Remediation of PAH-Contaminated Soils and Sediments: A Literature Review

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Abstract

Polycyclic aromatic hydrocarbons (PAHs) are the product of incomplete combustion, i.e. the burning of fossil fuels, forest fires, coal tar, creosote, diesel and cigarette smoke. These organic chemicals are found almost everywhere and pose a risk for human health because of their potentially carcinogenic nature and bioavailability in water, soil, sediment, and air resources that humans come in contact with daily. Because PAHs are emitted naturally through forest fires and volcanoes, microorganisms have the ability to breakdown PAHs and contaminated sites can be remediated through microbial and environmental manipulations. Previous research on remediation of PAH contaminated resources have been conducted in situ (superfund and industrial sites), ex situ in bioreactors, or in a lab setting with soils spiked with various levels of PAHs. Very few studies have focused on the risk or cleanup techniques involved with the transport and remediation of PAH contaminated materials, such as dredge sediments.

The focus of this literature review is the degradation of PAHs in dredge sediments placed in an upland setting, where anaerobic conditions exist during initial dewatering and shift to aerobic conditions during soil formation. Dredging operations involve the removal of underwater sediments to maintain ports and waterways around the United States. Finding beneficial uses for the dredged sediment, such as beach nourishment, dewatering for topsoil material, aggregate, and fill, is an important component to these operations from an environmental and economic viewpoint. Previously, clean dredged sediment (without salts or organics) has successfully been placed in upland confinements for dewatering and future use as agricultural soil. However, there is a limited amount of clean dredge material, so there is a growing interest in accepting and remediating contaminated dredge sediments from rivers and ports that have been impacted with industrial byproducts and contain varying levels of PAHs.

This literature review provides information on:
- PAH chemistry
- behavior and PAH concentration ranges in different environments
- PAH bioavailability
- transfer, degradation and sequestration of PAHs in sediments and soils
- biological techniques for enhancing PAH degradation
- chemical techniques for enhancing PAH degradation
- regulations pertaining to dredge material contaminated with PAHs
- sampling and analytical methods

Basic and Detailed Chemistry

The following section addresses basic and detailed PAH chemistry and should provide sufficient background for a clear understanding of the type and nature of organic contaminants we are addressing in the upland placement of dredge sediments.

What are polycyclic aromatic hydrocarbons?

Polycyclic aromatic hydrocarbons (PAHs; also known as polyarenes, polynuclear aromatic hydrocarbons) are a product of incomplete combustion. Different types of PAHs form based on combustion temperature; where high temperatures (i.e. coking process) create simple PAHs, and low temperatures (i.e. smoldering) result in more complex PAHs (Harvey, 1997, 1998). They are formed of two or more rings of carbon and hydrogen atoms bonded in either a linear, angular or clustered way (Sims and Overcash, 1983; Dabestani and Ivanov, 1999; Harvey, 1997). Generally, PAHs are organic pollutants that are widely distributed in the environment, are toxic, and very persistent (Cerniglia, 1992; Bjorseth et al., 1979; Gao and Zhou, 2004; Haeseler et al., 1999).

Polycyclic aromatic hydrocarbon compounds are formed and released into the environment through both natural and anthropogenic sources. Natural sources include volcanoes and forest fires. Anthropogenic sources include (ASTDR, 1995; Harvey, 1997):

- combustion of fossil fuels, including motor vehicle emission and power generation
- wood burning
- municipal and industrial waste incineration
- coal tar, coke, asphalt, crude oil, creosote, asphalt roads, roofing tar
- discharges from industrial plants and waste water treatment plants
- hazardous waste sites, coal-gasification sites, smoke houses, aluminum production plants,
- atmospheric contamination of leafy plants
- cigarette smoke
- charbroiled meat

Anthropogenic sources are the primary source of PAHs in atmospheric pollution (Grimmer, 1983). Activities like power generation, refuse burning, and coke production provide 50% of the annual benzo[a]pyrene (BaP) emissions, which are widely used as a standard of PAH emissions. The emissions of PAHs by vehicles are believed to be responsible for up to 35% of the total emission in highly populated urban areas of the United States (Dabestani and Ivanov, 1999). Diesel power is a source of lighter molecular weight PAH, while gasoline power is a major source of heavy molecular weight PAH (Juhasz and Naidu, 2000). Although most PAHs enter the environment via the atmosphere, sediment and soil is the primary environmental repository (Dabestani and Ivanov, 1999; Juhasz and Naidu, 2000).

Molecular weight, structure, water solubility, and ***vapor pressure*** of each PAH compound affects the potential for PAH transfer (i.e. volatilization, absorption, leaching and erosion) degradation (biological and chemical), and sequestration (adsorption and diffusion) (Jones et al., 1996; Pierzynski et al., 2000; Reid et al., 2000a). Understanding the fate of each PAH compound in the natural environment based on its specific characteristics is important in determining appropriate remediation techniques.

Molecular weight

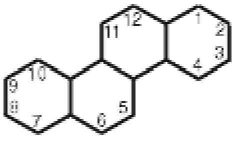
Polycyclic aromatic hydrocarbons are classified as *low molecular weight* (LMW) if they have two or three fused rings or *high molecular weight* (HMW) if they have four or more fused rings. LMW PAHs are degraded and volatilized more rapidly than HMW PAHs (Harvey, 1997). As molecular weight increases, hydrophobicity/lipophilicity increases, water solubility decreases, vapor pressure decreases, and the compound will have a more *recalcitrant* (difficult to degrade) structure. High molecular weight PAHs persist in the environment because of low volatility, resistance to leaching, and recalcitrant nature (Jones et al., 1996; Wild and Jones, 1995). Molecular weights of select PAHs are provided in Table 1.

Structure

Polycyclic aromatic hydrocarbons are also classified into two groups based on ring structure: alternant and nonalternant. Alternant PAHs such as anthracene, phenanthrene, and chrysene are derived from benzene by fusion of additional six-membered benzoid rings, and contain fewer than eight benzoid rings (Harvey, 1998). Nonalternant PAHs may contain rings with fewer than six carbon atoms in addition to six membered rings. This group is extremely broad in structure and greatly increases PAH diversity (Harvey, 1998). Examples of four-, five-, and six-membered rings are fluorine and fluoranthene (Harvey, 1997; Dabestani and Ivanov, 1999).

Notice the difference in the two structures of alternate and nonalternate PAHs in the below diagrams. Chrysene consists of four fused, six carbon benzene rings. Fluoranthene, on the other hand, contains naphthalene and a benzene unit connected by a five-membered ring (in the center of the structure) and is indicative of lower temperature and less efficient combustion. Information on number of rings for select PAH compounds are provided in Table 1.

Alternate (Chrysene)



Nonalternate (Fluoranthene)

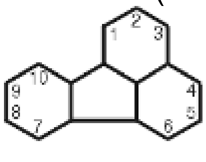


Table 1. US EPA's 16 priority pollutant PAHs and selected properties (adapted from Lundstedt, 2003; Bojes and Pope, 2007).

PAH name	**Number of rings**	**Molecular weight (g mole^{-1})**	**Solubility in water (mg L^{-1})**	**Vapor pressure (Pa)**	**Log K_{ow}**
Naphthalene	2	128.17	31	11.866	3.37
Acenaphthene	3	154.21	3.8	0.500	3.92
Acenaphthylene	3	152.2	16.1	3.866	4.00
Anthracene	3	178.23	0.045	3.40×10^{-3}	4.54
Phenanthrene	3	178.23	1.1	9.07×10^{-2}	4.57
Fluorene	3	166.22	1.9	0.432	4.18
Fluoranthene	4	202.26	0.26	1.08×10^{-3}	5.22
*Benz[a]anthracene**	4	228.29	0.011	2.05×10^{-5}	5.91
*Chrysene**	4	228.29	0.0015	1.04×10^{-6}	5.91
Pyrene	4	202.26	0.132	5.67×10^{-4}	5.18
*Benzo[a]pyrene**	5	252.32	0.0038	6.52×10^{-7}	5.91
*Benzo[b]fluoranthene**	5	252.32	0.0015	1.07×10^{-5}	5.80
*Benzo[k]fluoranthene**	5	252.32	0.0008	1.28×10^{-8}	6.00
*Dibenz[a,h]anthracene**	6	278.35	0.0005	2.80×10^{-9}	6.75
*Benzo[g,h,i]perylene**	6	276.34	0.00026	1.33×10^{-8}	6.50
*Indeno[1,2,3-cd]pyrene**	6	276.34	0.062	1.87×10^{-8}	6.50

*The U.S. EPA has classified PAH in italics as possible human carcinogens

Solubility

Solubility of PAH compounds in water is dependent upon temperature, pH, ionic strength (concentration of soluble salts), and other organic chemicals (i.e. dissolved organic carbon) (Pierzynski et al., 2000).

Solubility is estimated by:

- chemical structure
- octonol-water partition coefficients

Chemical structure: In general, as the number of benzene rings in a PAH compound increases, solubility decreases (Wilson and Jones, 1993). There are, of course, exceptions to the rule. Symmetry, planarity, and the presence of substituents affect PAH solubility in organic solvents. Solubility has been found to increase in linearly-fused PAH as the number of rings increase because the bonds become weaker (olifinic) in character, but has not observed in angularly-fused PAH (Harvey, 1997). Planar PAHs are less reactive (i.e. less soluble) and biologically less toxic (Dabestani and Ivanov, 1999). Substituted PAHs are those in which a functional group in the compound has been replaced with another functional group. For example, in a methyl-substituted PAH, one of the functional groups has been replaced by a univalent compound with the general formula CH_3^-.

Alternant PAH compounds that are planar and symmetrical require a relatively high energy of solubilization because of their ability to fit closely in a lattice. Thus, they tend to be less soluble (Harvey, 1997). As the compounds deviate from planarity or symmetry they tend to be more soluble in organic solvents. Methyl and polar substitution may also increase the solubility of PAHs in certain solvents (Harvey, 1997). Most byproducts of PAH biological and chemical degradation tend to be more polar and have higher solubility in the environment than the parent compounds.

Octanol-water partition coefficients: There are substantial amounts of data on the relationship between aqueous solubility and octonol-water partition coefficients (K_{ow}) for the partitioning of PAH between water and organic matter in soils (Mackay and Callcott, 1998). There is an inverse relationship between K_{ow} and solubility which is determined with the following equation:

$$K_{ow} = \frac{\text{amount of organic chemical in octanol (mg L}^{-1}\text{)}}{\text{amount of organic chemical in water (mg L}^{-1}\text{)}}$$

The octanol-water coefficient is often expressed as the log K_{ow}. Naphthalene has a log K_{ow} of 3.37, while Indeno[1,2,3-cd]pyrene K_{ow} is 6.50. In this case, naphthalene is more soluble than Indeno[1,2,3-cd]pyrene. This is also in agreement with the influence of chemical structure on solubility. Solubility and K_{ow} of select PAH are provided in Table 1.

Vapor pressure

Vapor pressure defines the point at which PAHs in the solid state either evaporate into a gaseous form or condense back to a solid state. The higher the vapor pressure (at normal temperatures), the more volatile the compound is. Naphthalene (11.866 Pa) and is more volatile and would readily evaporate more rapidly than dibenz[a,h]anthracene (2.80×10^{-9} Pa) at normal temperatures (Mackay and Callcott, 1998). Polycyclic aromatic hydrocarbon vapor pressures are important for determining risk associated with dredge sediments, transfer between two resources (soil and air) as well as field sampling and lab safety. Vapor pressures of select PAH are presented in Table 1.

Priority PAH

The U.S. EPA has placed 16 PAH compounds on the Priority Pollutant List created under the Clean Water Act (Table 1). Pollutants are chosen for this list because of potential for toxicity and frequency of occurrence in hazardous waste. Seven of these 16 PAHs are considered to be possible or probable carcinogens (ATSDR, 1995). Diagrams of molecular structures of these PAHs can be found in Figure 1.

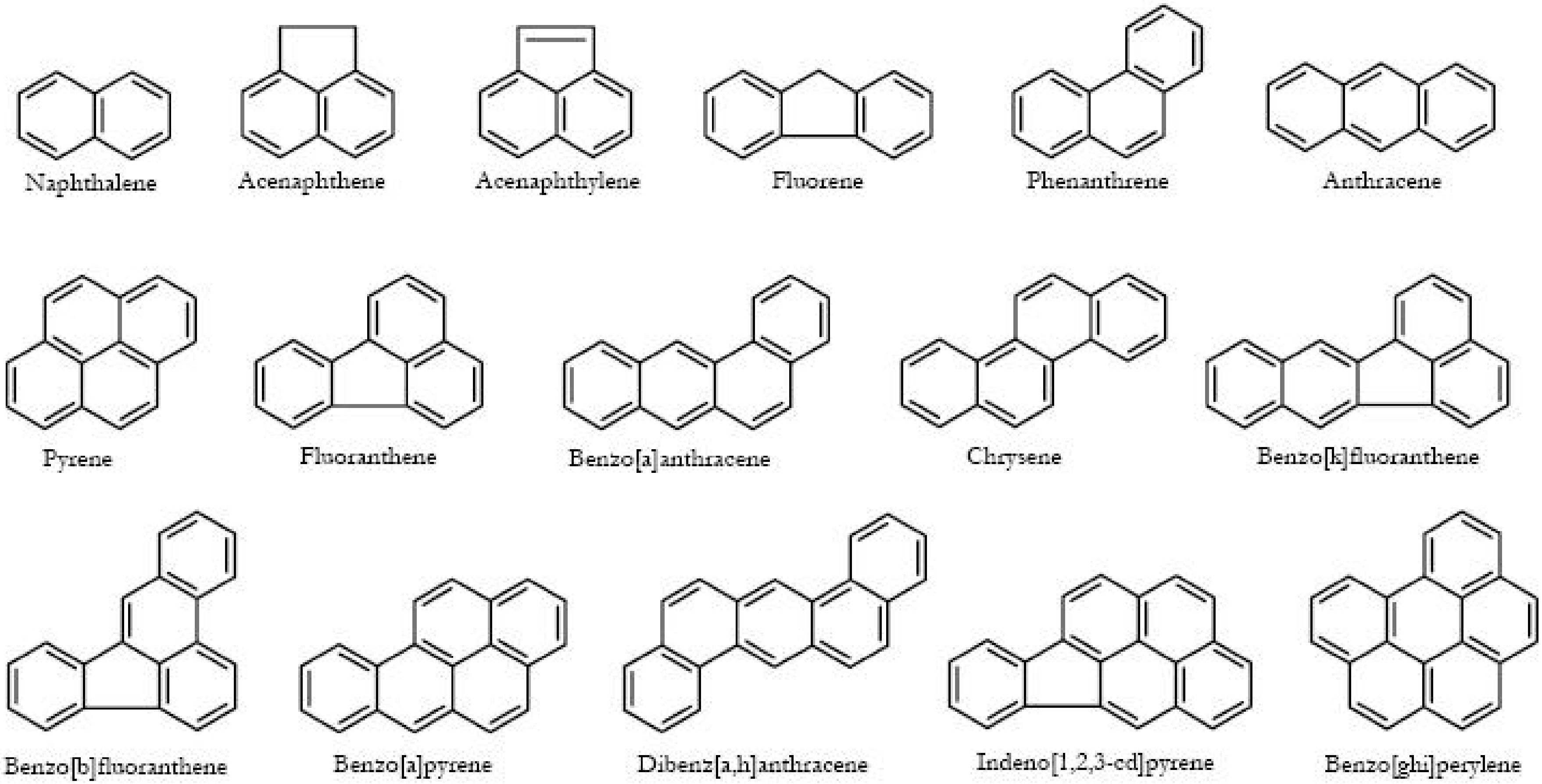


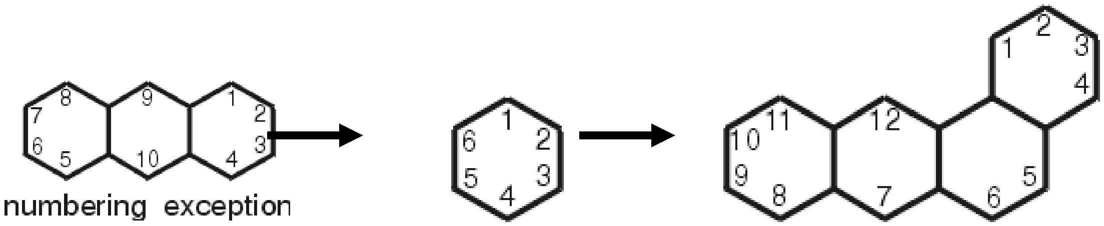
Figure 1. Structures of US EPA's 16 priority pollutant PAH (Lundstedt, 2003).

PAH nomenclature

Names given to PAH compounds are undoubtedly confusing, especially with discrepancies among European and American scientists, exceptions and old and new literature. In the International Union of Pure and Applied Chemistry (IUPAC) naming system (which will be used in this document), the following rules apply (Harvey, 1997; Dabestani and Ivanov, 1999):

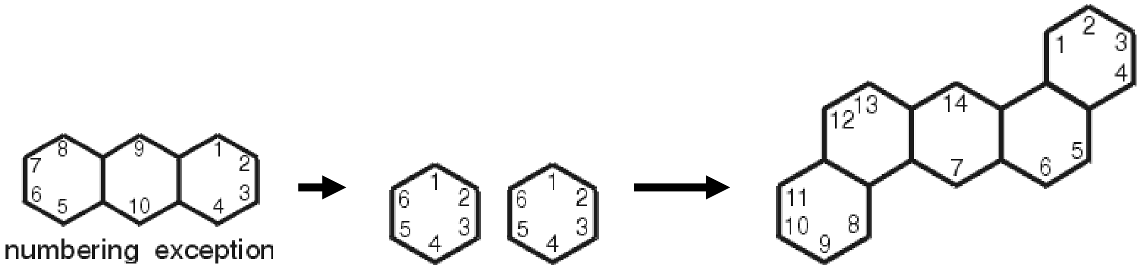
- Names of basic ring systems with a long history of use are retained by the IUPAC, such as chrysene and naphthalene.
- “-ene” indicates the compound is in an oxidized state and contains the maximum number of conjugated double bonds (represented by small lines inside the benzene ring). These are the “basic structures” referred to in the following text. Compounds ending in “-acene” are linearly fused and those ending in “-phene” angularly fused.
- More complex compounds are named based on prescribed hydrocarbons (such as anthracene, chrysene, naphthalene etc) which come before names of additional rings of the PAH. When naming a structure, try to pick out the largest “basic structure” in the compound and the simplest attachments (i.e. benzene rings). For example, the “basic structure” of benz[a]anthracene is anthracene. When you add an additional benzene ring to the structure on the 1-2 side (which is then called “a”; described in more detail on the next page) of the anthracene compound, this label is inserted in between the benz and anthracene in brackets as demonstrated below.

Anthracene + benzene ring = benz[a]anthracene



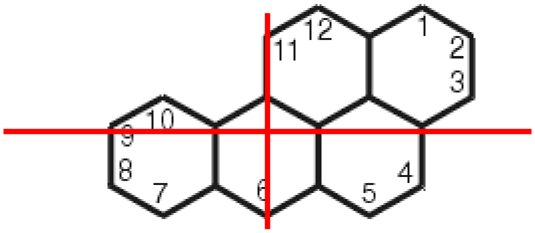
- If you were to add 2 benzene rings to the “basic component” (anthracene), the preface would become dibenz, and you would include the additional binding site; “h” in this case.

Anthracene + 2 benzene rings = Dibenz [a, h] anthracene



- Common abbreviated prefixes include: acenaphtho-, anthra-, benzo-, naphtho-, phenanthro-. The “o” is dropped when it prefaces another vowel, for example, benz[a]anthracene NOT benz**o**[a]anthracene.
- For more complex naming as seen in the above example, there is a numbering system for ring positions of the “basic component” (with the exception of phenanthrene and anthracene which maintain their historical numbering system). Once compounds are added to each other, the numbering system changes and “1” is assigned to the carbon atom in the most counterclockwise position, in the uppermost ring, farthest to the right. The numbering then proceeds in the clockwise direction and skips atoms at ring junctions.
- The spaces where numbers were not assigned are given “letters”.
- Orientation of the PAHs is also important. The PAH is orientated so that (a) the maximum number of rings are on the horizontal axis and (b) the maximum number of rings fall in the upper right quadrant (or the horizontal line formed by the “basic structure”).

Benzo[a]pyrene



PAHs in the Environment

Polycyclic aromatic hydrocarbons are widespread and found in air, water, terrestrial and biological systems (Cerniglia, 1992; Bjorseth et al., 1979; Gao and Zhou, 2004; Haeseler et al., 1999). Additionally, PAH compounds transfer between these resources, i.e. leaching of PAH from a soil resource into ground water, or transport of particulate soil PAH in the atmosphere (Figure 2). The following section describes contamination in atmosphere, water, sediment, soil and biological (plants and humans) systems and ranges of contamination found in each system.

