on the chemical in question, is site specific as well as organism specific. Hence, it-is necessary that the nature and characterization of the chemical and sites be conducted for environmental impact and risk assessment. Likewise, plants species as well as cultivars within a species also vary in their susceptibility to contaminants. In general, however, contaminants, especially metals tend to be more mobile and bioavailable in acidic soil environments.

In addressing soil quality with regard to contamination, it also is important to simultaneously consider the effect on groundwater quality. Soils have a finite capacity to retain chemicals that depends-on multiple, interacting and dynamic physical, biological, and chemical processes.

4-5 SUMMARY

Contaminants in soil may come from natural or anthropogenic sources, point and nonpoint-sources, incidental and accidental releases. or planned and unplanned activities. Most of the wastes in contaminated sites are from industrial processing or waste by-products. Infrequently, however, some raw materials for industrial purposes are accidentally released. Also, the sources may be airborne, such as those from emission stacks, or from fugitive emissions. Some may be released from the ground surface, and some may be released from below the surface. Initially, chemicals released from airborne sources and those from immediately above the ground affect primarily the soil surface. Since the soil surface generally has high organic matter content and buffering capacity for chemicals, these substances tend to be immobile and nonbioavailable. Those released below the soil surface will not have the benefit of this buffering capacity; therefore, contaminants are more subject to migration. Contaminants may occur in soil singly, in a mixture with other contaminants from the same class, or as complex mixture of inorganics and organic substances. Mixed waste often occurs in many hazardous sites, including the DOE facilities where organics, metals, and radionuclides are often found together. Because of their mobility, bioavailability, and potential risk to the environment and humans, it is necessary to characterize the nature and extent of chemical contamination, the soil geologic. setting of the affected sites, and the presence of indigenous microbial communities. While the traditional way of treating organic chemicals in soils is through microbial activity, this approach may only have limited efficacy for certain-metals. For example,. Hg, Se, Cr, and possibly As may be transformed through microbial activity or facilitated through mycorrhizal associations fungi and bacteria. Metals resistant to microbial action. such as Pb, Cd, and Zn may be bioremediated using phytoremediation techniques. This may include phytostabilization, phytoimmobilization, and phytoextraction. The disappearance of nitrate, which is a more common problem in agricultural soils, may be facilitated through denitrification. It is important to note that the capacity for soil to accumulate chemicals will have an eventual bearing on the quality of the underlying groundwaters.

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