

**Literature Review, Computer Model and Assessment
of the Potential Environmental Risks Associated With
Creosote Treated Wood Products
Used in Aquatic Environments**

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April 25, 1995

Revised

June 1, 1997

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Literature Review, Computer Model and Assessment of the Potential Environmental Risks Associated With Creosote Treated Pilings Used in Marine Waters

Introduction

Creosote has been widely used to protect wood from attack by fungi, marine borers and insects in the United States since 1865. It is a distillate derived from coal tar produced by the carbonization of coal, and consists chiefly of liquid and solid aromatic hydrocarbons.

The treatment of wood products is generally accomplished in accordance with the American Wood-Preservers' Association (AWPA) Standard C1-92. Average creosote penetration using the "empty cell" process in Douglas Fir is 1.5 inches and retention is 20 pounds per cubic foot (pcf) for marine applications and 17 pcf for freshwater (Arsenault, 1992; Baechler & Alpen, 1964). In 1996, AWPA reduced the required retention in temperate marine waters from 20 to 16 pcf.

Creosote is a complex mixture of at least 160 detectable hydrocarbon compounds, all 18 major components are cyclic and aromatic. According to Environment Canada (1992), 80% of creosote is composed of polycyclic aromatic hydrocarbons (PAH). Some low molecular weight creosote compounds, such as the naphthalenes, have densities less than one. However, most of the components are heavier than seawater and sink in a water column.

Public concern has been raised by recognition that creosote contains many of the 16 PAHs known to be acutely and chronically toxic to marine animals. Several of these compounds, most notably benzo[a]pyrene, can degrade to carcinogenic, teratogenic and mutagenic intermediates during metabolism. As with most potentially harmful substances, pathological responses are a matter of exposure (concentration and length of time).

The purpose of this report is to review the literature pertaining to creosote, its potential toxic effects, and to assess the potential environmental risks associated with its use in aquatic environments. To properly address these issues, there are a number of questions that must be answered. Is creosote toxic and at what levels? What are normal background levels of PAH in the environment and how do creosote treated pilings contribute to those levels? A spreadsheet (Microsoft EXCEL and LOTUS) based computer model is described. This model quantitatively predicts environmental levels of PAH associated with treated wood. Lastly, this report will assess the environmental risks associated with the release of PAH from creosote treated wood products.

The report has been organized to provide background information and then to use that information to assess potential environmental risks. There is a growing body of "gray literature" concerning creosote and its impacts. By gray literature, I mean reports such as this one, the Monroe (1992) report, and the 1993, Department of Ecology report by Tera Hegy in *Coastal Currents*. Gray literature consists of material published without the scrutiny of peer review. This author has, for several years provided environmental mediation services to both local government and the Governor's Natural Resource Sub-cabinet. He has listened to testimony and read thousands of pages from the gray literature and peer reviewed literature. Both forms of literature are often written to present a point of view. Selected statements may be extracted from either source and used in a way that the original author did not intend. A thorough bibliography is provided with this assessment to facilitate review of original documentation.

The compounds of concern are the PAHs found in creosote. Most of the following discussion will focus on these polycyclic aromatic hydrocarbons. There are multitudes of sources contributing PAHs to marine environments and there is a considerable body of literature discussing them.

Sources of PAH in Aquatic Environments

Polycyclic aromatic hydrocarbons are formed by a variety of processes, including indirect and direct biosynthesis, fossil fuel production and distribution and incomplete combustion of organic matter. Once formed, PAHs can be transported into an aquatic environment by a number of pathways including fossil fuel distribution, stormwater runoff and sewage effluent.

Biosynthesis. Indirect biosynthesis of PAH occurs when extended quinones and related polycyclic materials (mostly plant and animal pigments) are exposed to the reducing conditions found in anoxic sediments. The resulting PAHs tend to accumulate in the sediments where they were formed. De novo biosynthesis of PAHs by aerobic and anaerobic bacteria, fungi, and plants is controversial. However, Niaussat *et al.* (1969), Niaussat (1970), Mallet *et al.* (1972) and Brisou (1972) conclude that both aerobic and anaerobic bacteria can biosynthesize benzo[a]pyrene (B[a]P) and certain other PAHs using fatty acids, sterols, plant pigments and aliphatic terpenes as substrates. In most cases where PAH biosynthesis has been reported, accumulation of PAH in the organisms

purported to have synthesized them could also have been attributed to uptake of PAH from exogenous sources.

In light of all of the literature reviewed, it appears that PAH biosynthesis may occur to a limited extent under special environmental conditions when necessary bacterial growth substrates are present. Eisler (1987) suggested that, on a global scale, biosynthesis annually contributes 5,952,420 pounds of PAH to aquatic environments.

Fossil fuels including peat, coal, and petroleum are relatively rich in complex assemblages of PAHs. These compounds reach aquatic environments through surface runoff, in waste water, and as a result of petroleum spillage. Eisler (1987) estimates that spilled petroleum contributes 374,782,200 pounds of PAH to aquatic environments each year. This source overwhelms all others in terms of global inputs.

Pyrolysis of organic matter at temperatures between 400 and 2000 °C results in the generation of a wide variety of PAHs. Reducing conditions (insufficient oxygen) in the pyrolytic environment favor PAH production. Forest and grass fires, industrial processes, heating, power generation and petroleum refining release significant amounts of PAH into the atmosphere.

These products of combustion are subject to chemical- and photo-oxidation. However, their residence time in the atmosphere is long enough to allow wide dispersal and they are a major source of PAH to aquatic environments. According to Eisler (1987), forest and prairie fires together with agricultural burning release nearly 72 million pounds of PAH into the atmosphere. This is three times the amount from all other pyrolytic sources combined (24,000,000 lbs.)

Petrolytic Sources. Johnston and Harrison (1984) report that B[a]P deposition along a United Kingdom motorway is $2.8 \mu\text{g m}^{-2} \text{ week}^{-1}$. Note that B[a]P is approximately 0.5 to 2.5% of some PAH mixtures and a direct extrapolation suggests that the total PAH loading along a well used highway may be $560 \mu\text{g m}^{-2} \text{ week}^{-1}$.

Winter levels of PAH in coastal areas are higher than summer levels. This is attributed to increased pyrolytic input from the burning of fossil fuels for power generation and heating (Bouloubassi and Saliot, 1991). Broman *et al.* (1990) suggested that primary PAH inputs in the Baltic region were from exhaust emissions associated with automobiles, domestic heating, refuse incineration plants, ships and aircraft.

Neff (1979) reports that little used (224 km) motor oil contains 6.4 ppb B[a]P equivalent to nearly 1,280 ppb total PAH. Dunn and Stich (1976) found up to 22,000 ppb B[a]P in well used crankcase oil. This is equivalent to 4.4 parts per thousand total PAH. In 1989, Washington State had 4,179,000 vehicles registered. These vehicles produced 21,000,000 gallons of used crankcase oil each year. That may represent as much as 625,000 pounds of PAH available to the environment.

Industrial and domestic wastewaters are rich in PAH. Secondary sewage treatment removes some PAH, but most are released to aquatic environments through

STP outfalls . Eisler (1987) notes that untreated, raw sewage contains 100 to 500 ppb total PAHs and sewage sludge contains 200 to 1,750 ppb PAH.

Hoffman *et al.* (1984) noted that stormwater runoff from urban areas and highways accounted for 71% of the high molecular weight PAHs and 36% of the total PAH loading to Narrangansett Bay. More than 30% of all pyrolytic PAHs in the coastal sediments of Washington State are supplied by riverine transport of suspended particulate materials, while direct atmospheric input accounts for a maximum of 10% (Prahl *et al.*, 1984).

Observed levels of PAH in aquatic environments. As a result of the many natural sources, polycyclic aromatic hydrocarbons have been ubiquitous in aquatic environments for thousands of years. However, significantly increased levels have been recorded in ocean sediments since the turn of this century. Neff (1979) reviews the distribution of PAHs in aquatic environments. He found very low (<1 - 2 ppb) levels of PAH in the water column of pristine areas.

High molecular weight PAH tend to accumulate in sediments and Neff (1979) recorded low sediment contamination in pristine areas (< 50 ppb) and higher levels (to 15,000 ppb) associated with industrialized areas and/or human population centers.

Eisler (1987) found a similar distribution of sediment PAH levels. Levels in pristine areas of Alaska, Africa and the Amazon Basin ranged from 5 to 544 ppb. Levels in urbanized and industrialized areas ran as high as 791,000 ppb in the United Kingdom.

Cerniglia and Heitkamp (1991) measured sediment PAH levels ranging from 5 ppb for an undeveloped area in Alaska to 1.79×10^6 ppb at an oil refinery outfall in Southampton, England. Sediment PAH concentrations in other industrialized areas ranged from 198 to 232,000 ppb.

O'Connor (1991) reports PAH concentrations in sediment at U.S. sites ranging from undetectable to nearly 60,000 ppb in Boston Harbor, MA. Elliott Bay, WA has >28,000 ppb PAH in its sediment.

The Puget Sound Environmental Atlas (1992) lists high molecular weight PAH (hPAH) levels in sediments from the Bellingham area at generally less than 2,000 ppb. However there are two sites adjacent to the City of Bellingham where sediment levels are between 2,000 and 5,999 ppb.

Summary. Eisler (1987) summarizes PAH loading to aquatic environments from a number of sources. Values are in pounds of PAH per year.

Petroleum spillage	374,782,200
Atmospheric deposition (from combustion)	110,230,000
Wastewater	9,700,240
Surface land runoff	6,481,524

There is a consistent thread running through research and reviews by Bouloubassi and Saliot (1991), Neff (1979), Eisler (1987) and others cited above. These papers indicated that PAH are ubiquitous in marine and terrestrial environments. There are numerous natural sources of PAH including volcanoes, forest and prairie fires, natural oil seeps and biosynthesis. According to the sediment record, PAHs have been present in our environment since there was life. Historically, most of the natural sources of PAH were either the result of biosynthesis, in which case the PAH remained stable in the anoxic environments where they were formed, or the inputs resulted from volcanoes or forest and prairie fires. These pyrogenic PAH were widely distributed over large geographic areas and resulted in relatively low background levels (< 10 to 50 ppb).

Anthropogenic inputs from oil spills, wastewater, stormwater and petrolysis tend to be concentrated in urban and industrial areas. This may result in concentrating PAHs in aquatic environments and the sediments that underlie them. It is these higher concentrations that are of concern. Petroleum spills represent the major PAH input to our oceans and can have devastating, although probably short term (2 to 5 year) impacts on aquatic resources.

The literature suggests that sediment PAH levels of less than 200 to 500 ppb may be expected in pristine areas. Worldwide, urban areas such as Puget Sound have much higher background sediment PAH levels in the range of 500 to several thousand ppb. Heavily industrialized areas may have PAH levels of 10,000 to several hundred thousand ppb. In non-industrial areas of Puget Sound, the background level of PAH in sediments is likely to be 500 to 1500 ppb.

Fate of PAH in the Marine Environment

Introduction. Polycyclic aromatic hydrocarbons form a family of compounds and the routes of degradation and fates are different for the major classes of PAH. In water, PAHs evaporate, disperse into the water column, become incorporated into bottom sediments, concentrate in aquatic biota, or experience oxidation and biodegradation.

The most important degradative processes for PAHs in the marine environment are photo-oxidation, chemical oxidation, and biological transformation by bacteria and animals (Neff 1979). Most PAHs in aquatic environments are associated with particulate materials and only about a third are present in dissolved form.

Dissolved PAHs will likely degrade rapidly through photo-oxidation (EPA 1980). They degrade most rapidly at higher concentrations, at elevated temperatures and oxygen levels, and at higher levels of solar irradiation. Different PAHs vary significantly in their relative sensitivity to photo-oxidation.

Heavier molecular weight PAH. Because of their low aqueous solubility and hydrophobic character, the higher molecular weight PAH readily adsorb to particulate materials and solid surfaces in water. The ultimate fate of PAHs that accumulate in sediments is believed to be biotransformation and degradation by benthic organisms (EPA 1980). PAHs in sediments degrade very slowly in the absence of oxygen and may persist indefinitely in anaerobic conditions (Neff 1979).

Microbial metabolism. Cerniglia and Heitkamp (1991) address microbial degradation of PAHs in aquatic environments. They note that a wide variety of bacteria, fungi and algae have demonstrated the ability to metabolize PAH. Low molecular weight PAHs, such as naphthalene, degrade rapidly. The higher molecular weight PAHs such as benz(a)anthracene and benzo(a)pyrene are more resistant to microbial attack. They also note that the most rapid biodegradation of PAHs occur at the water/sediment interface. This is because prokaryotes oxidize PAH as a first step in metabolism. Deeper sediments usually contain little oxygen, thus inhibiting microbial metabolism.

Cerniglia and Heitkamp (1991) summarized the available literature describing the half life of PAH in various environments. The results are highly variable and depend on PAH species together with a range of environmental and biological factors. Bacterial communities in polluted areas metabolize PAH more quickly than communities in unpolluted areas. Lighter weight PAHs are metabolized more quickly than heavier PAH. Naphthalene has a short turnover time (days to weeks) whereas the five ringed Benzo(a)pyrene has a long turn over time (years under unfavorable conditions).

Ingram (1982) observed that the concentration of creosote in leaching vats increased to greater than 700 ppb in the first 72 hours and then decreased to less than 34 ppb at the end of 20 days. He attributed that decrease to bacterial metabolism of the low molecular weight PAH being leached from the pile sections in his study.

Tagatz *et al.* (1983) noted that creosote concentrations decreased by 42% over an 8 week period in sediments artificially contaminated as part of their mesocosm studies. They attributed the decrease to microbial metabolism.

Summary. Neff (1979) attempts to integrate the degradative processes associated with PAH removal from aquatic environments. He concludes that the residence time of PAH in marine waters is brief. The lower molecular weight aromatics (benzene to phenanthrene) are removed primarily by evaporation and microbial activity. Higher molecular weight PAH are removed mainly by sedimentation and photo-oxidation. Degradation of PAH by animals in the water column is of minor importance. In nutrient rich, biologically active, aerobic, sediments, the degradation of PAH is dramatically increased by healthy bacterial and fungal communities. In anaerobic sediments, the heavier molecular weight PAH (4 through 7 rings) may persist for years.

Bioconcentration and Bioaccumulation of PAH

in the Marine Environment

Introduction. Bioconcentration and bioaccumulation of contaminants is of special importance because some aquatic species, most notably bivalves, have demonstrated an ability to rapidly bioconcentrate contaminants in water to high tissue levels. The concern is that persistent contaminants may move up the food chain, biomagnifying to higher concentrations in each trophic level, until contaminants found at non-toxic levels in the ambient environment reach concentrations where they do cause stress and disease. For effective biomagnification and movement of contaminants through the food chain, several conditions must be met.

First, organisms must have the ability to bioconcentrate low levels of contaminants from the water column or their food. Second, these contaminants, or their toxic metabolic intermediates, must be retained, unaltered, in the tissues of the organism until it falls prey to an animal at a higher trophic level.

There are a number of factors that mitigate against biomagnification. If contaminants are not absorbed, they cannot accumulate. Numerous organisms, particularly vertebrates, have the ability to either metabolize or to excrete contaminants. The gut, liver, kidney and gall bladder are common sites of PAH concentration, metabolism and excretion in vertebrates. If the contaminants are either rapidly excreted, or they are metabolized to non toxic compounds, then the chain is broken and biomagnification is not effective in passing contaminants upward through the food chain.

DDT is an excellent example of a persistent compound that was bioconcentrated from low levels in the water to higher levels; first in plankton, then in fish, and finally in bird populations with devastating consequences.

Bioconcentration of dissolved PAH from the water column. Neff (1982) reports that all species of marine organisms studied to date, rapidly bioconcentrate polycyclic aromatic hydrocarbons (PAH) from low concentrations in the ambient water.

Bivalve mollusks, particularly the commercially important mussel (*Mytilus edulis*) and oysters of the genera *Ostrea* and *Crassostrea* have received far more attention than other aquatic invertebrates, plants, or fish. They are excellent subjects for monitoring pollutants because they filter substantial quantities of water over large and highly permeable gills. For these reasons mussels have been the subject of numerous studies such as the Global Mussel Watch Program. Many of these studies have focused on the accumulation of metals and the highly carcinogenic molecule benzo[a]pyrene (B[a]P).

Benzo[a]pyrene levels recorded in Neff (1979) for uncontaminated areas fall in the undetectable to perhaps 50 ppb range. Dunn and Stich (1975, cited in Dunn and Stich, 1979) recorded tissue levels averaging 59 ppb in areas associated with marinas and higher levels, averaging 402 ppb, on creosote treated pilings. Dobroski and Epifanio (1980) found that direct uptake of B[a]P from seawater by diatoms was much greater than the rate of trophic transfer from the diatoms to clam larvae.

Eisler (1987) recorded elevated PAH concentrations, especially benzo(a)anthracene, chrysene, fluorene, phenanthrene, and pyrene in oyster tissues and

sediments from the vicinity of marinas. These levels are notably higher in cooler months, when lipids and glycogen are being stored preparatory to spawning (Marcus and Stokes, 1985).

For mussels, the general trend towards lower levels of higher molecular weight PAHs relative to the levels in associated sediment suggests an uptake mechanism that involves the solution of PAH in water. Supporting this hypothesis is the observed rapid turnover and shorter half-life of the more soluble, lower molecular weight PAHs (Dunn, 1980 in Eisler, 1987). This suggests that the more soluble (and more bioavailable) PAH are effectively removed from sediments and metabolized by bivalves. The higher molecular weight PAH (associated with chronic stress and genetic disorders) remain in the sediments because of their low solubility. However, once absorbed hPAH are not readily metabolized by bivalves.

Polycyclic aromatic hydrocarbon levels in fish are usually low because this group rapidly metabolizes all PAHs (Lawrence and Weber, 1984; West *et al.* 1984) or they excrete them. High concentrations of PAH are typically found in the gut, liver and bile. Raw fish from unpolluted or moderately polluted water seldom contain detectable amounts of PAH. However, smoking and cooking of fish can increase PAH content to significant levels. The smoky, crunchy, taste we love in BBQ steaks is very high in PAHs.

Neff (1982) reports bioconcentration factors (BCF) for several PAHs in the clam *Rangia cuneata*. It should be emphasized that the BCF values, which range from 6.1 to 32, are for PAH dissolved in water. Eisler (1987) has summarized BCF values from the literature. The BCF values reported in his own paper contradict his assertion that bivalves accumulate PAHs more rapidly than fish. For all of the values given in his review the averages are:

Bivalves	82 (n = 8)
Fish	6,844 (n=34)

Note: Eisler's (1987) paper reported bioconcentration values from 6 to 236 in the clam *Rangia cuneata*. Four of the five values were less than 33. For fish, bioconcentration values range from 44 to 82,916 with most values in the hundred to thousand times range.

Bioconcentration of PAH from sediments. The ultimate fate of most heavier molecular weight PAH deposited in aquatic environments is sedimentation. Roesijadi *et al.* (1978) examined the accumulation of Prudhoe Bay crude oil and specific PAH from oil-contaminated sediments by three infaunal invertebrate species, the sipunculid worm *Phascolosoma agassizii* and the clams *Macoma inquinata* and *Protothaca staminea*. They found that the efficiency of PAH uptake from sediments was much lower than from water. Bioconcentration factors for uptake of the four PAH from contaminated sediments were 0.2 or less, indicating no significant bioconcentration of PAH by this

route. However, bioconcentration factors for uptake of these four PAH from seawater were in the 10.3 to 1349 range indicating a low to moderate potential for bioconcentration.

Eisler (1987) suggests that bivalves readily take up PAH from sediments. This hypothesis is contradicted by the results of numerous studies. O'Connor (1991) found that at 117 National Status and Trend Sites where there were both mollusks and fine-grained sediments, the average ratio of mollusk tissue to sediment concentration was only 1.2 for total PAH. He also noted that mollusks accumulate the low molecular weight (and more highly soluble) PAHs to a greater extent (2.0) than the high molecular weight PAH (0.64). Eaton and Zitko (1978) noted that PAH levels in clams and mussels were two orders of magnitude below those detected in sediments. Neff (1979) cites Perdriau's (1964) finding that in no case did benthic animals contain elevated levels of B[a]P compared with sediments collected from the French coast. Tissue concentrations in the animals were, on average, 36% of the sediment concentration.

Numerous studies cited above and in Neff (1982) lead to the general conclusion that sediment-adsorbed PAHs are not readily assimilated by benthic animals. Accumulation of PAH from sediment, when it occurs at all, may be attributed in large part to uptake of PAH desorbed from sediment particles into the interstitial water. This hypothesis is supported by Swartz *et al.* (1989) who conclude that the concentration of chemicals in interstitial water is the primary determinant of sediment toxicity - not the bulk concentration in the sediment.

Depuration of PAH. Southworth *et al.* (1980) found a half life of less than one hour for all PAHs metabolized by *Daphnia pulex*. Jackim and Lake (1987) reported that the half life of PAHs in most bivalves is on the order of 2 to 16 days. These studies suggest that PAHs are either rapidly metabolized or excreted. At least by these species.

Bioaccumulation from food. Neff (1979) reports that the annelid, *Neanthes arenaceodentata*, has little, if any, ability to accumulate 2-methyl-naphthalene from its food. However, the situation is quite different in marine crustaceans and fish where uptake from food was much more efficient than uptake from water. Arthropods (crabs, amphipods, shrimp and etc.) rapidly accumulate the lighter weight PAH and very rapidly excrete or metabolize these compounds. The half life of B[a]P in *Callinectes sapidus* was six days. Neff's (1979) conclusion was that all results dramatically demonstrate the importance of metabolism in eliminating PAH from contaminated crustaceans.

Broman, *et al.* (1990) examined the trophic transfer of PAHs in a study involving seston, the blue mussel (*Mytilus edulis*) and the eider duck (*Somateria mollissima*). Contrary to biomagnification, they observed decreasing PAH concentrations with increasing trophic levels.

Summary. Aquatic organisms are able to efficiently bioconcentrate PAH from the water column. It appears that direct transfer from sediments to organisms living within and on those sediments is minimal. Benthic organisms rarely contain higher concentrations of PAH than are found in the sediments in which they live.

PAHs are rapidly metabolized and excreted by vertebrates and arthropods. In bivalves, which do not efficiently metabolize PAHs, the half-life of most PAHs examined was in the range of 2 to 16 days. These data suggest that PAHs are not persistent in the tissues of aquatic species and that the movement of PAHs through the food chain to higher trophic levels is minimal, if it occurs at all.

Neff (1979) concludes that: "From the limited data available, it would appear that there are large interspecific differences in ability to absorb and assimilate PAH from food. Polychaete worms have a very limited ability to absorb and assimilate PAH, whereas fish absorption of PAH from the gut is limited and variable depending on species of fish, the PAH, and possibly the food matrix in which PAH is administered. Crustaceans, on the other hand, apparently readily assimilate PAH from contaminated food. In all cases where assimilation of ingested PAH was demonstrated, metabolism and excretion of PAH were rapid. Thus, the potential for food chain biomagnification of PAH seems to be limited. For such biomagnification to occur, the material must be readily absorbed from food, and once assimilated, it must be relatively resistant to metabolism or excretion."

Creosote and PAH Toxicity in the Marine Environment

Introduction. Aquatic organisms have been exposed to background levels of PAH for aeons. The diversity of life in aquatic environments attests to aquatic species ability to tolerate these background levels (1 to 2 ppb in the water column and 10 to 500 ppb in sediments). The question asked here is, at what level do PAHs cause pathological responses at the organismal and population levels? In answering that question we will consider two types of toxicity; acute and chronic.

Acute toxicity causes observable physiological lesions and is usually measured by mortality. PAH can interact with cells in several ways to cause toxic responses. As an example, they may bind reversibly to lipophilic sites in the cell and thereby interfere with cellular processes. Potentially impacted and important intracellular organelles include lysosomes which contain strong enzymes important in intracellular digestion of complex organic molecules and in the immune response. Increased lysosomal membrane permeability can result in the unregulated flow of these enzymes into the cytoplasm or blood serum with pathological consequences including autophagy. Eisler (1987) notes that the lower molecular weight, unsubstituted PAH compounds, containing 2 or 3 rings, such as naphthalene, fluorene, phenanthrene and anthracene have significant acute toxicity to some organisms. Whereas the higher molecular weight, four to seven ring aromatics, do not. However, these heavier molecules contain numerous potentially carcinogenic and mutagenic intermediates.