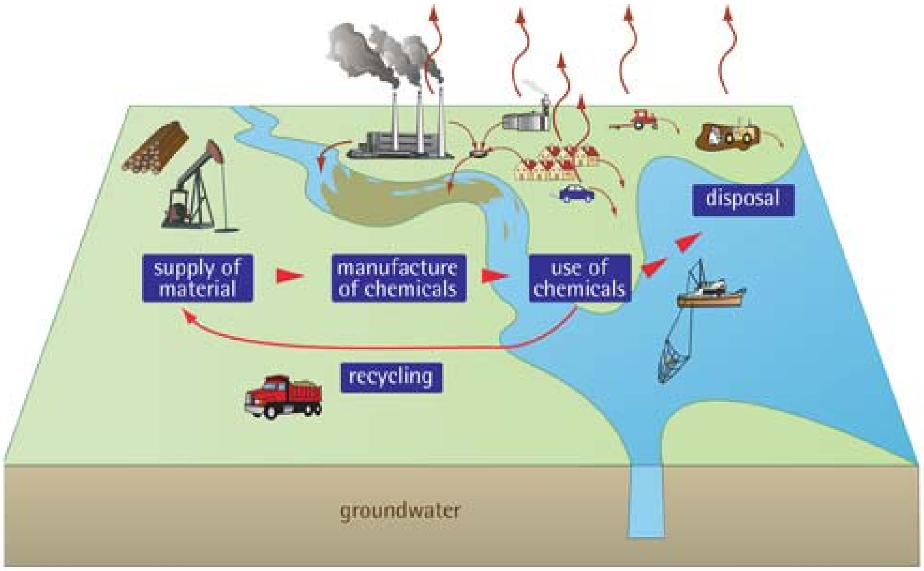


Figure 2. Diagram of the transfer of PAHs in the environment. Source: www.sepa.org.uk

PAHs in the atmosphere

Many PAH compounds enter water, sediment, soil and biological resources through the atmosphere. Wide ranges in atmospheric PAH concentrations have been measured, with the highest concentrations occurring in urban areas. Atmospheric PAH levels are usually higher in the winter because of combustion products from heating and reduced thermal- and photo-decomposition (Greenberg et al., 1985; Harvey, 1997; Juhasz and Naidu, 2000). In North America, PAH concentrations in the air range from 3.7-450 ng m^{-3}. Phenanthrene, fluoranthene and pyrene usually dominate the atmospheric PAH profile (Arey and Atkinson, 2003).

Nitrated PAH compounds are formed by the gas-phase reaction of PAHs with nitrous oxides in the atmosphere (Arey, 1998). Nitrated PAHs are found at lower concentrations than non-nitrated PAHs in the atmosphere (typically in the low ng g^{-1} range), but are of concern because of their persistence in the environment and their mutagenic and carcinogenic potential, which is generally higher than that of non-nitrated PAHs (Bamford et al., 2003).

Polycyclic aromatic hydrocarbon compounds in the atmosphere are either present in the gaseous phase or associated with particulates and tend to condense onto particles at temperature below 150° C temperatures (Schure and Natusch, 1982). At ambient temperatures, most atmospheric PAHs are in the particulate phase. The partitioning of PAHs into gas and particulate phases also depends on vapor pressure of the specific PAH (Wania and Mackay, 1996). At ambient air temperatures, 2- to 4-ring PAH and 2-ring nitrated PAH compounds are the predominant PAHs in the gas phase, while PAH compounds with 5 or more rings and 4-ring nitrated PAHs are associated with particulates (Arey and Atkinson, 2003). The fate of atmospheric PAHs is influenced by whether the PAHs are in the gaseous or particulate form. The residence time of small particles in the atmosphere can be one to two weeks, which would permit long range transport assuming there is no precipitation to cause wet deposition (Atkinson and Arey, 1994).

PAHs in water

The main sources of PAHs in water bodies are atmospheric particulate matter deposition, runoff of polluted ground sources and pollution of river and lakes by industrial effluents, municipal wastewater discharge, and oil spills (Latimer and Zheng, 2003; Dabestani and Ivanov, 1999). Since PAHs have low solubility and tend to adsorb to particulate matter, they are usually found in low concentrations in water bodies. Some PAH concentrations that have been measured in water include: marine waters with levels of non-detected to 11 µg L^{-1}, wastewater in North American and European municipalities with levels of <1 to 625 µg L^{-1} and urban runoff in the U.S. with levels of <0.05 to 560 µg L^{-1} (Latimer and Zheng, 2003).

PAHs in sediment

Polycyclic aromatic hydrocarbon compounds tend to accumulate in sediments rather than water (Meador et al., 1995; Juhasz and Naidu, 2000). Concentrations of PAH compounds in a particular sediment can range from µg kg^{-1} to g kg^{-1} levels depending on the proximity of the area to PAH sources such as industries, municipalities, and on water currents. In North America, total PAH concentrations in marine sediments usually range from 2.17-170,000 ng g^{-1} sediment (Latimer and Zheng, 2003). Sediment core studies have shown an increase in PAH concentrations in the past 100-150 years with concentrations peaking in 1950 (Meador et al., 1995). Polycyclic aromatic hydrocarbon profiles in sediments are usually dominated by the more hydrophobic 4-, 5-, and 6-ring compounds.

PAHs in soils

Accumulation of PAH soils without direct industrial contamination is believed to result mainly from atmospheric deposition after long-range transport (Greenberg et al., 1985). Forest fires and airborne pollution deposition are the main source of soil PAHs in remote areas. Soil levels of PAHs resulting from natural processes are estimated to be in the range of 1-10 µg kg^{-1} (Edwards, 1983). Jones et al. (1989a) reported a total PAH concentration of 0.1-55 mg kg^{-1} in Welsh soils that resulted strictly from atmospheric deposition with no direct industrial pollution.

Levels of PAHs in soils have increased in the past 100-150 years because of growing industrial activities. Polycyclic aromatic hydrocarbon concentrations in urban industrial soils can be 10-100 times higher than in remote soils (Wild and Jones, 1995). In soils at industrial sites, PAH concentrations and type of PAH found vary depending on the type of industry. For instance, Juhasz and Naidu (2000) in a review of the literature, reported total PAH concentrations of 5863 mg kg^{-1} at a creosote production site, 18,704 mg kg^{-1} at a wood preserving site, 821 mg kg^{-1} at a petrochemical site, and 451 mg kg^{-1} at a gas manufacturing plant site.

The major pathway of PAH loss in soil is degradation by microbial metabolism. The physical and chemical properties of the particular PAH compound being degraded will affect this process, as well as environmental factors such as soil temperature, moisture, pH, and oxygen concentration (Manilal and Alexander, 1991; Weissenfels et al., 1992). Sims and Overcash (1983) concluded that photolysis, hydrolysis and chemical oxidation processes did not contribute measurably to loss of PAHs from soil, but Wild and Jones (1993) reported some abiotic loss of LMW PAHs from soil by volatilization. Degradation by various mechanisms will be discussed in detail later.

PAHs in plants

Polycyclic aromatic hydrocarbons accumulate in vegetation mainly through atmospheric deposition on and uptake by above-ground parts of the plant. Concentrations of PAHs in plant tissue in nonindustrialized regions range from 50-80 µg kg^{-1} (Edwards, 1986), although specific plant tissue concentrations will depend on plant species, type of PAH, and environmental conditions (Salanitro et al., 1997). Vegetation in urban areas can have up to 10 times higher PAH levels than rural vegetation (Juhasz and Naidu, 2000). Sims and Overcash (1983) and Edwards (1986) found that PAHs can be adsorbed onto plant roots, but translocation to the above-ground parts was negligible because plants are unable to transport hydrophobic compounds such as PAHs in xylem.

PAH in humans

The carcinogenicity of PAHs was first discovered in the mid-1930's and gave way to new research on the influences of PAHs on human health and the environment. Data concerning human exposure and carcinogenicity of PAHs have been from occupational workers exposed to PAHs during coke production, roofing, oil refining and coal gasification (Wynder and Hoffman, 1967; Lloyd, 1971; Mazumdar et al., 1975; Hammond et al., 1976; Maclure and MacMahon, 1980). However, human exposure is not limited to inhalation, absorption or ingestion through working environments. Nearly every person is exposed to PAHs on a daily basis due to widespread atmospheric distribution.

As stated earlier, PAH concentrations are generally higher in the winter months as a result of fossil fuel combustion (Harvey, 1997), making human exposure during this time higher than in summer months. Particulate matter containing PAHs are a major contributor to accumulation of PAHs in urban areas. A study in Taiwan found human exposure through inhalation to be between 0.4 and 1.55 ng day^{-1} (Kuo et al., 2003). Menzie et al. (1992) found PAH levels to be 15-50 ng m^{-3} in urban areas. In addition to particulate matter, inhalation of cigarette smoke greatly increases human exposure to PAHs. Tobacco smoke contains more than 150 compounds in the gas phase and >2000 in the particulate phase (Harvey, 1997), making tobacco use the single greatest factor contributing to respiratory cancers. Humans are also exposed to PAHs through ingestion and absorption. Drinking water has been found to contain 1-10 ng PAH L^{-1} and high levels (10's of ng PAH kg^{-1}) have been found in leafy vegetables, grains, fats, oils, grilled and smoked meats (Menzie et al., 1992). It is suspected that humans inhale, ingest and absorb 1-5 ng PAH per day from food, 0.02-3.0 ng PAH per day from air, and 0.0002-0.12 ng PAH per day from water (Menzie et al., 1992).

PAH Bioavailability

Polycyclic aromatic hydrocarbon transport, degradation and sequestration in the environment are dependent upon the bioavailability of the PAHs. There is no universally accepted definition of bioavailability (Semple et al., 2004; Stokes et al., 2006; Harmsen, 2007); however, it is generally acknowledged to be related to the possibility of a substance to negatively or positively affect an organism (Pierzynski et al., 2000). Reliable estimates of PAH bioavailability are extremely important for understanding the adverse effects of PAH, but adequate tests to evaluate bioavailability in dredged sediments and contaminated soils are lacking. Total PAH levels, which are often used to determine remediation success, are not adequate as a measure of bioavailability (Talley et al., 2002, Harmsen, 2007) is discussed further in the *Analytical Methods* section*.*

PAH bioavailability is affected by (Stokes et al., 2006; Harmsen, 2007):

- physical properties of the specific PAH compound (LMW, HMW)
- soil characteristics (clay and organic matter content, structure)
- receptor organisms (bacteria, earthworms, arthropods etc)

First of all, HMW PAH compounds are more recalcitrant and less bioavailable in the environment than LMW (Cerniglia, 1992). Low molecular weight PAHs are removed faster by physicochemical and biological processes due to their higher solubility and volatility and the ability of different microorganisms to use them as a sole carbon source (Alexander, 1999). Bioavailability will change with time and weathering stage (Uyttebroek et al., 2007).

Soil properties like organic matter content, texture and aggregation also influence PAH bioavailability. In addition, heterogeneity of soil greatly influences PAH bioavailability (Eweis et al., 1998). Nam and Alexander (1998a) found declining PAH bioavailability to phenanthrene degraders with time in soils with >2% OM. Hundal et al. (2001) reported on the retention of large amounts of phenanthrene by smectite clays. Soil structure, such as aggregation has also been found to decrease PAH availability through physical protection of PAHs on the interior of aggregates (Wu and Gschwend, 1986). However, PAH availability is not always correlated to single or multiple soil properties such as organic matter content and/or clay content, making it hard to predict (Chung and Alexander, 2002). It is important, when looking at research, to consider the organic matter and clay percentages of the soil used in the experiment as well as pretreatment (i.e. sieving size) prior to the treatment additions.

Bioavailability also varies based on receptor organisms (Alexander, 1999). For example, in an environment dominated by microbial population “A”, a certain compound may be bioavailable and readily degraded; however, in that same environment with microbial population “B”, that same compound may not be bioavailable to that specific group of microorganisms and the compound will persist in the soil (Alexander, 1999). Interestingly, some microorganisms have evolved mechanisms to overcome decreased bioavailability in soils and sediments such as production of biosurfactants to increase contaminant solubility or adhesion to the surface of the contaminant making it more accessible to degradation (This is discussed further in the *Biological Techniques for Enhancing PAH Degradation* Section).

Consideration of PAH bioavailablity based on physical characteristics of the PAH compound, sediment/soil characteristics and receptor organisms is important in the remediation of dredge sediments. The composition of PAH compounds might change during dewatering, where some LMW PAHs volatilize and HMW persist, soption to organic matter and clays may occur as the sediments age and the microbial communities will undoubtedly change as the sediment shifts from anaerobic to aerobic. Thus an important question remains unanswered: do PAHs which are not currently bioavailable pose a threat with time to the environment or to humans?

PAH Transfer, Degradation and Sequestration

Polycyclic aromatic hydrocarbon compounds are transferred, degraded and sequestered in soils and sediments. Transfer is the process by which PAHs are relocated without altering their structure, degradation is the process where PAH structures are altered from their original form, and sequestration occurs when PAHs are removed from bioavailable pools and stored for long periods of time. The following section will expand upon processes presented in Table 2 and the relative rates of transfers from pools presented in Figure 3.

Table 2. Movement and fate of organic chemicals, such as PAHs, in the environment (adapted from Pierzynski et al., 2000).

Process	Consequence	Factors
Transfer ***(processes that relocate PAHs without altering their structure)***		
Volatilization	Loss of PAHs due to evaporation from soil, plant, or aquatic ecosystems	Vapor pressure, wind speed, temperature
Absorption	Uptake of PAHs by plant roots or animal ingestion. Polycyclic aromatic hydrocarbons usually do no transfer into aboveground biomass from soil.	Cell membrane transport, contact time, susceptibility, plant species
Leaching	Translocation of PAH either laterally or downward through soils	Water content, macropores, soil texture, clay and organic matter content, rainfall intensity, irrigation
Erosion	Movement of PAH by water or wind action	Rainfall, wind speed, size of clay and organic matter particles with adsorbed PAH on them
Degradation ***(processes that alter the PAH structure)***		
Biological	Degradation of PAHs by microorganisms, biodegradation and cometabolism	Environmental factors (pH, moisture, temperature, oxygen), nutrient status, organic matter content, PAH bioavailability, microbial community present, molecular weight of PAH (LMW or HMW)
Chemical	Alteration of PAHs by chemical processes such as photochemical (i.e. UV light) and oxidation-reduction reactions	High and low pH, structure of PAH, intensity and duration of sunlight, exposure to sunlight, and same factors as for microbial degradation
Sequestration ***(processes that relocate PAHs into long-term storage without altering structure)***		
Adsorption	Removal of PAHs from bioavailable pools through interaction with soils and sediments	Clay and organic matter content, clay type, moisture
Diffusion	Diffusion of PAH into soil micropores where it is unavailable for microbial degradation	Hydrophobic nature of micropores and PAH

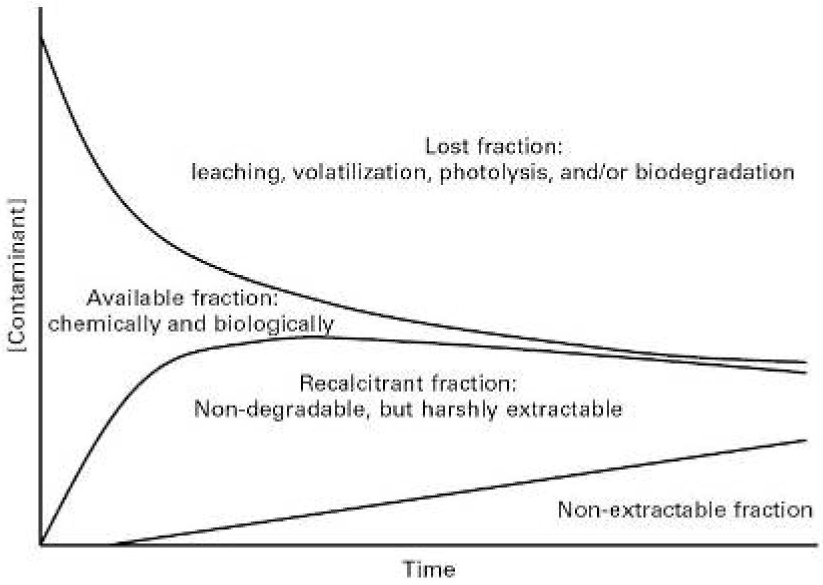


Figure 3. Relative PAH concentrations with time under the following processes: transfer (lost fraction), degradation (available fraction) and sequestration (recalcitrant fraction) (Stokes et al., 2006).

PAH Transfer

Polycyclic aromatic hydrocarbons are readily transferred among water, air, terrestrial and biological systems. The following processes will be discussed as PAH transfers *from* soil or sediments *to* air, water or biological systems.

Volatilization: This is an important transfer process of PAHs in both soil and water resources through diffusion and is expressed with Henry's Law. Henry's Law is based on that fact that when two phases are not in equilibrium, a concentration gradient forms and a net flux will occur from one phase to the other (Eweis et al., 1998).

Henry's Law:

$$m = HRT = \frac{C_G}{C_L} RT$$

Where, m is Henry's Law coefficient
H is the dimensionless Henry's Law coefficient
R is the universal gas constant
T is the temperature in Kelvins
C_G is the gas-phase contaminant concentration (g m^{-3})
C_L is the liquid-phase contaminant concentration (g m^{-3})

Henry's Law coefficient (*m*) is indicative of the tendency of a chemical to volatilize. If $m > 3 \times 10^{-7}$ atm-m^3 mol^{-1}, then the chemical is volatile, but if $m < 3 \times 10^{-7}$ atm-m^3 mol^{-1}, then volatilization is not an important transfer (Eweis et al., 1998). Because of the mixture of PAHs in contaminated soil and sediment, volatilization rates are essential for determining PAH persistence in soil and are dependent upon:

- intrinsic physiochemical properties of the PAHs (vapor pressure, solubility, structure)
- soil properties (moisture, porosity, organic matter and clay)
- environmental factors (temperature, humidity, wind speed)

Polycyclic aromatic hydrocarbon compounds have different vapor pressures (Table 1), as a result of solubility and PAH structure, and this causes variable rates of volatilization. In general, LMW PAHs have higher vapor pressures and are more soluble making them more likely to volatilize at room temperature (20˚C) than HMW PAHs (Stronguilo et al., 1994; Huesemann et al., 1995; Mackay and Callcott, 1998). Half lives are a way to express how long an organic chemical will persist in the environment under the effects of volatilization and degradation (it is difficult to separate the two processes). Two-ring PAHs (LMW) have half lives of days in the atmosphere, weeks in water, months in soils and a year in sediments, while three to four-ring PAHs have half lives about double the two-ring PAHs. Compounds with five or more rings have half lives of weeks in the atmosphere, months in water, and years in both sediments and soils (Mackay and Callcott, 1998).

Soil properties are also important to consider with volatilization. Soil moisture influences PAH volatilization through diffusion rates. At low soil moisture contents, diffusion decreases because of adsorption. Adsorption sites that would normally be occupied by water will accept PAHs when the soils are unsaturated (Hamaker, 1972). However, the solubility of the specific PAH needs to be considered along with soil moisture content. If the PAH is soluble, then it will diffuse less rapidly in wet soils than in dry soils (Hamaker, 1972). Soil porosity affects the path the gas takes from the soil to the atmosphere (also referred to as tortuosity). With variable pore size distribution, the twists and turns a gas must travel through to get from the soil to the atmosphere increases, meaning the tortuosity increases and the flux of the gas decreases (Hamaker, 1972). Organic matter and clays often reduce the ability of PAHs to volatilize through sorption, which decreases diffusion (Hamaker, 1972).

Vapor pressures controlling volatilization have been found to be dependent upon temperature, humidity and wind speed. Volatilization of PAHs from soil, atmospheric particles, water and vegetation increases with air temperature (Ausma et al., 2001; Sofuoglu et al., 2001). Lower molecular weight PAH volatilization is more dependent upon air temperature than the HMW PAHs, where 23-49% of the variability of acenaphthene and chrysene concentrations in the gas phase was attributed to temperature variations. High molecular weight PAH volatilization is less dependent upon temperature with only 1-6% of the variability in concentrations in the gas phase accounted for by temperature (Sofuoglu et al., 2001). Wind speed above the soil surface also contributes to PAH volatilization (Currado and Harrad, 2000; Sofuoglu et al., 2001).

There are two methods to measure trace gas emissions from soils. The first involves micrometeorlogical methods and the second, chamber operations (Ausma et al, 2001). Micrometeorlogical methods are nondestructive and result in continuous measurements (Ausma et al., 2001), where chamber operations can be destructive (Dupont and Reineman, 1986). Using micrometeorlogical methods, Ausma et al. (2001) found 131 µg C m^{-2} s^{-1} emission rates from landfarmed PAH contaminated soils. When oil-contaminated biosolids were applied in this same study, the flux increased to 185 µg C m^{-2} s^{-1} and with biosolid application to a separate treatment, the flux was only 17 µg C m^{-2} s^{-1}. These rates declined with time for all treatments, indicating that volatilization is an important transfer of PAHs in the early stages of remediation.

Absorption: Adsorption refers to the transfer of PAHs from contaminated soil onto plant roots and animal ingestion of contaminated soils, water or vegetation. Factors influencing absorption include:

- cell membrane transport
- contact time
- susceptibility
- plant species

Plants, humans and animals absorb PAHs daily as discussed in the *PAHs in the Environment* section. Polycyclic aromatic hydrocarbons absorbed by plant roots from soil usually accumulate on roots and do not transfer to aboveground biomass because the xylem is unable to move hydrophobic PAH compounds within the plant (Sims and Overcash, 1983; Edwards, 1986).

Leaching: Leaching refers to the transport of water soluble or colloidal PAHs laterally or downward through soils. The following factors need to be considered when addressing PAH leaching (Bedient et al., 1994):

- Soil water content
- Soil properties (macropores, texture, clay, organic matter)
- Rainfall intensity/irrigation

The above properties all influence the rate of saturated water flow in soils and sediments which is usually described by Darcy’s Law, which is a simple equation describing water flow through soils.

Darcy's Law:

$$q = -k\ (\Delta H / \Delta L)$$

Where:
q = volume of water flowing per unit time per area
k = hydraulic conductivity of the soil/sediment
$\Delta H / \Delta L$ = hydraulic gradient or the change in head per unit distance of water movement.

Hydraulic conductivity (k) is the most important component of Darcy's Law and affects the relative leaching of PAHs through soils because it is dependent up on soil moisture content and pore size distribution. The rate of water movement in unsaturated soils is very slow (< 1 cm/day) due to suction forces (negative potentials). However, once the soil becomes saturated, water flow rates can increase dramatically (Letey and Oddson, 1972) and are controlled principally by soil texture and structural development, particularly by the extent and interconnectivity of macropores. For example, coarse textured or well aggregated soils have large pores and higher saturated conductivity (Ksat) values. The hydraulic gradient ($\Delta H / \Delta L$) is basically the change in water head (or relative elevation) across or down the measured flow path. As dredge soils dewater, water flow (i.e. leaching) and PAH transfer rates will obviously change based on changes in Ksat, particularly as deep cracking and aggregation lead to the development of continuous vertical macropore.