A common measure of acute toxicity is the concentration of a toxicant that causes 50% mortality in a test population within some specified period of time (often 96 hours). This parameter is referred to as the 96-h LC50. Borthwick and Patrick (1982) and Neff (1979) reported 96-h LC50 values for several marine animals. These are summarized in Table 1.

Table 1. Acute toxicity of various PAH to marine organisms as measured by 96-h LC50 values.

Species	96-h LC50
mysids (<i>Mysidopsis bahia</i>) 1	18 to 21 ppb
oysters (<i>Crassostrea virginica</i>)1	700 ppb
pink shrimp (<i>Penaeus duorarum</i>)1	240 ppb
Sheepshead minnows (<i>Cyprinodon variegatus</i>)1	3,500 ppb
Mosquito fish (<i>Gambusia affinis</i>)1	150,000 ppb naphthalene
Mosquito fish (<i>Gambusia affinis</i>)2	1,180,000 ppb toluene
Dungeness crab larvae (<i>Cancer magister</i>)2	8 ppb naphthalene
Dungeness crab larvae (<i>Cancer magister</i>)2	170 ppb naphthalene

Sources: 1 Borthwick and Patrick (1982)

2 Neff (1979)

Interestingly, in Neff's (1979) discussion of the effects of PAH on aquatic animals, he cites Caldwell *et al's.* (1977) finding that continuous exposure to naphthalene concentrations of 19 to 170 ppb had no effect on the survival of Dungeness crab larvae. No explanation was given for the very low (8 ppb) value reported in Neff's (1979) paper or for the differences in the values reported. One might expect that exogenous factors contributed to the discrepancy. The LC₅₀ values reported in the literature for most organisms and PAH compounds are in the 500 to 5,000 ppb range.

Neff (1979) found that in all but a few cases, the concentrations of aromatic hydrocarbons that are acutely toxic to aquatic animals are several orders of magnitude higher than concentrations found even in the most heavily polluted marine and fresh waters. However, sediments from polluted regions may contain aromatic hydrocarbons at concentrations similar to, or higher than, those which are acutely toxic. The limited bioavailability of sediment-adsorbed PAHs probably renders them substantially less acutely toxic than PAHs in solution. He also notes that PAH induced stress is cumulative and exacerbated by exogenous stress factors such as abnormal thermal and osmotic conditions.

PAH toxicity to aquatic plants. The effect of various PAHs on aquatic plant growth is highly variable. At low concentrations (10 - 20 ppb) several PAHs act as a stimulant to plant growth. At 300 ppb, chrysene was observed by Boney (1974, cited in Neff, 1979) to induce a 58% increase in the growth of the red alga, *Antithamnion plumula*. Other PAHs (anthracene and 2-methylanthracene) caused declines of -20% and -12% in the same alga at 300 ppb. In general, PAH concentrations greater than 1,000 ppb inhibit algal growth.

Chronic Toxicity. Neff (1979) addresses chronic stress associated with PAH contamination. He cites Ott *et al.* (1978) and notes that the copepod, *Eurytemora affinis*, suffered statistically significant reductions in the length of life, total number of nauplii produced, and brood size when exposed to 10 ppb naphthalene, 2-methylnaphthalene, 2,6-dimethylnaphthalene, or 2,3,5-trimethylnaphthalene for the duration of their lives. Documented instances of chronic stress will be discussed, by effect, in the following paragraphs.

Reduced Fecundity. Nearly all PAHs are hydrophobic and lipophilic. Thus, there is a potential for these compounds to become associated with stable lipid pools in aquatic organisms. Energy is generally stored as glycogen in bivalves until gametogenesis when the glycogen and lipid stores are converted into eggs and sperm. The eggs contain significant lipid reserves and can become a repository for lipophilic PAH. Moore *et al.* (1989) cited Lowe and Pipe's (1985) observation that long term exposure to diesel oil at 30 and 130 ppm caused a decrease in the mass of gametes produced by *Mytilus edulis* and *Macoma balthica*.

Reduced Feeding. Mollusks elicit reduced ventilation (feeding) rates at PAH levels as low as 30 to 40 ppb in seawater (Widdows *et al.* 1982, 1985). The feeding inhibition probably results from the narcotic effect of hydrocarbons, particularly aromatic hydrocarbons. These compounds have a direct effect on cilia, muscles and/or the nervous system which controls their activity. Reduced feeding rates result in a reduction in "scope for growth," a commonly measured parameter that quantitatively describes the energy available for tissue growth, reproduction and activity. In bivalves, the major problem caused by reduced scope for growth is poor reproductive capacity. While this does not have immediate consequences at the organismal level, the long term consequences of reduced recruitment can be significant for the population.

Summary. Neff (1979) concludes his discussion of PAH induced chronic toxicity by suggesting that while environmentally realistic PAH water column concentrations of 1 - 50 ppb can cause potentially detrimental, sublethal responses in aquatic organisms, in most cases, the PAH concentrations required to elicit significant sublethal responses are higher than those normally encountered in all but the most heavily polluted aquatic environments.

From the preceding discussion on the uptake of PAH from water, food and sediments, it appears that PAH concentrations in the water column (including interstitial water in sediments) is the parameter of greatest significance in defining chronic stress. Furthermore, it appears from the preceding discussion that sustained water column concentrations of 30 to 50 ppb PAH can have subtle, but important chronic impacts on populations of marine organisms.

Neoplasia. Hyperplastic and neoplastic like growths have been reported in fish for a number of years. These same types of lesions are far less common in bivalves and other invertebrates.

Promotion of carcinogenesis. In vertebrates, enzymes produced by the cytochrome P-450, Mixed-Function Oxidase (MFO) and Aryl Hydrocarbon Hydroxylase (AHH) systems are responsible for initiating catabolism of lipophilic compounds (including PAH). These systems render hydrophobic molecules more water soluble and therefore increase their potential for excretion and detoxification. In the case of certain high molecular weight PAH, the intermediate metabolic products of these enzyme systems can be highly toxic, mutagenic or carcinogenic. Oxidative metabolism of some PAH (like B[a]P) results in the production of arene oxides, some of which bind covalently to DNA and RNA (particularly with guanine). The resulting chromosomal lesions can result in unregulated cell growth and division (cancer).

The ability to metabolized high molecular weight PAH (hPAH) varies significantly between the phyla. Among invertebrates, the mollusks have low AHH activity and a limited ability to metabolize hPAH. Arthropods and annelids show increased activity and some marine crustaceans have demonstrated significant cytochrome P-450, MFO and AHH activity.

Vertebrates, including fish, demonstrate high MFO, AHH and cytochrome P-450 capabilities (Payne, 1973). The liver is the primary site of MFO activity in fish and the liver, gut and gall bladder are primary sites of PAH concentration, metabolism and excretion. These organs are not normally consumed by humans. In Crustaceans, the hepato-pancreas, green gland (excretory organ), pyloric stomach, gill, testes and eyestalk are major sites of PAH accumulation and AHH enzyme activity. Again, these are tissues not normally consumed by humans, although, the hepato-pancreas is sometimes eaten as "crab butter."

Melanomacrophage centers are an integral part of the teleost immune system. Payne and Fancey (1989) observed that the numbers of melanomacrophage centers were increased in the liver of fish exposed to total PAH concentrations in the range of 25,000 to 50,000 ppb. These concentrations are found only in heavily polluted harbors, industrially polluted sites, or oil spills. Payne, *et al.* (1988) observed changes in mixed-function oxygenase (MFO) enzyme levels and liver fat content in fish exposed to low hydrocarbon levels of 1000 ppb (perhaps even as low as 200 to 300 ppb PAH).

The increased levels of P-450, MFO and AHH enzymes in fish and crustaceans exposed to very high levels of PAH suggest active catabolism of these molecules. Enzyme induction is not a sign of stress, per se. However there is concern because some of the intermediate products of hPAH catabolism are carcinogenic, mutagenic and teratogenic.

Bioindicator Studies. Are genotoxicity and enzyme induction tests appropriate indicators of environmental risk? There is growing interest in enzyme induction and genotoxicity tests as indicators of environmental risk. The following, simple-minded

discussion, is not meant to be condescending. However, it is important to put this issue in proper context.

Background. Effects at the organismal level, associated with external factors, are mediated by numerous levels of protection. Detrimental factors (abnormal temperature, xenobiotics, desiccation, disease organisms, low DO, high levels of pollution, UV radiation, etc.) are often avoided by mobile animals. Sessile animals (shellfish) isolate themselves within tightly closed valves in an attempt to avoid harmful conditions.

At the next level of protection, an animal's integument isolates internal organs and structures from harmful conditions. The skin and gut epithelia are capable of selective absorption of material. For instance, high molecular weight PAH, adsorbed to sediments, apparently pass through the digestive tract of many annelids without being absorbed through the gut epithelia.

Once foreign materials are absorbed into the blood serum through the skin, gills or gut, organisms respond by sequestering them in vacuoles, metabolizing them in the liver or cleansing them from the serum as it passes through the kidney. Whether or not a molecule is metabolized or excreted, depends, in great part, on its ability to penetrate cell membranes. The plasma lemma is highly permeable to essential molecules such as glucose, amino acids and lipids. These phospholipid bilayers are not very permeable to ions or to large uncharged polar molecules. The four to seven-ring hPAH are generally not charged and therefore they do pass across the cell membrane and are actively metabolized by vertebrates.

It is well documented that some metabolic intermediates of high molecular weight PAH, particularly arene oxides, can bind covalently to guanine, producing DNA lesions which may result in unregulated cell growth (cancer). These metabolic intermediates are frequently found in the digestive gland (liver or hepatopancreas) where metabolism is most active. The literature contains many citations regarding hepatic lesions (including hepatic carcinomas) in demersal fish associated with PAH contaminated sediments. However, the levels of contamination observed at Eagle Harbor, the Duwamish River, Elizabeth River, etc., at which significant increases in hepatic carcinomas are observed are generally greater than 25 to 50 ppm. In some cases, Eagle Harbor sediments contain as much as 6,000 ppm PAH.

Mixed Function Oxidases (MFO), Cytochrome P450, Ethoxy Resofurin-O-Deethylase (EROD), and Aryl Hydrocarbon Hydroxylases (AHH) are important enzyme systems for the metabolism of hPAH. There are numerous reports in the literature suggesting that PAH metabolizing enzyme systems are activated at sediment PAH levels as low as 1.0 ppm.

As previously stated, intermediate PAH metabolites, such as arene oxides can covalently bind to DNA resulting in lesions. However, DNA contains numerous mechanisms that repair miscoded or damaged sequences. This repair is achieved by a suite of enzymes capable of recognizing damaged or mismatched base pairs and excising them. Environmental and/or random damage to DNA is not unusual and the presence of nicks or double stranded breaks in nuclear (or ribosomal) DNA does not often lead to

unregulated cell growth. Increased DNA damage obviously increases the risk for failure of these repair mechanisms resulting in a number of diseases.

The point is that there are numerous levels of protection involved in maintaining the biological integrity of an organism. In evaluating environmental risks, we must recognize the importance of these cellular safeguards. The questions we ask must recognize that different levels of biological organization will respond differently to the same level of insult. Therefore, our questions must be posed carefully and caution should be exercised when extrapolating biological responses at one level of organization to responses at another level. Put simply, the sun feels good on our skin and it is necessary for the synthesis of vitamin D. Peel away the skin and expose the underlying tissue to the same beneficial sun and the underlying cells die. Almost anyone would recognize that evaluating sunlight, based on the response of a naked cell, has nothing to do with an organisms response to the same level of light. This may seem simplistic, but these same principles must be applied to genotoxicity tests.

What question is asked by genotoxicity tests. Ernst (1994) reports the results of genotoxicity tests on subtidal sediments collected at varying distances from a wharf constructed of creosote treated wood. PAH were extracted from the sediments, dried and re-dissolved in dimethylsulfoxide (DMSO).

Trout hepatocytes were exposed to varying concentrations of the PAH preparation and genotoxicity assayed using the nick translation assay (NTA) of Gagne and Blaise (1994) and a modified version of the alkaline precipitation assay (APA) described by Olive *et al.* (1988).

The results were quantified by defining a toxicity threshold (TT) which is the geometric mean of the Lowest Observed Effects Concentration (LOEC) and the No Observed Effects Concentration (NOEC).

This test measures the response of DNA in naked digestive gland cells to isolated PAH suspended in a material which is an exceptionally powerful solvent for both polar and nonpolar compounds. DMSO is often used as a reaction medium for bimolecular nucleophilic reactions in which the attacking nucleophile (arene oxide) bears a negative charge. It's use in these genotoxicity studies greatly facilitates transfer of PAH across the plasma lemma and of arene oxides into the nucleus.

Based on the preceding paragraphs, it appears that the question being asked is: "How many DNA nicks and breaks occur when we eliminate, or impair, all of a cells nuclear defense mechanisms and expose DNA to PAH and their intermediate metabolic products?" This is an interesting question, and as expected, we find that the degree of DNA insult is proportional to the PAH exposure. In other words, this study revealed a quantifiable dose-response relationship. The dose is isolated PAH and the response is from naked cells whose nuclear and cell membranes have been compromised in the presence of DMSO.

Does our current understanding of bioindicators allow their use in assessing environmental risks? There are numerous weaknesses in our current understanding. Consider the following:

**Genotoxicity Test
in
Environment**

1. PAH are desorbed and extracted from sediments. They are made very available to the test cells.
2. No organismal epithelium present
3. No kidney present to clear PAH. clear rapidly
4. Plasma lemma compromised by DMSO restricts
5. Lysosomal membranes compromised contain by DMSO.
6. Nuclear membrane compromised by DMSO another

**Organismal Environment
Open Aquatic Systems**

1. PAH are bound to sediments. They are not readily available in the water column.
2. After desorption from sediments, PAH must cross an external epithelium (skin, gills, gut) before entering the blood stream for delivery to the digestive gland.
3. Kidney present. Functions to some xenobiotics. Fish excrete some PAH.
4. Cell membrane selectively movement of some PAH into the cell. This increases the probability of excretion and decreases the probability of metabolism.
5. Lysosomal membranes help intermediate metabolites during metabolism.
6. Nuclear membrane provides

level of protection for DNA.

7. DNA lesions assumed to result in reduce the unregulated cell growth.

7. DNA repair mechanisms probability of cancer.

Creosote and PAH do result in disease in demersal fish. The study reviewed here is valuable in that it provides us with insight into the mechanisms leading to observed hepatic carcinomas. However, before these genotoxic tests can be used to establish environmental criteria, we need to correlate the observed cellular responses with responses at the population or organismal levels of organization. The response of a naked cell, with at least seven layers of protection stripped away, to isolated PAH, does not describe the response of whole organisms living in close association with sedimented PAH.

Other Bioindicator Tests of Pollution. Other bioindicator tests (primarily enzyme induction tests) suffer from the same weakness. The response of an enzyme system to an appropriate substrate has little to do with the response of the organism to that substrate. Bioindicators certainly have a future in environmental studies. However, adequate correlations between cellular or genetic responses and organismal or population responses to pollutant levels have not been made. There appears to be a great deal of haste in adapting an emerging technology to contemporary problems without completing our homework.

Payne, *et al.* (1993) reported a study supporting the hypothesis that many point sources of hydrocarbon contamination could be harmful to fish health. They found that MFO enzyme levels were altered at hydrocarbon levels as low as 1.0 ppm. The authors note that PAH levels in this range are encountered over a broad range of aquatic environments, many of which are not associated with pollution. They suggest that hydrocarbons often occur in sufficient concentrations to affect biological responses in fish. They conclude by recognizing that **meaningful bioindicators must distinguish between effects per se. and either chronic or acute effects.**

The development of simple, timely, and effective tests to evaluate the risks posed by pollutants to aquatic organisms is important work. However, I submit that until we obtain a better understanding of the correlation between effects observed in bioindicator studies and the response of organisms and populations of organisms living in open environmental systems, bioindicators will have little value as a regulatory tool or for assessing environmental health.

Case Studies. Vogelbein *et al.* (1990) described hepatic neoplasms in the Mummichog (*Fundulus heteroclitus*) from a site with high levels (22,000 ppb) of creosote in the sediment. Ninety three percent of the Mummichogs collected at this site had gross hepatic lesions and 33% of these fish had hepatocellular carcinomas. It should be noted that fish from a site of lower contamination (63 ppb) did not show signs of hepatic

lesions or carcinomas. Similar cellular lesions have been described in fish from a highly urbanized area (the Duwamish River estuary) in Puget Sound (Pierce, *et al.*, 1978).

Mutagenicity. Colwell (1986) examined mussels and sea water associated with creosoted marine pilings at the Roosevelt Roads Naval Station Complex in Puerto Rico. She employed *Salmonella typhimurium* in the familiar Ames test (Ames *et al.*, 1975) for mutagenicity and found no detectable mutagenic activity in bacteria from either the water or mollusks associated with the creosote. She concluded that the creosote did not exhibit any appreciable leaching into the surrounding water.

Effects of PAH contamination on populations of marine organisms.

Mesocosm studies by Stekoll *et al.* (1980), Widdows *et al.* (1982), and Widdows *et al.* (1985) report similar community responses to petroleum and PAH contamination. Significant, long term, reductions in the abundance and diversity of invertebrate fauna are reported when ambient water levels contain as little as 130 ppb diesel oil over prolonged periods of time. Less significant population effects were observed on a rocky shore community exposed to 30 ppb diesel oil for two months.

Tagatz *et al.*, (1983) examined the impacts of creosote contaminated sand on macrofaunal communities. He found that the lowest creosote (in sediment) concentration, at either of his sites, that affected the number of individuals or species was 844,000 ppb for mollusks and 177,000 ppb for echinoderms, annelids and arthropods.

Community Adaptation. The adaptation of microbial communities in the gut of *Limnoria tripunctata* and in sediment are well documented and discussed in Neff (1979). Similar adaptations are discussed by Wade *et al.*, (1989) in Gulf of Mexico hydrocarbon seep communities including numerous species of annelids, crustaceans, bivalves and fish. Tissue PAH concentrations indicate that these organisms are chronically exposed to high levels of PAH. The seep organisms are able to survive and thrive in an environment of high PAH exposure. The apparent ability to cope with these elevated levels of PAH may involve specially adapted and/or evolved enzyme systems.

Summary. The low molecular weight PAHs (benzene and naphthalene) produce acute toxic effects in marine animals. Acute intoxication in the sensitive larval stages of marine invertebrates may occur at water column concentrations as low as 8 to 10 ppb. However, for most species, the literature suggests that water column concentrations of greater than 20 ppb are required for significant responses. Low molecular weight PAH are highly volatile and are rapidly metabolized by bacteria and other aquatic organisms. The potential for their accumulation to toxic levels is very small except when introduced in large quantities such as occurs in petroleum spills. However, laboratory (including mesocosm) studies have demonstrated photo-enhanced toxicity associated with fluoranthene and anthracene at levels as low as 3 ppb in the water column.

Because of their low biological availability, sedimented PAHs have a low potential to cause acute pathological responses at either the organismal or population levels in

aquatic species. However, sediment levels of creosote exceeding 177,000 ppb have been shown to cause significant impacts on populations of the most sensitive taxa. Furthermore, bacteria and eukaryotes have demonstrated a remarkable ability to adapt to relatively high levels of background PAH.

Chronic toxicity is more difficult to measure than acute toxicity. This review suggests that chronic stress can occur in many organisms, including bivalves at concentrations as low as 30 to 40 ppb in the water column. Chronic stress causes reduced scope for growth and reduced reproductive capacity which can have long term consequences for populations of aquatic species.

In addition to direct physiological stress, there is a potential for the high molecular weight PAHs (particularly B[a]P) to form carcinogenic, mutagenic and teratogenic compounds during metabolism by crustaceans and vertebrates. Neff (1979) summarizes his section on neoplasia by noting that while carcinogenic PAH can produce cancer-like growths and cause teratogenesis and mutagenesis in some aquatic invertebrates and vertebrates, there are no reports of the induction of cancer by exposure of aquatic animals to environmentally realistic levels of carcinogenic PAH in the water, food, or sediments. More recent work points out increases in the number of hepatic lesions and carcinomas with sediment PAH burdens as low as 25 to 50 ppm.

Potential for Human Pathology Associated with PAH in Shellfish

The author receives several calls every year from people asking if it is safe to eat mussels growing on creosoted pilings. Neff (1979) and Stegeman (1981) indicate that consumption of PAH-contaminated mollusks probably constitutes a minor source of human dietary PAH, in comparison to PAH in smoked foods, charcoal-broiled meats, and even many vegetables. Moore (1989) agrees with the caveat that "except possibly where animals have been exposed to very high concentrations of PAH such as those occurring following an oil spill."

Average concentrations of 402 ppb B[a]P were reported in Neff (1979) for mussels from creosoted pilings. Numerous other authors have associated high B[a]P levels in mollusks with proximity to creosoted pilings. Eisler (1987) lists human health criteria proposed by the EPA and others for various PAH compounds. The proposed maximum human consumption of benzo(a)pyrene is $1.6 \mu\text{g}\cdot\text{day}^{-1}$. Consuming as little as four grams of mussel tissue from a creosoted piling would exceed this value. That is approximately two mussels. I always tell people not to eat mussels from newly creosoted pilings.

It is interesting to note that Mallet *et al.*, (1963) observed a B[a]P concentration of 55 ppb in *Mytilus edulis* collected from a pristine area on the coast of Greenland. The authors attributed this high level to biosynthesis of B[a]P by sediment-dwelling anaerobic bacteria. It is also possible that B[a]P could be leaching from peat deposits which are extensive in that part of Greenland. Neff (1979) reported high levels of Perylene (3,010 ppb) in Glastonbury peat from Avalon, England. This observation once again points to the ubiquitous nature of PAH and the multitude of natural and anthropogenic sources.

The potential toxicity of creosote is well recognized by the American Wood - Preservers' Association . The association provides a list of precautions to be taken in the use and handling of creosoted material. This list includes precautions against using creosote in human or animal habitations where direct contact can occur. They recommend that creosoted materials used above grade in homes be well sealed and that creosoted materials not be used in close association with either human or animal feedstuffs. However, the EPA label for creosote does allow its incidental use in associated with human water supplies.

Creosote contamination of drinking water supplies. Table 2 lists limits for creosote constituents in drinking water established by the Council of European Communities (CEC), the Canadian Council of Ministers of the Environment (CCME), the British Columbia Ministry of the Environment and the U.S. EPA. Of these, benzo[a]pyrene is the compound of most concern.

Table 2. Canadian and United States regulatory limits for drinking water and/or ground water.

Compound	Authority	Remediation Level (ppb)
Total carcinogenic PAH	CEC	0.200
Benzo[a]pyrene	British Columbia	0.100
	CCME	0.010
	U.S. EPA	1.6 µg/day

The Council of European Communities directive relating to the quality of water intended for human consumption sets a maximum PAH level of 200 parts per trillion, based on the amount of fluoranthene, **benzo(b)fluoranthene**, **benzo(k)fluoranthene**,

benzo(a)pyrene, benzo(ghi)perylene and indeno(1,2,3-cd)pyrene. The highlighted components are listed in Eisler (1987) as potential human carcinogens. Based on the creosote compositions given in Environment Canada (1991) and Cooper (1994), it appears that the sum of the concentrations of the potentially carcinogenic compounds represents 2.20% of creosote. Fluoranthene is not considered a carcinogen but is a major constituent of creosote comprising 11% of the PAH. Regulatory levels for all of these compounds have not been established (or I am unaware of them). For this discussion we will compare predicted levels of these compounds in the immediate vicinity of a freshly treated piling installed in a freshwater drinking supply.

Water column concentrations associated with creosote treated piling. The CREORISK computer model for steady state currents, presented later in this document was used to estimate water column concentrations of PAH. In this analysis, we have set the sediment partition coefficient to zero and the water column partition coefficient to 1.0. This forces the model to assume that all of the PAHs migrating from the piling enter the water column and that none are sedimented. Inputs assume fresh water (salinity = 0.0), an initial creosote retention of 17.0 pcf in piling that average 15 centimeters in radius, installed in very slow, steady state currents of 1.6 centimeters/second. Maximum tidal current speed is set to zero. We assume the piling is newly installed (Age = 0). In addition, we have set the ambient water temperature at a relatively high value (20 °C). With a flow of 1.6 cm/sec, the model predicts total PAH water column concentrations of 1.2886 parts per billion within a few centimeters of the piling. If we conservatively assume that the, carcinogenic, high molecular weight, PAH migrate at the same rate as the more water soluble and volatile low molecular weight PAH, then it appears that the concentration of carcinogens contributed by a creosote treated piling would be on the order of 0.028 parts per billion. In Table 3 we consider all potential carcinogens in creosote and compare their predicted concentrations with regulatory levels.

Table 3. Anticipated levels of potentially carcinogenic PAH found in association with a newly installed, creosote treated (retention = 17 pcf) piling in a river flowing with steady state currents of 1.6 cm/sec. Regulatory levels for drinking water or ground water are provided. All values are reported in parts per billion.

Potential carcinogens Concentration	Regulatory Level	Percent In Creosote	Predicted
Benzo(a)anthracene		0.85	0.0101

Benzo(k)fluoranthene		0.40	0.0048
Benzo(ghi)perylene		0.08	0.0010
Indeno(1,2,3-cd)pyrene		0.05	0.0010
Benzo(b)fluoranthene		0.60	0.0071
Benzo[a]pyrene	0.010	0.20	0.0039
Sum for carcinogens	0.200 (CEC)	2.18	0.0278

Eisler (1987) describes proposed PAH criteria for human health protection. He suggests that for a cancer risk of 10^{-5} , the concentration of carcinogenic PAH in drinking water should be less than $0.028 \mu\text{g/liter}$ (28 pp trillion). This analysis suggests that if a drinking water intake were placed immediately adjacent to a newly installed piling, a minimum current speed of 1.6 cm-sec^{-1} would be required to meet Eisler's (1987) criteria. An examination of Table 3 suggests that all other regulatory criteria for drinking water are met as well. The incidental use of creosote treated piling is allowed in the EPA sponsored *Consumer Information Sheet* for creosote treated wood.

The assumptions made in developing these models are very conservative. In an ongoing study with Environment Canada, the Battelle Marine Sciences Laboratory used polyethylene collectors (Semi-permeable membrane devices or SPMDs) to evaluate water column concentrations of PAH within 15 cm of a newly installed, six piling, dolphin in Sooke Basin, British Columbia. In this very poorly circulated marine environment, total PAH were predicted at 398.5 parts per trillion and they were measured at 17.9 to 30.8 parts per trillion. The sum of carcinogens was predicted at 0.014 parts per trillion and observed at 0.0001 parts per trillion in the water column. For total PAH, the model predictions are 16 times higher than observation and for the more hydrophobic carcinogens, the model predictions were 137 times too high. This suggests first, that little PAH is actually dissolved in the water column and second, that our initial assumption that the high molecular weight compounds are dissolved into the water column in proportion to their presence in creosote is not valid. There are two points that this discussion emphasizes, the first is that water column concentrations of PAH associated with creosote treated piling are very low and the second is that the model tends to be very conservative.

The analysis presented above is intended as a worst case analysis. When coupled with environmentally realistic currents and temperatures, this analysis suggests that cancer risks associated with the carcinogenic PAH found in small to moderate quantities in creosote treated wood pose a drinking water risk far less than 10^{-5} or 10^{-6} (the basis for federal drinking water standards).

This analysis is very consistent with the findings of Colwell (1986) and Wade (1987). Polycyclic aromatic hydrocarbons (PAH) are very difficult to detect in the water column between sediments and surface sheens. When measured, they are found to be in the very low parts per trillion range. In addition, these findings are consistent with the EPA label allowing incidental use of creosote treated wood in association with drinking water supplies.

Empirical evidence of creosote (PAH) accumulation in aquatic organisms.

Dunn and Stich (1976) observed that mussels taken from rocks underneath and near a creosoted wharf were contaminated with 54 to 78 ppb (wet tissue weight) of B[a]P, while those growing directly on the creosoted barricade were contaminated with 215 ppb B[a]P. They concluded that the creosoted pilings and timbers, rather than the moored vessels, were the major sources of contamination. They also note that mussels from aged (clean) pilings show considerably lower levels of contamination. They found an overall half-life of B[a]P in mussel tissues of approximately 16 days.

Colwell (1986) examined mussels and seawater associated with creosote treated marine pilings at the Roosevelt Roads Naval Station Complex in Puerto Rico. She concluded that the creosote did not exhibit any appreciable leaching into the surrounding water.

Dunn and Stich (1976) have detected significant amounts of PAH in mussels from treated pilings. They note that the levels detected are dependent on the age of the piling and the proximity of mollusks to the pilings. They suggest that as pilings age, the more toxic components leach out, or are degraded.

A Spreadsheet Model Predicting

Creosote Treated Wood

Contributions of PAH to the Water

Column and Sediments in

Aquatic Environments

Introduction. Based on the preceding chapters and the analysis presented in this chapter, a model has been developed to predict water column and sediment levels of PAH associated with creosote treated wood. The model is intended as a tool for engineers to be used in the conceptual stages of design, and as a regulatory tool providing site and project specific assessments of the environmental risks associated with creosote treated wood in aquatic environments.

The model is reasonably complete and includes 13 easily measured input parameters. However, it does have certain limitations. It is general in nature and does not include provisions for complex, turbulent or chaotic current or mechanically induced distributions of sedimented PAH. Adequate studies and data were not available for all input parameters such as retention, salinity, temperature and piling age. Estimates of some parameters, such as the effect of creosote retention on subsequent migration, were based primarily on anecdotal evidence. There are major flaws in existing studies evaluating salinity effects on creosote migration and future studies may require modification of the algorithms used to describe this and several other parameters

Polycyclic Aromatic Hydrocarbon migration data is not available for creosote treated wood processed using newly designed Best Management Practices (BMPs). The data used to develop migration rates is from non-BMP produced piling that was

frequently overtreated. The use of BMPs is expected to significantly reduce the early (piling age less than 5 years) migration of creosote. Therefore, migration rates calculated in this model are probably excessive. The model can be easily changed to reflect new data on these pilings when it becomes available.

This model does not include PAH accumulation in sediments associated with the mechanical loss of creosote treated wood fibers from structures. Impregnated wood can be heavier than water and may sink to the bottom around creosote treated piling. For economic, as well as environmental, reasons, treated wood should be protected from excessive abrasion such as that found in association with ferry dolphins and wingwalls.

Recognizing these limitations, the model has been tested and those tests, included in this report, suggest that the model adequately predicts sediment and water column concentrations of PAH associated with the use of creosote treated wood.

Lastly, in every case, the author intended to be conservative (from the environment's point of view) in evaluating the parameters which make up this model. That is to say, if there is an error in this model, the error should cause an overestimation of the accumulation of PAH in aquatic sediments and in the water column.

Water Quality Standards. The information gathered in preceding chapters indicates that PAH dissolved in the water column can cause acute toxicity at low levels in the most sensitive taxa. The larval stages of some invertebrates experience acute toxicity at levels ≥ 8 to 20 ppb. However, for most taxa the threshold is more likely to be 100 ppb or higher. Chronic toxicity can be more subtle and there is considerable data to show that water column levels of 30 to 40 ppb can create stress with long term detrimental consequences for populations of marine organisms. However, numerous investigations have failed to find significant levels of PAH in the water column associated with the use of treated wood. For purposes of this model, the water quality standard will be set at 3 ppb total PAH. This is the lowest level at which photo-enhanced PAH toxicity is well documented. In addition, it is the numerical criteria for total PAH adopted by New Zealand and Australia. However, this is a user entry and therefore it can be modified to reflect local standards.

Sediment Quality Standards. PAHs adsorbed to particulate matter in the sediment do not appear to be biologically available and sediment concentrations ($> 20,000$ ppb) have been associated with significant biological effects. As an example, based on Apparent Effects Thresholds (AETs), Washington State has set Marine Sediment Quality Standards (WAC 173-204-320) at the following levels:

Washington State Apparent Effects Threshold Based Sediment Criteria

Compound Class Weight Sediment TOC)	Criteria (ppm organic carbon)	Criteria (Sediment Dry @ 2%
--	--	--

	HPAH ₁	960	19.2 ppm
	LPAH ₂	370	7.4
ppm	Total PAH	1,330	26.6 ppm

- Notes: 1) HPAH includes fluoranthene, pyrene, benzo(a)anthracene, chrysene, Total benzofluoranthenes, benzo(a)pyrene, indeno (1,2,3,-c,d)pyrene, dibenzo(a,h)anthracene, and benzo(g,h,i)perylene).
- 2) LPAH includes naphthalene(s), acenaphthylene, acenaphthene, fluorene, phenanthrene and anthracene.

For purposes of this model, we will use the Washington State criteria, expressed in ppm organic carbon as the level at which there are Apparent (Biological) Effects associated with PAH sediment loading. WAC 173-204-420 includes Maximum Chemical Criteria for sediment management. These values represent the maximum sediment values authorized for issuance of a Sediment Impact Zone without an exception being authorized by the Department of Ecology. Sediments exceeding these values are considered unacceptable and may require remediation.

Washington State PAH Maxima for Establishment of a Sediment Impact Zone

Compound Class	Criteria	Criteria (Sediment Dry Weight)
	(ppm organic carbon)	@ 2% sediment TOC)
HPAH	5300	106.0 ppm
LPAH	780	15.6 ppm
Total PAH	6080	121.6 ppm

In this model, predicted sediment loading associated with the use of creosote treated wood will be compared with each of these criteria as an aid in the decision making process. The Microsoft EXCEL spreadsheet version of the model allows users to input alternate standards.

Physics and chemistry of creosote. Creosote is a complex mixture of compounds derived from the coking of coal. Leach (1976) describes how the kind of coal, kind of coke oven, coking temperature and time all effect the composition of creosote. Ingram *et al.* (1982) estimated that 50 to 65% of creosote was composed of PAH. Neff (1979) gives a more thorough analysis and found 44.4% PAH in coal tar. Neff (1979) quotes Lijinsky *et al.* (1963) who found only 93 grams PAH in a kilogram of creosote (9.3%). The difficulty in determining the composition of creosote from the literature is seen in Table 4. Environment Canada (1992) reported a comprehensive analysis of the

composition of creosote, estimated that marine grade creosote contains 80.2% TPAH, and will be used as a basis for the following discussion.

Table 4. Variation in the percent composition, by weight, of various Polycyclic Aromatic Hydrocarbons in marine grade creosotes as reported in the literature.

Compound	Literature Source				
	USDA (US) <i>al.</i> (1984)	USDA (German) (1984)	Env. Canada (1992)	Ruddick & Ruddick (1992)	Ingram, <i>et al.</i> (1982)
naphthalene 7.1	7.1	14.7		5.4 - 29.8	17.5
phenanthrene 21.0	21.0	12.6		4.7 - 21.0	10.2
acenaphthene 9.0	9.0	4.1		2.7- 14.7	5.6

Most of the material migrating from treated wood is composed of the lower boiling point, water soluble fractions. Table 5 contains information for the low molecular weight polycyclic aromatic hydrocarbons (LPAH) with boiling points $\leq 340^{\circ}\text{C}$. All of these low molecular weight PAH contain one, two, or three rings. They have variable, but relatively high water solubility's and moderately low octanol/water partition coefficients (K_{ow}) implying moderate affinity for lipids. Their low to moderate Organic Carbon Partition Coefficients (K_{oc}) implies relatively low potential for binding to sediments and their high vapor pressures (P_v) imply high volatility from either the surface sheen or the portion of the piling exposed to the air.

Table 5. Physical and chemical characteristics of low molecular weight PAH in creosote.

Compound %Creosote	Mol. wt.	B.P.	S_w (ppm)	$\log K_{ow}$	Log K_{oc}	P_v (mPa)
Phenols 0.80	94	182	93,000	1.48	1.15	45,466
Naphthalene(s) 3.4-28.6	128	218	32	3.29-3.36	2.97	11,600
Cresol 0.34	143	235	3,850	3.10	2.78	667
Acenaphthylene 0.45- 2.0	152	265	4	3.27	3.40	3,866
Acenaphthene 206.7 2.7-14.7	154	279	3.42		3.98-4.03	3.66
Carbazole 1.2- 5.1						
Dimethylnaphthalene 2.0- 2.3						

Dibenzofuran 5.0- 7.5						
Fluorene 94.7 3.1- 11.8	166	293	1.69	4.18-4.47	3.86	
Phenanthrene 128.0 4.7- 21.4	178	340	1.00	4.45-4.57	4.15	
Anthracene 0.4- 2.5	178	340	0.044	4.45-4.54	4.15	2.3

Total average LPAH as a percent of Marine Grade Creosote

60.57%

Note that benzene and phenols are listed as initial components of marine grade creosote. They are not PAH. These compounds have been reported, in low concentrations, in the air at treating plants. However, neither component has been observed in environmental samples or reported as a component of treated wood. They both have high vapor pressures (12,693,33 and 45,466 respectively) and high water solubility's (1780 and 93,000 ppm respectively). These components of new creosote oil appear to evaporate, or they are solubilized during the treating process. They do not appear to be present in treated wood and therefore do not pose a risk associated with the use of creosote treated wood products in aquatic environments.

The high molecular weight PAH (HPAH) have three or more rings. These compounds have much lower water solubility, moderately high lipid and sediment affinities, and low vapor pressures. Therefore, these compounds are unlikely to evaporate from the water column and their fate involves photo or chemical oxidation, incorporation into the biota where they are sequestered or metabolized, or they may be sedimented where they are metabolized by fungi and bacteria in aerobic conditions. In anaerobic conditions HPAH may persist in sediments for very long periods of time. Because of the relatively higher K_{oc} values, they are less likely to be solubilized from the sediments. High molecular weight PAH are described in Table 6. For purposes of this report, we will assume that creosote contains 19.57% HPAH, 60.57% LPAH and a total PAH content of 80.14%.

Table 6. Physical and chemical characteristics of high molecular weight PAH in creosote.

Compound % creosote	Mol. wt.	B.P.	S_w (ppm)	log K_{ow}	Log K_{oc}	P_v (mPa)
Fluoranthene 3.1-11.8	202	375	0.26	4.90-5.22	4.58	0.7000
Pyrene 2.1- 8.5	202	393	0.13	4.90-5.18	4.58	0.3000
Methylfluorenes 2.3- 3.0						
Benzo[a]anthracene 0.60-1.1	228	400	0.0057	5.61	5.30	0.0029
Chrysene 0.26-3.0	228	448	0.0018	5.61-5.91	5.30	0.0008

Benzo[b]fluoranthene 0.60	252		0.14	6.06	5.70	0.0670
Benzo[k]fluoranthene 0.40	252	480	0.0043	6.06	5.70	0.0067
Benzo[a]pyrene 0.15- 0.5	252		0.0038	6.06-6.50	6.74	0.00075
Benzo[ghi]perylene 0.06- 0.1	276	222	0.00026	6.51-7.10	6.20	0.00001
Indeno[1,2,2-cd]pyrene 0.06- 0.1	276	530	0.00053	6.51	6.20	0.00001
Dibenzo[a,h]anthracene 0.20	278	275	0.0005	6.84-7.19	6.52	0.00001

Total HPAH

19.57%

Total LPAH

60.57%

Total PAH

80.14%

Proportions LPAH and HPAH reported from highly contaminated sites.

Data provided by Malins (1984) provides a basis for assessing the proportion of LPAH to HPAH in creosote contaminated sediments associated with Eagle Harbor, Washington. At Eagle Harbor, Site B, there is a total of 113,660 ppb (dry sediment weight) PAH. Of those, 100,750 ppb or 87% are HPAH and 13% are LPAH. These values are consistent with our knowledge regarding the relative insolubility of HPAH and greater solubility of LPAH. In addition, later sections of this report will clearly demonstrate that LPAH are more readily degraded by marine prokaryotes, further explaining the observed reversal of LPAH/HPAH proportions observed between creosote oil and sediments.

For purposes of this model, we will assume that HPAH and LPAH migrate from the piling in the same proportions in which they are found in whole creosote. If we assume minimal mineralization of HPAH in the water column, then by combining the relative proportions of LPAH and HPAH in whole creosote oil with the relative proportions reported above for contaminated sediments, it appears appropriate to suggest that 95.17% of the LPAH migrating from creosote remain in the water column or form a surface sheen from which they either evaporate, photochemically degrade or are biologically metabolized. Based on these arguments, this model will assume the following:

- 1) **High Molecular Weight PAH are adsorbed to the silt-clay fraction and sedimented.**
- 2) **4.83 percent of the Low Molecular Weight PAH are sedimented.**
- 3) **95.17 percent of the Low Molecular Weight PAH are dissolved in the water column where they reside with determinable half-lives. Note that we conservatively assume no evaporation of LPAH.**

Relative solubility of creosote as a function of salinity. Ingram, *et al.* (1982) found that 15 PAH varied in their migration from creosote treated piling into fresh water and marine water at 20, 30 and 40°C. The results of their study are provided in Table 7. It should be noted that these studies used distilled fresh water (axenic) and seawater from Alabama City, Alabama, Gulf of Mexico. The time of testing the seawater was not given. Numerous authors, reviewed in another section of this document, have noted significant bacterial degradation of PAH by microbes within 72 hours. It is possible that at least some of the difference between observed marine and fresh water migration rates could be attributed to the presence of natural bacterial flora in the unsterilized sea water samples. These bacteria and yeast, which are absent in distilled, water, may have metabolized some of the PAH in Ingram's unsterilized seawater samples.

Table 7. Relative migration of PAH from creosoted piling into fresh water and seawater.

Compound corrected	Fresh Water (ppb)	Sea Water (ppb)	FW/SW	% in creosote	FW/SW ⁽¹⁾
LPAH					
Naphthalenes	3342	1158	2.9	15.45	0.7899
2-Methylnaphthalene	1151	784	1.5	2.15	0.0568
1-Methylnaphthalene	982	784	1.3	included in Naphthalenes	
Biphenyl	196	155	1.3	1.35	0.0310
Acenaphthylene	256	238	1.1	1.02	0.0196
Acenaphthene	688	640	1.1	8.70	0.1687
Dibenzofuran	482	463	1.0	6.25	0.1102
Fluorene	405	388	1.0	7.45	0.1313
Phenanthrene	660	620	1.1	12.90	0.2492
Anthracene	169	135	1.3	1.45	0.0332
LPAH Migration Ratio (FW/SW)					1.5901
HPAH					
Carbazole	368	207	1.8		
Fluoranthene	184	124	1.5	7.45	0.7665
Pyrene	103	59	1.7	5.30	0.6180
1,2-Benzanthracene	43	25	1.7	0.20	0.0233
chrysene	36	9.7	3.7	1.63	0.4136
HPAH Migration Ratio (FW/SW)					1.8214⁽²⁾
Total PAH Migration Ratio (FW/SW)					1.6466

Notes:

1. Corrected FW/SW Ratios = the % compositions of each PAH species x FW/SW migration ratio / sum of the % composition for all LPAH or HPAH.
2. This suite of HPAH represents only four of the 11 HPAH reported earlier. However, they represent the only information available and their sum is 14.58%, compared with the

19.57% HPAH in creosote. For purposes of this analysis, we will assume that these listed HPAH are representative of the HHHH remaining compounds.

Summary. The analysis used in this report will assume the following:

Compound Class	Percent Creosote Composition	Migration Ratios (FW/SW)
HPAH	19.57	1.8214
LPAH	60.57	1.5901
Total PAH	80.14	1.6466

Both the high molecular weight and low molecular weight fractions are more soluble in fresh water than in sea water (28 o/oo). It should be noted that naphthalene(s) will be a prominent constituent in the leachate from creosote treated wood. This relatively soluble ($S_w = 32$ ppm) chemical is relatively toxic at low concentrations, but is quickly biodegraded in the water column and has little, or no potential for bioaccumulation. However, naphthalene is 2.9 times more soluble in fresh water than in seawater making it more bioavailable, particularly to filter feeding bivalves. Because of its reduced solubility in seawater, naphthalene is more likely to migrate to the surface; where, as part of the surface sheen, it evaporates into the air.

Effects of pH on PAH in Aquatic Environments. Most PAHs do not possess functional groups that can be effected by pH. Subsequently, PAH adsorption is not effected by moderate changes in pH (pH 6.0 to 8.0). For the purposes of this model, we will assume that pH is not a factor in the migration of PAH from creosote treated wood. In addition, we will assume that pH does not effect the dynamics of PAH binding to inorganic sediments, organic carbon, or the solubility of sedimented PAH.

Total Organic Carbon. In addition to sorption to sediment, PAHs in aquatic environments bind to dissolved humic material (Hoffman and Grudey, 1990). A direct relationship exists between the hydrophobicity of a PAH and the affinity for binding to dissolved humic material and therefore, the sediment partition coefficient (K_p) for PAH is directly related to the organic carbon content of the sediment. Because dissolved humic materials are more mobile than inorganic sediments, they may facilitate transport of PAHs in aquatic environments (Hoffman and Hrudey, 1990). In this model, worst case scenarios involve the adsorption of migrating creosote onto suspended silt with subsequent sedimentation in the immediate vicinity of the pile. Increased DOM (dissolved organic matter) in the water column will ameliorate this condition by distributing PAH over a larger area and reducing sediment concentrations. We will ignore this beneficial contribution and assume that creosote derived PAH is adsorbed to the silt-clay fraction.

Quantifying the Total Organic Carbon in adjacent sediments has value in understanding the hydrodynamics of a site, in assessing the potential for contributions

from distant sources and in assessing sediment oxygen depletion created by the Biological Oxygen Demand (BOD) associated with organic material. This model will rely on the Redox Potential Discontinuity (RPD) to evaluate sediment oxygen content. Total Organic Carbon will only be used to evaluate Washington State sediment standards (expressed as ppm total organic carbon).

Sediment Grain Size (SGS). The silt-clay (< 63 micron) fraction sequesters PAH at much higher concentrations than do coarse-grained sediments. In addition, sediments containing high proportions of silt and clay are characteristic of low energy, depositional sites. Therefore a simple sieve and pipette analysis to determine the sediment grain size (SGS), can give a subjective assessment of local water circulation and sedimentation. Coupled with TOC, SGS may provide important information regarding deposition of fine grained material (and PAH) in localized areas.

This model is based on the deposition of silt adsorbed PAH. A quantitative assessment of silt deposition can be obtained through the application of Stokes Law for the settling velocities of small particles (Shepard, 1963). This law is expressed in Equation (1).

Equation (1) Stokes law for the settling velocities of small particles:

$$w = \frac{g D^2(\rho_s - \rho_w)}{18 \mu}$$

Where: g = gravitational constant

D = particle diameter

ρ_s = particle density

ρ_w = density of water

μ = Coefficient of molecular viscosity

For clay particles or finely divided organic material, the resulting vertical velocities are very small (10^{-6} cm/sec). In this model we will assume that PAH is adsorbed to silt particles with vertical velocities in sea water (10°C) of 2×10^{-1} to 10^{-3} cm/sec. An intermediate value of 5×10^{-2} cm/sec will be used in computing silt adsorbed PAH deposition to the benthos. It should be noted that this is a very conservative number and that actual deposition, particularly in areas where sediments have high total organic carbon or clay fractions, may be significantly lower. The EXCEL Spreadsheet includes provisions for user defined settling velocities.

Currents. Tidal currents may be very complex and depend on highly variable factors such as wind velocity, tidal exchange, lunar period, local geography, season and barometric pressure. A very simple tidal model is being used in this analysis. We will

assume that tidal flows are harmonic with a frequency of 12 hours. The instantaneous tidal current can be simply modeled by the harmonic:

$$V_t = V_{\text{maximum}} \times \text{Sin}(t/12)$$

Integrating this equation from $t = 0$ to $t = 6$ gives: Distance = $V_{\text{max}} \int \text{Sin}(t/12) dt$,
or:

Equation (2) Distance = 3.82 (hours) x V_{maximum} = 1.3752 x 10⁴ (sec) x V_{maximum}

where V_{maximum} is measured in cm/hour or cm/sec respectively

V_{maximum} is measured (using either a drogue or a current meter) at a time midway between Mean High Water (MHW) and Mean Low Water (MLW). MHW does not vary significantly from tide to tide. However, V_{maximum} should be measured during a tidal exchange when the low tide is as close to MLW (18.6-year average of all low tides) as possible. Ideally, two velocity measurements should be made at mean water depth, once on the ebb tide and again on the flood tide. These two measurements should be averaged to provide a value for V_{maximum} . This procedure will give a crude, but reasonable, estimate of the average, annual, current speed at a site.