Minimal leaching (33 µg total PAH) of freely dissolved PAHs was observed from a soil containing 2077 µg total PAH after two years of landfarming (Saison et al., 2004). Leaching of PAH compounds dissolved in water is likely a negligible transfer process (Stroo et al., 2000), but leaching of PAHs attached to colloidal organic matter is of concern (Jones et al., 1989b; McCarthy and Jimenez, 1985; Maxin and Kogel-Knabner, 1995). Therefore, leaching needs to be monitored in a field and greenhouse situation, especially when studying dredge sediments.

Erosion: Soil erosion is primarily affected by climate, topography, soil and land use cover (Toy et al., 2002). Transfer of PAH compounds specifically through erosion (both wind and water transport) is influenced by the following:

- Rainfall (amount and intensity)
- Wind speed
- Size of clay and organic matter particles with adsorbed PAH compounds
- Soil aggregation

As dredge sediments dewater, erosional processes increasingly influence the transfer of PAHs from the sediments. Erosion is the detachment, entrainment and transfer of soil particles (which may or may not have PAHs adsorbed). With increasing rainfall intensity or wind speed, soil particles are more likely to be detached and transported (Toy et al., 2002).

PAH Degradation

Degradation rates of PAHs vary depending on molecular weight and solubility of the PAH compound (Alexander, 1999). Polycyclic aromatic hydrocarbon compounds can be grouped into different degradation and sequestration fractions in both soil and sediments depending on their bioavailability. Brion and Pelletier (2005) suggested dividing them based on decreasing availability into the following phases:

- water-extractable phase (or easily degraded)
- slow molecular diffusion of PAHs into microsites (transition)
- sequestered residual phase which requires extraction with organic solvents

The ultimate goal of degradation is the complete mineralization of PAHs to CO_2, water, microbial carbon, and other inorganic compounds (Lundstedt, 2003). Unfortunately, degradation of PAHs may result in the accumulation of metabolites (mainly ketones, quinones, dicarboxylic acid anhydrides and coumarins) that can be more toxic and/or more soluble than the parent compound (Lundstedt, 2003). For example, fluoranthene degradation has been found to produce more soluble and potentially leachable metabolites (Vessigaud et al. 2007). Haeseler et al. (2001) showed enhanced, but incomplete, degradation of PAH compounds in a field study and noted a brief spike in leachate toxicity due to the accumulation of more soluble metabolites. However, after remediation was complete, final toxicity was negligible because the metabolites tended to be less stable and more soluble than the parent compounds, making them more available to degraders (Haeseler et al., 2001). Intermediates of PAH degradation are not always bioavailable and can also be incorporated into the humic fraction of soil, making them less available and less toxic (Kastner et al., 1999).

Biological: Microbial communities (including bacteria and fungi) can biologically degrade PAH compounds during direct microbial metabolism of carbon and energy sources or by cometabolism while consuming another substrate (Lundstedt et al., 2007). Biological degradation is highly dependent upon several abiotic soil factors, including (Eweis et al., 1998; Huesemann, 2004):

- nutrients
- pH
- metals
- temperature

- moisture
- salts

The amount of nutrients present and the state of the nutrients (organic, inorganic) is important for biodegradation. Addition of nutrients through fertilizers can enhance biodegradation. Soil pH also impacts microbial activity and can alter the community composition (i.e. fungal vs bacterial dominated). The ideal range for bacteria is generally between 6 and 8 while fungi dominate degradation at pH < 5.5 (Eweis et al., 1998). However, some species of bacteria such as sulfur-oxidizing bacteria are well adapted to acidic environments.

Soil pH also influences the mobility of nutrients and metals. For example, phosphorous solubility is maximized at pH 6.5 and metal mobility minimized at pH>6 (Sims et al., 1990). Availability of metals, which are toxic to some micoorganisms, can greatly reduce biodegradation of PAHs. Soil pH can be increased using lime and decreased with elemental sulfur or sulfur containing compounds (sulfuric acid, liquid ammonium polysulfide and aluminum and iron sulfates; Dupont et al., 1988).

The ideal soil temperature range for biodegradation is between 15 and 45˚C with maximum rates of biodegradation occurring from 25 to 35˚C (Sims et al., 1990). As a rule of thumb, with every 10˚C increase in temperature up to 45˚C, microbial activity and potential biodegradation of PAHs increases twofold (Eweis et al., 1998). Mulches (wood chips, compost, manure) can be used to control soil temperature. Moisture is also an important component for biodegradation. A major component of bacterial cells is water which also serves as the transport medium for PAHs in the soil. Most microbes function optimally when soil water is 50 to 75% of field capacity (Eweis et al., 1998). Salts, often present in dredge sediments, have a negative impact on microorganisms. With increasing levels of salinity, rates of hydrocarbon metabolism decrease (Ward and Brock, 1978). Excessive salts can be removed by leaching the soil.

The following topics of microbial degradation will be further addressed in this section:

- basics of biodegradation
- aerobic biodegradation
- anaerobic biodegradation
- cometabolism

Basics of biodegradation: Biodegradation is the transformation of organic compounds as a result of microbial activity and can be enhanced with specific management (discussed in the *Biological Techniques for Enhancing PAH Degradation* section). Since PAHs are widespread in the environment, their degraders can be found in both natural or contaminated sediments and soils. However, numbers of degraders and their degrading capacities are much higher in contaminated soils than uncontaminated soils (Carmichael and Pfaender, 1997).

Before discussing remediation techniques, it is important to identify the different microorganisms capable of degrading PAHs. Bacterial, fungal and algal species have been found to degrade PAH compounds, with bacteria constituting the most important group of degraders (Cerniglia et al., 1992; Kastner et al., 1994). Numerous bacteria genera and species can degrade 2- or 3-ring PAHs have been identified, but few genera have shown ability to degrade HMW PAHs (Table 3). However, some *Pseudomonas* species have been found to degrade 4-ring and 5-ring PAHs (Juhasz and Naidu, 2000).

Table 3. Some genera of PAH-degrading microorganisms (adapted from Frick et al., 1999).

Bacteria	**PAH compounds degraded**
Acidovorax	phenanthrene, anthracene
Alcaligenes	phenanthrene, fluorene, fluoranthene
Arthrobacter	benzene, naphthalene, phenanthrene
Mycobacterium	phenanthrene, pyrene, benzo[a]pyrene,
Pseudomonas	phenanthrene, fluoranthene, fluorene, benzo[a]pyrene
Rhodococcus	pyrene, benzo[a]pyrene
Sphingomonas	phenanthrene, fluoranthene, anthracene

The following studies are examples of biodegradation research:

- Liste and Felgentreu (2006) observed similar microbial species richness between a contaminated and pristine soil; however, PAH degraders (*Alcaligenes piechaudii*, *Pseudomonas putida*, and *Stenotrophomonas maltophilia*) were more abundant in the contaminated soil (1517 mg kg^{-1} total petroleum hydrocarbons; 71.4 mg kg^{-1} total PAHs) compared to pristine soil.

- Mueller et al. (1997) reported bacterial ability to degrade PAHs isolated from creosote-contaminated soils in the United States, Norway, and Germany. *Sphingomonas* strains showed the most ability to degrade 4- & 5-ring PAH.

- Kanaly and Harayama (2000) found that *Sphingomonas* species used compounds like fluoranthene and phenanthrene as a sole carbon source, while a *Mycobacterium* strain from PAH-contaminated freshwater sediments was capable of using phenanthrene, pyrene, and fluoranthene as sole carbon sources. Bacterial PAH degradation rates will be affected by environmental factors like temperature, moisture, and nutrient supply.

As stated earlier, biodegradability of PAHs slows as the number of rings increase (Alexander, 1999). High molecular weight PAHs are more recalcitrant because of their very low solubility, decreased bioavailability and high stability (Cerniglia, 1992; Wilson and Jones, 1993; Juhasz and Naidu, 2000). High molecular weight PAHs have a higher Log K_{ow} and tend to partition to solids. Low bioavailability of residual PAHs after initial rapid losses of LMW PAH compounds often limits further degradation (Erikkson et al., 2003).

In soil, PAH compounds generally undergo a two-phase loss process (Alexander, 2000; Reid et al., 2000a; Semple et al., 2004; Niqui-Arroyo and Ortega-Calvo, 2007):

- Rapid initial loss of LMW PAHs to degradation and transfer to the atmosphere through volatilization. This removes the more labile fraction and results in a HMW PAH-dominated profile.

- Slower loss as contact time increases (PAH aging).

For example, Uyttebroek et al. (2007) reported a biphasic loss upon spiking weathered contaminated soil with phenanthrene and pyrene. There was rapid degradation and volatilization of PAHs during the first 30 days, followed by slow but continuous degradation rates so that almost all the spiked amount was mineralized during the 140 day experimental period. For rapid biodegradation, PAH compounds must be in the aqueous phase where microorganisms can utilize them as a substrate (Ogram et al., 1985; Rijnaarts et al., 1990; Volkering et al., 1992; Bosma et al., 1997). Mass transfer through diffusion to the aqueous phase is the rate limiting step in biodegradation in soils because it often controls PAH availability to microorganisms (Volkering et al., 1992; Figure 4). Diffusion of PAHs into the aqueous phase can be modeled by Fick's First Law of Diffusion.

Fick's First Law of Diffusion:

$$Q/t = \frac{-DA(C_o-C_x)}{x}$$

Where:
Q = quantity of substrate (mol)
A = area (m^2)
t = time (seconds)
(C_o-C_x) = concentration gradient, Co is the concentration at the source (mol m^{-3}) and Cx is the concentration at the sink (mol m^{-3})
x = diffusion path length (m), distance between source and sink
D = diffusion coefficient (m^2 s^{-1}) for resistance of environment to diffusion

Ideal biodegradation of PAHs, where they are the sole bioavailable carbon source, can be broken into three distinct phases based on diffusion of PAH into the aqueous phase as shown in Figure 4 (Johnsen et al., 2005):

I. Exponential growth phase
II. Pseudo-linear growth as the dissolved PAH concentrations stabilize but microbial biomass still increases linearly
III. Pseudo-stationary phase where biomass, PAH dissolution and concentrations all stabilize

This ideal situation is somewhat complicated in soil because of adsorption of PAH to organic matter and diffusion into small pores (both mechanisms of PAH sequestration). It is suspected that microbial communities in soils remain in Phase III (pseudo-stationary) as a result of the rate limiting diffusion of PAHs into the aqueous phase (Johnsen et al., 2005). Transfer to the aqueous phase is especially important for HMW hydrophobic compounds with low aqueous solubility which tend to partition to the solid phase (especially organic matter) in soils and sediments.

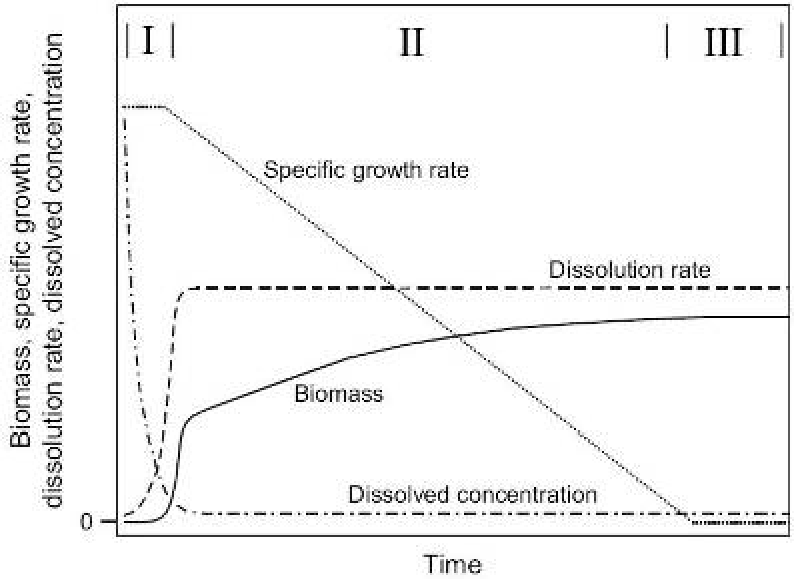


Figure 4. Schematic diagram for microbial biomass, specific microbial growth rate, PAH dissolution rate and dissolved PAH concentration of bacterial batch grown on solid PAHs (Johnsen et al., 2005).

Aerobic biodegradation: Aerobic PAH biodegradation is well studied and widespread in soil due to the presence of large numbers of aerobic degraders (Pothuluri and Cerniglia, 1994; Shuttleworth and Cerniglia, 1995; Sutherland et al., 1995; Juhasz and Naidu, 2000; Kanaly and Harayama, 2000). Bacteria and fungi degrade PAHs through different pathways shown in Figure 5.

During aerobic degradation by bacteria, PAHs are oxidized to cis-dihydrodiols through incorporation of an oxygen molecule into the PAH. The cis-dihydrodiols are further oxidized to aromatic dihydroxy compounds (catechols) and then PAH rings are cleaved with intracellular dioxygenases (Cerniglia, 1984; Alexander, 1999; Johnsen et al., 2005). Oxidation of unsubstituted PAHs with very high thermodynamic stability, often results in PAH compounds that are less stable than the parent compounds and more susceptible to cleavage (Volkering and Breure, 2003). Oxygenase production by bacteria can be increased using biostimulants: for example, salicylic acid is a known inducer of naphthalene dioxygenase. Yi and Crowley (2007) found that linoleic acid is a powerful stimulant of pyrene and benzo[a]pyrene degradation by gram positive bacteria. The addition of humic substances also greatly enhances microbial degradation of PAHs (Holman et al., 2002; Bogan and Sullivan, 2003).

White rot fungi have also been shown to oxidize some PAHs (i.e. anthracene, fluoranthene, and benzo[a]pyrene) through destabilizing the rings using non-specific enzymes, lignin peroxidase and Mn-dependent peroxide enzymes. These enzymes produce highly reactive intermediates which are then oxidized to produce quinones (Cerniglia et al., 1992; Juhasz and Naidu, 2000). Cytochrome P450, an enzyme found in almost all life forms, uses PAHs as a substrate for a monooxygenase reaction where oxygen is inserted into the benzene ring during biodegradation by white-rot fungi. The accumulation of fungal degradation byproducts of some PAHs, like benzo[a]pyrene, is of concern since monooxygenase oxidizes these PAHs to diol epoxides and trans dihydrodiols (the active molecules implicated with the carcinogenicity of PAHs). For instance, Cerniglia and Gibson (1980) found that fungal transformation of Benzo[a]pyrene produced Benzo[a]pyrene 7,8-diol-9,10-epoxides, which are the carcinogenic form of Benzo[a]pyrene in higher organisms. This occurred within 12 hours during an incubation experiment. Though this transformation has been documented, researchers are still unsure of what happens to the metabolites in a soil environment.

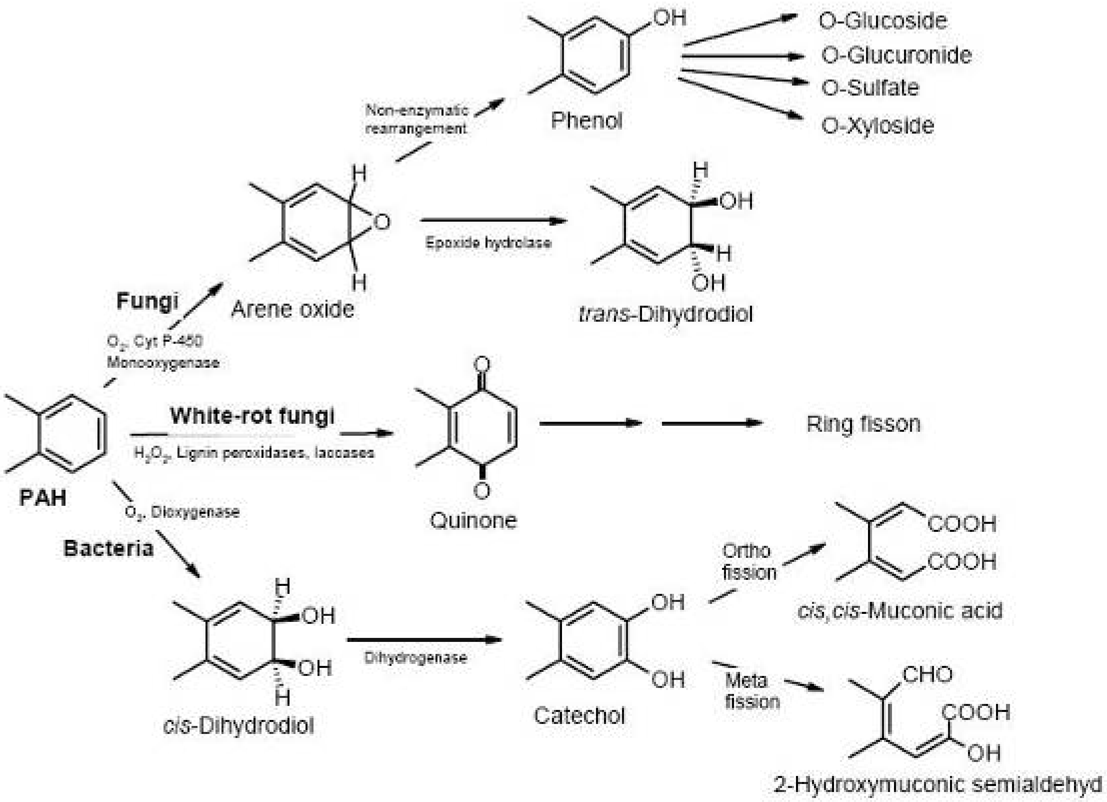


Figure 5. Aerobic degradation of PAH by general fungi, white-rot fungi and bacteria (Cerniglia, 1992).

Complete mineralization is common for LMW PAHs; however, partial degradation and transformation of PAHs to metabolites also occurs and leads to an accumulation of byproducts (Cerniglia, 1992). Ketones and quinones are common products of aerobic degradation (Lee and Hosomi, 2001; Kochany and Maguire, 1994; Mallakin et al., 1999), and hydroxylated polycyclic aromatic acids result from the partial degradation and/or transformation of some HMW PAHs (Kelley et al., 1993; Roper and Pfaender, 2001) (Table 4).

Table 4. Products of biodegradation (Alexander, 1999).

Substrate	**Products**	**Reference**
Acenaphthylene	1,8-Napthylenedicarboxylic acid	Komatsu et al. (1993)
Anthracene	3-Hydroxy-2-naphthoic acid	Rogoff and Wender (1957)
Fluorene	Phthalic acid	Grifoll et al. (1994)
Naphthalene	2-Hydroxybenzoic acid	Liu et al. (1992)
Phenanthrene	1-Hydroxy-2-naphthoic acid	MacGillivray and Shiaris (1994)

Anaerobic biodegradation: Anaerobic biodegradation of PAHs is not as well-documented as aerobic biodegradation. Polycyclic aromatic hydrocarbon compounds often persist or undergo slow degradation in anaerobic conditions (Alexander, 1999). Complete mineralization of PAHs usually involves three or more species of microorganisms in anaerobic conditions, where in aerobic sediments, only one species of microorganism is often necessary (Alexander, 1999). Abundance of electron acceptors in anaerobic conditions is usually the limiting factor for degradation (Alexander, 1999); however, transformation of 2- and 3-ring PAH compounds under methanogenic, iron-reducing and sulfate-reducing conditions have been reported (Volkering and Breure, 2003). The following are examples of PAH research conducted under anaerobic conditions:

- Coates et al. (1997) demonstrated that a number of PAHs can be degraded under sulfate-reducing conditions in contaminated sediments from San Diego Bay area. They reported mineralization of naphthalene, phenanthrene, methylnaphthalene, fluorene, and fluoranthene under sulfate-reducing conditions, but not pyrene or benzo[a]pyrene. Inoculating a less contaminated site where PAHs were not readily degraded with active PAH-degrading sediment from the San Diego Bay site stimulated naphthalene degradation in the less contaminated site.

- Johnson and Ghosh (1998) evaluated the feasibility of anaerobic biodegradation of PAHs in dredged river sediments from Jones Island, Wisconsin. In a bioslurry experiment, they reported a loss in PAHs without any additional treatment. This was attributed to the presence of high sulfate reducing bacteria in the sediments. When nitrate was added, there were no additional reductions in PAH levels.

Cometabolism: Cometabolism is the process by which microorganisms transform organic compounds simultaneously despite their ability to use only one of the substrates for energy or nutrition (Alexander, 1999). Organic byproducts of cometabolism are not incorporated into the degraders' cells as carbon and remain in the soil matrix for possible utilization by another microbial group or merely persist and accumulate. Polycyclic aromatic hydrocarbon compounds are cometabolized when the nonspecificity of microbial dioxygenase enzymes leads to the metabolism of a different PAH besides the ones used as a carbon source. For example, a microorganism may be utilizing naphthalene (which is easily degraded) or just simple organic matter as an energy or carbon source and, at the same time, degrading benzo[a]pyrene into other organic substrates or metabolites which then accumulate in the soil.

Cometabolism is explained by three basic reasons (Alexander, 1999):

- Initial microbial enzymes are used to convert a substrate into an organic product which is not further transformed by other enzymes specific to that microorganism. No metabolic intermediates used for biosynthesis or energy production are produced in this scenario and accumulation occurs.
- Initial substrate is transformed into enzyme inhibiting or growth suppressing organic products.
- An additional substrate that is not available at the time of the reaction is needed by the microorganism to complete the degradation of both substrates.