The "Distance" developed in this analysis is the average distance that a particle is carried, by the tides, in one direction, before its velocity is reversed and it is carried back toward the point of origin (source). The average tidally driven velocity is (3.82 hours/6 hours) V_{maximum} or 0.64 V_{maximum} . This procedure will integrate the effects of all currents influencing a site at the time the measurements are taken.

Where local water movement is not wholly driven by tides, other considerations may determine the value used for average water speeds. In relatively steady state conditions, a single measurement of water speed will suffice. We will refer to this steady state speed as V_{ss} .

In situations where local currents are a function of both steady state and tidally driven factors, three current measurements should be taken approximately three hours apart. In addition to the measurements required to determine V_{maximum} , the third measurement should be taken at slack tide. This measurement is V_{ss} . The appropriate velocity to be used in this mode can then be determined using Equation 3.

Equation 3. $V_{\text{model}} = V_{\text{ss}} + 0.64(V_{\text{maximum}})$

The author acknowledges that during the period of time in which tidal currents are opposed to steady state currents, low velocities may occur, resulting in higher deposition rates in sediments "upstream" from the source. Do to the variety and complexity of potential hydrodynamic interactions, this model will only examine average PAH deposition to the sediment.

The deposition to the benthos of PAH migrating from pressure treated wood equals $L \times P/dA$. Where L = the loss per unit area of piling = $M \times 2 R_p dh$, P is the *Sediment Partition Coefficient* and M is the creosote migration rate from the piling to be developed in Equation (10).

The parameter (M) has units $\mu\text{g-cm}^{-2}\text{-day}^{-1}$, P is dimensionless, and the PAH loss (L) has units $\mu\text{g-cm}^{-2}\text{-day}^{-1}$. Equation 4 is used to predict PAH deposition to sediments in this model.

$$(4) \text{ Deposition (D)} = M \times R_p \times P \times G / [(r + R_p) \times (V_{\text{model}}/V_{\text{vert}})]$$

D = deposition rate (excluding degradation factors) measured in $\mu\text{g cm}^{-2}\text{-day}^{-1}$

M = PAH Migration Rate ($\mu\text{g cm}^{-2}\text{-day}^{-1}$)

P = Sediment Partition Coefficient (0.280)

R_p = average piling radius measured in centimeters

G = the Geometry Factor (dimensionless)

V_{vert} = average vertical velocity of adsorption particles (silt = 0.05 cm-sec^{-1})

V_{model} = the Model Water Velocity = $V_{\text{ss}} + 0.64V_{\text{maximum}}$

r = the distance from the periphery of the treated wood at which the deposition is measured.

Note: Boundary conditions exclude evaluation of PAH accumulation in sediments at distances greater than the height of the piling (h), multiplied by the maximum tidal velocity and divided by the settling velocity. For a piling submerged in 5 meters of water flowing with a maximum horizontal velocity of 2 cm-sec^{-1} , this boundary condition limits predictions to a distance of 200 meters from the piling. This is not considered a limitation on the use of the mode because maximum PAH concentrations occur in the near field at distances less than one meter.

As an example, consider PAH migrating from treated wood at a rate of $30 \mu\text{g-cm}^{-2}\text{-day}^{-1}$. The PAH is adsorbed to silt ($V_{\text{vert}} = 0.05 \text{ cm/sec}$) suspended in a marine environment where model currents (V_{model}) are determined to be 2.5 cm/sec . Polycyclic Aromatic Hydrocarbon deposition at a radius (r) of 50 centimeters from a piling that is 15 cm in radius would be deposited at a rate equal to $0.138 \text{ micrograms-cm}^{-2}\text{-day}^{-1}$. In a previous section, we suggested that 100% of the HPAH and 4.83% of the LPAH reach the sediments. From that, we concluded that 28% of the TPAH migrating from a piling reaches the sediments. In this case that implies that the effective loading is $0.0501 \mu\text{g-cm}^{-2}\text{-day}^{-1}$.

PAH Degradation in Aquatic Environments. Polycyclic Aromatic Hydrocarbons are degraded in the water column by photo-oxidation, chemical-oxidation and microbial metabolism (Saylor and Sherrill, 1981; Colwell, 1986; Cerniglia and Heitkamp, 1992; Gardner, *et al.*, 1979; Borthwick and Patrick, 1982; MacGillivray and Shiaris, 1993; Herbes, 1981). Cerniglia and Heitkamp (1992) present a summary of PAH half-lives. Based on that report, the PAH half-lives presented in Table 8 will be used as a

basis for this model. Cerniglia and Heitkamp's data have been normalized to 20°C using the methods discussed in Table 9 and the analysis that follows.

Table 8. Sediment PAH half lives in moderately contaminated sediments (>1,000 ppb PAH), assuming aerobic conditions in the top 4 centimeters of sediment. Half-life values are based on data from Cerniglia and Heitkamp (1992) and normalized to 20°C.

LPAH (13% of sedimented TPAH). Half Life (T= 20°C) = 30.5 days.

Compound	Half-life	% in Creosote & (Contam. Seds.)	LPAH Half-Life Contribution
Naphthalene	18 days	15.45 (2.00)	8.7
2-methyl Naphthalene	101 days	2.15 (0.28)	6.8
Phenanthrene	29 days	12.85 (1.67)	11.7
Anthracene	72 days	1.45 (0.19)	3.3
	Sums	31.90 (4.14)	30.5 days

HPAH (87% of sedimented TPAH). Half Life (T= 20°C) = 242.3 days

Compound	Half-Life	% in Creosote & (Contam. Seds.)	HPAH Half-Life Contribution
Pyrene	246 days	5.30 (4.61)	160.6
Benzo[a]anthracene	20 days	0.85 (0.74)	2.1
Chrysene	100 days	1.63 (1.42)	20.1
Benzo[a]pyrene	>1448 days	0.32 (0.29)	59.5
	Sums	8.10 (7.06)	242.3 days

Continuing our assumption that 87% of sedimented TPAH are HPAH and that 13% are LPAH, the TPAH half-life would be 214.8 days.

Low Molecular Weight PAH Half-Life = 30.5 Days

High Molecular Weight PAH Half-Life = 242.3 Days

Total PAH Half-Life = 214.8 Days

From this analysis, it would appear that the phenanthrene, pyrene, chrysene and Benzo[a]pyrene would be the PAH species most likely found in sediments associated with creosote pilings. Recent studies (Environment Canada, 1994; EVS Consultants, 1994) showed elevated levels of pyrene, phenanthrene, chrysene and fluoranthene(s), within one meter of recently installed creosoted pilings. This EVS study also found that 83% of the sedimented PAH were high molecular weight and 17% were low molecular weight at the most contaminated station. These findings are in reasonable agreement with Malins (1985) values of 87% and 13% respectively.

Accumulation of PAH in Sediments and the Water Column Based on Half-Life. To determine the accumulation associated with these half-lives, the following expression was submitted to *Mathcad 4.0 for Windows*. The parameter (h) is the half life, and (t) is time, measured in days. Convergence of this expression is dependent on the value of (h). However, the computed value is asymptotic at between 3000 and 5000 iterations.

Equation (6)

$$h := 214.8$$
$$\sum_{t=0}^{5000} \exp\left\{-\frac{0.6931}{h} \cdot t\right\} = 310.412$$

(Dimensionless)

For the PAH half-lives of 30.5, 242.3 and 214.8 days the results of this analysis indicate that steady state conditions (PAH degradation = PAH deposition) when 310, 364 and 45 days of PAH accumulation have occurred. The values, provided in Table 6, will be used in this analysis.

Table 9. Steady state PAH accumulations in sediments at 20°C derived from half-life values.

PAH Class	Half Life	Steady State Accumulation Factor
LPAH	30.5 days	44.5
HPAH	242.3 days	364.5
TPAH	214.8 days	310.4

Additional factors affecting PAH degradation half-lives. PAH degradation and half-lives are a function of several physical and biotic factors:

Oxygen availability: Microbial metabolism of aromatic hydrocarbons requires molecular oxygen as a first step in breaking the ring by bacterial enzymes known as dioxygenases (Sayler and Sherrill, 1981). Dissolved oxygen is seldom depressed in the water column of open aquatic systems. However, oxygen diffuses slowly into sediments and is rapidly used by infauna, epifauna and microorganisms in the upper few centimeters of the substrate. Heavy organic loading, particularly in poorly flushed areas, can exacerbate oxygen deficits creating anoxic conditions on the surface of sediments or at very shallow depths (1 to 2 cm).

Hambrick *et al.* (1980) reported the effect of oxidation-reduction potential on the microbial degradation of naphthalene in aquatic sediments from a salt marsh stream near an oil field in Louisiana. The redox potential of submerged sediments may range from -300 mV for anoxic sediments up to +700 mV for highly aerobic sediments. They found that mineralization of naphthalene at pH values of 5.0, 6.5 and 8.0 increased as redox values increased from -250 to +510 mV and concluded that oxygen availability is an important factor for PAH mineralization. Degradation studies by Bauer and Capone (1985) suggest that PAH buried in anaerobic sediments may persist for many years.

The current model will evaluate sediment oxygen levels through measurement of the Redox Potential Discontinuity (RPD). This is simply the distance, below the sediment surface, at which the sediment color changes to dark gray or black. The black color is evidence of iron sulfides associated with anaerobic conditions. To measure the RPD, simply insert a clear plastic or glass cylinder vertically into the sediment and measure the depth of the discontinuity in centimeters. For purposes of this analysis, we will assume that sediment half lives should be adjusted for RPD by application of the following factor:

$$\text{Equation (7)} \quad \text{Half-life}_{\text{RPD}} = e^{[(4 - \text{RPD})/3]} \quad (\text{Dimensionless})$$

In working with the EXCEL Spreadsheet, RPD values greater than 4 cm should be entered as 4. The entry of larger values will give erroneous results. The Half-Life factor will correct PAH degradation half-lives by the following amounts:

Depth of RPD	Half-life Correction
≥ 4 cm	1.00
3 cm	1.03
2 cm	1.34
1 cm	2.72
0 cm	10.70

Temperature directly affects the rate at which PAH are degraded by microorganisms in natural ecosystems. Several investigators have reported seasonal fluxes in heterotrophic activity and PAH degradation rates. The highest activities are found in summer and the lowest in winter. The magnitude of temperature effects on PAH degradation was demonstrated in anthracene and naphthalene by Bauer and Capone (1985). Similarly, Sayler and Sherrill (1981) demonstrated increased phenanthrene degradation as a function of temperature in the range 5 to 37°C. For this model, the preceding data were normalized to a temperature of 20°C. Linear regression on the transformed data gave the results presented in Table 10. Further normalizing each of the component coefficients to their relative proportions in creosote oil PAH derived the coefficient for total.

Table 10. Relationship between phenanthrene, anthracene and naphthalene mineralization and incubation temperature. Data between 5 and 37°C were used in the analysis. For purposes of this analysis, the degradation coefficients were normalized to their proportional presence in creosote oil to obtain an estimate of the effect of temperature on total PAH degradation.

Compound Coef = 0.0	Regression	R_{a2}	Probability that
Phenanthrene	Degradation (D) = 2.033 T(°C)	0.937	P = 0.002
Anthracene	Degradation (D) = 0.568 T(°C)	0.979	P = 0.011
Naphthalene	Degradation (D) = 1.249 T(°C)	0.971	P = 0.014
Total PAH	Degradation (D) = 1.555 T(°C)		

To accommodate the needs of this model, the data used to develop Table 10 was normalized to a temperature of 20°C and the following relationship obtained:

Equation (8) PAH Thermal Degradation Factor (TDF) = 0.047T(°C)

At 8 °C, the model predicts degradation rates that are 37.6% of those observed at 20 °C. Likewise, at 30 °C, the model predicts degradation rates that are 141% of those observed at 20 °C. In this model, PAH degradation will be measured in half-lives at 20°C and corrected using this dimensionless factor.

Bacterial Population Density and Species. Bacterial populations (species) within a microbial community do not have the same spectrum of enzymatic

capability. Relatively few bacterial species are known to contain the necessary genetic material to code for the production of PAH degradative enzymes. It is generally accepted that bacterial enzymes have co-evolved with the presence of growth supporting substrates or as a response to the destruction of potentially toxic substrates. The complete mineralization of a growth supporting substrate is a result of multiple enzymes acting sequentially under complex systems of product and substrate regulation. Consequently, novel PAH substrates or PAH substrates reaching high concentrations due to anthropogenic sources may resist complete mineralization due to a lack of specific enzymes or enzyme complexes. Lack of a complete enzyme system may result in a phenomenon known as co-oxidation or co-metabolism in which a PAH substrate may be partially oxidized by a non-specific enzyme while the bacterial cell is growing at the expense of another substrate.

Bacterial enzymes involved in the metabolism of PAH are induced, meaning that they are synthesized due to an unknown, but finite, quantity of PAH interacting with DNA in the bacterial cell. There are no known active transport systems that facilitate the accumulation of PAH in the bacterial cell. The passive diffusion rate of PAH onto and into the bacterial cell is concentration dependent and potentially rate limiting if the bacterial cell is competing with inorganic and organic particle surfaces as sites for PAH adsorption. Therefore, the solubility of PAH, which ranges from 12.5 mg/l for naphthalene to 10 ng-L⁻¹ for Benzo [a]pyrene, is a major determinant effecting PAH availability to microbes.

It is generally thought that microbes metabolize low molecular weight PAH (2 and 3 rings) much more readily than high molecular weight PAH (4 or more rings). In part, this is due to the reduced solubility of HPAH. PAH with more than three condensed benzene rings do not serve as sole substrates for microbial growth, though they may be subject to slow co-metabolism when there is another substrate available.

For the purposes of this analysis, we will assume that sufficient PAH are released, over an extended period of time, such that microbial communities with PAH metabolizing enzyme systems are stimulated and that there are sufficient quantities of LPAH and other primary substrates allowing for the co-metabolism of HPAH. No corrections for microbial community adaptation will be included in this model.

Polycyclic Aromatic Hydrocarbon Degradation Model. Combining the results of the above arguments provides a degradation model based on temperature and dissolved oxygen distribution in the sediments:

$$\text{Equation (9)} \quad \text{PAH}_{\text{degrade}} = (\exp^{(4-RPD)/3})/0.047T(^{\circ}\text{C})$$

Migration of creosote from treated wood. Several mechanisms contribute to the migration of creosote from treated lumber and piling. When treated wood is first placed in the water, the wood fibers quickly swell during hydration. It is this initial hydration, coupled with surface residues, that result in the sheen frequently observed during the installation of creosote pilings. These direct physical losses are generally of short

duration in properly treated wood. The sheen quickly evaporates and studies by Colwell (1986) and Wade, *et al.* (1987) have clearly shown that water column levels of PAH under the sheen are exceedingly low or undetectable. This model does not correct water column PAH concentrations for short-term losses of low molecular weight hydrocarbons observed in the sheen from newly installed creosote treated wood. This model conservatively assumes that all LPAH are dissolved into, and diluted by, the water column.

There are additional mechanisms that result in the long-term loss of creosote from pressure treated wood used in aquagrading would be unlikely in distilled water. Therefore, this author questions the significance of the leaching rates observed by Ingram, *et al.* (1982) in distilled fresh water when compared with natural marine water.

Estimating rs. At 10 meters, both predicted and observed levels of PAH are very low. Small scale hydrodynamic features appear to be redistributing sedi along the Pacific coastline of Vancouver island - an area rich in algal growth, while the highest levels were found in muss

Creosote Part I Bibliography

The following is a comprehensive list of references held by the Western Wood Preservers Institute. The list includes those references cited in this document plus others that provide background for those desiring a comprehensive review of the aquatic risks associated with creosote treated wood. For information or copies (0.50 per page plus postage) contact the Western Wood Preservers' Institute at (206) 693-9958 or Dr. Kenneth M. Brooks at (206) 732-4464.

1. American Industrial Health Council. Exposure Factors Sourcebook; 1994. AWPI. Contains human health risk assessment information.
2. American Wood-Preservers' Association. Standards, 1992. American Wood-Preservers' Association, P.O. Box 286, Woodstock, MD 21163-0286: American Wood- Preservers' Association; 1992.

In the judgment of the membership of the American wood-Preservers' Association, these standards represent the preferred wood preservation specifications, processes, penetration, and retention in the present state of research and technical knowledge. Because of possible variations in materials, applications, and manner of use, however, AWPA cannot be responsible for results of use or performance of products treated in accordance with these standards.

3. Ankeley, G.T., R.J. Erickson, G.L. Phipps, B.R. Mattson, P.A. Kosian, B.R. Sheedy, and J.S. Cox. 1995. Effects of light intensity on the phototoxicity of fluoranthene to a benthic macroinvertebrate. Environmental Science and Technology. Vol. 29,

No. 11, pp. 2828-2833.

Conceptual models suggest that the toxicity of photoactivated polycyclic aromatic hydrocarbons (PAHs) should be a direct function both of chemical (PAH) dose and intensity of the ultraviolet (UV) light to which the organism is exposed. However, there have been only limited studies with aquatic organisms to quantify the relationship between PAH dose and UV intensity in producing phototoxicity. In this study, oligochaetes (*Lumbriculus variegatus*) were exposed, via the water, to multiple concentrations of fluoranthene, a PAH known to be phototoxic, and then placed under UV light at three different intensities. The resultant phototoxicity clearly was a function of both of PAH dose and light intensity. Time-dependent mortality of the oligochaetes could be accurately predicted through evaluation of the product of fluoranthene dose (in the tissue of the animal) and light intensity to which the organisms were exposed. These results indicate that criteria for phototoxic chemicals should incorporate consideration not only of xenobiotic exposure but also of light intensity in specific aquatic environments.

4. Army Corps of Engineers (US Department of the Army). Puget Sound Dredged Disposal Analysis Program; PSDDA Biennial Report; Dredged Material Management Years 1992/1993. Seattle District, Corps of Engineers, P.O. Box 3755, Seattle, WA 98124-2255; US COE; 1994.

This report summarizes the application of the PSDDA sediment evaluation guidelines to dredging projects during Dredging Years (DY) 1992 and 1993. It also describes the disposal of tested material at the eight PSDDA open-water disposal sites in Puget Sound during that period.

5. Arsenault, R.D. (AMINEX). 1992. Critique of Report by Monroe Toxicology Professionals on Potential Human Health and Environmental Impacts Associated With Creosote-Treated Foundation Pilings Flynn Street Project, Lake Whatcom. Final ed. Shelton, WA: AMINEX.
6. ASTM Committee E-47 on Biological Effects and Environmental Fate (Spons.). 1995. Fifth Symposium on Environmental Toxicology and Risk Assessment: Biomarkers and Risk Assessment—Program and Abstracts. 1916 Race Street, Philadelphia, PA 19103-1187

This booklet is the Program and Abstracts of the Fifth Symposium on Environmental Toxicology and Risk Assessment: Biomarkers and Risk Assessment. It

was sponsored by the ASTM Committee E-47 on Biological Effects and Environmental Fate at the Denver Marriott City Center in Denver, Colorado.

7. Augspurger, T.P., R.L. Herman, J.T. Tanacredi and J.S. Hatfield. 1994. Liver Lesions in Winter Flounder (*Pseudopleuronectes americanus*) from Jamaica Bay, New York: Indications of Environmental Degradation. *Estuaries*. Vol. 17, No. 18, pp. 172-180.

Liver sections of winter flounder (*Pseudopleuronectes americanus*) collected from Jamaica Bay and Shinnecock Bay, New York, in 1989, were examined microscopically to determine the pervasiveness of liver lesions observed previously in Jamaica Bay winter flounder. Neoplastic lesions were not detected in fish from Jamaica Bay or the Shinnecock Bay reference site. Twenty-two percent of Jamaica Bay winter flounder examined (n = 103) had unusual vacuolization of hepatocytes and biliary pre-ductal and ductal cells (referred to hereafter as the vacuolated cell lesion). The lesion, identical to that found in 25% of Jamaica Bay winter flounder examined in 1988, has previously been identified in fishes taken from highly polluted regions of the Atlantic coast (e.g., Boston Harbor, Massachusetts, and Black Rock Harbor, Connecticut). Prevalence of the vacuolated cell lesion in winter flounder from Jamaica Bay was significantly greater ($p < 0.0001$) than in 102 specimens collected from Shinnecock Bay. Current scientific literature indicates vacuolated hepatocytes and cholangiocytes are chronically injured and that the extent of their deformity is consistent with the action of a hepatotoxicant. The high prevalence of vacuolated hepatocytes in Jamaica Bay winter flounder and absence of the lesion in flounder from reference sites strongly supports the hypothesis that this impairment is a manifestation of a toxic condition in at least some portions of Jamaica Bay.

8. Baechler, R.H., B.R. Richards, A.P. Richards and H.G. Roth. 1970. Effectiveness and Permanence of Several Preservatives in Wood Coupons Exposed to Sea Water. *Journal of the American Wood-Preservers' Association*. 47-65.

Pine coupons treated with different preservatives at several levels of loading were exposed in two harbors and removed at 6-month intervals for observation of biological attack and for chemical analyses to determine residual preservative in outer zones. Losses of preservatives tended to level off after 6 months. After 5 years, heavily treated coupons showed minimal attack. Considerable attack by *Limnoria tripunctata* was found on coupons treated to moderate retentions of creosote. When creosoting was preceded by treatment with copper-arsenic compounds, attack was prevented except in lightly treated series. The lower retentions of copper-arsenic salts without supplementary creosoting permitted teredinid attack. No definite relation was found between the amount of residual preservative and the onset of borer attack. Infrared studies of extracted creosote yielded no clues on loss of effectiveness of the creosote.

9. Baechler, R.H. and R.M. Alpen. 1964. Extraction of Borings Removed from Fender Piles in San Francisco-Oakland Bay Bridge. *Journal of the American Wood-Preservers' Association*; 32-37.

This study was made of Douglas-fir fender piling in the San Francisco-Oakland Bay Bridge built in 1934. After 25 years, 11 percent of the piles had shown some attack by marine borers. Borings taken from sound piles in 1962 in most cases showed appreciably more creosote than borings taken from piles showing borer damage. Samples of creosote that had been received by the plant during the period of treatment were found to be low-residue oils with high specific gravity's of fractions, showing that they were derived from high temperature tar.

10. Baechler, R.H. and H.G. Roth. (Date unknown). Further Data on the Extraction of Creosote From Marine Piles. *Journal of the American Wood-Preservers' Association*; unknown: 120 - 132.

The residual oil was determined in disks from 60 southern pine and 23 Douglas-fir marine piles of variable age and condition. The recovered oil was subjected to simple tests to ascertain its general nature. Except when untreated wood was exposed by mechanical damage, attack by toredo was negligible even in piles showing only moderate retention. Attack by *limnoria* was more frequently encountered. A heavy retention of an oil that is essentially free from saturated hydrocarbons is recommended for treating piles to be used where *limnoria* are active.

11. Barrick, R.C. 1982. Flux of Aliphatic and Polycyclic Aromatic Hydrocarbons to Central Puget Sound from Seattle (Westpoint) Primary Sewage Effluent. *Environ. Sci. Technol.* 16: 682 - 692.

Concentrations and mass emission rates are reported for hydrocarbons in a 20-month evaluation of primary municipal waste water discharging to marine waters of Puget Sound from Seattle, WA. On the average, METRO (Westpoint) discharges 475 metric tons/year of aliphatic hydrocarbons and approximately 1 metric ton/year of 3-7 ring polynuclear aromatic hydrocarbons (PAH), corresponding to discharges of 2.6 and 0.005 g/(capita day), respectively. Effluent PAH containing >-4 rings apparently derive principally from storm-water contributions. A comparison of METRO's yearly average discharge of different hydrocarbon components with observed hydrocarbon fluxes in adjacent Puget sound surface sediments suggests negligible accumulations of the resolvable alkanes (derived from the effluent), partial accumulations of an unresolved complex mixture and phenanthrene, and substantial accumulations of the >-4-ring PAH. The discharge accounts for a major portion of the sedimentary aliphatic fossil hydrocarbon flux and is one of several important PAH contributors.

12. Barrick, R.C. and F.G. Prahl. 1987. Hydrocarbon Geochemistry of the Puget Sound Region - III. Polycyclic Aromatic Hydrocarbons in Sediments. *Estuarine, Coastal and Shelf Science*; 25: 175-191.

Polycyclic aromatic hydrocarbon (PAH) distributions and sources are characterized in 96 sediment samples from 24 ²¹⁰Pb-dated cores collected at locations in the greater Puget Sound. The highest PAH concentrations are found within a few kilometers of several sources including industrial facilities in northern Puget Sound, urban areas in central Puget Sound, and river systems draining coal-bearing strata. Regional patterns of combustion-derived PAH in surficial sediments indicate little atmospheric or waterborne exchange of PAH between different regions of the Sound. Significant subsurface maxima in combustion-derived PAH concentrations (²¹⁰Pb dated at the 1950s) occur only in sediment cores collected near urban centers. Perylene apparently derives from erosion of a terrestrial source with little or no evidence of in-situ production at depth in sediment cores. coal fragments are carriers of a characteristic suite of alkylated phenanthrene, chrysene, and pyrene derivatives concentrated near river mouths in central and southern Puget Sound.

13. Battelle Marine Sciences Laboratory for EPA (Battelle, MSL). Contaminant Loading to Puget Sound From Two Marinas. I ed. Seattle, WA: EPA, Region 10; 1989; EPA 910/9-89-014.

Reports sediment and water column concentrations of PAH and other contaminants to Puget Sound from two local marinas.

14. Bauer, J.E. and D.G. Capone. Degradation and Mineralization of the Polycyclic Aromatic Hydrocarbons Anthracene and Naphthalene in Intertidal Marine Sediments. *Applied and Environmental Microbiology*; 1985: 81 - 90.

The degradation of the polynuclear aromatic hydrocarbons (PAHs) anthracene and naphthalene by the microbiota of intertidal sediments was investigated in laboratory studies. No mineralization of either PAH was observed in the absence of oxygen. both rates and total amounts of PAH mineralization were strongly controlled by oxygen content and temperature of the incubations. Inorganic nitrogen and glucose amendments had minimal effects on PAH mineralization. The rates and total amounts of PAH mineralized were directly related to compound concentration, pre-exposure time, and concentration. Maximum mineralization was observed at the higher concentrations (5 to 100 micrograms/g [ppm]) of both PAHs. Optimal acclimation to anthracene and naphthalene (through pre-exposures to the compounds) occurred at the highest acclimation concentration (1,000 ppm). However, acclimation to a single concentration (100 ppm) resulted in initial relative mineralization rates over a range of re-exposure concentrations (1 to 1,000 ppm) being nearly identical. Maximum mineralization of both PAHs occurred after intermediate periods (1 to 2 weeks) of pre-exposure. The fraction of

the total heterotrophic population capable of utilizing anthracene or naphthalene as sole carbon source was also greatest after 2 weeks.

15. Bauer, J.E. and D.G. Capone. Effects of Co-Occurring Aromatic Hydrocarbons on Degradation of Individual Polycyclic Aromatic Hydrocarbons in Marine Sediment Slurries. *Applied and Environmental Microbiology*; 1988; July: 1649-1655.

Rates of polycyclic aromatic hydrocarbon (PAH) degradation and mineralization were influenced by preexposure to alternate PAHs and a monoaromatic hydrocarbon at relatively high (100 ppm) concentrations in organic-rich aerobic marine sediments. Prior exposure to three PAHs and benzene resulted in enhanced [¹⁴C]naphthalene mineralization, while [¹⁴C]anthracene mineralization was stimulated only by benzene and anthracene preexposure. Preexposure of sediment slurries to phenanthrene stimulated the initial degradation of anthracene. Prior exposure to naphthalene stimulated the initial degradation of phenanthrene but had no effect on either the initial degradation or mineralization of anthracene. For those compounds which stimulated [¹⁴C]anthracene or [¹⁴C]naphthalene mineralization, longer preexposures (2 weeks) to alternative aromatic hydrocarbons resulted in an even greater stimulation response. Enrichment with individual PAHs followed by subsequent incubation with one or two PAHs showed no alteration in degradation patterns due to the simultaneous presence of PAHs. The evidence suggests that exposure of marine sediments to a particular PAH or benzene results in the enhanced ability of these sediments to subsequently degrade that PAH as well as certain other PAHs. The enhanced degradation of a particular PAH after sediments have been exposed to it may result from the selection and proliferation of specific microbial populations capable of degrading it. The enhanced degradation of other PAHs after exposure to a single PAH suggests that the populations selected have either broad specificity for PAHs, common pathways of PAH degradation, or both.

16. Bauer, J.E., R.P. Kerr, M.F. Bautista, C.J. Decker and D.G. Capone. Stimulation of Microbial Activities and Polycyclic Aromatic Hydrocarbon Degradation in Marine Sediments Inhabited by *Capitella capitata*. *marine Environmental Research*; 1988; 25: 63-84.

The effect of the polychaete *Capitella capitata* on a variety of sediment microbial activities was determined for 5 months in marine microcosms with or without chronic treatment with the polycyclic aromatic hydrocarbon anthracene. Rates of microbial D[U-¹⁴C] glucose assimilation and respiration as well as rates and total amounts of [9-¹⁴C] anthracene mineralization were consistently greater in sediments with resident populations of *Capitella*. anthracene treatment only affected ¹⁴C-anthracene mineralization such that after 5 months all sediments under chronic anthracene treatment mineralized ¹⁴C-anthracene more rapidly than sediments without anthracene or those containing only *Capitella*. microbial incorporation of [methyl-³H]thymidine showed no consistent pattern among treatments.

The colonization of sediments by total numbers of meiofauna and meiofauna-sized larvae was suppressed in microcosms dosed with anthracene, in contrast to the increased numbers in *Capitella*-inhabited microcosms. However, when *Capitella* was also present in anthracene-dosed microcosm sediments, the suppression of total meiofauna numbers was partially offset.

17. Baumann, P.C., J.C. Harshbarger, and K.J. Hartman. 1990. Relationships between liver tumors and age in brown bullhead populations from two Lake Erie tributaries. *Sci. Total Environ.* 94, pp. 71-87.

We compared liver tumor frequencies, and age and length characteristics of brown bullheads (*Ictalurus nebulosus*) of greater than 250 mm total length from two Lake Erie tributaries. Bullheads taken from Old Woman Creek (n = 144) had no grossly observable liver tumors, while those collected in the highly industrialized Black River (n = 532) had a 30% frequency of grossly visible liver tumors during 1981-1982. Liver lesions diagnosed histologically in a randomly collected sample (n = 125) of brown bullheads from the Black River included both biliary and hepatic lesions, with cancerous neoplasms occurring in 38.4% of the fish. Black River bullheads of combined ages 4 and 5 had a significantly (p < 0.05) greater prevalence of biliary carcinomas (35.5%) than those of ages 2 and 3 combined (18.4%). Biliary carcinomas was significantly more prevalent than hepatocellular carcinoma in age 5 fish (sexes combined) and in males of ages 3 and 4. The prevalence of hepatocellular carcinomas in age 4 fish (sexes combined) and in males of ages 3 and 4. The prevalence of hepatocellular carcinomas was significantly higher in females than in males. Age distributions of bullheads differed significantly between the two sites, while length distributions were similar. No brown bullheads of ages 6 or 7 were collected in the Black River, while these age groups composed 18% of the catch in Old Woman Creek. Brown bullheads of age 5 were almost six times more numerous in the Old Woman Creek than in Black River collections. These age and length distributions are consistent with the hypothesis that brown bullheads in the Black River were subjected to an age-selective mortality associated with high prevalences of liver carcinoma.

18. Baumann, P.C. and J.C. Harshbarger. 1995. Decline in Liver Neoplasms in Liver Neoplasms in Wild Brown Bullhead Catfish after Coking Plant Closes and Environmental PAHs Plummet. *Environmental Health Perspectives*. Vol. 103, No. 2, pp. 168-170.

Polycyclic aromatic hydrocarbons (PAHs) in both sediment and brown bullhead catfish tissues from the Black River in Lorain County, Ohio, declined by 65% and 93%, respectively, between 1980 and 1982. Sediment PAHs declined an additional 99% by 1987, coincident with the closure of a coking facility in 1983. Contemporaneously, liver cancer in 3 to 4 year old brown bullheads declined to about one-quarter the 1982 frequency (10% versus 39%) by 1987, while the percentage of livers without any

proliferative lesions doubled (42% versus 20%). These changes were significant within age group. Our data affirm a cause-and-effect relationship between PAH exposure and liver cancer in wild fish. The data also support the efficacy of natural, unassisted remediation once the source of the pollution is eliminated.

19. Baumann, P.C. and J.C. Harshbarger. 1985 Frequencies of liver neoplasia in a feral fish population and associated carcinogens. *Marine Environ. Res.* 17, pp. 324-327.

Previous research had documented prevalent liver neoplasia within feral fish populations from half a dozen polluted waterways of North America. A brown Bullhead, *Ictalurus nebulosus*, population in the Black River, Ohio, and a 33% prevalence of grossly observable liver tumors in fish older than 2 years compared to 0% in 249 bullhead from a reference location (Buckeye Lake). To approximate the actual prevalence of gross plus microscopic lesions combined in the Black River population, we captured 125 bullhead at least 250 mm in length in 1982. Livers were preserved for histopathology and pectoral fin spines were removed for aging. On average, each liver was sectioned at five levels for diagnosis. Bullhead (whole fish) and Black River sediment were analyzed for polynuclear aromatic hydrocarbons (PAHs) by gas chromatography-mass spectrometry as previously reported. Bullheads were found to have a higher incidence of liver tumors than was grossly apparent and to contain elevated levels of polynuclear aromatic hydrocarbons (PAHs).

20. Bay, M. and J.S. Goldberg (King County and Seattle). Contaminants in Vector Waste and Disposal Options. 32-33 ed. Olympia, WA: Puget Sound Water Quality Authority, PO Box 40900, Olympia, WA 98504-0900; 1994 Puget Sound Notes.

Maintenance of stormwater systems results in a large quantity of solid and liquid wastes that have high concentrations of many pollutants. These "vector" wastes (so called after the trade name of specialized pieces of removal equipment) require special handling, storage, treatment and disposal to minimize further contamination of the environment.

21. Baya, A.M., P.R. Brayton, V.L. Brown, D.J. Grimes, E. R. Cohen and R.R. Colwell. Coincident Plasmids and Antimicrobial Resistance in Marine Bacteria Isolated From Polluted and Unpolluted Atlantic Ocean Samples. *Applied and Environmental Microbiology*; 1986; 51(6): 1285-1292.

Sewage effluent and outfall confluence samples were collected at the Barceloneta Regional Treatment Plant in Barceloneta, Puerto Rico; outfall confluence samples at ocean City, Md., were also collected. Samples from uncontaminated open ocean areas served as clean-water controls. Bacteria were enriched in marine broth 2216 amended with 1 microgram of one of a set of chemicals selected for study per ml: nitrobenzene, dibutyl

phthalate, m-cresol, o-cresol, 4-nitroaniline, bis(tributyltin)oxide, and quinone. MICs of the chemicals were determined individually for all isolates. Bacterial isolates were evaluated for resistance to nine different antibiotics and for the presence of plasmid DNA. Treated sewage was found to contain large numbers of bacteria simultaneously possessing antibiotic resistance, chemical resistance, and multiple bands of plasmid DNA. Bacteria resistant to penicillin, erythromycin, nalidixic acid, ampicillin, m-cresol, quinone, and bis(tributyltin)oxide were detected in nearly all samples, but only sewage outfall confluence samples yielded bacterial isolates that were resistant to streptomycin. Bacteria resistant to a combination of antibiotics, including kanamycin, chloramphenicol, gentamicin, and tetracycline, were isolated only from sewage effluent samples. It is concluded that bacterial isolates derived from toxic chemical wastes more frequently contain plasmid DNA and demonstrate antimicrobial resistance than do bacterial isolates from domestic sewage-impacted waters or from uncontaminated open ocean sites.

22. Beaulieu, P.D., Editor (Puget Sound Council of Governments). Puget Sound Water Quality Conference; September 30, 1983 to October 1, 1983; Seattle, WA. Seattle: Puget Sound Council of Governments; 1983. 139 pages.

Variety of discussions regarding water quality in Puget Sound, Washington.

23. Becker, D.S., T.C. Ginn, and G.R. Bilyard (PTI Environmental Services and Tetra Tech, Inc.). Comparisons Between Sediment Bioassays and Alterations of Benthic Macroinvertebrate Assemblages as Measures of Sediment Toxicity. Bellevue, WA; unknown.

The results of this study indicate that chemical contamination and biological effects in Commencement Bay exhibited a patchy distribution, with the most severely polluted stations occurring near the four major contaminant sources evaluated in the Bay. In general, bioassay responses and alterations of benthic macroinvertebrate assemblages were closely related to sediment chemical contamination, suggesting that most of the observed biological effects resulted from chemical toxicity. Although all three bioassays were reasonably successful in predicting the presence or absence of moderately to severely altered benthic assemblages, considerable differences were found in the ability of the tests to specifically identify only the altered assemblages. The Microtox bioassay was the most sensitive of the three tests because it successfully identified the highest percentage of altered assemblages. By contrast, the oyster larvae abnormality bioassay was the most efficient of the three tests because it falsely predicted the lowest percentage of altered assemblages. By using the results of the Microtox and oyster larvae abnormality bioassays in a tiered design, the strengths of both tests could be combined to improve the accuracy with which altered assemblages are identified.

24. Becker, D.S., G.R. Bilyard and T.C. Ginn. Comparisons Between Sediment Bioassays and Alterations of Benthic Macroinvertebrate Assemblages at a Marine Superfund

Site: Commencement Bay, Washington. Environmental Toxicology and Chemistry; 1990; 9: 669-685.

Laboratory sediment bioassays and alterations of benthic macroinvertebrate assemblages were evaluated at 43 stations in Commencement Bay, Washington, and at 4 stations in Carr Inlet, Washington (a reference embayment). Three bioassays were evaluated: the amphipod mortality test using *Rhepoxynius abronius*, the oyster larvae abnormality test using *Crassostrea gigas* and the Microtox test using *Photobacterium phosphoreum*. Alterations of benthic assemblages were determined using numerical classification analysis.

Bioassay responses and alterations of benthic assemblages were closely related to chemical contamination, suggesting that most biological effects resulted from chemical toxicity. Although all three bioassays were reasonably successful in predicting the presence or absence of moderately to severely altered benthic assemblages, considerable differences were found in the ability of the tests to identify only the altered assemblages. The microtox bioassay successfully identified the highest percentage of altered benthic assemblages. By contrast, the oyster larvae abnormality bioassay falsely predicted the lowest percentage of altered assemblages. Tiered application of results of both the Microtox and oyster larvae tests improved the accuracy with which altered assemblages were identified.

25. Belas, M.R., A. Zachary, D. Allen, B. Austin, and R.R. Colwell. Microbial Colonization of naphthalene/Creosote-Treated Wood Pilings in a Tropical Marine Environment. Journal of the American Wood-Preservers' Association; 1979: 1 - 8.

Microbial colonization of wood pilings treated with naphthalene-enriched creosote and untreated wood in a harbor in Puerto Rico was investigated, using the techniques of numerical taxonomy to identify the bacterial species, and scanning and transmission electron microscopy to follow the attachment and subsequent biofouling process. Wood exposed to seawater in situ was rapidly colonized by *Hyphomicrobium vulgare*. Old wooden piling samples revealed a much more diverse array of microorganisms in the biofouled wood. Floc formation by bacteria under laboratory conditions was found to be associated with rapid microbial attachment to surfaces and production of extracellular fibrils by the bacteria. Retardation of microbial colonization was observed for wood treated with naphthalene-enriched creosote. Retardation of bacterial attachment and subsequent micro-fouling of wood surfaces may influence subsequent settling of macro-organisms.

26. Bender, M.E., W.J. Hargis, R.J. Huggett and M.H. Roberts. Effects of Polynuclear Aromatic Hydrocarbons on Fishes and Shellfish: An Overview of Research in Virginia. Marine Environmental Research; 1988; 24: 237-241.

This paper discusses the following topics related to polynuclear aromatic hydrocarbon pollution in estuaries: (1) the use of oysters (*Crassostrea virginica*), hard clams (*Mercenaria*) and brackish water clams (*Rangia cuneata*) in residue monitoring; (2) the effects of elevated PAH residues on oyster condition; (3) three years of field studies relating PAH sediment contamination to abnormalities in fishes; and (4) laboratory bioassays for effects and bioconcentration modeling. Oysters, hard clams and *Rangia* have been shown, from 3 years of field studies, to be good monitors of pollution inputs as one proceeds along salinity gradients from 25 o/oo to 0.5 o/oo. Effects of increased body burdens of PAHs are shown by a lowering of the oysters' condition index, as measured by lipid levels. Fishes inhabiting the Elizabeth River, VA, which is highly contaminated with PAHs, have abnormalities (cataracts, skin lesions, abnormal fins, etc.). These abnormalities have higher incidence in regions of the river where the sediments are more heavily contaminated. Laboratory studies utilizing contaminated sediments have reproduced some of the abnormalities observed in the field. Bioconcentration of PAHs from sediments has been studied with oysters and hard clams. Oysters generally accumulate three times the body burdens of clams exposed to the same suspensions. A faster depuration rate (k_2) for clams appears to be responsible for the higher equilibrium body burden of oysters.

27. Bernuth, P.K. Creosote Oil - Its Importance for Wood Preservation and Technical Requirements and Environmental Aspects in Western Europe. *Journal of the American Wood-Preservers' Association*; 1987: 297-306.

A historical and practical review of creosote oil as a wood preservative is given, with particular reference to its utilization in the United States. Aspects of the Western European situation, namely source, markets, methods of impregnation, as well as the specifications of the West European Institute for Wood Impregnation, which were dictated by environmental aspects, are briefly described.

West German and Norwegian studies have shown that there is no increased cancer risk for workers employed in wood impregnation plants. Dutch research demonstrated that for treated timber, used in waterways, only the creosote oil adhering to the surface is extracted without significantly lowering the oil content of the timber. Research on decreasing tar acids content of creosote oil, while maintaining performance, has been carried out successfully. Similarly, research is now in progress to lower the high boiling polycyclic aromatic hydrocarbon content. With continued research into technical and process aspects, it is expected that future restrictions in specification can be met.

28. Bernuth, P.K. Creosote Oil - Its Importance for Wood Preservation and Technical Requirements and Environmental Aspects in Western Europe. *Journal of the American Wood-Preservers' Association*; 1987: 297-306.

A historical and practical review of creosote oil as a wood preservative is given, with particular reference to its utilization in the United States. Aspects of the Western European situation, namely source, markets, methods of impregnation, as well as the specifications of the West European Institute for Wood Impregnation, which were dictated by environmental aspects, are briefly described.

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With continued research into technical and process aspects, it is expected that future restrictions in specifications can be met.

29. Black, J.J., R. Robinson, and K. Soloman. 1995. HPLC studies of PAH pollution in a Michigan trout stream. *Chemical Analysis and Biological Fate: Polynuclear Aromatic Hydrocarbons*. Edited by M. Cooke and A.J. Dennis, Fifth International Symposium. Battelle Press, Columbus Ohio, pp. 343-355.

This study addressed the pollution in the Hersey River (Osceola County, MI) due to the sewage discharges at Reed City. The sewage treatment facilities were improved, benefiting the river conditions and increasing fishing opportunities downstream from the treatment plant. However, there were reports of "medicine-like" flavored fish. Investigations indicated a black, oily material characterized by a naphthalene-like odor. It was discovered that the area was the former site of a wood preservation facility where creosote leakings, spillage and drippings had caused extensive site contamination. The problem had only recently been recognized through angler use of the trout fishery afforded by water quality improvements.

Results of analytical studies of the distribution of PAH compounds in sediments and biota from this aquatic system as determined with high pressure chromatography (HPLC) are presented here.

30. Borgmann, U., K.M. Ralph, W.P. Norwood. 1989. Toxicity test procedures for *Hyalella azteca*, and chronic toxicity of cadmium and petachlorophenol to *H. azteca*, *Gammarus fasciatus*, and *Daphnia magna*. *Arch. Environ, Contam. Toxicol.* Vol. 18, No. 5, pp. 756-764.

Survival, growth, and reproduction of *Hyalella azteca* were determined under various test conditions. Reproduction by a cohort begins when the amphipods are 5 to 6 weeks old, peaks at 8 to 12 weeks, and then declines due to continuing adult mortality. Full life-cycle test can be completed in 12 to 14 weeks at 25° C. Reproduction is poor when only artificial plastic substrate is provided. A substrate of cotton gauze results in dramatic improvements in both reproduction and growth. Better reproduction can be obtained by culturing the amphipods in some sediments, but this makes weekly enumeration difficult. Increased mortality during chronic exposure to cadmium was observed at 1 µg/L for *H. azteca* and 3.2 µg/L for *Gammarus fasciatus*. Reproduction during longer exposure was not reduced at concentrations lower than those causing increased mortality within six weeks. Chronic toxicity of pentachlorophenol was observed at 100 µg/L for both species. Chronic toxicity to *Daphnia magna* was similar to that of the amphipods for cadmium, but lower for pentachlorophenol. Amphipods are at least as sensitive as *Daphnia* to a variety of toxicants during chronic exposure.

31. Borthwick, P.W. and J.M. Patrick. Use of Aquatic Toxicology and Quantitative Chemistry to Estimate Environmental Deactivation of Marine-Grade Creosote in Seawater. *Environmental Toxicology and Chemistry*; 1982; 1: 281-288.

The acute toxicity of marine-grade creosote, expressed as the 96-h LC50 is 0.018 mg/L for mysids (*Mysidopsis bahia*), 0.24 mg/l for pink shrimp (*Penaeus duorarum* Burkenroad) and 0.72 mg/l for sheepshead minnows (*Cyprinodon variegatus*, Lacepede). The 96-h EC50 (shell deposition) for Eastern oysters (*Crassostrea virginica*, Gmelin) is 0.71 mg/l. Mysid bioassays and chemical analyses estimate the half-life (< 1 week) for marine-grade creosote in seawater.

32. Bos, R.P. W.J.C. Prinsen, J.G.M. van Rooy, F.J. Jongeneelen, J.L.G. Theuws and P.T. Henderson. Fluoranthene, a volatile mutagenic compound, present in creosote and coal tar. *MUTAT.-RES*; 1987; vol. 187; no. 3: 119-125.

Creosote, a coal-tar distillation product, contains mutagens which are volatile at 37 degrees C. After distillation of creosote it was found that these volatile mutagens were present in the distillation fraction with the highest boiling range (> 360 degrees). The “volatile mutagenic activity” was connected with the presence of fluoranthene, a polycyclic aromatic hydrocarbon. Commercially available fluoranthene was positive in the so-called “taped-plate assay” (the test system used for the detection of volatile mutagens) towards the strains TA98 and TA100 in the presence of S9 mix. The tested creosote and coal tar contained fluoranthene in concentrations of 5.2 and 2.2%, respectively.

33. Bouloubassi, I and A. Saliot. Composition and Sources of Dissolved and Particulate PAH in Surface Waters from the Rhone Delta (NW Mediterranean). *Marine Pollution Bulletin*; 1991; 22(12): 588-594.