In the first part of the cometabolism degradation reaction, the following equation can be used to represent substrates (A, B, C, D) and enzymes (a, b, c, d):

$$A \xrightarrow{a} B \xrightarrow{b} C \xrightarrow{c} D \rightarrow\rightarrow\rightarrow\rightarrow CO_2 + \text{energy} + \text{cell-carbon}$$

Enzyme “a” might have low substrate specificity and can act on A or on the product of A (or A’). The product of B (or B’) might differ in the same way that A and A’ differ, but enzyme “b” has higher substrate specificity and cannot degrade B’. So, B’ would accumulate as represented by the following equation:

$$A' \xrightarrow{a} B' \not\!\nrightarrow$$

The substrate of these cometabolic reactions persists in the soil and is not mineralized into CO_2, microbial energy and cell-carbon. In the case of PAHs, the product of naphthalene (A’) may continue to be degraded, but the product of Benzo[a]pyrene (B’), or metabolite, may not be further degraded and accumulate in the soils. Though Benzo[a]pyrene may be degraded as mentioned earlier, the problem with this situation is that metabolites can be more carcinogenic than the initial substrate (Alexander, 1999).

Scientifically supported degradation of HMW PAHs in the presence of LMW PAHs is discussed or reviewed in the following literature:

- Juhasz and Naidu (2000) reviewed several studies where the presence of LMW PAHs enhanced the degradation of benzo[a]pyrene through co-metabolism.

- Hwang and Cutright (2002) reported enhancement of pyrene degradation through cometabolism with the addition of phenanthrene.

- The presence of naphthalene was found to enhance *Pseudomonas* degradation of pyrene and phenanthrene in pure cultures, but phenanthrene inhibited pyrene degradation by the same bacteria (McNally et al., 1999).

- Rodrıguez and Bishop (2005) studied biodegradation of naphthalene, phenanthrene, and pyrene as sole substrate or in combination in biofilm (a porous media system inoculated with enrichment culture from an activated sludge aeration tank). They found phenanthrene and pyrene could not be used as sole substrates in the system. Co-substrate or degradation intermediates from a more soluble and easily degradable compound such as acetate or naphthalene were needed for biodegradation of 3-ring and 4-ring rings to occur. The presence of naphthalene and acetate supplements stimulated the degradation of pyrene or phenanthrene with a noticeable increase in removal efficiency. Additionally, the presence of phenanthrene inhibited pyrene, possibly because the competition for the common enzymes in the system led to the inhibition of HMW PAHs.

- Beckles et al. (1998) reported the co-metabolism of fluoranthene by bacteria growing on naphthalene.

Cometabolism is considered just another type of microbial transformation (Alexander, 1999). There are two constants in the cometabolism process: (1) accumulation rates of metabolic products are consistent as the microbes are not utilizing the substrates as a carbon or energy source, and (2) accumulation of secondary products is evident (Alexander, 1999). In an ideal situation, microorganisms capable of breaking down secondary products are present in soils and completely mineralize the material into CO_2 and biomass (Lundstedt, 2003).

Nonbiological degradation: Degradation of PAHs by nonbiological pathways occurs via oxidation reactions in the same way that the microbially mediated enzymatic reactions occur. Three known nonbiological pathways of PAH degradation are: (1) direct photooxidation, (2) radical oxidation reactions, and (3) oxidation reactions initiated by atoms of high oxidation state (e.g. Mn^{7+}). Thermal decomposition is also a nonbiological degradation pathway but will not be covered in this section. The resulting products of chemical degradation may or may not be more biologically inert or toxic than the parent compound (Dabestani and Ivanov, 1999).

Oxidative degradation: Oxidation is the removal of one or more electrons from a molecule and the subsequent reduction, or addition of the electron(s), to the oxidizer. Redox potential measures the tendency of a substance to accept or donate electrons. The redox potential is positive or high in strongly oxidizing systems and negative or low in strongly reducing systems. Some of the common redox potentials encountered in environmental conditions are presented in Table 5 (Essington, 2004; Bohn et al., 1985):

Table 5. Reduction reactions and redox potential for general environmental conditions.

Reduction Reactions	Measured Redox Potential (V)
$O_2 \rightarrow H_2O$	0.6 – 0.4
$NO_3 \rightarrow NO^{2-}$	0.5 – 0.2
$MnO_2 \rightarrow Mn^{2+}$	0.4 – 0.2
$FeOOH \rightarrow Fe^{2+}$	0.3 – 0.1
$SO_4 \rightarrow HS^-$	0.0 – $^-$0.15
$2H+ \rightarrow H_2$	$^-$0.15 – $^-$0.22
$R \rightarrow CH_4$	$^-$0.15 – $^-$0.22

In general, for a species to become oxidized, an electron from another species possessing a higher oxidation state needs to be transferred. Polycyclic aromatic hydrocarbons have high oxidation states (see Table 6) due to their unique chemistry previously described. For reference, stable humic acids found in soils have oxidation potentials near 0.3 – 0.4 V (Stevenson, 1994). Few non-enzymatic naturally occurring molecules have oxidation potentials that exceed the oxidation potential of PAHs. The most common class of reactants which possess oxidation potentials exceeding those of the PAHs is free radicals. Free radicals contain an unpaired electron, creating a species having a very high affinity for electrons (Silberberg, 2006). This leads to very reactive, non-specific oxidizers, capable of attacking benzene rings. (Ferrarese et al., 2008).

Table 6. Oxidation potentials for select PAHs (Dabestani and Ivanov, 1999).

Compound	Oxidation Potential
	$(E^{ox}_{1/2})$
Acenaphthene	1.21
Acenaphthylene	1.21
Anthracene	1.09
Benz[a]anthracene	1.18
Benzo[a]pyrene	0.94
Benzo[ghi]perylene	1.01
Chrysene	1.35
Dibenz[ah]anthracene	1.26
Fluoranthene	1.45
Naphthalene	1.54
Phenanthrene	1.50
Pyrene	1.16

There are many molecules which can become free radicals and several pathways exist for their presence in natural ecosystems. The most common and reactive group of free radicals is that of the oxides (Figure 6) and nitrates ($NO_3^{\bullet}$), both of which are readily created in the troposphere by absorption of sunlight radiation (λ =290-335nm) (Arey and Atkinson, 2003). Nonbiological radical oxidation is most important for volatile PAHs or particle associated PAHs in the atmosphere because of the low concentration of free radicals in sediments and their very quick reaction time (less than 1 second) time in aqueous systems.

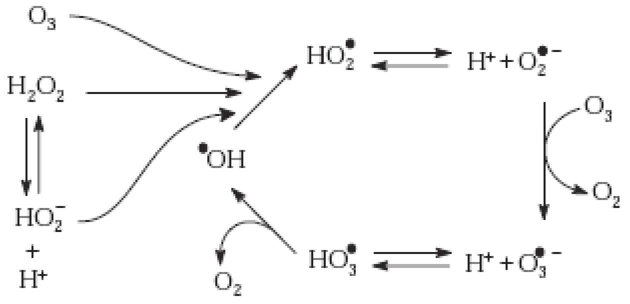


Figure 6. Common ozone reactions that occur in the atmosphere (Miller and Olejnik, 2004)

Nonbiological oxidation reactions induced for the purposes of PAH degradation have been accomplished by the following advanced oxidation processes (Rivas, 2006; Alderman et al., 2007; Isosaari et al., 2007; Ferrarese et al., 2008):

1. Fenton's reagent – formation of hydroxyl radical (to be discussed in more detail in *Chemical Techniques for Enhancing PAH Degradation)*

   $H_2O_2 + Fe^{2+} \rightarrow {}^{\bullet}OH + OH^{-} + Fe^{3+}$

2. Ozone – formation of hydroxyl radical or direct oxidation by ozone radical (to be discussed in more detail in *Chemical Techniques for Enhancing PAH Degradation)*

   $O_3 \rightarrow HO_2^{-} \rightarrow {}^{\bullet}OH$
   $O_3 + O_2^{\bullet -} \rightarrow O^{\bullet 3-}$

3. Sodium persulfate – formation of persulfate anions (standard oxidation potential of 2.0V); additions of metals can subsequently create sulfate radicals (standard oxidation potential of 2.6V)

   $Na_2S_2O_8 \rightarrow S_2O_8^{-} + 2Na^{+}$
   $S_2O_8^{-} + Fe^{2+} \rightarrow 2SO_4^{\bullet -} + Fe^{3+}$

The mechanism by which free radicals attack PAHs is similar for all free radicals and works by the following examples of hydroxyl radical oxidation with reaction 1 usually initiating ring cleavage (Ferrarese et al., 2008; Flotron et al., 2005):

1) $R + {}^{\bullet}OH \rightarrow {}^{\bullet}ROH$ (hydroxyl addition)
2) $ROH + {}^{\bullet}OH \rightarrow {}^{\bullet}R + H2O$ (hydrogen abstraction)

In recent investigations the use of potassium permanganate ($KMnO_4$) has also shown some success. The reaction proceeds without the formation of a radical species. The reaction occurs due to the high oxidation state (+7) of the manganese atom in the permanganate salt.

$$MnO_4^{-} + 4H^{+} + 3e^{-} \rightarrow MnO_2(s) + 2H_2O$$

Although permanganate is a strong oxidant, with a standard oxidation potential of 1.7V, it lacks the ability to attack the benzene ring. The inability to attack the benzene ring has limited the use of potassium permanganate in PAH degradation (Ferrarese et al., 2008).

In complex soil mixtures, the use of advanced oxidation processes can become complicated by soil organic matter, which has the ability to scavenge non-selective oxidants as well as sequester PAHs into hydrophobic pores. To overcome PAH solubility issues, previous investigations have increased oxidant concentrations. Care must be taken when using this approach; however, as over application of the oxidant can cause self consumption of the radical species (Ferrarese et al., 2008). Other investigations have sought to overcome low PAH solubility with the additions of: surfactants, sub/supercritical water extraction and electrokinetics (Rivas 2006; Isosaari et al., 2007).

Electrokinetic degradation: Use of electrokinetics for PAH remediation is often integrated as an assist in nonbiological or biological oxidation steps. Electrokinetic remediation is the process of inducing an electric current through a body of contaminated sediment. The technology works by placing a series of wells coupled with electrodes around the zone of contamination; connection of the electrodes to a power supply creates cathodic and anodic zones. Inside of this energized zone the cations in the soil solution (electrolyte solution), located beyond the shear zone of soil particles diffuse double layer, begin to flow towards the cathodic zone in a process called electroosmosis or electroosmotic flow. The movement of the electrolytic solution drags uncharged molecules, such as PAHs, into the flow where they can be removed via the wells and treated at wastewater facilities (Figure 7). The charge induced during electroosmosis also increases the dispersion and formation of radical species during treatments utilizing chemical oxidants (i.e. H_2O_2, $Na_2S_2O_8$), leading many researchers to suggest that electrokinetic remediation be integrated with other treatment techniques. Some advantages and disadvantages of electrokinetic degradation are listed below:

Advantages:

- if integrated with chemical oxidants, electrokinetics have the potential to limit the effects of untreated zones
- works well in sediments of high clay or organic matter that have small capillary pores
- is an effective in-situ remediation strategy for saturated sediments

Disadvantages:

- high ionic strengths collapse the diffuse double layer and reduce the area prone to electroosmotic flow
- low ionic strengths cease electroosmotic flow by removal of the charged particles that facilitate flow
- the contaminated zone must be saturated for electroosmosis to occur, which poses PAH leaching hazards
- electroosmosis will not occur in compacted sediments with overlapping diffuse double layers

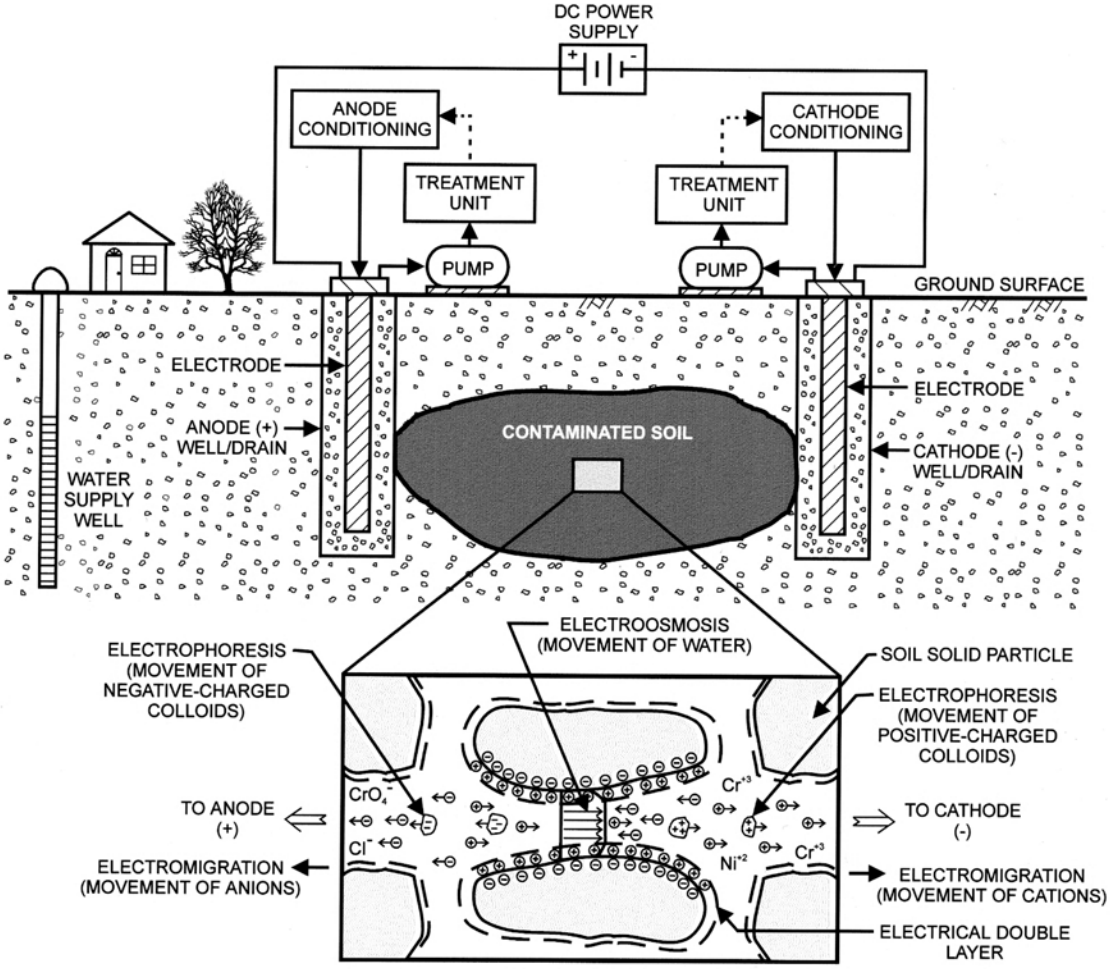


Figure 7. Schematic of integrated electrokinetic technique (Saichek and Reddy 2005)

Photochemical degradation: Photochemical degradation or photooxidation involving sunlight is an important process for surface and atmospheric degradation of PAHs (Harvey, 1998; Pierzynski et al., 2000). During direct photooxidation the PAH, is directly oxidized after the absorption of sunlight radiation by the PAH. The PAHs must absorb radiation above 290-335 nm (below this level ozone absorbs solar radiation) for photooxidation to occur (Table 7). Chemical transformation rates during direct photooxidation depend upon sunlight intensity, and overlapping spectral characteristics of solar radiation and the PAHs.

Table 7. Range of adsorption spectra for selected PAHs (Dabestani and Ivanov, 1999).

Compound	Adsorption Spectra Range (λ)
Acenaphthene	227 – 320
Anthracene	221 – 374
Benz[a]anthracene	222 – 342
Benzo[a]pyrene	221 – 347
Benzo[b]fluoranthene	223 – 342
Benzo[ghi]perylene	210 – 363
Benzo[k]fluoranthene	216 - 352.5
Chrysene	218 – 344
Dibenz[ah]anthracene	217 - 321.5
Fluoranthene	236 – 359
Fluorene	219 – 299
Indeno[1,2,3-cd]pyrene	210 – 386
Naphthacene	273 – 470
Naphthalene	220.5 - 310.5
Phenanthrene	213 – 330
Pyrene	232 - 351.5

Indirect photooxidation occurs when other substances (clay, organic matter, and inorganics) absorb sunlight energy and transmit the energy to the PAHs through electron orbital interactions (Pierzynski et al., 2000). Sunlight intensity and subsequent photooxidation are expected to be greatest during the summer months and in locations with less water vapor interference.

The mechanism by which photooxidation actually degrades PAHs is still unclear, but likely involves a process similar to that shown in Figure 8. The electron delocalization of the PAH in the atmospheric oxygen seems to be essential since many studies show that direct oxidation in anaerobic environments is limited (Vione et al., 2006). Interestingly, research also suggests that the rate of degradation for HMW PAH is higher than LMW PAH during photooxidation which is opposite that of all other known forms of PAH degradation (Guieysse et al., 2004).

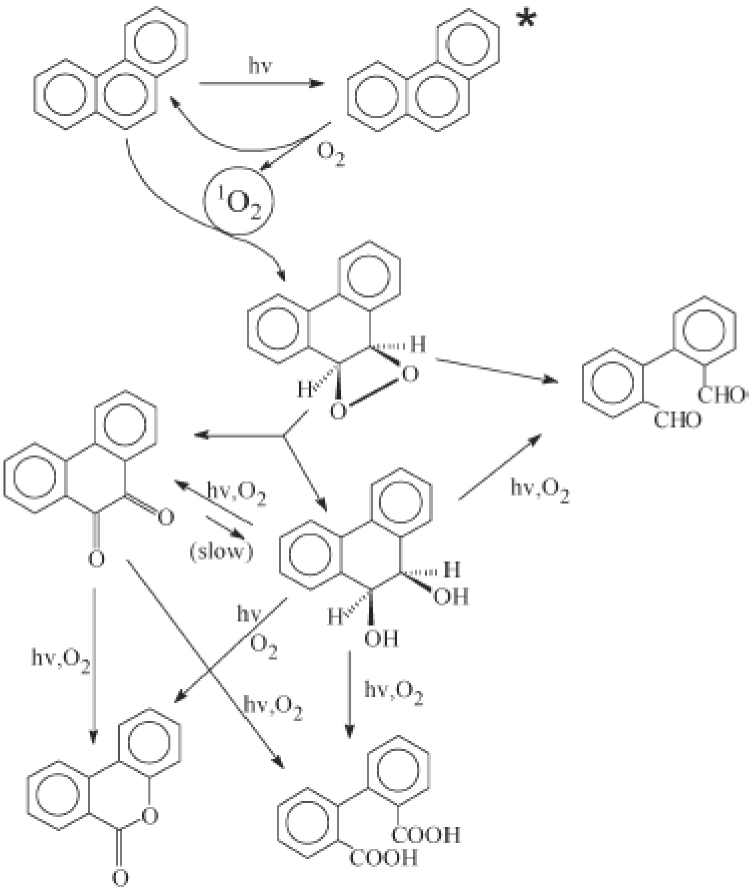


Figure 8. Possible mechanism for direct photooxidation of PAHs (Vione et al., 2006)

As mentioned previously PAHs are hydrophobic and therefore tend to be found in PAH-particle associations. The rate of photooxidation is dependent upon the nature of the particle associated with the PAH. Research has found that PAH-black carbon associations have much longer half lives than do PAH-dissolved organic matter. The changes to photooxidation rates are most likely the result of particle color and therefore the quantity of wavelengths that the material can absorb. Black carbonaceous materials tend to absorb the wavelengths that may have photooxidized the associated PAH. Research conducted on PAH-particle associations with white materials such as silica and alumina support this conclusion and have resulted in higher rates of photooxidation (Vione et al., 2006).

PAH Sequestration (Aging)

The most recalcitrant PAH fraction consists of residual PAHs in soil or sediments and seems to increase with aging or soil-PAH contact time (Hatzinger and Alexander, 1995; Semple et al., 2003). Even distribution of two- to six-ringed PAHs in a soil sample may indicate a “young” PAH profile, since environmental processes such as natural degradation and evaporation are known to cause a reduction in the concentrations of LMW PAHs. A higher proportion of HWM PAHs generally indicates that there has been more aging in the contaminated soils or sediments (Haeseler et al., 1999; Braida et al., 2001).

Polycyclic aromatic hydrocarbon aging can be summarized as a combination of the following two processes (Chiou et al., 1979; Steinberg et al., 1987; Vessigaud et al., 2007):

- Adsorption to soil organic matter and black carbon
- Diffusion into three dimensional micropores of soil particles or residual charcoal in the soil matrix

Although sequestration of PAHs is primarily controlled by soil organic matter (Bogen and Sullivan, 2003), this is not the sole factor governing PAH sequestration. Intra-aggregate diffusion of PAHs protects them from microbial degradation or solvent extraction by local sorption on hydrophobic pore walls or by entrapment in voids due to constricted geometry (Pignatello and Xing, 1996; Nam and Alexander, 1998a). With time, PAHs will adsorb to soil components and diffuse to be trapped in soil micropores (Semple et al., 2003), which will limit bioavailability. Microbial activities also affect sequestration of PAHs in soils (Kastner et al., 1999).

Adsorption: Adsorption of PAHs to organic matter and black carbon can affect the bioactivity, persistence, biodegradability, leachability, and volatility of the PAHs (Pierzynski et al., 2000). Though there are several adsorption equations, organic chemical (in this case, PAHs) adsorption is usually modeled using the Freundlich adsorption equation.

Freundlich adsorption equation:

$$x/m = K_f C^{1/n}$$

where:

x/m = mass of organic chemical adsorbed per unit weight of soil
K_f and n = empirical constants
C = equilibrium concentration of organic chemical

K_f is a measure of the extent of sorption, so the above equation can be transferred into a linear form through log transformation:

$$\log (x/m) = \log K_f + 1/n \log C$$

The linear form will plot a straight line, where K_f is the y-intercept and $1/n$ is the slope.

Modifications of Freundlich adsorption equation for organic chemicals:

$$K_d = \frac{x/m}{C}$$

where:

x/m = organic chemical adsorbed per unit weight of soil (mmol kg^{-1})
K_d = distribution constant for organic chemical between soil and solid phases
C = equilibrium concentration of organic chemical (mmol L^{-1})

We can use $\boldsymbol{K_d}$ along with the soil organic carbon content to determine a coefficient ($\boldsymbol{K_{oc}}$) describing the distribution of the organic chemical between aqueous and soil organic matter phases. If we know the $\boldsymbol{K_{oc}}$ of the contaminant, we can back out the $\boldsymbol{K_d}$ to define the distribution of the organic chemical between soil solid and solution phases.

$$K_{oc} = \frac{K_d}{f_{oc}}$$

where:

f_{oc} = the fraction of soil organic carbon (i.e. %organic carbon / 100)

Walter et al. (2000) modified the Freundlich equation to apply to 9 PAHs:

$$\log K_{oc} = 0.62 \log K_{ow} + 0.70$$

Sorption to the organic matter fraction in soil and sediment dominates the sequestration process of organic contaminants (Hatzinger and Alexander, 1995; Alexander, 2000), but the exact sorption interaction with the organic matter fraction is not clearly understood (Stokes et al., 2006). Polymeric compounds, such as organic matter, are thought to have two types of structures: *rubbery* (or expanded) and *glassy* (or condensed, with nano-sized pores; Pignatello and Xing, 1996). The rubbery region is where PAH adsorption takes place, and this is followed by entrapment in the nanostructures of the glassy region (Pignatello and Xing, 1996; Xing and Pignatello, 1997).

Black carbon (soot) formed during pyrolysis of fossil fuel is an important fraction to which PAHs preferentially sorb over organic carbon. Black carbon serves as both as a sink for PAHs early in the formation process and as preferential partitioning phase for petrogenic PAHs (Gustafsson et al., 1997; Accardi-Dey and Gschwend, 2002). Sorption of PAHs to black carbon can be 1000 times as great as sorption of PAHs to organic matter (Jonker and Koelmans, 2002), and thus the presence of black carbon in sediments will drastically limit the solubility and bioavailability of PAHs (Gustafsson and Gschwend, 1997; Accardi-Dey and Gschwend, 2002.

Black carbon has been found to have a large aromatic fraction and a surface area close to 100 m^2 g^{-1} (Gustafsson and Gschwend 1997). Chemical analysis and X-ray evidence suggests that black carbon may actually be made up of sheets of 30 ring PAHs that are bridged together via carbon-carbon and carbon-oxygen linkages. Analysis of globally distributed black carbon indicates that nearly 90% of its structure is aromatic, which would explain increased sorption of PAHs in the presence of black carbon.

Black carbon is ubiquitous in the environment because of the several different mechanisms thought to be responsible for its creation. Many researchers have subdivided black carbon into a 3-30 nm diameter class and a larger aggregated class based on spectrographic observations (Gustafsson and Gschwend 1997). The smaller of these two classes is thought to form shortly after pyrolysis from condensation of aromatics. This fine grain black carbon would be intimately associated with any PAHs present and persist in this relationship after deposition.

In addition to organic matter and black carbon, PAHs can also be associated with the clay/silt fraction. Each fraction each has a different PAH level, release rate and desorption activation energy (Talley et al., 2002). After bioslurry treatment of highly contaminated sediment from Milwaukee harbor, they found reduced PAHs in the silt/clay fraction but not in the black carbon fraction. Loss of PAHs from the silt clay fraction to water in the harbor was correlated to lower toxicity. They concluded that total PAH concentrations in sediment did not correlate with risk of toxicity because the PAHs in the black carbon fraction had very limited bioavailability.

Diffusion: Weber et al. (1992), Weber and Huang (1996), and Xing and Pignatello (1997) have modeled the chain of events for PAH aging. As previously discussed, PAHs initially partition into and onto humic and fulvic acids (highly complex and stable forms of organic matter) followed by the diffusion into soil micropores. This second step in PAH aging and sequestration has been found to be further enhanced by the hydrophobic nature of both the interior wall of micropores and the PAHs (Nam and Alexander, 1998b). Although part of this fraction can be extracted with harsh organic solvents, portions are still irreversibly bound (recalcitrant) and usually non extractable (Jones et al., 1996; Reid et al., 2000a).

Some researchers feel that aging (through adsorption and diffusion) can reduce the bioavailability and toxicity of PAHs, so much that conventional extraction methods will overestimate risk (Kelsey et al., 1997; Alexander, 2000; Macleod et al., 2001). The magnitude of the potential risk of recalcitrant fractions, however, is still a matter of debate (Semple et al., 2004). It has been shown that that organisms such as bacteria, earthworms, or plants are able to access these supposedly unavailable fractions by “facilitated desorption processes” (Park et al., 2001; Stokes et al., 2006) or diffusion back out of the micropore (Johnsen et al., 2005; Figure 9). Dissolved organic matter has also been shown to considerably increase water solubility of PAHs in contaminated soil (MacKay and Gschwend, 2001), but bonding to humic substances have been found to reduce the toxicity of PAHs such as pyrene, fluoranthene, and anthracene (Perminova et al., 2001).

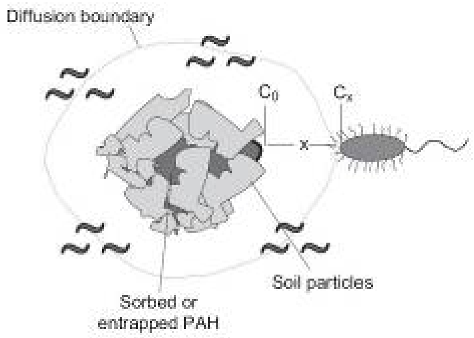


Figure 9. Diffusion of entrapped PAH out of micropores to become available to bacteria (Johnsen et al., 2005). (C_o-C_x) is the concentration gradient over distance x.

Summary

Polycyclic aromatic hydrocarbons are transferred, degraded and stored through a variety of mechanisms. These mechanisms contribute to the complexity of research conducted with PAH contaminated soils and sediments. All processes (transfers, losses and persistence) must be considered when conducting experiments as well as during site remediation. A summary of the important processes is presented in Table 8.

Table 8. Properties which influence the transfer, degradation and sequestration of PAH with approximate range or rates for environmental processes (adapted from Pierzynski et al., 2000). Ranges of properties for organic chemicals are presented in the top portion of the table, while the fate of the organic chemical with specific property ranges is listed in the lower part of the table. For example, if water solubility of an organic chemical is in the range of 10-1,000 mg L^{-1}, then the fate of this chemical is variable for solubility, volitalization with an intermediate persistence and leaching potential. This table can be compared to Table 1 of general properties of 16 EPA priority PAHs.

Property	**Ranges for Organic Chemicals**		
Water solubility (mg L^{-1})	<10	10-1,000	>1,000
Octanol/water (log K_{ow})	>3.0	2.7-3.0	<2.7
Sorption (log K_{oc})	>4.0	3.0-4.0	<3.0
Photolysis ($t_{1/2}$)	> 90 days	30-90 days	<30 days
Vapor pressure (Pa)	<0.00013	0.00013-1.33	>1.33
Process	**Environmental Fate**		
Soluble	Negligible	Variable	Yes
Photolyzes	Negligible	Variable	Yes
Volatilzes	Negligible	Variable	Yes
Adsorption potential	High	Intermediate	Low
Persistence potential	High	Intermediate	Low
Leaching potential	Low	Intermediate	High
Runoff potential	Low	Intermediate	High
Bioaccumulates	Yes	Variable	Negligible
Biodegradable	Slowly	Intermediate	Yes

Biological Techniques for Enhancing PAH Degradation (Bioremediation)

Biodegradation is the biological transformation of molecules into smaller molecules with less toxicity (preferably water and carbon dioxide which is then termed "mineralization"). *Bioremediation* is the application of biodegradation to decrease pollutant concentrations (Olson et al., 2003). In this section, we will be discussing techniques to enhance biodegradation of PAHs during bioremediation.

Several factors may limit the biodegradation of PAH in contaminated soils including (Alexander, 1999; Olson et al., 2003; Straube et al., 2003; Harmsen et al., 2007):

- limited supply of bacterial nutrient or carbon sources
- nonoptimal abiotic conditions of temperature, pH, salts, oxygen concentration and toxins
- lack of bacterial species that can degrade PAH compounds or low microbial biomass in general
- low PAH bioavailability to degrading organisms
- physiochemical characteristics of PAH compound

Manipulations of the above limitations are the basis for bioremediation with the subsequent goals of: (1) improving soil microbial habitat through fertilizer additions, tillage, liming, and/or (2) plant establishment to promote microbial functional groups capable of degrading PAHs, while at the same time (3) increasing the bioavailability of the PAHs. *Biostimulation* techniques are used to improve the soil microbial habitat and *bioaugmentation* strategies manipulate the microbial community structure to make it more capable of degrading PAHs.

Biostimulation

Lack of sufficient carbon and nutrient sources to sustain the growth of biodegrading microorganisms may affect bioremediation success (Odokuma and Dickson, 2003; Ward and Singh, 2004). Nutrient and carbon additions can enhance microbial activities which may promote cometabolism (Untermann et al., 2000). Abiotic conditions can also affect ioremedation, since oxygen is often the most limiting factor in microbial growth. Oxygen can be manipulated through physical (landfarming, composting) and chemical (injection of manganese peroxide) techniques to stimulate microbial communities (Ward and Singh, 2004).

Remediation efficiency increases due to the addition of nutrients has been reported mostly in small-scale studies:

- Haddox et al. (1996) used two different combinations of nutrients: (1) low level of macronutrients and (2) high level of macronutrients and low level of micronutrients. The second treatment gave a much better remediation result, but it was unclear whether the increase in macronutrients or the addition of micronutrients was the reason.

- Liebeg and Cutright (1999) tried different combinations and levels of macro- and micronutrients to enhance bioremediation of an aged gas manufacturing plant soil (pH 7.5, organic carbon: 3.5%, and total PAH: 620 mg kg^{-1}) through biostimulation and/or bioaugmentation. Their best overall combination was a low level of macronutrients with phosphorous as the dominant macronutrient, combined with high levels of micronutrients. In augmentation with *Achromobacter* sp. (ATCC 21910) and *Mycobacterium* sp. (ATCC 21676), bioactivity was highest when a high level of micronutrients with no macronutrient addition was used. Bioaugmentation, however, did not significantly enhance PAH degradation.

- Mills and Frankenberger (1994) found that the addition of phosphorous increased the microbial activity in a diesel fuel contaminated site.

- Straube et al. (2003) carried out microcosm and pan studies to evaluate the effect of: (1) biostimulation with slow release N fertilizer (dried blood) and (2) bioaugmentation with biosurfactant-producing *Pseudomonas aeruginosa* strain 64 on Superfund site soils with 1300 mg kg^{-1} total PAH concentrations. Combining both biostimulation and bioaugmentation significantly increased both PAH degradation and Benzo[a]pyrene-equivalent toxicity reduction. In medium scale pan studies, combining biostimulation and bioaugmentation with soil tillage reduced PAH levels seven times more than the control after 16 months (86 % to 12%).

- Lei et al. (2005) observed considerable degradation of two-, three-, four- and five-ring aged PAHs just through the introduction of oxygen with landfarming (i.e. tillage). Reductions were much higher for LMW PAHs (50-80%) than they were for HMW PAHs (10%) after nine weeks.

- Yi and Crowley (2007) experimented with biostimulation with linoleic acid produced by plant roots. Soil was spiked with pyrene and 43 different plant root extracts were tested for their ability to stimulate degradation. Root tissue extracts of carrots, potatoes, radish and celery, which contains high concentration of linoleic acid, was most effective in enhancing biodegradation as compared to the control. Similar PAH dissipation results were obtained in soils spiked with sodium linoleate. The addition of celery root extract resulted in continuous linear disappearance of pyrene and benzo[a]pyrene. They found that linoleic acid is a powerful stimulant of pyrene and benzo[a]pyrene degradation by gram positive bacteria. They hypothesized that (1) linoleic acid increased numbers of degrading bacteria, or (2) linoleic acid acted as a surfactant to increase the bioavailability of the PAH, or (3) linoleic acid formed a coating on soil particles and increased the attachment of bacteria to hydrophobic sites, which enhanced their proximity to PAH compounds.

Bioaugmentation

Bioaugmentation is the introduction (or inoculation) of a specific competent microorganism or group of microorganisms to improve the metabolic capacity of the indigenous population of microbes (Gentry et al., 2004). For example, *Mycobacterium sp*. are known to have extremely lipophilic surfaces so they are better equipped to directly take up organic hydrophobic contaminants such as PAHs (Rehman et al., 1998; Bogan et al., 2003). Bioaugmentation can be especially useful in sites with high PAH concentrations, in recently polluted soils with limited adapted microbial populations, or in aged soils/sediments where the PAH profile is dominated by HMW PAHs (Mueller et al., 1989).

Successful field-scale applications of bioaugmentation are limited (Alexander, 1999). Bioaugmentation is still experimental with most successful cases reported in confined systems where conditions are controlled to favor the growth of added microbes. There are several reports of the usefulness of bioaugmentation in enhancing bioremediation of contaminated soils (Lendvay et al., 2003; Silva et al., 2004), and others reporting that the procedure has failed to improve biodegradation (Bouchez et al., 2000). Some lab-scale or demonstration-scale experiments and summaries are presented below:

- Pritchard et al. (2002) found that introducing *Sphingomonas paucinobilis* EPA 505 along with nutrients and biosurfactants in a lab microcosm containing Superfund soils did not improve PAH degradation. They suggested that the addition of microorganisms to improve biodegradation in such highly contaminated soils might be limited by the microorganisms' sensitivity to toxic components and competition with indigenous community.

- Microbes introduced to a field setting in liquid cultures have poor survival due to predation and competition (O'Reilly and Crawford, 1989). For successful bioaugmentation, the added microorganism must fill a non-utilized metabolic niche in the microbial community and be protected by encapsulation or addition in a biofilm (Watanabe et al., 2002; El Fantroussi and Agathos, 2005). Inert materials such as vermiculite can be used as carriers to extend the survival of microbial cultures (Weir et al., 1995). Other methods to assist microbial introduction include the addition of pre-adapted strains or consortia of degraders, the addition of genetically modified strains, and alteration of soil properties to support proliferation of the desired microbes (Lanthier et al., 2005; Da Silva and Alvarez, 2004; Dejonghe et al., 2001).

- Bioaugmentation has been shown to be more successful in sterilized soil (which is not found in a field setting) because of predation by nematodes and competition with indigenous microorganisms for resources (Van Veen et al., 1997; El Fantroussi et al., 1999).

- Gentry et al. (2004) suggested that adding soils that already contain indigenous degraders can be very effective in enhancing biodegradation.

- Hamdi et al. (2007) reported an increase in the degradation of pyrene and anthracene (but not benzo[a]pyrene) in spiked soil when either aged PAH-contaminated soil, sewage sludge, or decaying rice straw were added.

- Significant declines (87% of total PAHs) in a highly contaminated, aged PAH soil (13,000 mg kg^{-1} total PAHs) were observed following the introduction of *P. aeruginosa* strain 64 on a vermiculite carrier in a greenhouse study (Straube et al., 2003).

Different techniques are used at a field scale for biostimulation and bioaugmentation. Solid and slurried phase treatments can be implemented depending on the volume of material being remediated. Bioremediation strategies and literature discussed in the following text include:

- Solid phase treatments:
    - *Composting:* contaminated material is mixed together with an organic substrate (i.e. straw, wood chips or bark), supplemented with inorganic nutrients and placed in a pile.
    - *Landfarming*: a combination of biostimulation, bioaugmentation, and/or surfactants, combined with tilling and mixing the soil/sediment to improve distribution of the contaminants and supply oxygen.
    - *Phytoremediation:* growing specific plants with the ability to sequester or degrade contaminants.
    - *Surfactants and other compounds:* additions of surfactants or compounds such as vegetable oil and cyclodextrins to enhance PAH solubility availability to bacteria.

- Slurry phase treatments:
    - *Bioreactors:* treatment of contaminated sediment in slurry phase on site with mixers or removal of contaminated material to a specific reactor for treatment.

Composting

Composting is a form of biostimulation because it consists of nutrient additions, moisture and oxygen control in a contained system. In a properly-maintained compost pile, temperatures in excess of 55˚C are reached which kills most pathogens (Eweis et al., 1998) and is a technique most commonly used for treatment of municipal solid wastes. In applications for hazardous waste, contaminant organic compound concentrations and extremely high temperatures (>55˚C) cannot support microbial activity in a composting environment and additional organics must be added and temperatures controlled (Eweis et al., 1998).

Like all bioremediation techniques, composting is effective only if implemented properly. Optimization of four parameters is necessary for successful PAH degradation during composting; aeration, temperature, moisture and pH. Composting is a generally aerobic process with microsites of anaerobic activity; therefore, the pile must be aerated through mechanical mixing or additions of bulking agents to improve structure and porosity. Temperature of the pile must remain between 30 and 60˚C for optimal microbial community structure, solubility and mass transfer rates (Eweis et al., 1998). Addition of organic material, while maintaining a C:N ratio for 25:1, facilitates higher temperatures in compost piles and biodegradation. Moisture must be manipulated through water and amendment additions. Most compost piles are able to reach high temperatures with low moisture contents. To obtain optimum moisture content in the pile (50-80%), a bulking agent (wood chips and sewage sludge) can be added (Epstein and Alpert, 1980).

There are three types of composting systems; windrow, static piles and closed reactors (Eweis et al., 1998). Open systems (windrow and static piles) are more commonly used than the closed reactors. In a windrow system, the compost mixture is placed on an impermeable layer to prevent leaching of contaminants. The cross section of the pile must be such that high temperatures are maintained on the interior of the pile with minimal heat losses on the outside of the pile. Aeration is achieved through mechanical mixing (front end loader or turner). If the pile is too large to mix, pipes can be installed to increase aeration in the pile. Windrow piles are often covered with a high density, polyethelyne material or wood chips in outside environments to prevent leaching from the pile during rainfall events (Eweis et al., 1998). In static piles, compost material is placed on an impermeable platform with perforated pipes connected to a blower system. Piles are aeriated at either a fixed rate or variable rate depending on the microbial activity. Static piles are also covered with plastic sheeting, but the cover must allow air to enter the pile. Closed reactors are the least used systems because of size limitations, but are the most controlled. Closed systems are constructed as the name implies and contain mixing devices through drum rotation or mixing instruments within the tank (Eweis et al., 1998).

Extensive degradation of two-, three- and four-ring PAHs has been observed during composting at a bench scale; however, five- and six-ring degradation was not observed (Potter et al., 1999). In one study, there was an initial increase in HMW PAHs after 12 days of composting, followed by a decrease after 50 days (Johnson and Gosh, 1998). The initial increase was attributed to contaminant mobilization with soil shearing in the reactor. In general, soil to compost ratios of 2:1 on a dry weight basis produce the highest degradation of PAHs compared to those with higher ratios (Stegmann et al., 1991; Dooley et al., 1995).

Landfarming

Landfarming is a commonly used, inexpensive remediation technology for PAH removal from contaminated soils (Gray et al., 2000; Harmsen et al., 2007). This method became popular in the 1950's for treatment of hazardous material through leaching and volatilization; however, in the 1970's landfarming methods and ideas changed with increased regulations and the focus switched to biological removal of contaminants (Eweis et al., 1998).

In landfarming, contaminated material is spread evenly over an impermeable layer and treated with standard agricultural techniques (i.e. tillage). It is important to maintain oxygen diffusion throughout contaminated material throughout the treatment, so depth of material is an important consideration as well as tillage strategies.

Land treatment units must be established during landfarming of highly contaminated material. These units must have: (1) an impermeable layer, (2) a drainage system, (3) a soil treatment zone, (4) berms and swales, (5) a water storage pond, and (6) a monitoring system. The impermeable layer prevents water movement from the contaminated material to groundwater and can be a synthetic or clay liner or compacted soil. The drainage system collects the leachate and is a series of pipes in a sand layer with drainage to a tank. Soil treatment zones are not applicable to dredge sediments as they are being pumped into a basin and not on top of other soil. Berms and swales protect against cross contamination and are used to contain the material over the nonpermeable layer. Storage ponds collect the leachate and are treated according to contaminants. A monitoring system is necessary to ensure contaminants are retained within the unit. Monitoring systems include wells, and air monitoring systems (Eweis et al., 1998).

The purpose of landfarming is to stimulate indigenous microorganisms to degrade PAHs via (Straube et al., 2003):

- adding nutrients and a carbon source (amendments)
- mixing soil to better distribute amendments
- introducing oxygen into soil at depth
- increasing the chance of microbial contacts with contaminants

The addition of inorganic nutrients compensates for limiting nutrients values in the waste material. The optimum C:N:P ratio for degrading hazardous wastes is reportedly between 100:10:1 (Straube et al., 2003) and 300:10:1 (Eweis et al., 1998). Adding too much of any nutrient can greatly increase costs. Mixing, associated with tillage, breaks apart soil aggregates, exposes PAHs once entrapped within the aggregates to biotic and abiotic degradation and homogenizes PAH levels in the soil. During landfarming, it is possible to enhance the bioavailability and degradation rate of the rapidly desorbable fraction in large pores, but not the slowly desorbable fractions associated with organic matter and smaller pores (Harmsen, 2004). Microorganisms cannot enter into pores smaller than their own size, so PAHs strongly sorbed to organic matter are slowly degraded. The biodegradation of the slowly degradable fractions is thus controlled by diffusion (Harmsen et al., 2007).

Reducing PAHs to acceptable levels through landfarming can be a lengthy process and often does not result in levels low enough to meet EPA standards. In one study in Holland, rapid degradation of PAH compounds (550 mg kg^{-1}) in dredge sediment occurred within the first year, followed by slow degradation for the next seven years. After 15 years, PAH levels (22 mg kg^{-1}) were similar to the background soils in the same area (Harmsen et al., 2007).