PAH were determined in surface waters from the Rhone delta in winter and summer 1987. Both particulate and dissolved phases were analyzed by BC and BC/MS. Concentrations of major unsubstituted compounds associated with particles varied from a few to 20 ng/l, or from 0.42 to 6.0 micrograms/gram. The seasonal variations reflected higher inputs in winter resulting from the presence of highly PAH-enriched particles. Tetra- and penta-cyclic PAH with MW 202 and 252 predominated, which reflected a significant origin from pyrolytic processes. A rapid decrease of the level of higher MW PAH was observed seawards in both seasons. Study of the tricyclic compounds and their alkylated homologues demonstrated a mainly fossil origin in winter, whereas in summer a high heterogeneity of particles was observed. PAH in the dissolved phase were found at concentrations up to 31 and 50 ng/l in summer and winter, respectively. These levels were much higher than those encountered in the corresponding particulate phases. PAH with MW 178 and 202 predominated, and the alkylated homologues of the tricyclic compounds showed a major fossil origin in winter and a mixed origin in summer. In winter, dissolved PAH were transported through the delta into the marine environment without significant losses.

34. Bouloubassi, I and A. Saliot. The role of rivers in the deposit of organic pollutants in coastal zones: the case of polycyclic aromatic hydrocarbons (PAH) in the Rhone delta (Northwestern Mediterranean). unknown; unknown: 549 - 560. Note: In French.

Polycyclic aromatic hydrocarbons (PAH) were studied in surface waters from the Rhone delta in September 1986, January and June 1987. Both dissolved and particulate phases were analysed by GC and GC/MS following fractionation of PAH by HPLC. Major unsubstituted PAH in the particulate phase showed concentrations from 1 to 20 ng/l, or from 0.4 to 6 microgram/g. Seasonal variations indicated high inputs in winter and in late summer. Pyrolytic sources were predominant. PAH concentrations showed important decreasing trends seawards. PAH in the dissolved phase were more abundant than those associated with particles. Their concentrations varied from 4 to 119 ng/l and highest inputs occurred in winter. Within this phase, fossil sources were generally predominant. Our data evidenced a significant quantitative and qualitative decoupling of PAH between the two phases. This underlines the fact that a realistic assessment of PAH sources, fluxes and fate requires a simultaneous analysis of both reservoirs. Estimation of the in situ partition coefficient showed significant deviations from theoretical values.

35. Bowling, J.W., G.J. Leversee, P.F. Landrum and J.P. Giesy. 1983. Acute mortality of anthracene-contaminated fish exposed to sunlight. *Aquatic Toxicol.* 3, pp.79-90.

Acute mortality of bluegill sunfish (*Lepomis macrochirus*) dosed with anthracene at 12.7 µg/l and exposed to natural sunlight conditions was observed during a study of

anthracene fate in outdoor channel microcosms. No mortality was observed under control conditions (natural sunlight and no anthracene). Fish survived when held in the shade downstream of sunlit contaminated water, arguing against mortality due to toxic anthracene photoproducts in the water. Fish held 48 h in anthracene contaminated water (12 µg/l), in a shaded channel, died when placed in clean water and exposed to sunlight. After 144 h depuration in darkness, fish anthracene concentrations had decreased to pre-exposure concentrations and no mortality was observed when fish were subsequently exposed to sunlight. This observed photoinduced toxic response in anthracene contaminated fish may represent a significant environmental hazard of polycyclic aromatic hydrocarbons in aquatic environments.

36. Bramhall, G. and P.A. Cooper. Quality Comparison of Current Marine Piling with 25 and 40 Year Service Piling. *Journal of the American Wood Preservers' Association*; 1972: 194 - 202.

The creosoted piling of a 40-year old wharf in Vancouver harbor was inspected in place by four-hole boring and assay. Creosote concentration in the treated zone after this service was 74 percent of current minimum standards, averaging 15 pcf in the outer 1-1/2 inches. Whether this sub-standard retention was due to original treatment or leaching is not determinable. Penetration averaged 1.47 inches, with 1.7 percent less than 0.5 inch, compared with 1.11 inches average and 8.5 percent of samples less than 0.5 inch in 25-year old piling inspected in 1966, and 1.15 inches average and 7.7 percent less than 0.5 inch (before rejection of sub-standards) in piling produced in 1965. The physical characteristics of the creosote were practically identical with current standards. Piling was in very good condition, with insignificant damage due to *Bankia*, and 5 percent in fair condition due to *Limnoria*, whereas in the 25-year old piling, 5 percent were in fair condition due to *Bankia* attack and 5 percent in fair condition due to *Limnoria* attack. Detailed results confirm that low creosote concentrations permit *Limnoria* attack and emphasize the importance of deep penetrations in the protection of marine piling from *Bankia*. It was concluded that present AWPA or CSA standards, adhered to by conscientious inspection particularly with respect to penetration, will ensure the production of piling which will give over 40 years' service in conditions comparable to Vancouver harbor.

37. Breteler, R.J. (Springborn Laboratories, Inc.). Critique Provided On Behalf Of The American Wood Preservers Institute. Carle Place, LI NY: The Coalition to Preserve the Availability of Treated Wood; 1992. 1 - 5.

This reports is a response to three articles published by P. Weiss and J.S. Weis in 1991 and 1992.

38. Broman, D., C.N. Naf, I. Lundbergh and Y. Zebuhr. An In Situ Study on the Distribution, Biotransformation and Flux of Polycyclic Aromatic Hydrocarbons

(PAHs) in an Aquatic Food Chain (Seston-*Mytilus edulis* - *Somateria mollissima*) from the Baltic: An Ecotoxicological Perspective. Environmental Toxicology and Chemistry; 1990; 9: 429- 442.

This *in situ* study is focusing on the distribution, biotransformation and flux of 19 polycyclic aromatic hydrocarbons (PAH) in the food chain seston-blue mussel (*Mytilus edulis*) - common eider duck (*Somateria mollissima*) as well as the distribution in the gallbladder, liver, adipose tissue and egg of the duck. All samples were collected within the open northern Baltic proper coastal areas. analyses were carried out by gas chromatography/mass spectrometry with electron impact (GC-MSEI) and negative ion chemical ionization (GC-MSNICI). With a multivariate statistical method (SIMCA) a significant change in the PAH composition through the food chain was found. This change probably depends on an increasing metabolic activity with increasing trophic level, due to a selective biotransformation capacity for different PAHs. Decreasing PAH concentrations with increasing trophic level were found. The PAH concentrations in the different eider duck organs were: gallbladder>adipose tissue>liver. The theoretical inhalation of air-dispersed PAHs was of no significance compared to the exposure from food. The relatively high theoretical PAH flux through the food chain did not result in increasing concentrations with increasing trophic level, which indicates that PAHs are biotransformed quite fast. However, many intermediate metabolites of PAHs have a mutagenic and carcinogenic potential, which makes it important to observe these compounds when assessing ecotoxicological risks.

39. Brooks, J.M., M.C. Kennicutt, T.L. Wade, A.D. Hart, G.J. Denoux, and T.J. McDonald. Hydrocarbon Distributions around a Shallow Water Multiwell Platform. Environ. Sci. Technol.; 1990; 24: 1079 - 1085.

Polynuclear aromatic hydrocarbon (PAH) concentrations in nearshore coastal sediments offshore of Matagorda, TX, average 29+-28 (SD) ppb compared to 96+-112 ppb for the sediments in adjacent coastal estuaries and bays. PAHs were analyzed in bottom sediments collected in the vicinity of a multiwell platform in about 25 meters of water, where six wells had been drilled between May 1982 and November 1985. The most elevated PAH concentrations were restricted to within 25 meters of the platform discharge point. Mean pah concentrations for two samplings at 10 and 25 meters from the platform were 494+-251 and 757+-1820 ppb, respectively. The contaminated platform sites (<-25 meters distant) were dominated by two-ring aromatics while the estuarine/bay and noncontaminated coastal sites were dominated by four- and five-ring aromatic hydrocarbons. Pehnanthrene/anthracene ratios suggest a petroleum source for the hydrocarbons at platform stations and pyrolytic sources for the bay/estuarine hydrocarbons.

40. Brooks, K.M., Primary (Aquatic Environmental Sciences). Literature Review and Assessment of the Environmental Risks Associated with the Use of Treated Wood Products in Aquatic Environments. I ed. 601 main Street, Suite 401; Vancouver, WA 98660: Western Wood Preservers Institute; 1993. 63 pages.

This is a comprehensive assessment of the risks associated with the use of CCA, ACZA and creosote treated wood products in aquatic environments. Report includes a quantitative assessment of the associated risks.

41. Brown, R.A. and R.J. Pancirov. Polynuclear Aromatic Hydrocarbons in Baltimore Canyon Fish. Environmental Science and Technology; 1979; 13(7): 878 - 879.

This work provides the beginnings of a base-line study with regard to the present level of polynuclear aromatic hydrocarbons in selected marine tissue of the Baltimore Canyon. In case oil and/or gas production ever occurs in the Baltimore Canyon area, data of this type will be useful in establishing if the fish population has been contaminated by polynuclear aromatic hydrocarbons. This is extremely important because some of these hydrocarbons are potential carcinogens.

42. Bruner, K.A., S.W. Fisher, P.F. Landrum. 1994. The role of the zebra mussel, *Dreissena polymorpha*, in contaminant cycling: 1 The effect of body size and lipid content on the bioconcentrations of PCBs and PAHs. J. Great Lakes Res. Vol. 20, No. 4, 725-734.

The zebra mussel, *Dreissena polymorpha*, a recent invader to the Great Lakes, may influence contaminant cycling by bioconcentrating high levels of hydrophobic contaminants in its tissue. To better understand zebra mussel bioconcentration and ultimately, contaminant cycling, we measure bioconcentration factors (BCFs) and kinetic parameters for accumulation of polychlorinated biphenyl and polycyclic aromatic hydrocarbon congeners for two size classes of mussels and for a pre-spawning (high lipid) and post-spawning (low lipid) mussel population. High lipid, pre-spawning mussels had greater BCFs and faster uptake kinetics for the highly hydrophobic compounds, i.e., hexachlorobiphenyl and benzo(a)pyrene, than the low lipid, post-spawning mussels. BCFs and uptake kinetics determined for the less hydrophobic compounds, i.e., tetrachlorobiphenyl and pyrene, were not measurably influenced by differences in lipid content. Small mussels (15 mm shell length) had higher BCFs and faster uptake kinetics for all compounds compared to larger (21 mm shell length) mussels. Contaminant elimination was not affected by size or differences in lipid levels. For both lipid levels and size classes of mussels, the BCFs were positively correlated with compound log octanol:water partition coefficient. Hence, the lipid affinity of a compound can be a good indicator of mussel contaminant accumulation. Potentially large contaminant concentration in zebra mussels may alter contaminant cycling in the Great Lakes by

increasing contaminant transfer to mussel predators. Selective predation on small, pre-spawning (high lipid) mussels may present a greater hazard to predators than predation on larger, post-spawning (low lipid) mussels.

43. Burgess, R.M. and G.E. Morrison. 1994. A short-exposure, sublethal, sediment toxicity test using the marine bivalve *Mulinia lateralis*: statistical design and comparative sensitivity. *Environmental Toxicology and Chemistry*. Vol. 13, No. 4, pp. 571-580.

Over the last 10 years a great deal of research effort has concentrated on determining the effects of contaminated sediments on aquatic organisms. For marine systems, this effort has emphasized acute sediment toxicity test using amphipods, although a variety of other end points and species have been used. Another candidate species for marine, solid-phase, sublethal sediment toxicity testing is the bivalve *Mulinia lateralis*. Useful attributes of this euryhaline bivalve include a wide geographic distribution (along the North American Atlantic coast from Prince Edward Island to the Gulf of Mexico), easy lab culture, and amenability to toxicity testing applications (end points are mortality and growth [milligrams per organism dry weight]). Detailed in this paper are organism selection and culture, establishment of statistical design, and an estimate of organism mortality and sublethal response variability. Results of *Mulinia lateralis* toxicity test with 65 contaminated sediments from eight sites are reported, as well as results of comparative toxicity test using two amphipod species, *Ampelisca abdita* and *Eohaustorius estuarius*. Analysis of statistical power indicates treatment weight and survival responses that are 25% different from the site control responses can be detected with a probability of 95%. Results of comparative toxicity test illustrate that although *Mulinia lateralis* and amphipod acute end points are relatively similar in sensitivity, utilization of the *Mulinia lateralis* sublethal growth end point greatly increases test sensitivity. This paper describes a new marine sediment toxicity test that complements the existing suite of marine sediment toxicity assessment techniques.

44. Burns, K.A. Analytical Methods Used in Oil Spill Studies. *Marine Pollution Bulletin*; 1993; 26(2): 68-72.

Because of the recent confusion over the concept of 'legally defensible methods' for oil spill studies, often believed to be limited to the analysis of specific polynuclear aromatic hydrocarbons by gas chromatography-mass spectroscopy, I restate the need for a hierarchical scheme of methods to be used in environmental assessment studies. I illustrate the success of using several complementary methods in tandem with examples from the results of the Bahia las Minas (Galeta) Oil Spill Study, and present further evidence for reasons why methods must continue to be developed for an expanded range of polar oxidation products.

45. Butalla, J.H. (Duquesne University). [Letter to Tim Flint, Regional Supervisor, Marine Permits, Washington State Department of Fisheries.]. Duquesne University; 1993. 3 pages.

Discusses human health aspects of creosote treated wood.

46. Canada. Canadian Fisheries Act. R.S.C., 1985. c. F-14 ed.; 1992; RSC, 1985, c.F-14. These portions of the Canadian Fisheries Act discuss Fish Habitat Protection and Pollution Prevention.

47. Canadian Institute of Treated Wood. 1995 Environmental Program Report.

This Report Summarizes the Environmental Program in Canada, addressing such issues as Media Relations, Government Relations, Issues Management, Public Attitudes Research, Crisis Management, as well as Supporter Communications.

48. Canton, L. and J.O. Grimalt. Gas chromatographic-mass spectrometric characterization of polycyclic aromatic hydrocarbon mixtures in polluted coastal sediments. *Journal of Chromatography*; 1992; 607: 279 - 286.

A gas chromatographic-mass spectrometric (GC-MS) study of the polycyclic aromatic hydrocarbon (PAH) composition of a series of 72 marine sediments collected from the Guipuzcoan Coast (Bay of Biscay, Spain) showed three end-member distributions, one related to pyrolytic soot contributions (type A), another to combined paper mill effluents and soot inputs (type B) and the third to petrogenic residues (type C). The detailed composition of each of these end-member mixtures is given. Further examination of the pah extracts by GC-negative ion chemical ionization MS illustrated several previously unreported selectivity effects such as enhancement of the parent PAHs eluting with longer retention times and the increased response factor of the alkyl homologues corresponding to the m/z 252, 276 and 302 hydrocarbons.

49. Capuzzo, J.M. Biological Effects of Petroleum Hydrocarbons on Marine Organisms: Integration of Experimental Results and Predictions of Impacts. *Marine Environmental Research*; 1985; 17: 272-276.

Biological effects of petroleum hydrocarbons on marine organisms are dependent on their persistence and bioavailability, the ability of the organisms to accumulate and metabolize various hydrocarbons, the fate of metabolized products, and the interference of hydrocarbons with normal metabolic processes that may alter an organism's chances of survival and reproduction in the environment. In considering the long-term effects of petroleum hydrocarbons in the environment it is important to ascertain what biological effects may result in subtle ecological changes, changes in community structure and function, and possible impairment of fisheries resources. Although a wide range of stress

indices have been proposed for monitoring pollutant impacts on marine organisms, no single index can provide the predictive capability to evaluate population or community changes. Understanding the relationship and integration of multiple stress indices should improve our capabilities of predicting long-term change at organismal and population levels before irreversible damage occurs at the community and ecosystem levels.

50. Cardwell, R.D., S.F. Olsen, M.I. Carr and E.W. Sanborn. 1980. Biotic, Water Quality and Hydrologic Characteristics of Skyline Marina in 1978. Technical Report No. 54, Washington Department of Fisheries 115 General Administration Building, Olympia, WA 98504.

Fish, zooplankton, and water quality characteristics of Skyline Marina in north Puget Sound were compared to the marina's source water in monthly surveys conducted from March to October 1978. A companion study defined the marina's flushing properties. Fish were indexed mainly by purse seining and the food habits of seven species of salmon (*Oncorhynchus* spp.) and baitfish juveniles in terms of ontogenic-seasonal variation. Symbol surface zooplankton larger than 505 micrometers were indexed with push nets. Water quality was described through measurements of general parameters (E.G., temperature, phytoplankton, nutrients), heavy metal and organic concentrations in sediments, heavy metal residues in adult Pacific oysters (*Crassostrea gigas*), and acute toxicity of ambient waters to Pacific oyster larvae.

51. Casillas, E., D.A. Misitano, P.D. Plesha, D.D. Weber, C.R. Haley, S. Demuth, M.H. Schiewe, S. Chan and U. Varanasi. Sublethal and Lethal Effects in Two Marine Organisms, A Juvenile Echinoderm and a Larval Fish, Exposed to Contaminated Sediments. unknown; unknown: 402 - 407.

Toxicity is one of the major factors considered when, for example, disposal of dredged sediments from urban waterways is desired. To measure toxic effects of sediments, bioassays that use the marine amphipod, *Rhepoxinius abronius*, the oyster larva, *Crassostrea gigas*, and the luminescent bacterium, *Photobacterium phosphoreum* have been commonly employed. In this preliminary report, we describe two new bioassay systems for assessing sediment toxicity and report the relative sensitivity of mortality and impaired growth as indicators of toxicant effects on the test organisms. In these bioassays, juvenile sand dollars (*Dendraster excentricus*) and larval surf smelt (*Hypomesus pretiosus*) were exposed to serially diluted sediments from three urban areas with different types and levels of contamination. Physical and biochemical measures of growth (i.e. length or diameter, DNA content, and protein content) were then evaluated for dose-responsiveness and sensitivity and compared with mortality as biological indicators of toxicant effects.

52. Cerniglia, C.E. and M.A. Heitkamp. Chapter 2, Microbial Degradation of Polycyclic Aromatic Hydrocarbons (PAH) in the Aquatic Environment.

Describes microbial (prokaryotes and eukaryotes) degradation of PAH and the environmental fate of these compounds. Emphasis is on naphthalene, anthracene, phenanthrene and B[a]P.

53. Chapman, P.M. Four Independent approaches to Developing Sediment Quality Criteria Yield Similar Values for Model Contaminants. *Environmental Toxicology and Chemistry*; 1987; 6: 723-725.

Separate approaches to determining marine sediment quality criteria yielded similar values for three contaminants. These values, including concentrations at or below which biological effects have been shown to be minimal and lowest concentrations at which biological effects have been shown to occur, range from (dry weight sediment): lead, 50 to 300 micrograms/gram (ppm); polyaromatic hydrocarbons, 2.0 to 12.0 ppm; polychlorinated biphenyls, 0.06 to 0.13 ppm.

54. Chmura, G.L. and N.W. Ross (Rhode Island Department of Environmental Management - Marine Advisory Service NOAA/Sea Grant). *The Environmental Impacts of Marinas and Their Boats*. Final ed.: University of Rhode Island; University of Rhode Island, Marine Memorandum 45.

55. Cocchieri, R.A., A. Arnese and A.M. Minicucci. Polycyclic Aromatic Hydrocarbons in Marine Organisms from Italian Central Mediterranean Coasts. *Marine Pollution Bulletin*; 1990; 21(1): 15 - 18.

The level of 16 PAHs was investigated in 5 shellfish and in 14 fish along the coast of the Gulf of Naples. The average total amount of PAHs in shellfish was 217 micrograms/kg wet wt, with a range of 185 to 295 micrograms/kg and in fish species 94 to 1930 micrograms/kg wet wt. The total PAH levels found correspond to those polluted areas.

56. Colwell, R.R. (Department of Microbiology, University of Maryland). *Microbial Ecology Studies of Biofouling of Treated and Untreated Wood Pilings in the Marine Environment*. Final Report. Office of Naval Research: U.S. Navy; 1986; Contract No. N00014-75-C-0340 P0003. 22 pp.

The role of marine microorganisms in facilitating attachment, invasions, and subsequent destination, viz., biofouling, of solid substrata, especially wood, in the marine environment was studied. Relationships between microorganisms, primarily bacteria, and invertebrate macroorganisms that bore into wood were also investigated. It was concluded that naphthalene enrichment of creosote retards biofouling of wood pilings during the first year of placement of the treated wood into tropical marine waters. After that, little or no slowing of biofouling can be detected. The wood boring invertebrate,

Limnoria, appears to develop a gut microflora that is both naphthalene resistant and capable of naphthalene degradation. It was hypothesized that this gut microflora enabled the wood-boring Limnoria to survive on creosote/naphthalene-treated wood. Ames assay revealed no detectable mutagenicity in seawater samples collected near creosote/naphthalene-treated pilings.

57. Colwell, R.R. and R.A. Seesman. Progress Report on Roosevelt Roads Piling Project, Preliminary Work. Report to Koppers Company: Koppers; 1976. 7 pp. AWPI.

Water samples were collected at Roosevelt Roads, Puerto Rico, February 10, 1976 at Pier #3. Ten water samples were taken sequentially at ten different pilings. Samples of the wood were also collected. Approximately 10 ml of the surface water at the tidal zone at the pilings were collected and examined for total viable, aerobic heterotrophic microorganisms and those microorganisms capable of growth on naphthalene, creosote and creosote containing 40% naphthalene. This report examines the bacteriology and limnoria invasion of the piling.

58. Conradie, W.E. and A. Pizzi. The Permanence and Biological Effectiveness of Creosotes and Creosote/Waxy Oil Mixtures. unknown; unknown: 33 - 41. The permanence properties (leaching, water absorption, evaporation) and the biological effectiveness (protection against termite and fungal attack) of medium temperature creosote and high temperature creosote, and of creosote/waxy oil mixture were investigated. The high temperature creosote outperformed the medium temperature creosote in respect of leachability, but the latter was superior regarding performance against termite and fungal attack. The creosote/waxy oil mixture (70 percent medium temperature creosote, plus 30 percent waxy oil) proved to be more effective against termite attack, but especially against fungal attack, and showed reduced leaching, when compared with the pure creosotes.59. Cooper, P.A., D.N. Roy and S. Konar (1994) Investigation of the Residual

Creosote Content and Leaching of Creosote Components from Creosote Treated Ties Removed From Service. Final Report to Environment Canada. 50 pp.
Authors' address: University of Toronto, 33 Willcocks Street, Toronto, ONT.

M5S 1B1. "Also, the extracted creosote had a higher proportions distilling at the higher temperature ranges than the new creosote. While the creosote characteristics of the creosote initially used for the tie treatment no doubt varied among the ties and, in fact are unknown, the results confirm that more volatile and water soluble components have been preferentially lost in service. Thus emission during a second life cycle as landscaping timbers should be substantially lower than their initial use. The full tie leaching procedure resulted in significantly different proportions of creosote components in the leachate compared to the LEP method. Naphthalene and other low boiling components were at lower relative concentrations in this leachate than in either the extracted creosote or the leachate from the LEP test. Presumably the more volatile and soluble compounds were more extensively lost from the surface and were less available

for the full tie leaching test than for the LEP and extraction samples which represented the entire cross-section. These results confirm the observations of Ingram *et al.* (1982) that significant biological breakdown of PAH components of leach water after several days.

60. Couch, J.A. and J.C. Harshbarger, 1985. Effects of carcinogenic agents on aquatic animals: An environmental and experimental overview. *Environ. Carcinogen. Revs.* 3, pp. 63-105.

This article studies the effects of carcinogenic agents on aquatic animals. It addresses such issues as neoplasms in aquatic animal populations, indicator species, and monitoring with aquatic species. It also addresses the experimental effects and laboratory studies of carcinogenesis using aquatic animals in addition to the use and potential of aquatic animals in carcinogen studies.

61. Crecelius, E.A., T.J. Fortman, S.L. Kiesser, C.W. Apts and O.A. Cotter (Battelle,

MarineSciences Laboratory, Sequim, Washington). Survey of Contaminants in Two Puget Sound Marinas. U.S. EPA, 122 6th Avenue, Seattle, WA 98101: U.S. EPA; 1989; Contract No. 68-03-3319; Work Assignment No. 2-113.