Phytoremediation

Phytoremediation is an on-site remediation strategy that uses plants to reclaim contaminated areas mainly through increasing microbial activity in the rhizosphere while breaking down organic compounds in contaminated soils by metabolic processes (Salt et al., 1995; Barter, 1999; Liste and Alexander, 2000; Binet et al., 2000; Dzantor and Beauchamp, 2002). The rhizosphere is the small volume of soil immediately surrounding plant roots which has much higher concentrations of root exudates, CO_2 pressures, and microbial activity (20x) than surrounding bulk soil (Rovira and Davey, 1974; Hutchinson et al., 2003). Root morphology of various plant species impact phytoremediation success. Some important root morphological properties that affect the success of phytoremediation include: length, surface area, mass, depth of penetration, quantity and composition of dead roots and exudates, root hairs, and bacterial and fungal associations (Hutchinson et al., 2003). Selecting species with varying root properties can be beneficial during phytoremediation efforts.

Plants are thought to enhance PAH degradation mainly through mechanisms such as mobilization into the rhizosphere (thus increasing bioavailability) and enhancing bacterial populations in the rhizosphere (Liste and Alexander, 2000; Binet et al., 2000). Plant roots provide an easily degradable source of carbon to the soil (both through root turnover and exudates) which encourages microbial activity in the rhizosphere and promotes biodegradation of organic contaminants (Olson et al., 2003; Yu et al., 2006), but can also decrease PAH bioavailability through sorption (Hutchinson et al., 2003). Root contributions of carbon to the soil (exudates) vary based on lifeform and species. For example, annual plants transfer 30-60% of new fixed photosynthetic carbon to the roots of which 40-90% is transferred directly into the rhizosphere (Olson et al., 2003). A similar range of photosynthetic carbon, 30-70%, is transferred to the soil in perennial plants, where 25-80% is transferred from the roots to soil (Olson et al., 2003). These contributions of carbon from plants to the soil stimulate microbial communities and thus the degradation of PAHs (Liste and Alexander, 2000; Binet et al., 2000; Chen et al., 2003; Robinson et al., 2003; Yu et al., 2006; Kamath et al., 2004).

Though stimulation of microbial communities in the rhizosphere is the main process for PAH degradation, some studies have revealed that potential uptake and metabolism of PAHs is also possible (Harms, 1996). Uptake is controlled by molecular configuration and size as well as the capability for uptake by a specific plant species (Harms, 1996). Organic compounds with low water solubility (high log K_{ow}) tend not to be transported within a plant, but organics with log K_{ow} between 0.5 and 3.0 are likely to be transported within a plant (Burken and Schnoor, 1998; Olson et al., 2003). Additionally, plants typically transport LMW PAH compounds or HMW compounds that have been transformed outside the plant in the rhizosphere (Olson et al., 2003).

Phytoremediation also helps reduce the offsite transfer of contaminants by controlling runoff, wind erosion and leaching, and is a non-disruptive self-sustaining process which requires relatively little management. However, phytoremediation is a very lengthy process (1-3 years) that is often limited by phytotoxic contaminant levels, and is usually used as a secondary treatment in soils contaminated with residual levels of PAH (Joner et al., 2002; Cunningham et al., 1995). The success of the process will depend on environmental factors such as adequate supply of oxygen, water, and nutrients, as well as edaphic factors like the soil texture, pH, EC, and the levels of pollutants (Cunningham et al., 1995).

Some plant species that have been shown to have potential for remediation of petroleum hydrocarbons, including PAHs, and associated citations are listed in Table 9. Some examples of the influence of specific plant species on degradation of PAH compounds include:

- Reilley et al. (1996) found the total accumulation of pyrene and anthracene in roots and shoots of different plants accounted for <0.03% of total added. Thus, uptake of PAH by vegetation is insignificant for PAH reduction in soils.

- Saison et al. (2004) found that the growth of Italian rye-grass (*Lolium multiflorum* var. Fastyl) and red clover (*Trifolium pratense*) on coking plant soils with 2077 µg PAH g^{-1} soil was similar to plant growth in an uncontaminated control.

- Yu et al. (2006) found no effects on plant growth or any sign of stress in corn (*Zea mays* L.), white clover (*Trifolium repens*), and perennial ryegrass (*Lolium perenne* L.) grown in greenhouse pots spiked with phenanthrene and pyrene at rates of 0-375 mg kg^{-1}.

- Liste and Felgentreu (2006) reported up to a 50% decrease in root and shoot yield in summer vetch (*Vicia sativa* L.) , annual ryegrass (*Lolium multiflorum* Lam.) and white mustard (*Sinapsis alba* L.) growing on soil from an old coal gasification site (EPA Priority PAH content: 71.4 mg kg^{-1}; total petroleum hydrocarbons: 1517 mg kg^{-1}). Ryegrass was the most PAH-tolerant species in their study. The reduction in growth was thought to be due to toxicity of LMW constituents or to changes in physicochemical properties of the soil caused by petroleum hydrocarbon contamination.

- Yi and Crowley (2007) reported that the uptake of PAH by 43 different plants was insignificant. Less than 0.01 mg kg^{-1} was detected in the roots and shoots of tested plants.

- Increased degradation of HMW PAHs during phytoremediation has also been documented (Aprill and Sims, 1990; Binet et al., 2000; Paquin et al., 2002). Other researchers have found; however, that plants either inhibited or had little effect on biodegradation rates depending on the plant species and type of contamination (Watkins et al., 1994; Gunther et al., 1996).

- Liste and Felgentreu (2006) suggested that a slowing of PAH degradation during phytoremediation could be due to increased nitrogen demand, which decreased the amount of nitrogen available to degrading microorganisms. Incorporating a nitrogen-fixing component into a species mix during phytoremediation could prevent this.

When selecting phytoremediation species, there are several factors to consider; climate, water availability, salinity, and the presence of other phytotoxins (Hutchinson et al., 2003). Climate includes the length of growing season, rainfall and temperature patterns. Water availability is influenced by soil texture, bulk density, hydraulic conductivity and is related to climate. Dense clay soils have less water movement or lower infiltration, while sandy soils have greater infiltration and hydraulic conductivities. Sandy soils also drain quickly and have lower water storage. Salt resistant species selection for soils or sediments with high salinity is extremely important for establishment and health of plants. Other toxins are also a concern, as some contaminants can be too toxic in soils to support plants. Obviously, if the contaminant levels are too high, phytoremediation will not be successful (Hutchinson et al., 2003).

Table 9. Phytoremediation species and select research citations on success of these species.

Common Name	Latin Name	Select Successful Research on PAH Degradation
Alfalfa	*Medicago sativa L.*	Schwab and Banks, 1994; Reilley et al., 1996; Pradhan et al., 1998; Olson et al., 2007
Annual ryegrass	*Lolium multiflorum*	Schwab and Banks, 1994; Hutchinson et al., 2003; Rezek et al., 2008
Annual sunflower	*Helianthus annuus*	Olson et al., 2007
Barley	*Hordeum vulgare*	Kucerova et al., 2001
Bermuda grasss	*Cynodon dactylon L.*	Ferro et al., 1994; Banks et al., 1998; Hutchinson et al., 2003; Olson et al., 2007
Big bluestem	*Andropogon gerardii*	Aprill and Sims, 1990; Schwab and Banks, 1994; Rugh et al., 2004; Olson et al., 2007
Blue grama	*Bouteloua gracilis*	Aprill and Sims, 1990
Bottlebrush grass	*Hystrix patula*	Rugh et al., 2004
Bridsfoot trefoil	*Lotus corniculata*	Olson et al., 2007
Buffalograss	*Buchloe dactyloides*	Qui et al., 1997
Canada wild-rye	*Elymus canadensis*	Aprill and Sims, 1990

Carrot	*Daucus carota*	Wild and Jones, 1992
Green bulrush	*Scirpus atrovirens*	Rugh et al., 2004
Hybrid poplar	*Populus deltoides x nigra*	Jordahl et al., 1997
Joe pye weed	*Eupatorium purpureum*	Rugh et al., 2004
Kleingrass	*Panicum coloratum*	Wrenn and Venosa, 1996; Qui et al., 1997; Olson et al., 2007
Little bluestem	*Schizachyrium scoparius*	Aprill and Sims, 1990; Pradhan et al., 1998
Maxmilian sunflower	*Helianthus maximiliani*	Olson et al., 2007
Meadowsweet	*Spiraea alba*	Rugh et al., 2004
New England Aster	*Aster novae-anglicae*	Rugh et al., 2004
Perennial ryegrass	*Lolium perenne L.*	Gunther et al., 1996; Wrenn and Venosa, 1996; Binet et al., 2000; Nedunuri et al., 2000; Olson et al., 2007
Prairie chordgrass	*Spartina pectinata*	Rugh et al., 2004
Red clover	*Trifolium pratense*	Olson et al., 2007
Side oats grama	*Bouteloua curtipendula*	Aprill and Sims, 1990
Sorghum	*Sorghum bicolor*	Nedunuri et al., 2000
St Augustine grass	*Stenotaphrum secundatum*	Schwab and Banks, 1994; Nendunuri et al., 2000
Sticky geranium	*Geranium viscosissimum*	Olson et al., 2007

Stiff goldenrod	*Solidago rigida*	Olson et al., 2007
Sudangrass	*Sorghum vulgare L.*	Schwab and Banks, 1994; Lee, 1996; Reilley et al., 1996
Switchgrass	*Panicum virgatum*	Aprill and Sims, 1990; Reilley et al., 1996; Pradhan et al., 1998; Chen et al., 2003; Rugh et al., 2004
Tall fescue	*Festuca arundinaceae Schreb.*	Ferro et al., 1994; Schwab and Banks, 1994; Gunther et al., 1996; Reilley et al., 1996; Wrenn and Venosa, 1996; Banks et al., 1998; Banks et al., 1999; Chen et al., 2003; Hutchinson et al., 2003; Robinson et al., 2003; Huang et al., 2004; Olson et al., 2007
Western wheatgrass	*Agropyron smithii*	Aprill and Sims, 1990; Olson et al., 2007
Wheat	*Triticum aestivum*	Kucerova et al., 2001
Yellow sweetclover	*Melilotus officinalis*	Olson et al., 2007

Surfactants

Mass transfer of PAH compounds to the aqueous phase in the soil solution can be a major limiting factor in the bioremediation of PAHs (Volkering et al., 1992). Compounds like surfactants, cyclodextrins, and vegetable oil may be used to enhance PAH solubility.

Properly applied surfactants have been shown to improve desorption, apparent aqueous mobility and bioavailability of hydrophobic organic compounds such as PAHs (Bragg et al., 1994; Mata-Sandoval et al., 2002). Surfactants are amphiphilic (possess both hydrophilic and hydrophobic properties) molecules with a hydrophilic polar head (Gao et al., 2007). They can be classified by the charge on their polar head as anionic, cationic, nonionic or zwitterionic (Mulligan et al., 2001). At or above a certain concentration level called critical micelle concentration, the hydrophobic parts of the surfactants will tend to associate together to form a micelle (an aggregate of surfactant molecules dispersed in a liquid colloid) with a hydrophobic core (Santharam et al., 1997). Surfactants solubilize hydrophobic contaminants by partitioning them into the hydrophobic core of the micelle. If the concentration of surfactant exceeds the critical micelle concentration, solubility of hydrophobic compounds can increase by an order of magnitude over normal aqueous solubility (Edwards et al., 1991; Mulligan et al., 2001; Gao et al., 2007). The critical micelle concentration of a specific surfactant depends on temperature, ionic strength and surfactant chemistry.

- In mixed pollutant systems, the extent of solubilization will differ from those in single solutes. For example, Guha et al. (1999) found that naphthalene solubilized by surfactants increased the solubilization of other PAHs such as phenanthrene.

- Surfactants are thought to be able to solubilize sorbed organic compounds in a soil-water system only after critical micelle concentration is attained (Laha and Luthy, 1991; Gao et al., 2007).

- Several interactions affect the solubilization of hydrophobic compounds by surfactants. These include the micellular phase-organic interactions, surfactants monomer-organic interactions in the aqueous phase, and the interactions of surfactants and organic compounds with the solid phase (Mata-Sandoval et al., 2002).

- Soils with predominantly fine particles are generally found to reduce desorption efficiency of surfactants (Mulligan et al., 2001). Organic matter content and clay mineralogy also affect surfactant performance, but the effect differs depending on the type of surfactant used (Rodriquez-Cruz et al., 2005).

- Stimulatory effects, no effect, and inhibitory effects have been reported (Kim et al., 2001; Kim and Weber, 2003). Some of the negative effects of surfactants on biodegradation may be due to toxicity to microorganisms, prevention of bacterial access to contaminants through sequestration of micellar solubilized organics, or preferential biodegradation of the surfactant rather than the contaminant. For instance, phenanthrene solubilized by the surfactant Tween-80 was found to be unavailable for biodegradation by *Sphingomonas paucinobilis* because this microorganism preferred to use the hydrophobic portion of the surfactant as a carbon source rather than destabilizing the micelles.

Because of the above interactions, the determination of a critical micelle concentration for a surfactant in a complex medium such as soil can be difficult. Desorption occurs at surfactant concentrations greater than the critical micelle concentration, but at lower concentrations, admicelles (surface aggregates of surfactants, also called hemimicelles) may form, sorb onto soil, and act as additional sorption sites that can enhance PAH sorption instead of reducing it (Doong et al., 1996, Santharam et al., 1997).

Anionic and nonionic surfactants are more commonly used in remediation because they are less likely to sorb onto soil surfaces (Mulligan et al., 2001). Nonionic surfactants are also advantageous because they have a low critical micelle concentration, high cold water solubility, and low microbial toxicity (Kim and Weber, 2003; Zhao et al., 2005). Cuypers et al. (2002) and Conte et al. (2005) have shown that PAHs can be effectively desorbed using nonionic surfactants like dodecylbenzene sulfonate.

Biosurfactants: Some synthetic surfactants can be toxic to microorganisms, which may decrease the number of degraders in the soil (Sandbacka et al., 2000). The addition of biosurfactants (either surfactant producing microorganisms or natural compounds that act as surfactants) is one way to get around the problem of toxicity. Biosurfactant-producing microbes have been proposed as an alternative to chemical surfactants to enhance availability of hydrophobic compounds (Hunt et al., 1994; Oberbremer et al., 1990).

- *Pseudomonas* strains can synthesize biosurfactants called *rhamnolipids* (Nitschke et al., 2005).

- Surfactants that are produced by microorganisms tend to have lower toxicities and are effective at wider temperature, pH, and electrical conductivity ranges (Bordas et al., 2005).

- Atlas (1993) found that biosurfactant-producing indigenous bacteria achieved higher hydrocarbon degradation rates than those achieved by nutrient addition alone.

- Straube et al. (2003) showed that the introduction of *Pseudomonas aeruginosa* strain 64, a rhamnolipid-producing bacterium, enhanced the biodegradation of PAHs in highly contaminated soil.

- Conte et al. (2005) found that humic acid can be used as an effective surfactant for PAH desorption.

- Bogan and Sullivan (2003) reported that the addition of fulvic acid to soils that had low humic acid/fulvic acid content greatly enhanced pyrene mineralization by *Mycobacterium austoafricanum*. They also reported slower progress in PAH sequestration in a soil with high fulvic acid content.

Cyclodextrins: *Cyclodextrins* are cyclic oligosaccharides that are able to form complexes with hydrophobic molecules. They are the product of the action of cyclodextrin glycosytransferases on starch and are non-toxic and biodegradable in the environment. Cyclodextrins can be added to washing waters to solubilize PAHs and increase desorption from soil (Stokes et al., 2006).

Vegetable oil: Vegetable oil has been proposed as an economic and environmentally friendly solvent to dissolve PAHs and has been shown to be as effective as organic solvents like acetone and dichloromethane (Gong et al., 2005).

Bioreactors

Treatment of contaminated sediments in a slurry phase is completed in a bioreactor. Advantages of the slurry phase include: complete mixing of nutrients into sediment, increased contact between microorganism and contaminant, control (Eweis et al., 1998). Bioreactors are commercially available for this type of treatment but are expensive. Sediment is often put into the bioreactors in small batches; however, continuous flow operations are possible. With treatment, the slurry is mixed with nutrients and microbial cultures and aerated. The sediment then settles and the water is transferred to a treatment plant while the sediment is returned to a contained area (Eweis et al., 1998). For large quantities of sediment, this is a difficult option.

Chemical Techniques for Enhancing PAH Degradation

In situ chemical oxidation is a process where oxidants (ozone, hydrogen peroxide, hypochlorites, chlorine and chlorine dioxide) are injected into the contaminated soil to convert PAHs to more stable and less mobile forms (Figure 10) and/or to provide an oxygen source for microbes (coupled with bioremediation). It is important to consider soil properties and injection method when choosing the appropriate oxidant. There are several drawbacks to this process including, but not limited to:

- Oxidant introduction can negatively impact subsurface soils
- Decreased soil permeability (colloid formation)
- Release of previously sorbed metals to groundwater resources
- Toxic byproduct production
- Heat and gas production
- Logistics of handling and storing oxidizing chemicals

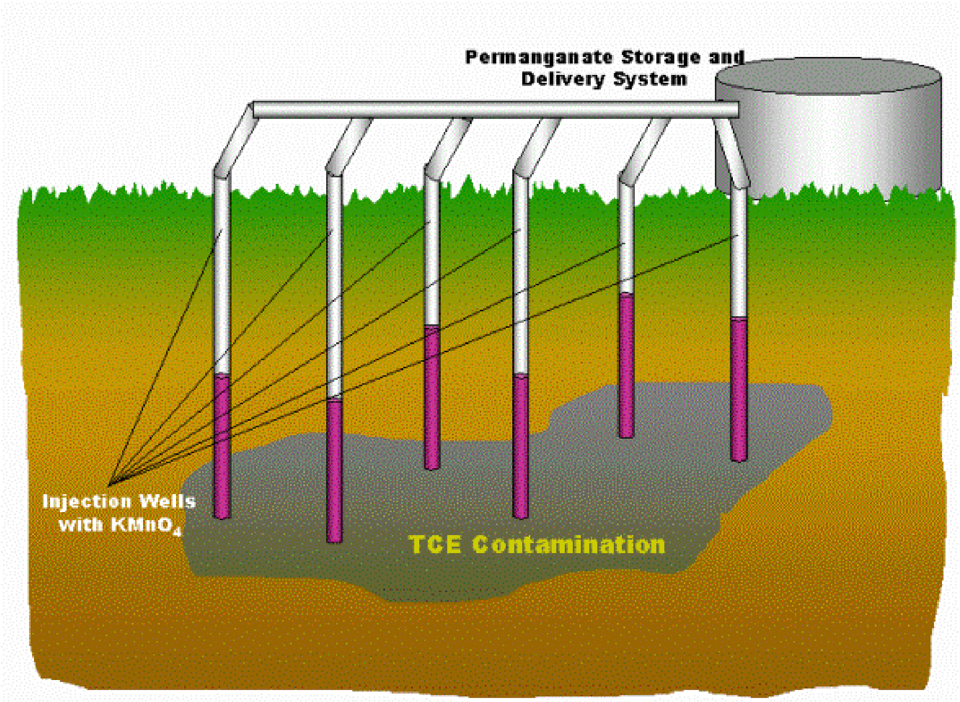


Figure 10. Injection of potassium permanganate for oxidation of PAHs in contaminated soils. Source: http://sve.ucdavis.edu/AlternativesDesc.htm

Bioremediation processes are efficient and economically feasible remediation strategies but tend to be slow, and have shown limited capacity to degrade HMW PAHs (Wilson and Jones, 1993; Lundstedt et al., 2003). The introduction of a strong chemical oxidant into the soil can overcome some of the limitations encountered with biodegradation, and may result in a faster and more efficient degradation of HMW compounds (Kawahara et al., 1995; Nam et al., 2001; Watts et al., 2002). Combining chemical oxidation processes with biodegradation may enhance PAH removal since chemical oxidation byproducts of PAHs are more water-soluble and available to biodegradation (Nam et al., 2001; Matscheko et al., 2002). Some researchers have suggested that biodegradation procedures be used as a polishing step after the bulk of contaminants is removed by other means (Lundstedt et al., 2006).

Chemical oxidation procedures have some other advantages over biodegradation in that the processes can be better controlled since the conditions can be modified. They are also relatively insensitive to external environmental disturbances (Rivas, 2006). Conversely, there is always a possibility of wastage of chemical reagent added, especially when the sediments/soils have high organic matter content, which will also be oxidized. High organic matter content may increase the cost of treatment but can also increase PAH availability since sorbed PAHs will be released from organic matter during oxidation (Rivas, 2006).

Remediation by chemical oxidation suffers from some of the same problems as other remediation technologies. Any treatment method designed to eliminate PAHs must consider the strong sorption of PAH compounds into micropores which may render them inaccessible to oxidation processes. Transfer to solution can be very slow and diffusion controlled; therefore, slowing degradation. More aged soils/sediments usually have a lower overall PAH availability and therefore the contaminant will be less susceptible to the chemical oxidation resulting in lower efficiency of removal (Bogan and Trbovic, 2003). When a complex mixture of PAH compounds has been present in soils for many years, remediation with chemical oxidation is far more difficult (Nam et al., 2001; Guha et al., 1999).

Soil chemical processes can be enhanced through several oxidation techniques to increase PAH degradation. The two most popular of these processes are (Yin and Allen, 1999):

- Ozone treatment
- Fenton’s reagents

Both methods utilize the formation of non-specific hydroxyl radicals oxidizing agents which are capable of oxidizing persistent organic contaminants. Hydroxyl radicals are strong, relatively unspecific oxidants that react with most organic contaminants, including PAHs (Haag and Yao, 1992). They degrade organic compounds either by hydrogen abstraction or by hydroxyl addition.