30 pp, plus appendices. The sediment and water samples from within the marinas were contaminated with Cu, Pb, Zn, PAH, TBT, and FC compared to samples taken outside the marina. Outside the marinas, sediment contamination was limited to stations within about 150 m of the marina entrances. The contaminant with the greatest elevation in marina sediments compared to reference sediments was TBT. Few of the sediments exceeded Puget Sound Apparent Effect Threshold (AET) sediment quality values, but most of them exceeded Puget Sound Dredged Disposal Analysis (PSDDA 1988) screening levels for in-water disposal of dredged sediment indicating more testing would be required in order to evaluate for in-water disposal. There are no AET or other sediment values for TBT. 62. Crecelius, E.A., D.L. Woodruff and M.S. Myers (Battelle, Pacific Northwest Laboratories). Survey of Sediment Quality, Contaminants in Fish Tissue, and

Incidence of Fish Disease in Four Non-Urban Bays of Puget Sound. Four non-urban bays of Puget Sound (Dyes Inlet, Gig Harbor, Port Angeles, and Oak Harbor) were surveyed to characterize contamination problems. These bays have not previously been extensively examined for contamination problems but have the potential for contamination from industry, marinas, sewage outfalls, and military bases. Sediment samples collected were analyzed for contaminants and bioassays conducted with amphipods. Flatfish collected were analyzed for contaminants, and livers of sole were examined for diseases or disorders. Some sediments contained elevated levels of As, Cd, Cu, Pb, Hg, Ag, Zn, PAH, PCB, and tributyltin. Only a few sediment samples exceeded the Puget Sound Apparent Effect Threshold (AET) sediment quality values for Hg, Ag, and PAH. None of the sediments tested by the amphipod bioassay indicated a toxic response. Some fish muscle and liver tissue contained elevated levels of PCBs with the

highest concentration found in English sole muscle tissue from Gig harbor. concentrations of PAH metabolites in bile indicated low to moderate exposure to petroleum and combustion hydrocarbons. The prevalence of idiopathic liver disease (no apparent association with an infectious agent) was similar to other reference areas in Puget Sound.

62a. Davensport, R. and A. Spacie. 1991. The acute phototoxicity of harbor and tributary sediments from lower Lake Michigan. *J. Great Lakes Research*, 17(1), pp. 51-56.

The phototoxicity of PAHs, together with their accumulation in sediments, suggest that dredging and other disturbances may pose a presently unrecognized environmental hazards. To test this, sediments contaminated with PAHs were collected from sites in the Grand Calumet River, the Indiana Harbor Canal, and Waukegan Harbor. The phototoxicity of the liquid-phase elutriates was tested using *Daphnia magna*. Phototoxicity was found in Grand Calumet River and Indiana Harbor elutriates, both in sunlight and 354 nm near-uv. None of the elutriates was toxic in the absence of light. These results reveal an important and previously unsuspected hazard to shallow water environments near dredging sites, and describe simple methods to detect phototoxicity which will be of value in the establishment of sediment quality criteria.

63. Dickhut, R.M. and K. E. Gustafson. 1995. Atmospheric Washout of Polycyclic Aromatic Hydrocarbons in the Southern Chesapeake Bay Region. *Environmental Science and Technology*. Vol. 29, No. 6, pp1518-1525.

Vapor washout of selected polycyclic aromatic hydrocarbons (PAHs), determined from discrete atmospheric and integrated precipitation samples collected every two weeks throughout 1991, was observed to be controlled by the Henry's law constant for the compound at the temperature of deposition (5-29 °C). Particle washout was found to be relatively constant for the various PAHs but to vary seasonally, with higher particle scavenging occurring in the spring and summer compared to fall/winter. Vapor washout coefficients were negatively correlated with rainfall intensity, with stronger dependencies on precipitation rate for high molecular weight PAHs relative to low molecular weight, volatile compounds. This observation indicates that gases of the less volatile PAHs may not achieve equilibrium between air and raindrops during extremely intense precipitation events. Particle washout coefficients for PAHs were positively correlated with rainfall intensity, indicating an increased efficiency for particle scavenging from the atmosphere with precipitation rate.

64. Di Toro, D., C.S. Zarba, D.J. Hansen, W.J. Berry, R.C. Swartz, C.E. Cowan, S.P. Bavlou, H.E. Allen, N.A. Thomas, and P.R. Paquin. 1991. Technical basis for establishing sediment quality criteria for nonionic organic chemicals using equilibrium partitioning. *Environ. Tox. Chem.* Vol. 10, pp. 1541-1583.

The purpose of this review paper is to present the technical basis for establishing sediment quality criteria using equilibrium partitioning (EqP). Equilibrium partitioning is chosen because it addresses the two principal technical issues that must be resolved: the varying bioavailability of chemicals in sediments and the choice of the appropriate biological effects concentration.

65. Dobroski, C.J. and C.E. Epifanio. Accumulation of Benzo(a)pyrene in a Larval

Bivalves via Trophic Transfer. *Can. J. Fish. Aquat. Sci.*; 1980; 37: 2318 - 2322.

The diatom *Thalassiosira pseudonana* was cultured in 10 microgram/l 14C-benzo(a)pyrene (B(a)P) and subsequently fed to larvae of the hard clam *Mercenaria mercenaria*. The rate of direct uptake of B(a)P from seawater by the diatoms was much greater than the rate of trophic transfer of B(a)P from the diatoms to the clam larvae. This was attributed to greater efficiency of direct uptake and to the larger quantity of B(a)P available in the water. A comparison of direct uptake by bivalves as reported in the literature) with trophic transfer measured in the present investigation indicated that the processes may be equally important in accumulation of B(a)P in natural populations of bivalves.66. Donkin, P., J. Widdows, S.V. Evans and M.D. Brinsley. QSARs for the sublethal

responses of marine mussels (*Mytilus edulis*). *The Science of the Total Environment*; 1991; 109/110: 461-476. The marine environment is contaminated with many organic compounds, some of which induce deleterious responses in biota. Biological impact can be assessed by measuring the physiological responses of mussels, though the task of establishing which of the bioaccumulated compounds cause the observed effects is complex. To facilitate this task, quantitative structure-activity relationships (QSARs) for the physiological responses are being established. In this paper, the responsiveness of ciliary feeding to alkanes and benzene-substituted alkanes is described and compared with a QSAR established previously for aromatic compounds. Most of the test compounds with aqueous solubility's > 70 micrograms/cm³ were toxic to feeding activity when bioaccumulated to similar concentrations, whereas compounds of lower solubility were less toxic. The only exceptions were the polyaromatic hydrocarbons pyrene and fluoranthene, which were less toxic than predicted from their solubility. These data are consistent with the hypothesis that the toxicity cut-off is due to solubility-related phenomena, the effect perhaps being enhanced by aromatic hydrocarbons dosed near to their solubility limits, by sequestration of crystals within the mussel tissues. These observations indicate that many organic contaminants detected by chemical analysis of mussels have no direct effect on filter feeding, whereas the less frequently determined volatile compounds are toxic. 67. Dunn, B.P. and H.F. Stich. Monitoring Procedures for Chemical Carcinogens in

Coastal Waters. *J. Fish. Res. Board Can.*; 1976; 33: 2040-2046. Sampling procedures and analytical techniques have been developed for evaluating the contamination of coastal waters by polycyclic aromatic hydrocarbon carcinogens. The procedures involve extraction and purification of hydrocarbon fractions from marine sediments or organisms, and determination of compounds by thin-layer chromatography

and fluorimetry, or gas chromatography. Sediment samples in the vicinity of a sewage outfall showed elevated levels of benzo(a)pyrene. Mussels (*Mytilus edulis*) taken from the outer Vancouver harbor showed lower BAP levels in the summer than in the winter, perhaps a result of seasonal discharges of sewage and storm drain water into the harbor. Elevated levels of BAP in mussels growing near creosoted timbers or pilings suggested that creosote may be a significant source of BAP in the marine environment. Direct evidence for this suggestion was obtained by comparison of gas chromatographic profiles of polycyclic aromatic hydrocarbons isolated from mussels and from creosoted wood.

The procedures developed are rapid, sensitive, and reproducible. They appear to be suitable for application in large-scale monitoring systems for carcinogenic hydrocarbons in coastal waters.⁶⁸ Dunn, B.P. and J. Fee. Polycyclic Aromatic Hydrocarbon Carcinogens in Commercial Seafoods. J. Fish. Res. Board Canada; 1979; 36: 1469-1476. Fresh and processed commercial seafoods were analyzed for the polycyclic aromatic hydrocarbon carcinogen benzo(a)pyrene using a thin-layer chromatographic separation technique and quantitation by fluorescence. Commercial samples of vertebrate fish did not contain detectable levels, except where fish were packed with vegetable oil, an exogenous source of carcinogens. Levels in most shellfish samples were generally less than 10 ng/g wet weight, but occasional samples contained up to 36 ng/g. Crab and shrimp samples contained little or no benzo(a)pyrene (ND to 0.5 ng/g). Commercial lobsters contained 0.8 to 7.9 ng/g. The source of contamination of lobsters was further investigated, utilizing high pressure liquid chromatography to measure 13 polycyclic aromatic hydrocarbon isomers. Freshly caught lobsters had less than 1 ng/g benzo(a)pyrene. Lobsters which had been kept in a commercial tidal pond constructed of creosoted timber contained highly elevated levels of benzo(a)pyrene and other carcinogenic hydrocarbons, including chrysene, benzo(a)anthracene, benzo(b)fluoranthene, dibenz(a,h)anthracene, and indeno(1,2,3-cd)pyrene. The maximum level of benzo(a) pyrene was 2300 ng/g wet weight in digestive gland, and 291 ng/g in edible tail meat. These levels are substantially higher than previously reported for any foodstuff, and are most probably attributable to creosote contamination during impoundment.⁶⁹ Dunn, B.P. and H.F. Stich. The Use of Mussels in Estimating Benzo[a]Pyrene Contamination of the Marine Environment. Proceedings of the Society for Experimental Biology and Medicine; 1975; 150: 49-51. The results point to a correlation between the level of B[a]P in mussels and industrial, urban, and recreational (e.g., powerboat) activity. Apart from a general contamination of mussels toward and within the harbor area, there are numerous local "hot spots" such as wharves, docks, and constructions utilizing pilings. Whether creosote from pilings or petroleum pollution is the main contributor to the higher B[a]P levels around marinas and wharves is difficult to assess at present. However, creosote does appear a major source of contamination of mussels located on pilings. Our results do not support the suggestion that large amounts of PAH in the marine environment originate by endogenous synthesis by marine flora. The lowest levels of B[a]P were recorded along the Pacific coastline of Vancouver island - an area rich in algal growth, while the highest levels were found in

mussels from a relatively barren inner harbor area. The results indicate that the level of B[a]P in mussels, which are easy to collect and abound in the areas of greatest interest, may represent a simple indicator for the degree of contamination of the marine environment by polycyclic aromatic hydrocarbons.⁷⁰ Eaton, P. and V. Zitko. Polycyclic Aromatic Hydrocarbons in Marine Sediments and Shellfish Near Creosoted Wharf Structures in Eastern Canada. International

Council for the Exploration of the Sea; 1978; E:25: 1 - 6. Samples of sediment, mussels, clams, and periwinkles were collected in the vicinity of creosote treated wharf and bridge structures at various locations along the Atlantic coast of Eastern Canada. These were analysed, by a spectrofluorometric technique, to detect and roughly quantify the levels of polynuclear aromatic hydrocarbons (PAH). Selected samples were analysed by GC/MS to quantify specific hydrocarbons. Significant levels of PAH were detected in sediment and shellfish. Levels in shellfish were generally higher close to the creosoted structure and decreased with increasing distance from the wharf or bridge, however, sediments did not conform as closely to this pattern. The relationship between distance from creosoted structures and levels of PAH is examined and the influence of the age of the structure is determined. The levels found suggest that creosoted structures should not be used in the construction of aquaculture facilities.⁷¹ Eganhouse, R.P. and R.W. Gossett. Chapter 10, Historical Deposition and Biogeochemical Fate of Polycyclic Aromatic Hydrocarbons in Sediments Near a Major Submarine Wastewater Outfall in Southern California. unknown:

unknown; unknown. Chapter contains information describing the contribution of PAH from STP outfalls and the fate of those PAHs.⁷² Ehrhardt, M.G. and K.A. Burns. Petroleum-derived dissolved organic compounds concentrated from inshore waters in Bermuda. J. Exp. Mar. Biol. Ecol.; 1990; 138: 35 - 47. In conjunction with the IOC/GEEP Workshop of September 1988, lipophilic dissolved organic material was concentrated from Bermuda inshore waters by liquid-solid adsorption on Amberlite XAD-2. Water samplers were moored at depths of 1 to 2 meters on the reef platform and in inland seawater basins (Hamilton Harbor, Castle harbor). Sample volumes were 221 - 435 l. The adsorbed material was eluted from the resin with refluxing aqueous acetone in a specially designed apparatus. Fractions containing aliphatic and aromatic hydrocarbons were obtained by liquid chromatography on silica gel. Single compounds were identified and quantified by capillary GC/MS. Alkylated PAH with minor contributions of unsubstituted parent compounds were detected in the basins, strongly suggesting a fossil fuel origin. Concentrations diminishing steeply over a short distance between contaminated harbor water and a control station suggest a source of limited spatial extension for unsubstituted PAH. An even steeper concentration gradient of alkyl substituted PAH may indicate their more rapid environmental alteration. Thus, predominance of unsubstituted over substituted PAH in environmental samples could have two causes: a significant contribution of pyrolysis products or easier conversion/degradability of substituted PAH. Photochemically generated hydroxyl and carbonyl derivatives of alkylbenzenes were also measured. Concentrations of hydroxyl derivatives exceeded those of carbonyl derivatives in harbor water with a high load of

dissolved organic material, as indicated by total lipid weight and UV fluorescence measurements. In waters with lower organic carbon load, concentrations of carbonyl derivatives were essentially similar but concentrations of hydroxyl derivatives dropped below the detection limit. We propose that the total concentration of dissolved organic material in the water influences the degree of oxidation and thus the composition of products formed. Combined concentrations of specific photo-oxidation products such as alkylacetophenones, alkylbenzaldehydes, quinones, alkylbenzyl alcohols, alkylphenylethanols were up to more than seven times higher than those of the parent hydrocarbons, indicating rapid conversion rates in this subtropical environment. These results support the need for further assessment of the relative toxicities of the reaction products in addition to those of the parent hydrocarbon contaminants in marine ecosystems.

73. Ehrlich, G.G., E.M. Godsy, D.F. Goerlitz, and M.F. Hult. Microbial Ecology of a Creosote-Contaminated Aquifer at St. Louis Park, Minnesota. Symposium: Microbiology of Subsurface Environment; Unknown: Ch. 18: 235-245.

Bacterial populations were sampled in creosote-contaminated and undisturbed zones of anaerobic, surficial Middle Drift aquifer at St. Louis Park, Minnesota. The densities of several types of bacteria including total aerobes, total anaerobes, nitrate-respirers, and iron-reducers were about the same in the contaminated and undisturbed zones. Chemical analyses suggested that nitrate-respiration and iron-reduction were occurring in the contaminated zone. Conversion of phenolic compounds to methane occurred in the contaminated zone. Methanogenic bacteria were found only in the contaminated zone. In laboratory culture, methane was evolved when contaminated ground water was inoculated with bacteria from the contaminated zone. In laboratory culture, methane was evolved when contaminated ground water was inoculated with bacteria from the contaminated zone. Obligate anaerobic bacteria isolated from laboratory reactors include; a methanosarcina: a short methanobacterium; and a longer, crooked methanobacterium. *Pseudomonas stutzeri*, a nitrate-respiring bacterium, was isolated from both the laboratory reactors and the contaminated zone of the aquifer. These *Ps. Stutzeri* strains used phenol as an electron source for nitrate reduction. The methanogenic consortium found in the laboratory reactor appears similar to those described in other studies of the methanogenic fermentation of aromatic compounds.

74. Eisler, R. (U.S. Fish and Wildlife Service). Polycyclic Aromatic Hydrocarbon Hazards to Fish, Wildlife, and Invertebrates: A Synoptic Review. Final ed. Patuxent Wildlife Research Center, Laurel, MD 20708: U.S. Department of the Interior; 1987; Contaminant Hazard Reviews, Report No. 11. 81. This report synthesizes technical literature on ecological and toxicological aspects of polycyclic aromatic hydrocarbons (PAH) in the environment, with special reference to fisheries and wildlife resources. Subtopics include: chemical properties, sources, and fate; background concentrations in biological and nonbiological samples; toxic and sublethal effects of PAH

to flora and fauna; and proposed criteria and research needs for the protection of sensitive, nonhuman organisms.

75. Elder, J.F., and P.V. Dresler. 1988. Accumulation and bioconcentration of polycyclic aromatic hydrocarbons in a nearshore estuarine environment near a Pensacola (Florida) Creosote contamination site. *Environmental Pollution* 49, pp. 117-132.

Long-term accumulation of creosote wastes at a wood-preserving facility near Pensacola, Florida, has produced high levels of organic contamination of groundwaters near Pensacola Bay. Impacts of this contamination on the nearshore environment of the bay were examined by analysis of water, sediment and tissues of two mollusc species. One of the species (*Thais haemastoma*) was native to the study area. Individuals of the other test species (*Crassostrea virginica*) were placed in cages at the test sites for a 6-week period. Contamination at the nearshore estuarine sites was assessed by comparison to a control site in an uncontaminated area of the bay, as well as a small stream which forms a direct surface-water link between the creosote storage ponds and the bay. The study focused on polycyclic aromatic hydrocarbons (PAH), the primary component of creosote.

Very little PAH in water or in the surface layer of estuarine sediments was detected, despite heavy pollution of the stream sediments. This is attributed to various degradation processes which attack the PAH compounds once they discharge into the estuary, and to the likelihood of intermittent and localized release of contaminants to the estuary. Examination of sediment cores and mollusc tissues, which provide a record integrated over time and space, revealed some accumulation of a few PAH, notably fluoranthene, pyrene, benzo(a) anthracene, chrysene and phenanthrene. In the sediments, the highest concentrations of these compounds appeared below the surface, within a depth range of 8-13 cm.

Bioaccumulation of fluoranthene, pyrene and phenanthrene in both mollusc species was up to ten times greater at test sites than at the control site. This contrast with naphthalene, the bioaccumulation of which was no greater at test sites than at the control site. These differences in bioaccumulation factors relate to structural chemistry of the compounds which control their solubility, bioavailability, susceptibility to degradation and capacity for depuration by the organism.

76. Elskus, A.A. and J.J. Stegeman. Induced Cytochrome P-450 in *Fundulus heteroclitus* Associated with Environmental Contamination by Polychlorinated Biphenyls and Polynuclear Aromatic Hydrocarbons. *Marine Environmental Research*; 1989; 27: 31-50.

Fundulus heteroclitus were collected from two sites in Rhode Island during the non-spawning season and analyzed for hepatic monooxygenase activities and for whole-body concentrations of polychlorinated biphenyls (PCB) and polynuclear aromatic hydrocarbons (PAH). Microsomal protein, total spectral cytochrome P-450 and

cytochrome b5 content did not differ between Seekonk River and Succotash Salt marsh fish. Ethoxyresorufin O-deethylase (EROD) activity was significantly higher (3-fold) in *Fundulus* from the Seekonk River than in fish from Succotash Salt Marsh. Similarly, levels of the immunodetectable homolog of P-450E in *Fundulus*, a representative of the major PAH-inducible P-450 form (P450IA1) in teleosts, were higher in fish from the Seekonk River. In contrast, rates of aldrin epoxidase (AE) activity were the same in fish from the two sites. Concentrations of PCB were 1000-fold, and PAH 60-fold, greater in Seekonk River sediment than in Succotash Salt Marsh sediment. The bioavailability of these contaminants is not known.

77. Environment Canada. Konasewich, D., N. Hutt and G.E. Bruderemann. Background Technical Report; Creosote Impregnated Waste materials. Environment Canada, Western and Northern Region, Edmonton, Alberta: Environment Canada; 1992; None given. 111 pages, plus appendices. A comprehensive document describing creosote, creosote waste and the extent of creosote contaminated sites.
78. Environment Canada. Review - Canadian Wood Preservation Industry Survey - Conducted by EC Regions - 1991/1993. Final ed. Environment Canada, Industrial Sectors Branch, Place Vincent Massey, 351 Boul. St. Joseph, Hull, QC K1A 0H3: Environment Canada; 1994; none given. 22 pages, plus appendices. Taking the individual results at face value, the following conclusions could be drawn: The industry conformance to the TRD recommendations declined somewhat from 69% to 64% since the last survey. Items of apparent improvement are chemical delivery areas, drip areas for freshly treated wood, waste storage and disposal practices as well as routine environmental monitoring. Items of apparent decline are chemical mixing systems, personnel protection and spill/fire responses. The most important deficiencies appeared to be the inadequate containment in chemical storage and process areas. Other wide-spread shortcomings were the lack of environmental monitoring, emergency response planning and the lack of consistent use of personnel protection equipment.
79. Environmental Management Associates, Calgary, AB. Canada Creosote Project: Ecological Impact Evaluation and Risk Assessment. DRAFT ed. Calgary, Alberta: Environmental Management Associates; 1993; 922-7068. Executive summary only. The Canada Creosote Site is located on the south bank of the Bow River, on the western edge of downtown Calgary. The site was used for wood treating operations for nearly 40 years, which resulted in the accumulation of large amounts of creosote (primarily polycyclic aromatic hydrocarbons [PAH]) and other wood preservatives in the soil and ground water underlying the site. Creosote contamination has also been observed in the Bow River, where it may pose a hazard to aquatic organisms. The purpose of this study was to evaluate existing ecological impacts of contamination originating from the Canada Creosote Site on the Bow River ecosystem; establish cause-effect relationships between contaminant levels in environmental media and biological tissues and effects documented in the field; develop models for predicting contaminant levels in river sediments and biological tissues; and finally, to estimate the risk of alternative remediation strategies to the Bow River ecosystem.

This investigation documented creosote contamination in Bow River sediments and porewater adjacent to and downstream of the Canada Creosote Site. Field surveys of fish, benthic invertebrate and aquatic macrophyte distribution, laboratory toxicity tests, health/condition examinations and tissue residue analyses documented a low level exposure to creosote-derived contaminants in the contaminated zone and limited effects on a small number of species. Although these impacts were measurable, the majority of results generated by this study suggest that during the fall of 1992, the ecosystem of the Bow River was not substantially impaired by creosote contamination originating at the Canada Creosote Site.

The existing river berm has largely contained the direct DNAPL loading to the river, and there has been a corresponding reduction in river water concentrations. Similar reductions have likely occurred in river sediments and fish tissues, with the possible exception of benzo(a)pyrene type compounds.

The risk of direct mortality of juvenile and adult fish is non-existent with or without site remediation. The existing berm has likely reduced the incidence of fish tainting and containment should essentially eliminate any tainting potential. Without direct action to deal with contaminated surficial riverbed sediments, the impact on south shore benthic invertebrates will likely persist for a prolonged period of time even after loading to the river from the site are effectively eliminated.⁸⁰ EPA, Region IV. Coastal Marinas Assessment - Guidance Handbook. DRAFT. ed.

Atlanta, Georgia: EPA; 1984.

81. Ernst, B. 1994. Creosote from Wharves Study. Memorandum dated May 11, 1994 from Bill Ernst to Miles Constable transmitting raw genotoxicity and bioassay data on sediments from the vicinity of creosoted wharves.

81a. Eves Consultants. 1994. Creosote Evaluation Project. FOR: Fraser River Estuary Management Program, #301-960 Quayside Drive, New Westminster, BC V3M 6G2. BY: EVS Consultants, 195 Pemberton Avenue, North Vancouver, BC V7P 2R4 (EVS Project No: 3/620-01).

This project's objectives was to conduct a literature review of available information on the effects of creosote and conduct a field sampling program to determine PAH concentrations and the toxicity of sediment from sites potentially impacted by the use of creosote pilings. It also was to collect and preserve benthos samples for possible future analysis of benthic community effects. Recommendations were going to be based on sediment PAH concentrations and the sediment toxicity results. Appropriate biological studies to determine bioaccumulation of PAH in tissues and other biochemical and physiological indicators of contaminant exposure in fish were going to be recommended. This document reports on these objectives.