Ozone treatment

Ozone treatment is carried out with injection of gaseous or aqueous ozone (Choi et al., 2001). Ozone can transform PAHs into a polar, more soluble, and thus more biodegradable oxygenated intermediate. Oxidation of organic matter by ozone also can release some of the sequestered PAHs making them more available to biodegradation (Goi and Trapido, 2004; O'Mahony et al., 2006; Nam and Kukor, 2000). The presence of metal oxides can catalyze the formation of hydroxyl radicals which are more aggressive oxidant than ozone.

Ozone treatment can be made more effective when it is used as a part of an integrated strategy such as extraction before ozonation, or ozonation followed by biodegradation. The extraction step improves the oxidation efficiency of ozone due to the increase of accessibility to oxidation. Organic solvents with low toxicity and the ability to dissolve high amount of ozone are good choices for extractants since they can be used as a carrier to introduce ozone in the system (Rivas et al., 2004).

Zeng and Hong (2002) used ozonation to treat sediments contaminated by coal tar and reported that ozonation modified the inorganic and organic content of the sediments so as to improve the subsequent biodegradability. Kulik et al. (2006) found that ozonation removed more HWM PAH while biodegradation removed more LMW PAH. Stehr et al. (2001) reported that ozonation had a negative effect on the subsequent biodegradation of benzo[a]pyrene and phenanthrene.

Disadvantages of ozonation include the production of intermediates which can be more toxic than the parent compound. Ozonation can also destroy the indigenous microbial degraders. The destruction of the indigenous microbial community, however, might improve the chance of successfully inoculating the system later with specific bacteria that have high degradation potential (Rivas, 2006).

Fenton's reagents

Fenton's reagents use peroxide at different concentrations (3 to 35%) along with ferrous iron (Fe II) as a catalyst to oxidize organic chemicals (Flotron et al., 2005). Peroxide (H_2O_2) decomposes into highly reactive nonspecific hydroxyl radicals with the help of ferrous iron. Optimum pH for the reaction is 3-5, since if the pH is too high, iron will precipitate as iron oxides and will decompose peroxide. The iron can be artificially added with the peroxide, but if the soil has high enough iron oxide content (goethite, hematite or magnetite); there is no need to add iron (Watts et al., 2002; Kawahara et al., 1995). The decomposition process of peroxide is exothermic. The heat generated might enhance the volatilization of some compounds, so safety issues must be considered, especially when using a concentrated peroxide solution.

The success of a Fenton's reagent treatment is strongly dependent on solid matrix characteristics and the contaminant availability (Flotron et al., 2005; Nam et al., 2001). Hydrophobic contaminants in aged soils are less susceptible to chemical oxidation because of their adsorption to organic material and diffusion into micropores. This renders them unavailable for the hydroxyl radicals produced during Fenton's reactions, which are generated in the aqueous phase (Sedlak and Andren, 1994; Bogan et al., 2003). The presence of black carbon, for example, will limit the availability of PAHs to chemical oxidation (Lundstedt et al., 2006).

The amount of organic matter present also affects oxidation success. Bogan and Trbovic (2003) showed that Fenton's reagents can be more successful at higher organic matter contents. Since most PAH compounds partition to organic matter, oxidation of organic matter by the reagent will release PAH compounds and render them more available to chemical oxidation. They found that if less than 5% organic matter was present, the pollutants were adsorbed in the micropores and were less available for chemical oxidation. However, large amounts of organic matter will also result in scavenging of the OH^- radicals, so higher reagent concentrations must be added to achieve PAH oxidation (Flotron et al., 2005; Lundstedt et al., 2006).

The addition of a cosolvent may improve the oxidation process by enhancing compound desorption. Ethanol addition has been shown to increase the removal of Benzo[a]pyrene (Lee and Hosomi, 2001). Others have reported beneficial effects from using vegetable oil (Bogan et al., 2003), surfactants (Nadarajah et al., 2002) and cyclodextrins (Lindsey et al., 2003) as cosolvents to improve the extraction of recalcitrant HMW PAHs and make them more available to oxidation. Bogan et al. (2003) and Lee et al. (2002) used vegetable oil or ethanol extractions before oxidation to enhance desorption of PAHs and improve the overall degradation process. Lundstedt et al., (2006) found that ethanol pre-treatment enhanced the PAH transformation thereby making them more available for the hydroxyl radicals. However, they also found that Fenton's reagent caused an increase in oxidation products, mostly quinones. Compounds like 1-indanone, anthracene-9,10-dione, 1-methylanthracenedione, 2-methylanthracenedione, 1,8-naphthalic anhydride, benz[a]anthracene-7,12-dione and two compounds tentatively identified as hydroxy-9-fluorenones were found at higher concentrations after treatment. These compounds are generally less toxic and more susceptible to microbial degradation (Moody et al., 2005).

Fenton's oxidation can also be used in combination with bioremediation techniques (Nam et al., 2001). However pH adjustment is not practical under field conditions and is prohibitive to microbial growth. A modified Fenton's treatment with no pH adjustment or no addition of Fe has shown to be effective.

Jonsson et al. (2006) used both Fenton's reagent and ozonation on nine samples from five different contaminated sites and found that Fenton's reagent was generally more efficient in degrading PAHs than ozone treatment. Fenton's reagent removed 40-86% of the initial PAHs, as opposed to 10-70% removal by ozone oxidation. Ozonation was more effective in degrading LMW PAHs than HMW PAHs, while Fenton's reagent removed PAHs of all weights. However, most researchers have found that the oxidation rate of LMW PAH compounds by Fenton's reagents is generally higher than that of HMW PAHs (Wilson and Jones, 1993). Some exceptions to this are anthracene and benzo[a]pyrene, possibly due to their high reactivity towards hydroxyl radicals (Lundstedt et al., 2006). Both Nam et al. (2001) and Flotron et al. (2005) found that benzo[a]pyrene was more easily oxidized by Fenton's reagent than many smaller PAH compounds, probably due to its lower oxidation potential.

Regulatory Framework

Dredged material has been commonly found to have elevated levels of PAHs as well as metals and other organics (National Research Council, 2007). Because of the nature of and risk associated with dredged material, upland placement is heavily regulated either through standards specific to dredge material or solid waste. The following section includes a summary of federal, state and regional regulations as well as a general summary on the development of the regulations.

Federal, State and Regional Acts and Agencies

Handling, utilization and acceptable contaminant limits of dredge materials are regulated by federal, state and occasionally regional agencies. The Environmental Protection Agency (EPA) is separated by region (Figure 11) to federally regulate the handling, monitoring and final use of dredge material through several acts including, but not limited to, the Clean Water Act (CWA), National Environmental Policy Act (NEPA), Resource Conservation and Recovery Act (RCRA) and the Comprehensive Environmental Response, Compensation and Liability Act (CERCLA). The purpose of each act is summarized in Table 9 at the end of this section.

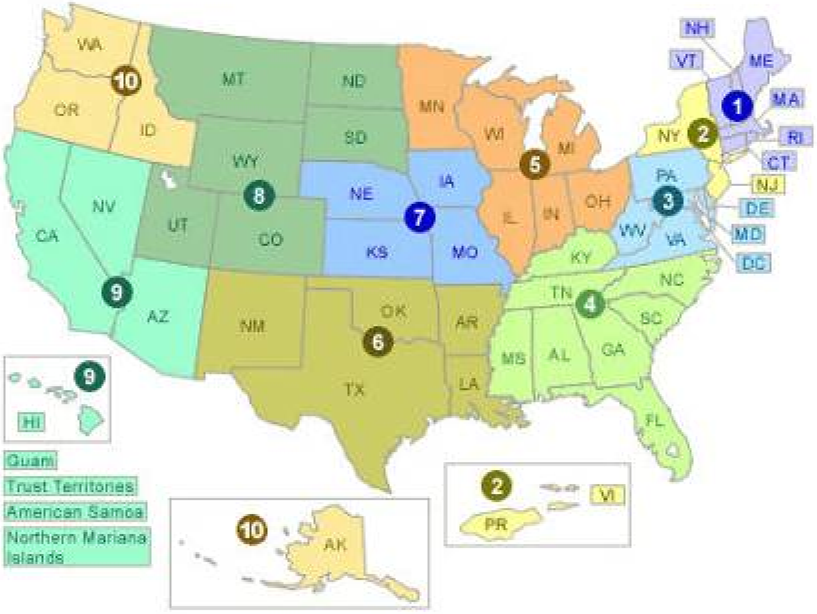


Figure 11. EPA regions for regulation of contaminated materials. http://www.epa.gov/osw/regions.htm

The span of federal acts controlling dredged material creates issues with overlap between the acts and general confusion. For example, the Hazardous Remediation Waste Management Requirements Final Rule in 1998 was written to help with the overlap between RCRA and the CWA regulations on dredge material. However, this rule only added to the confusion by further breaking dredged material into hazardous and non-hazardous waste. Furthermore, the transition of dredge material from slurried sediments to soils in upland settings is not fully regulated under the CWA. The CWA only applies to dredge material management while in-water or dewatering, and not to the soils resulting from upland placement (Childs et al., 2002). In general, water quality guidelines apply to the first phase of dredge sediment dewatering, and cleanup/solid waste program regulations apply during the second phase where the dredge material is considered a soil (Figure 12).

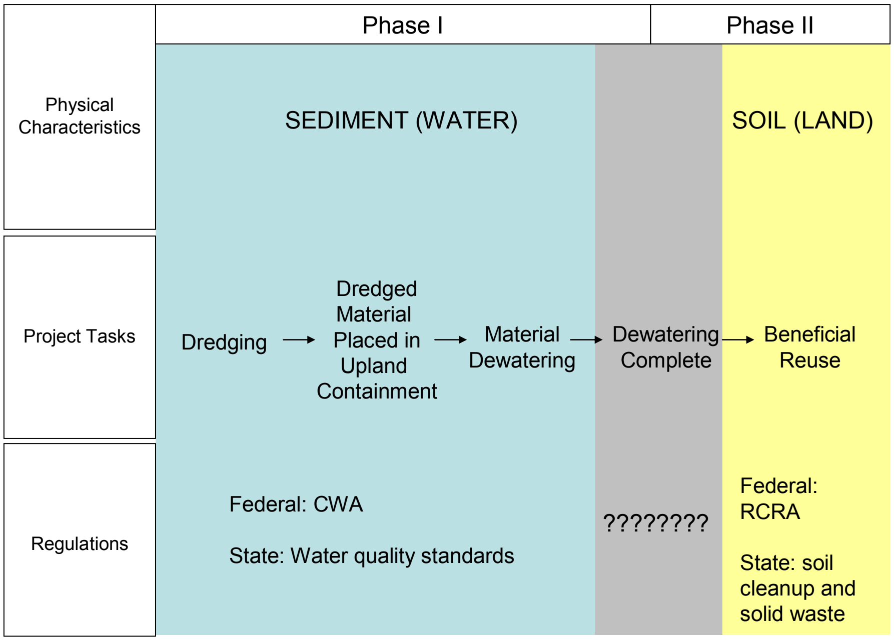


Figure 12. Sediment and soil phases for dredged material. Grey area indicates the overlap between water and soil quality regulations and confusion. Adapted from Childs et al. (2002).

Under the umbrella of federal regulations and EPA guidelines are state regulatory agencies such as the Virginia Department of Environmental Quality (or other state entity). Each state agency creates state-specific water and soil quality regulations and guidelines for handling, utilization and acceptable contaminant limits of dredge material. These guidelines can vary immensely among states in degree of specificity, stringency and perspectives on beneficial uses of dredge sediments. Most states, such as Illinois (IEPA, 2007) Minnesota (MPCA, 1999), and Oregon (Childs et al., 2002) regulate dredge sediments based on preexisting site remediation standards (water quality standards and solid or hazardous waste guidelines or biosolid application guidelines). New Jersey (NJDEP, 1997), in attempt to deal with the overlap and confusion, developed regulations specific to dredge sediments, that are not regulated by either water or soil regulations already in place. This has eliminated the transition phase between slurried sediments and soils, as well as set more realistic guidelines for cleanup. Beyond the previously described differences, state regulations and standards vary based on the intended beneficial use (beach nourishment, compost/topsoil, final cover at a landfill or superfund site, residential or industrial uses, or aggregate/fill) of a given dredge sediment.

In the states of the Great Lakes Commission (Illinois, Indiana, Michigan, Minnesota, New York, Ohio, Pennsylvania and Wisconsin), there is also a regional framework of guidelines and standards to aide in the proper management and beneficial use of dredged sediments (GLC, 2004). Currently, dredge sediments are considered a waste product rather than a resource (GLC, 2004). One of the goals of the Great Lakes Commission (GLC) is to combine knowledge from existing case studies, policy, guidance, and regulations to utilize dredge sediments as a resource, especially in upland placement settings.

Risk Assessment

Contaminants, including PAHs, are assessed for risk based on their toxicity and exposure. Low molecular weight PAHs are considered directly toxic (Sims and Overcash, 1983) and HMW PAH compounds are considered *genotoxic*, or capable of causing damage to DNA (Lijinsky, 1991). Toxicity is mainly the result of PAH metabolic transformations in the human body into a complex mix of quinones, quinines, cis- and trans-dihydrodiols, phenols, epoxides and other oxidized metabolites depending on the hydrocarbon and the metabolic route (Harvey, 1997; Dabestani and Ivanov, 1999; Volkering and Breure, 2003). Some of these reactive metabolic intermediates can covalently bind to nucleic acids to induce strand breaks and DNA damage, leading to mutation and tumor initiation (Harvey, 1997). The carcinogenic and mutagenic potential of PAHs depends on their metabolites.

Humans can be exposed to both directly toxic and genotoxic compounds through ingestion, inhalation, and dermal exposure (i.e. drinking contaminated water, consumption of plants or animals that have come in contact with the contaminant, breathing PAH particulates, or holding PAH contaminated soil in your hand). Once humans come in contact with the PAH compound, it is distributed, metabolized, stored in the human body or excreted. Once in the human body, the PAHs can impact the respiratory, reproductive, and neurological systems, cause birth defects, and cancer (Figure 13).

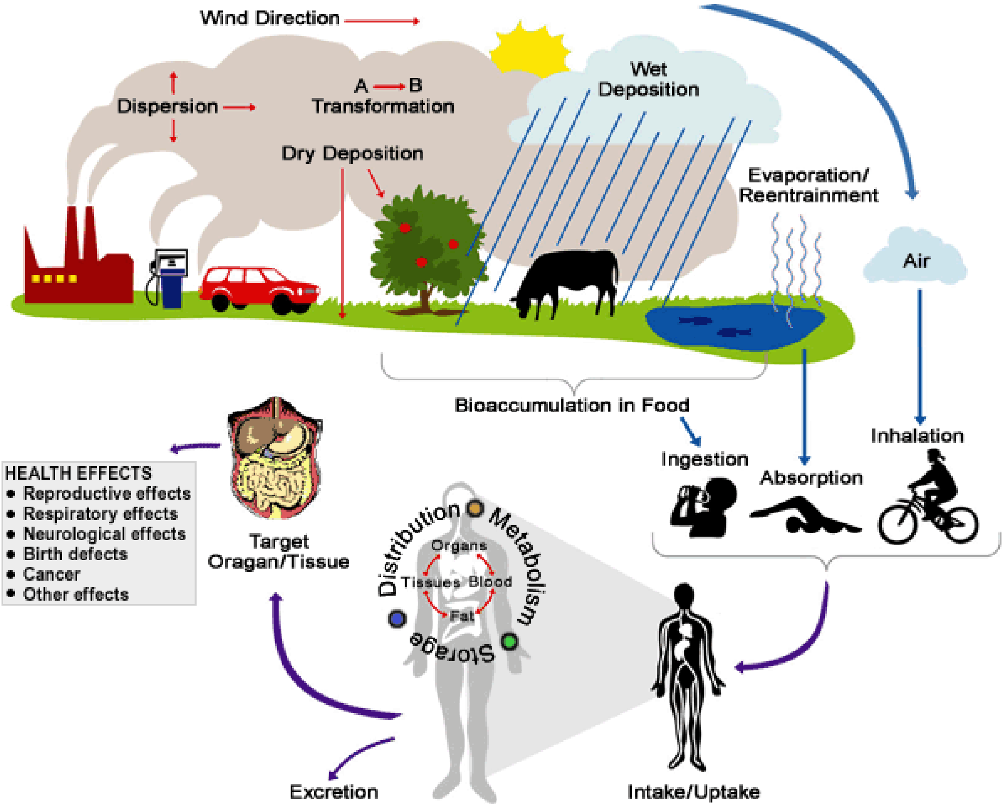


Figure 13. Risk based exposure to contaminants. Source: http://www.in.gov/idem/risk/

Risk based criteria (RBC) and soil screening levels (SSLs) were developed by the EPA to determine and minimize the risk associated with certain contaminants.

Risk based criteria: Risk based criteria equations combine pathways of human exposure and EPA toxicity data to determine SSLs for contaminated sites (EPA, 1996). Different values can be plugged into these equations to make the RBCs site specific. For example, the EPA (2003) uses the following equation to calculate residential soil ingestion risk for a generic carcinogenic material. (http://www.epa.gov/reg3hwmd/risk/human/rbconcentration_table/equations.htm)

$$\text{RBC} = \frac{\text{TR} * \text{ATc}}{\text{EFr} * (\text{IFS}_{\text{adj}} / 10^6) * \text{CSFo}}$$

Where RBC is the risk based criteria in mg kg^{-1}, TR is the target cancer risk (standard value = $1*10^{-6}$), ATc is the average time exposed to carcinogens (365 days/yr*70 yr = 25550), EFr is the exposure frequency in days year^{-1}, IF S_{adj} is the age adjusted soil ingestion factor in mg year kg^{-1} day^{-1} (114.29), CSFo is the oral carcinogenic slope factor in risk per mg kg^{-1} day^{-1} (EPA, 2003).

In addition to equation manipulation, conceptual models can also be developed with site specific information on soil parameters such as bulk density, percent clay or organic matter. Because of the binding of contaminants to organic matter and clays and the influence of soil pore space (as expressed by bulk density) on PAH fate, these soil properties are considered the most important for determining remediation goals (IEPA, 2004).

Despite the use of equations for determining RBCs for contaminants of concern, they are difficult to find in regulatory documents. This leads to considerable interest in the basis for SSLs and criteria for dredge sediment monitoring and reclamation standards on a state by state basis. Each state determines SSLs based on some type of risk assessment, i.e. Illinois and New York utilize standards suggested by the Integrated Risk Information System (IRIS) and Health Effects Assessment Summary Tables (HEAST), New Jersey bases some limits on “practical quantitation” (NJDEP, 1997), and Virginia divides the EPA RBC and divides it by 10 for noncarcinogenic contaminants (VDEQ, 2008). Additionally, Illinois allows for background determination of inorganics based upon statewide background data or statistically valid site specific data (IEPA, 2007; TACO, Appendix A, Table G) and New York State provides a table of background inorganic levels found in eastern United States for basis of comparison (NYDEC, 1994; TAGM 4046, Table 4). Some states list EPA levels for inorganics without consideration of background levels. It is important to have state specific, risk based standards which account for background levels to avoid problems during site evaluation, more specifically criteria for determining “clean” dredge sediment. Information on state regulatory documents can be found in Table 10.

Soil Screening Levels: Soil screening levels are an expression of the RBCs and were originally developed as a tool to generically standardize and accelerate the remediation of contaminated sites for future residential land use (EPA, 1996). Upon creation, SSLs were tailored to the cleanup goals of sites listed on the National Priorities List (NPL) for superfund sites, but have since been used by different states as goals or to calculate acceptable levels for the cleanup of contaminated residential and industrial sites. Residiential site use SSLs are more strict than industrial because of the risk associated with human contact in a residential setting. Environmental Protection Agency SSLs are not intended to be used as national cleanup standards, rather to identify areas and contaminants where no further action is required under CERCLA and to provide the framework for calculating site specific SSLs (EPA, 1996).

Table 10. Summary table of overview documents, federal and state regulations pertaining to dredge sediment remediation.

Name	Year Published	Weblink	Title of Document and Summary
Dredge Overview Documents and Reviews of Guidelines			
Summary of Available Guidance and Best Practices for Determining Suitability of Dredged Material for Beneficial Use	2007	http://el.erdc.usace.army.mil/elpubs/pdf/trel07-27.pdf	*ERDC/EL TR-07-27.* Review through US Army Corps of Engineers, Engineer Research and Development Center. Includes information on remediation techniques, beneficial use, and an extensive appendix of SSLs for EPA and several states
Testing and Evaluating Dredged Material for Upland Beneficial Uses: A Regional Framework for the Great Lakes	2004	www.glc.org/dredging/publications	Review of dredging operation regulations for states in the Great Lakes Region. Also includes soil testing/evaluation, material handling guidelines, case studies, and annotated bibliography
Federal Regulations Applying to Dredging			
Clean Water Act, Section 401	1994	http://www.usace.army.mil/inet/functions/cw/cecwo/reg/sec401.htm	*33 USC 1341, Public Law 92-500*. Permitting, potential discharges from dredge containments must meet state water quality and upland criteria
Clean Water Act, Section 404	1994	http://www.usace.army.mil/inet/functions/cw/cecwo/reg/sec404.htm	*33 USC 320-330, Public Law 92-500*. Guidance for regulation of leachates, discharge of dredge sediments into lakes, rivers or wetlands. Does not apply to upland placement

Coastal Zone Management Act (CZMA)	1972	http://www.epa.gov/oecaagct/lzma.html	Preserve, protect, develop and restore coastal natural resources
Comprehensive Environmental Response, Compensation and Liability Act (CERCLA)	1980	http://www.epa.gov/superfund/policy/cercla.htm	Also known as *Superfund*, designed to respond to situations involving abandoned hazardous waste disposal sites both in short- and long-term situations. Though this is not dredge specific, some state use guidelines for dredge sediments guided by CERCLA
Endangered Species Act (ESA)	1973	http://www.fws.gov/endangered/whatwedo.html	Requires assurance endangered species will not be impacted by activities, in this case, dredging
Fish and Wildlife Act	1956	http://www.fws.gov/laws/lawsdigest/fwact.html	Protects fish, shellfish and wildlife
Marine Protection, Research and Sanctuaries Act	1972	http://www.epa.gov/history/topics/mprsa/index.htm	Also known as the *Ocean Dumping Act*, which prohibits the dumping of material into the ocean that would endanger human health or degrade marine environments
National Environmental Policy Act (NEPA)	1969	http://www.epa.gov/compliance/resources/policies/nepa/	Requires federal agencies to consider environmental values in decision making process
Resource Conservation and Recovery Act (RCRA)	1976	http://www.epa.gov/osw/laws-reg.htm	Governs disposal of solid and hazardous wastes
Rivers and Harbors Act (RHA)	1899	http://www.usace.army.mil/cw/cecwo/reg/rhsec10.htm	Required all work in navigable waters to be permitted

Standards for the Use of Disposal of Sewage Sludge, US EPA	1999	http://www.epa.state.oh.us/dsw/sludge/503_08_04_99.pdf	*40 CFR 503. Passed under CWA, Section 405, D and E*. Regulates use of biosolids and could easily be applied to dredge sediment screening levels
Submerged Lands Act	1953	http://www.usace.army.mil/cw/cecwo/reg/rhsec10.htm	Three miles of submerged lands off of states belong to the federal government. Mainly created for natural resource exploration, but applies to dredging activities
Water Resources Development Act (WRDA)	1992	http://epw.senate.gov/wrda92.pdf	*Section 204, WRDA 1992.* Aquatic ecosystem restoration guidelines, not applicable to upland placement of dredge sediments

Federal Soil Cleanup Guidelines

EPA Regions Homepage	NA	http://www.epa.gov/osw/regions.htm	Allows user to click on EPA regions to find information on solid waste and cleanup values
EPA Region I	NA	http://www.epa.gov/region01/newseven/index.html	Includes CT, ME, MA, NH, RI, and VT. Use general EPA SSLs created in 1996
EPA Region II	NA	*Homepage:* http://www.epa.gov/region2/ *Dredge Specific:* http://www.epa.gov/region02/water/dredge/index.html	Includes NJ, NY and PR. No specific SSLs for this region, but dredge regulations were found
EPA Region III	NA	*SSLs:* http://www.epa.gov/reg3hwmd/risk/human/index.htm *Soil Screen Guidance:* http://rais.ornl.gov/calc_start.htm	Includes: DE, DC, MD, PA, VA and WV. Soil Screening Levels (SSL) based on literature for this region. Updated in 2007
EPA Region IV	NA	*Homepage:* http://www.epa.gov/region4/index.html *Waste and Cleanup:* http://www.epa.gov/region4/waste/	Includes: AL, FL, GA, KY, MS, NC, SC, and TN

EPA Region V	NA	http://www.epa.gov/R5Super/ecology/html/screenguide.htm	Includes: IL, IN, MI, MN, OH, and WI. Soil Screening Levels (SSL) based on literature for this region.
EPA Region VI	NA	*Homepage:* http://www.epa.gov/earth1r6/index.htm *Risk Assessment Document:* http://www.epa.gov/region6/6en/xp/eri.pdf	Includes: AR, LA, NM, OK, and TX. Risk assessment document for region that would apply to dredged materials, but no specific SSLs
EPA Region IX	NA	*Homepage:* http://www.epa.gov/region09/index.html *SSLs and Guidance:* http://www.epa.gov/region09/waste/sfund/prg/#prgtable	Includes: AZ, CA, and NV. SSLs for superfund sites (which can be applied to dredge material) located in PRG 2004 table on website link, and helpful documents for interpretation of SSLs located on listed website
EPA Region X	NA	*Homepage:* http://www.epa.gov/region10/ *SSLs:* http://www.nws.usace.army.mil/PublicMenu/Menu.cfm?sitename =dmmo&pagename=RSET	Includes: AK, ID, OR, and WA. The USACE has a dredge material management office for the state of WA, with SSLs
NOAA SQUIRT	2006	http://response.restoration.noaa.gov/book_shelf/122_squirt_cards.pdf	Set of quick reference guides for soil and water contaminant levels. Updated 2006

Web-Available Coastal State Regulations and Guidelines

Links to State Environmental Quality Webpages through EPA	NA	http://www.epa.gov/epaoswer/osw/stateweb.htm	Can click on states to find environmental agencies and further information on solid and hazardous wastes (which regulates most PAH contaminated soils and dredge material in absence of specific dredge regulations)[1]

Connecticut Department of Environmental Protection	1996	http://www.ct.gov/dep/lib/dep/regulations/22a/22a-133k-1through3.pdf	Not specific to dredge sediments[2]. *Regulations of Connecticut State Agencies Sections 22a-133k-1 through 22a-133k-3*. Risk based soil remediation guidelines which apply to the cleanup of contaminated sediments
Delaware Department of Natural Resources and Environmental Control	1999	http://www.dnrec.state.de.us/DNREC2000/Divisions/AWM/sirb/DOCS/PDFS/Misc/RemStnd.pdf	Not specific to dredge sediments. *Remediation Standards Guidance under the Delaware Hazardous Substance Cleanup Act*. SSLs divided into restricted use (industrial) and unrestricted use (residential) categories, and critical water resource areas and non-critical water resource areas
Florida Department of Environmental Protection	1994	http://www.dep.state.fl.us/water/monitoring/seds.htm	Specific to dredge sediments. Flo*rida Sediment Quality Assessment Guidelines (SQAGs), Chapter 6*. Extremely low SSLs and not really applicable to upland placement of dredge material
Illinois Environmental Protection Agency	2004	http://www.epa.state.il.us/land/taco/	Not specific to dredge sediments. *Tiered Approach to Corrective Action (TACO)* for remediation of contaminated soil and groundwater. SSLs are set by risk based criteria. Section 742, Appendix A and B (Tier 1 SSLs); Section 742, Appendix C, Table A (risk based SSL equations)

Indiana Department of Environmental Management	2001	http://www.in.gov/idem/programs/land/risc/index.html	Not specific to dredge sediments. *Risk Integrated System of Closure (RISC) and Solid Waste Guidelines Evaluation of Reclamation Criteria and SSLs, Appendix 1* (updated in 2006). Cost effective program to be used in conjunction with other regulations for the closing of contaminated sites, see technical guide tab from website for full document. SSLs are dependent upon pH (regular closure levels determined for pH 6-8) and based on equations from the EPA Soil Screening Guide (1996)
Maine Department of Environmental Protection	2006 (revised)	*Basics on Dredge:* http://www.maine.gov/dep/blwq/docstand/fsdredg.htm *Regulations:* http://www.maine.gov/dep/rwm/solidwaste/index.htm	Specific to dredge sediments, upland placement. Section under *Solid Waste Management Regulations, Beneficial Uses of Solid Wastes, Chapter 418*
Maryland Department of the Environment	2001	http://www.mde.state.md.us/assets/document/hazcleanup_Aug2001.pdf	Not specific to dredge sediments, soil cleanup standards for voluntary cleanup and superfund scenarios. *Cleanup Standards for Soil and Groundwater.* Appendix in document with SSLs, calculations for determining SSLs, and background levels for the state
Massachusetts Department of Environmental Protection	2007	http://www.mass.gov/dep/recycle/laws/drdgmat.htm	Proposal to regulate dredge material under federal clean water act instead of hazardous materials act for MA. If the material is considered hazardous, both regulations will apply. No SSLs

Michigan Department of Environmental Quality	2005	*Document:* http://www.deq.state.mi.us/documents/deq-wmd-swp-pt115rls.pdf *Criteria:* http://www.deq.state.mi.us/documents/deq-wmd-swp-AppendixC.pdf	Not specific to dredge sediments. *Solid Waste Management Act, Part 115.* Regulates dredge sediment under solid waste. *Act 307, Type B* contains clean up criteria for soil. Background levels from natural geology taken into consideration
Minnesota Pollution Control Agency	1999	*Document:* http://www.pca.state.mn.us/cleanup/pubs/srv3_99.pdf *Tier 1 SRVs:* http://www.pca.state.mn.us/publications/risk-tier1srv.xls *Tier 2: SRVs:* http://www.pca.state.mn.us/publications/risk-tier2srv.xls	Not specific to dredge sediments. *Soil Reference Values (SRV) and Soil Leachate Values (SLV).* Specific exposure standards, Tier 1: conservative screening, Tier 2: generalized site specific criteria, Tier 3: case specific evaluation for material not meeting Tier 1 or 2 standards. Excel spreadsheets available to calculate risk for site based contaminant concentrations
New Jersey Department of Environmental Protection (NJDEP)	1997	http://www.njstatelib.org/digit/r588/r5881997.html	Specific to dredge sediments. *The Management and Regulation of Dredging Activities and Dredge Material in New Jersey's Tidal Waters*. Addresses permitting, open water and upland placement, and beneficial use alternatives. Direct Contact Soil Cleanup Criteria for residential and non-residential

New York State Department of Environmental Conservation	1994	http://www.dec.ny.gov/regulations/2612.html	Not specific to dredge sediments. *Technical and Administrative Guidance Memorandum (TAGM): Determination of Soil Cleanup Objectives and Cleanup Levels (4046)*. Created to establish criteria to clean up superfund sites. SSLs for carcinogens based on human health levels in HEAST, human health based levels for systemic toxicants, calculated from Reference Doses (RfDs), groundwater and drinking water standards, background values of contaminants and detection limits. Goal is to remediate to background levels
Ohio Environmental Protection Agency	2007	http://www.epa.state.oh.us/legal/pubnots/071228.pdf	No clear regulations specific to dredge material. Regulated under solid waste unless contaminated. Then regulated under biosolids (*OAC 3745-40*)
Pennsylvania Department of Environmental Protection	2001	http://www.depweb.state.pa.us/ocrlgs/cwp/view.asp?A=1459&Q=518871&landrecwasteNav=|	Not specific to dredge sediments. Soil screening levels for cleanup of superfund and other hazardous sites. Will use dredge sediments for abandoned mine land reclamation, but difficult to locate general dredge regulations
Rhode Island Department of Environmental Management	2003	http://www.dem.ri.gov/pubs/regs/regs/water/dred0203.pdf	Specific to dredge sediments. *Rules and Regulations for Dredging and the Management of Dredged Material.* Limited screening levels. Values for total petroleum hydrocarbons, PCBs and several metals only

Texas Commission on Environmental Quality	2006	http://www.tceq.state.tx.us/remediation/rrr.html	Not specific to dredge sediments, *Risk Reduction Rule, Title 30, Texas Administrative Code Chapter 335, Subchapter S.* Sets forth requirements for risk reduction standards for undertaking of remediation. Referenced in Texas dredge documents
Virginia Department of Environmental Quality	2008, updated webpage	http://www.deq.virginia.gov/vrprisk/raguide.html	Not specific to dredge sediments. *Voluntary Remediation Program, Risk Assessment Guidance*. Tiers I and II have unrestricted use, Tier III is restricted use. SSLs are based on EPA Region III Risk Based Concentrations and EPA Soil Screening Level Guidance. Recognize that background levels (such as those for Arsenic) may exceed SSLs and suggest site specific measurements to make adjustments. SSLs for non-carcinogenic material are determined by dividing the EPA Region III Risk Based Concentration by 10
Washington State Department of Ecology	1989	http://www.ecy.wa.gov/pubs/9406.pdf	Not specific to dredge sediments. *Model Toxics Control Act Statute and Regulation (MTCA).* Regulates cleanup of superfund sites as well as hazardous waste disposal, site specific, unrestricted use and industrial use SSLs

[1] The following coastal states were searched, but regulations were not clear and/or not stated to apply to dredge material: Alabama, California, Georgia, Louisiana, Mississippi, North Carolina, Oregon, South Carolina, and Wisconsin.

[2] The statement, “not specific to dredge sediments” means that the document referenced was referred to for management and regulation of dredge sediments, but was not created specifically for the management and regulation of dredge sediments.

Analytical Methods

The following is a summary of the different methods in the EPA SW-846 manual (EPA, 2007) used for the extraction, cleanup, and analysis of PAHs.

Sample handling

Recommendations on sample handling from EPA (2007) (Table 11):

- Stock standard solutions should be stored in polytetrafluoroethylene (PTFE)-sealed containers at 4 C or below.
- Containers used to collect samples for the determination of semivolatile organic compounds should be of glass or Teflon, and have screw-caps with Teflon lined septa. Plastic containers or lids may not be used for the storage of samples due to the possibility of sample contamination from the phthalate esters and other hydrocarbons within the plastic.
- Sample containers should be soap and water washed followed by methanol (or isopropanol) rinsing.
- A surrogate should be added to each sample, blank, laboratory control sample (LCS), and matrix spike sample just prior to extraction or processing to monitor for unusual matrix effects, gross sample processing errors, etc. Recommended surrogates:
    - For EPA 8100 (GC): 2-Fluorobiphenyl (also recommended for EPA 8270), and 1-Fluoronaphthalene.
    - For EPA 8310 (HPLC): Decafluorobiphenyl.

Extraction

Table 11. U.S. EPA recommended extraction methods for PAHs (EPA, 2007)

Method	Matrix	Extraction Type	Remarks
3510	Aqueous	Separatory Funnel Liquid-Liquid Extraction	• Inexpensive glassware, fairly rapid. • Labor intensive. • Large volumes of solvent required. • Subject to emulsion problems.
3520*	Aqueous	Continuous Liquid-Liquid Extraction	• Excellent for samples with particulates (up to 1% solids). • No hands-on manipulation. • More expensive glassware. • Fairly large volumes of solvent. • Lengthy extraction time (6 to 24 hours).
3535	Aqueous	Solid-Phase Extraction (SPE)	• Allow extraction of water containing particulates. • Relatively fast. • Use small volumes of solvent. • Require specialized pieces of equipment.
3540*	Solids	Soxhlet Extraction	• Relatively inexpensive glassware. • No hands-on manipulation. • Efficient extraction. • Lengthy (16 to 24 hours). • Fairly large volumes of solvent. • Rugged extraction method; very few variables can adversely affect extraction efficiency.
3541	Solids	Automated Soxhlet Extraction	• Allows equivalent extraction efficiency in 2 hours. • Requires a rather expensive device.
3545	Solids	Pressurized Fluid Extraction (ASE) (Heat & Pressure)	• Rapid and efficient. • Uses small volumes of solvent. • Expensive extraction device.
3550	Solids	Ultrasonic Extraction	• Fairly rapid (three, 3-minute extractions followed by filtration). • Uses relatively large volumes of solvent. Requires a somewhat expensive device. • much less efficient than the other • Extraction techniques.
3560/1	Solids	Supercritical Fluid Extraction (SFE)	• Relatively rapid extraction. • Expensive device.

*EPA Note: Method 3520 (continuous liquid-liquid extraction of aqueous samples) or Method 3540 (Soxhlet extraction of solid samples), seems to be the most robust ones as these methods have the broadest applicability to environmental matrices.

Sample Cleanup

After extraction, cleanup methods are used to reduce and or eliminate sample interferences. Most soil and waste extracts require some degree of cleanup, but cleanup for water extracts may be unnecessary.

For PAH analysis, the recommended cleanup methods are:

- Gel permeation chromatography (3640). This is the most universal cleanup technique for a broad range of semivolatile organics. It is capable of separating high molecular-weight, high boiling material from the sample analytes. It has been used successfully for all the semivolatile base, neutral, and acid compounds associated with the EPA Priority Pollutant and the Superfund Target Compound list to clean up samples prior to GC/MS analysis for semivolatiles and pesticides.
- Alumina (EPA 3610 and 3611). Method 3611 may be used for fractionation of aliphatic, aromatic, and polar analytes.
- Florisil (EPA 3620)
- Silica gel (EPA 3630).

The decision process in selecting between the different options available generally depends on the amount of interferences/high boiling material in the sample extract and the degree of cleanup required by the determinative method. For analysis with either the 8100/8310 determinative methods, the cleanup methods 3611, 3630, and 3640 are preferred.

Analysis

Determination procedures include:

- EPA 8100 GC Packed and capillary column with FID (flame ionization detector)
- EPA 8310 HPLC Reverse Phase with UV/ Fluorescence detectors.
- EPA 8270 GC MS
- EPA 8275 Thermal extraction/GC MS
- EPA 8410 GC, capillary column FT-IR

The Mass Spec procedures are generally more specific, but less sensitive than the appropriate gas chromatographic (GC)/specific detection method. Many GC methods with either selective or non-selective detectors are more appropriate for use where the target analytes are known, are of limited number, and of significantly greater concentration than potential interfering materials. When the site where samples are taken from is not well characterized, and the researchers are concerned about a large numbers of analytes, analysis by GC/MS or HPLC/MS may be more appropriate.

Capillary columns usually generally provide more complete separation of the analytes of interest, while packed columns are most appropriately employed when the list of analytes to be determined is relatively short. However, the packed column GC method cannot adequately resolve the following four pairs of compounds:

1. anthracene and phenanthrene
2. chrysene and benz[a]anthracene
3. benzo[b]fluoranthene and benzo[k]fluoranthene
4. dibenz[a,h]anthracene and indeno[1,2,3-cd]pyrene.

The use of a capillary column instead of the packed column, may adequately resolve these PAH. However, unless the purpose of the analysis can be served by reporting a quantitative sum for an unresolved PAH pair, either liquid chromatography (Method 8310) or gas chromatography/mass spectroscopy (Method 8270) should be used for these compounds. See Table 12 for recommened methods and Table 13 for detection limits.

Table 12. Recommended analytical methods for specific PAH compounds (EPA, 2007).

Compound	Determinative Methods
Acenaphthene	8100, 8270, 8275, 8310, 8410
Acenaphthylene	8100, 8270, 8275, 8310, 8410
Anthracene	8100, 8270, 8275, 8310, 8410
Benz[a]anthracene	8100, 8270, 8275, 8310, 8410
Benzo[b]fluoranthene	8100, 8270, 8275, 8310
Benzo[j]fluoranthene	8100
Benzo[k]fluoranthene	8100, 8270, 8275, 8310
Benzo[g,h,i]perylene	8100, 8270, 8275, 8310
Benzo[a]pyrene	8100, 8270, 8275, 8310, 8410
Chrysene	8100, 8270, 8275, 8310, 8410
Dibenz[a,h]anthracene	8100, 8270, 8275, 8310
Fluoranthene	8100, 8270, 8275, 8310, 8410
Fluorene	8100, 8270, 8275, 8310, 8410
Indeno[1,2,3-cd]pyrene	8100, 8270, 8275, 8310
Naphthalene	8100, 8270, 8275, 8310, 8410
Phenanthrene	8100, 8270, 8275, 8310, 8410
Pyrene	8100, 8270, 8275, 8310, 8410

Table 13. Detection limits for certain polycyclic aromatic hydrocarbons (EPA, 2007).

Compound	Detection Limit (µg L^{-1})	
	UV	Fluorescence
Naphthalene	1.8	
Acenaphthylene	2.3	
Acenaphthene	1.8	
Fluorene	0.21	
Phenanthrene		0.64
Anthracene		0.66
Fluoranthene		0.21
Pyrene		0.27
Benz[a]anthracene		0.013
Chrysene		0.15
Benzo[b]fluoranthene		0.018
Benzo[k]fluoranthene		0.017
Benzo[a]pyrene		0.023
Dibenz[a,h]anthracene		0.030
Benzo[g,h,i]perylene		0.076
Indeno[1,2,3-cd]pyrene		0.043

Bioavailability Analytical Methods

Sites contaminated with PAHs can be evaluated using several different measurements: total extraction, mild organic extraction to assess desorbable fractions, and *bioassays* (assessments of bioavailability by uptake and/or toxicity to microorganisms). Although there are a range of bioassays available to assess PAH availability, they are time-consuming and can be expensive. An alternative is to use rapid, reproducible chemical tests to assess bioavailability.

Although total extractable PAH levels are routinely used to assess of contaminated sites, they will grossly overestimate bioavailable PAHs, and thus cannot be used to assess or predict the fraction of PAHs that is accessible to biota (Alexander, 2000; Semple et al., 2003). Different researchers have proposed several mild organic/aqueous extraction procedures to assess the readily available PAH fraction in soil and sediments. Some of these extraction procedures include:

- *Extraction with n-butanol:* Kelsey et al. (1997) reported that availability of phenanthrene to bacteria and earthworms could be accurately predicted with n-butanol extraction. Liste and Alexander (2002) also found good correlation between butanol extraction and PAH availability to earthworms. Bogan and Sullivan (2003) found that the n-butanol extractability of 13 PAH compounds was dependent on soil organic matter content.

- *Triton X-100 shake:* Cuypers (2001) found extraction with Triton X-100 overpredicted PAH availability.

- *Solid phase extraction with Tenax beads:* In this method, Tenax A (a porous polymer of 2,6-diphenyl-p-phenylene-oxide) removes the rapidly desorbing fraction that is equivalent to bioavailable PAH (Uyttebroek et al., 2007). Cuypers (2001) found extraction with Tenax A to correlate well with bioavailable PAH.

- *Aqueous β cyclodextrin shake:* Reid et al. (2000b) proposed β cyclodextrin aqueous solution extraction to predict availability, and found that this solution predicted the amount of phenanthrene available to bacteria. Both Cuypers (2001) and Allan et al. (2006) found extraction with β Cyclodextrin to correlate well with bioavailable PAHs. Papadopolous et al. (2007) compared aqueous cyclodextrin extraction to mineralization of phenanthrene in 4 different soils with different organic matter content ranging from 4.8 to 27 %. High correlation was found between cyclodextrin extractability and microbial mineralization of phenanthrene by indigenous bacteria.

However, no one chemical test predicts the availability of all PAH contaminants to different organisms in all soils. Thus, these tests are better used along with bioassays to assess PAH bioavailability in soils (Stokes et al., 2006).

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