82. Fabacher, D.L., C.J. Schmitt, J.M. Besser and M.J. Mac. 1988. Chemical characterization and mutagenic properties of polycyclic aromatic compounds in sediment from tributaries of the great lakes. *Environ. Toxicol. Chem.* 7, pp. 529-

Sediments from four inshore Industrial sites and a reference site in the Great Lakes were extracted with solvents and characterized chemically for polycyclic aromatic compounds (PACs). An aqueous phase and a crude organic extract were obtained. The crude organic extract was further resolved into fraction A-2 (polycyclic aromatic hydrocarbons) and A-3 (nitrogen-containing polycyclic aromatic compound), which were analyzed for PACs by gas chromatography and gas chromatography-mass spectrometry. The extracts and fractions were tested for mutagenicity in three assays: Ames, rat hepatocyte uncheduled DNA synthesis, and Chinese hamster ovary hypoxanthineguanine phosphoribosyl transferase (CHO/HGPRT). Sediments from the industrial sites contained 27 to 363 µg/g. Qualitative differences in the residue profiles among the sites were attributable to the probable sources of the PACs (petroleum versus combustion). Only one industrial site yielded measurable (0.1 µg/g or more) concentrations of individual nitrogen-containing PACs. In the Ames assay, only the highest doses of the A-2 fractions from two sites approached positive results. Conversely, the crude organic extract and A-2 and A-3 fractions from all sites induced unscheduled DNA synthesis. Crude organic extracts and the A-2 and A-3 fractions from all industrial sites gave well-defined dose-response relations in the CHO/HGPRT assay. We established the presence of chemical mutagens in sediment that could be correlated with neoplasm in fish from many of the sites; however, the mutagenicity of the sediment extracts was not completely related to the degree of contamination by PACs. We also discuss the utility of mutagenicity assays in the evaluation of complex chemical mixtures and recommend the use of a CHO/HGPRT-type assay in which cells are not required to proliferate in the presence of potential interfering chemicals.

83. Flynn, M.B. (Canadian Department of Fisheries and Oceans). An Overview of the Effects of Petroleum and Selected Hydrocarbon Products on the Aquatic Environment. Final ed. Water Quality Unit, Habitat Management Division, Fisheries Branch, Department of Fisheries and Oceans.: Canadian Department of Fisheries and Oceans; 1988; none. 7 pp.

Report provides a brief summary of anticipated effects of spilled petroleum on aquatic vertebrates and invertebrates.

84. Folmar, L.C., J. Harshbarger, P.C. Baumann, G. Gardner, and S. Bonomelli. 1995. Pathological and Serum Chemistry Profiles of Brown Bullheads (*Ameiurus nebulosus*) from the Black River and Old Woman Creek, Ohio. Bull. Environ. Contam. Toxicol. 54, pp.50-59.

During the past two decades there have been numerous reports concerning epizootics of neoplasia in feral fish (Baumann et al. 1990; Baumann 1992; Harshbarger and Clark 1990). One of those reviews (Harshbarger and Clark 1990) identified 41 locations with such epizootics in North America alone. While some neoplasm in fish are

of viral origin, many investigations have linked both benign and malignant neoplasms to carcinogenic contaminants in the environment (Baumann et al. 1990); Harshbarger et al. 1993). Serum chemistry measurements have been made on fish exposed to a variety of xenobiotic chemicals in the laboratory and on fish collected from highly contaminated areas in the environment (Folmar 1993). There is, however, little information on relationships between serum chemistry and neoplastic lesions in feral fish (Casillas et al. 1985; Folmar et al. 1993b). The purpose of this investigation was to determine whether serum chemistry measurements could be used as predictive indices of neoplasia in tumor-bearing brown bullheads (*Ameiurus nebulosus*) collected from the Black River, Ohio.

85. Forest Products utilization Laboratory, Mississippi State University. Migration of Creosote Components From Treated Poles Into the Soil. Mississippi State University: US Forest Products Laboratory; 1981; Cooperative Agreement Number 12-186. 31 pages. The analysis of 56 soil samples taken radially around 14 creosote-treated poles indicates that the migration of creosote into surrounding soil is limited mainly to the first few inches of soil. Naphthalene, 2-methylnaphthalene, 1-methylnaphthalene and biphenyl were not consistently found at measurable concentrations (25-50 ng/g) even in samples taken close to the treated pole. Acenaphthylene, acenaphthene, dibenzofuran, fluorene, phenanthrene and anthracene were found in lower concentrations relative to those occurring in whole creosote. Vaporization, water solubility and biological degradation may be an important factor in the fate and movement of the above named compounds. Fluoranthene and pyrene, along with carbazole, 1,2-benzanthracene and chrysene were the more persistent compounds occurring in soil samples from around creosote-treated poles. The concentration of these compounds in soil decreased sharply as the distance from the pole increased.86. Foster, G.D. and D.A. Wright. Unsubstituted Polynuclear Aromatic Hydrocarbons in Sediments, Clams, and Clam Worms from Chesapeake Bay. Marine Pollution Bulletin; 1988; 19(9): 459-465. Concentrations of unsubstituted polynuclear aromatic hydrocarbons were measured in sediments, *macoma balthica* and *Nereis succinea* at seven Chesapeake Bay habitats to determine animal-sediment bioaccumulation factors. Bioaccumulation factors for both species ranged between 0.2 and 4 for sediments with more than 0.5% organic carbon. Levels of unsubstituted polynuclear aromatic hydrocarbons in animal lipids were directly related to corresponding concentrations in sediment. coarse grained sediments low in organic carbon content (<0.5%) provided animal-sediment bioaccumulation factors that were much larger than fine grained sediments, and greater than estimations obtained from a thermodynamic model. Bioaccumulation was not related to the hydrocarbon concentrations present in sandy bed sediments.

87. Gala, W.R. and J.P. Giesy. 1992. Photo-induced toxicity of anthracene to the green alga, *Selenastrum capricornutum*. Arch. Environ. Contam. Toxicol. 23, pp. 316-323.

The photo-induced toxicity of the polycyclic aromatic hydrocarbon (PAH), anthracene, to the green alga, *Selenastrum capricornutum*, was characterized. The dose-

response relationships among anthracene concentration, ultraviolet (UV) radiation intensity, and alga growth rate and ^{14}C -bicarbonate incorporation were determined. The 22 h EC_{50} for specific growth rate was inversely related to UV-A radiation intensity and ranged from 37.4 to 3.9 $\mu\text{g/L}$ anthracene. For ^{14}C -bicarbonate incorporation on a volume basis (primary production), the 24 h EC_{50} ranged from 24.0 to 3.3 $\mu\text{g/L}$ anthracene depending on the UV-A intensity. The incorporation of ^{14}C -bicarbonate incorporation on a per cell basis (cellular photosynthesis) was more resistant than cell growth or primary production. The threshold for photo-induced toxicity of anthracene was 1.5-3 $\mu\text{g/L}$ anthracene, however, no UV-A radiation threshold was evident for many of the measurements of toxicity studied. Algae appeared to be slightly more resistant to photo-induced toxicity of anthracene than fishes and invertebrates. An environmental hazard assessment suggests that some aquatic systems are sufficiently contaminated by PAH that a hazard to natural algal communities due to photo-induced toxicity of PAH may be present.

88. Gardner, W.S., R.F. Lee, K.R. Tenore and L.W. Smith. Degradation of Selected Polycyclic Aromatic Hydrocarbons in Coastal Sediments: Importance of Microbes and Polychaete Worms. *Water, Air, and Soil Pollution*; 1979; 11: 339 - 347. Rates of degradation of polycyclic aromatic hydrocarbons (PAH) were examined after addition of crude oil enriched with anthracene, fluoranthene, benz(a)anthracene, and benzo(a)pyrene to coastal sediments in a laboratory (20 deg C) flowing seawater system. Three types of sediment (fine sand, medium sand, and marsh sediment) with and without the benthic polychaete worm, *Capitella capitata*, were used. After extraction from the sediment, PAH concentrations were measured by liquid chromatography with fluorescent detection. Microbial degradation was studied by incubating sediments with radioactive PAH and measuring subsequent production of $^{14}\text{C}\text{O}_2$. Concentrations of the four PAH decreased significantly with time in fine and medium sized sands. PAH levels also decreased in marsh sediment but trends were not significant ($P < 0.05$). *C. capitata* stimulated PAH degradation. Microbial degradation was more rapid in upper surfaces than in lower layers of the sediments.

88a. Garrigues, P., C. Raoux, P. Lemaire, A. Mathieu, D. Ribera, J.F. Narbonne, and M Lafaurie. 1990. *In situ* correlation between Polycyclic Aromatic Hydrocarbons (PAH) and PAH Metabolizing System Activities in Mussels and Fish in the Mediterranean Sea: Preliminary Results. *Intern. J. Environ. Anal. Chem.* Vol. 38, pp. 379-387.

Biochemical indices based on enzymatic activities have been determined in fish and mussels sampled in various different coastal location in the Mediterranean Sea. Preliminary results show a good agreement between biochemical measurements in marine organisms and chemical analyses of polycyclic aromatic hydrocarbons present in sediments. The results obtained suggest the use of biochemical indices for application in chemical contaminant biomonitoring.

89. Gensemer, R.W., R.D. Robinson, K.R. Solomon, and K.E. Day. 1994. PAH Toxicity to Aquatic Organisms in the Presence of Creosote Impregnated Waste Materials (Project Description and Interim Report of Activities from Field Season #1). Centre for Toxicology, University of Guelph, 620 Gordon Street, Guelph, Ontario N1G 1Y4.

90. Gjovik, L.R. (U.S. Forest Products Laboratory, USDA). Migration of Creosote Components from Treated Poles into the Soil. Final ed. Forest Products Utilization Laboratory, Mississippi State University.: U.S. Forest Products Laboratory,

USDA; 1981; Cooperative Agreement Number 12-186. 31 pages. The analysis of 56 soil samples taken radially around 14 creosote-treated poles indicates that the migration of creosote into surrounding soil is limited mainly to the first few inches of soil. naphthalene, 2-methylnaphthalene, 1-methylnaphthalene and biphenyl were not consistently found at measurable concentrations (25-50 ng/g) even in samples taken close to the treated pole. Acenaphthylene, acenaphthene, dibenzofuran, fluorene, phenanthrene and anthracene were found in lower concentrations relative to those occurring in whole creosote. Vaporization, water solubility and biological degradation may be an important factor in the fate and movement of the above named compounds. Fluoranthene and pyrene, along with carbazole, 1,2-benzanthracene and chrysene were the more persistent compounds occurring in soil samples from around creosote-treated poles. The concentration of these compounds in soil decreased sharply as the distance from the pole increased.91. Goodrich-Mahoney, J.W. (EPRI). Creosote-Treated Wood Poles: Sampling and Analysis for the TCLP. EPRI: EPRI; unknown; EPRI RP2485-9, 2979-6. 3 pages.

Total cresol concentration in the TCLP leachates ranged from below the level of detection to 14.95 mg/L. Thirty-five samples (64.8%) had cresol concentrations that were less than 0.5 mg/L or were not detected. The mean concentration for all 54 samples was 1.63 mg/L. The TCLP leachate concentrations of cresols in all samples were well below the TC regulatory level of 300 mg/L for cresols (individual isomers or summed). Thus, utility poles and crossarms used in this study would be classified as non-hazardous wastes on the basis of the TC as it applies to cresols.

Pole top samples contained higher extractable concentrations of cresols than the samples taken from the groundline portion or from the pole butt below ground. Top section samples had a mean concentration of 3.8 mg/L versus 0.9 mg/L for the groundline samples and 0.6 mg/L for the butt section samples.92. Gordon, D.C., P.D. Keizer and N.J. Prouse. Laboratory Studies of the

Accommodation of Some Crude and Residual Fuel Oils in Sea Water. Journal of the Fisheries Research Board of Canada; 1973; 30(11): 1111-1118.

Concentrations of oil accommodated in sea water under laboratory conditions are directly related to the amount added and the degree of turbulence, but inversely related to temperature. The major fraction (87-98%) of this oil is in particulate form ranging in size from about 1 to 30 microns, presumably small droplets. The exact ratio of the particulate

to subparticulate fractions is directly related to the apparent viscosity of each individual oil. Of the total amount of oil initially added, 9-15% appeared in sea water at the end of the 7-days experiments. Except in the proximity of recent oil slicks, the oil concentrations observed in these experiments are one to two orders of magnitude greater than the concentrations generally observed in the marine environment off eastern Canada.⁹³ Government of Canada, Environment Canada and Health Canada (Canadian Government). Creosote Impregnated Waste Materials; Background Technical Report. I ed.: Government of Canada; unknown. This report contains a wealth of specific data regarding the composition, nature, and environmental fate of creosote.⁹⁴ Graham, J.S. (National Timber Piling Council). Pressure-Treated Wood Effect on Marina Environment. New York: National Timber Piling Council, 350 Theodore Fremd Avenue, Rye, New York 10580; 1991. 9 pp. Pressure treated Southern Pine and Douglas Fir are the most commonly used materials for marina construction in the United States. The preservatives currently used, creosote, chromated copper arsenate (CCA), and ammonical copper zinc arsenate (ACZA), are restricted use pesticides, and registered with the U.S. Environmental Protection Agency. The effect of these preservatives on marine life and subsurface ground water at marina sites is reviewed based on available research data. Included is a discussion on the leachability and migration characteristics of the preservatives. The conclusion advises engineers how to properly specify pressure-treated wood without disturbing marine life or contaminating the subsurface ground water.⁹⁵ Grall, G. Pillar of Life. National Geographic ed.; 1992. Describes fouling communities on Chesapeake Bay pilings.

96. Gruson, L. Problem With Clean Harbor: Creatures Devour Waterfront. The New York Times. Unknown.

This newspaper article addresses the issue of the now clean water restored to New York Harbor and how now voracious mollusks and crustaceans have returned, devouring waterfront. Once protected by polluted waters, bridges collapse as a result of speeded corrosion due to clean water. Environmental progress is something of a double-edged sword, states the author.

97. Haeggbloom, M.M., M.D, Rivera, I.D. Bossert, J.E. Rogers and L.Y. Young. 1990. Anaerobic biodegradation of Para-cresol under three reducing conditions. MICROB.-ECOL. Vol. 20, no.2, pp. 141-50.

The anaerobic degradation of *p*-cresol was studied with one sediment source under three reducing conditions—denitrifying, sulfidogenic, and methanogenic. Loss of *p*-cresol in all the anaerobic systems took initially 3 to 4 weeks. In acclimated cultures *p*-cresol was degraded in less than a week. *p*-Cresol was completely metabolized under denitrifying, sulfidogenic, and methanogenic conditions, with formation of nitrogen gas, loss of sulfate, and formation of methane and carbon dioxide, respectively. *p*-Cresol metabolism proceeded through *p*-hydroxybenzaldehyde and *p*-hydroxybenzoate under

denitrifying and methanogenic conditions. These compounds were rapidly degraded in cultures acclimated to *p*-cresol under all three reducing conditions. These results suggest that the initial pathway of *p*-cresol degradation is the same under denitrifying, sulfidogenic, and methanogenic conditions and proceeds via oxidation of the methyl substituent to *p*-hydroxybenzaldehyde degradation was high in both the unacclimated cultures and in the cultures acclimated to *p*-cresol, suggesting that this step is nonspecific. Benzoate was additionally detected as a metabolite following *p*-hydroxybenzoate in the methanogenic cultures, but not in the denitrifying or sulfidogenic cultures. The degradation pathway therefore may diverge after *p*-hydroxybenzoate formation depending on which electron acceptor is available.

98. Hamilton, E.M., J.A. Whipple and R.B. MacFarlane. Striped Bass Populations in Chesapeake and San Francisco Bays: Two Environmentally Impacted Estuaries. *Marine Pollution Bulletin*; 1988; 19(9): 466-477. Striped bass populations have declined precipitously in both Chesapeake Bay and the San Francisco Bay Delta system. Parallel declines in both systems indicate possible common climatic patterns or trends affecting both populations. Climatic instability on both coasts with accompanying changes in average rainfall, outflow and temperature may be interacting with deteriorating water quality and pollution resulting in declining populations of striped bass in both areas. Declines in east coast striped bass stocks have been attributed to: overfishing; nutrient enrichment of the habitat and the resultant, temperature-oxygen squeeze on subadults; deterioration of the near-shore habitat for juvenile striped bass resulting from the loss of submerged aquatic vegetation; decreased survival of larval striped bass due to environmental pollution; poor nutritional state of larvae; and fluctuations in the physical environment and predation. In the San Francisco Bay Delta area the decline has been attributed to the interactive effects of reduced freshwater outflow and increased freshwater diversion, and decreased by flushing and increased pollutant burdens which have adversely affected both egg production and egg and larval survival.⁹⁹

Hamilton, H. (Environmental Management Associates). Canada Creosote Project: Ecological Impact Evaluation and Risk Assessment. DRAFT ed. Calgary, AB: H.E.L.P. Project Alberta Environment, Edmonton, AB; 1993; 922-7068. 10 page summary. This investigation documented creosote contamination in Bow River sediments and porewater adjacent to and downstream of the Canada Creosote Site. Field surveys of fish, benthic invertebrate and aquatic macrophyte distribution, laboratory toxicity tests, health/condition examinations and tissue residue analyses documented a low-level exposure to creosote-derived contaminants in the contaminated zone and limited effects on a small number of species. although these impacts were measurable, the majority of results generated by this study suggest that during the fall of 1992, the ecosystem of the Bow River was not substantially impaired by creosote contamination originating at the Canada Creosote Site.

The existing river berm has largely contained the direct DNAPL loading to the river, and there has been a corresponding reduction in river water concentrations. similar reductions have likely occurred in river sediments and fish tissues, with the possible

exception of benzo[a]pyrene type compounds. The risk of direct mortality of juvenile and adult fish is non-existent with or without site remediation. The existing berm has likely reduced the incidence of fish tainting, and containment should essentially eliminate any tainting potential. Without direct action to deal with contaminated surficial riverbed sediments, the impact on south shore benthic invertebrates will likely persist for a prolonged period of time even after loadings to the river from the site are effectively eliminated.100. Harrington, J.M. and D.B. Crane (California Department of Fish and Game). Water Pollution Control Laboratory. Presence of Target Compounds from Creosote Impregnated Timber in Water and Tissue of the Asiatic Clam (*Corbicula fluminea*) Near Ryer Island Ferry, Sacramento River Delta. Final ed. California Department of Fish and Game, Water Pollution Control Laboratory, 2005 Nimbus Road,

Rancho Cordova, CA 95670: California Department of Fish and Game; 1994; None Given. 9 pp. The California Department of Transportation (CALTRANS) placed creosote impregnated timber at the site of the Ryer Island Ferry in the Sacramento River Delta. The California Department of Fish and Game (CDFG) is concerned about possible creosote contamination in California waters. During the summer of 1993, samples of Asiatic clams (*Corbicula fluminea*) were collected from Lake Isabella, Kern County and transplanted to a site approximately 3 km above the Ryer Island Ferry, at the Ryer Island Ferry and approximately 80 m below the Ryer Island Ferry. The corbicula samples were collected after six weeks of exposure. Water samples were collected when the corbicula were deployed and retrieved. Water and tissue samples were analyzed at the CDFG Water Pollution Control Laboratory.

Concentrations of target compounds from creosote were not detected above the method reporting limits (MRLs) in water. No PAH were detected above the method reporting limit in corbicula from the Cache Slough site above Ryer Island. Corbicula tissue residues of anthracene, phenanthrene, pyrene, fluoranthene, benzo (a) anthracene and benzo (b) fluoranthene were 0.16, 0.30, 0.37, 0.45, 0.24 and 0.18 mg/kg dry weight, respectively at the Ryer Island Ferry site. Corbicula tissue residues of pyrene and fluoranthene were 0.15 and 0.20 mg/kg dry weight at the site directly downstream of the Ferry.

We concluded that there is probably no environmental hazard associated with creosote treated pilings at the Ryer Island Ferry because of the high volume of water moving past the pilings.

101. Hegeman, W.J.M., C.H. Van Der Weijden, and J.P. Gustav Loch. 1995. Sorption of Benzo[a]pyrene and Phenanthrene on Suspended Harbor Sediment as a Function of Suspended Sediment Concentration and Salinity: A Laboratory Study Using the Cosolvent Partition Coefficient. *Environ. Sci. Technol.* 29, pp. 363-371.

The sorption of benzol[a]pyrene (BaP) and phenanthrene (PHE) on sediment collected in the harbor of Rotterdam was studied in batch experiments using ¹⁴C-labeled compounds. In order to simulate various estuarine conditions, we investigated the effects

of various sediment concentrations and salinities on sorption of these compounds. We determined the apparent partitioning as well as the cosolvent partitioning between the liquid and solid phases. The apparent partition coefficient (K_p^{APP}) is influenced by the presence of colloids and dissolved organic matter. The influence of these components is minimized by the use of the cosolvent method in which the partition coefficient (K_p^*) is determined by extrapolation of the partition coefficients obtained in a variety of solutions with water and methanol. The effect of sediment concentration on sorption was investigated at five different sediment concentrations ranging from 0.064 to 10.8 g/L. In contrast to K_p^* , K_p^{APP} was found to be sensitive to the sediment concentration. $\log K_p^*$ (with K_p^* in L/kg), determined for different sediment concentrations, was 5.2-6.3 for BaP and 2.8-3.6 for PHE. The salt concentration was varied with dilutions of Milli-Q water and seawater; the salinity ranged from 0 to 35. The influence of salinity on K_p^* was small; the increase in $\log K_p^*$ from freshwater to seawater is approximately 0.2 for BaP and 0.1 for PHE.102. Hegy, T. (Washington State Department of Ecology). Is Creosote Safe in the

Aquatic Environment? Vol. XVII Number 7 ed. Coastal Currents, Volume XVII, #7, January, 1993: Department of Ecology; 1993.103. Hegy, Tera (Washington Department of Ecology). Focus. Creosote-Treated Wood in the Aquatic Environment. Olympia, Washington: Department of Ecology; 1993; F-TC-93-122. Article designed to discourage the use of creosote treated wood.104. Hellou, J., G. Stenson, I. Ni and J.F. Payne. Polycyclic Aromatic Hydrocarbons in Muscle Tissue of Marine Mammals from the Northwest Atlantic. Marine Pollution Bulletin; 1990; 21(10): 469 - 473.

There are virtually no data available on polycyclic aromatic hydrocarbons (PAH) in marine mammals. Total PAH concentrations were determined in terms of chrysene and petroleum hydrocarbon equivalents in muscle tissues of four species of seals and six species of whales from waters around Newfoundland and Labrador. Values expressed on a dry weight basis ranged from 0.10 to 1.21 ppm in terms of chrysene equivalents and 0.26 to 5.51 ppm in terms of petroleum equivalents. The relatively high levels found in some animals from fishing areas demonstrates a need for more comprehensive information on PAH in marine mammals.

105. Henningson, B. 1983 Environmental Protection and Health Risks in Connection with the Use of Creosote. Holz als Roh- und Werkstoff. 41, 471-475.

The use of creosote as a wood preservative has been examined with regard to environmental protection and health risks, mainly by reference to relevant literature. The examination considers toxic and hazardous problems caused by creosote, before, during and after its application to timber in impregnation plants as well as possible environmental problems posed by treated timber in service and during its final destruction. Although there are certain problems surrounding the use of creosote it may be concluded that these problems are not severe and that they can be reduced or avoided

by using fairly simple protective measures. The main problem at present, however, concerns creosote bleeding which must be solved in the near future. 106. Herbes, S.E.

Rates of Microbial Transformation of Polycyclic Aromatic

Hydrocarbons in Water and Sediments in the Vicinity of a Coal-Coking Wastewater Discharge. *Applied and Environmental Microbiology*; 1981;

41(1): 20-28. To facilitate predictions of the transport and fate of contaminants at future coal conversion facilities, rates of microbial transformation of polycyclic aromatic hydrocarbons were measured in stream water and sediment samples collected in the vicinity of a coal-coking treated wastewater discharge from November 1977 through August 1979. Six radiolabeled polycyclic aromatic hydrocarbons were incubated with sediment and water samples; $^{14}\text{CO}_2$, cell-bound ^{14}C , and polar transformation products were isolated and quantified. Whereas $^{14}\text{CO}_2$ and bound ^{14}C were major transformation products in sediment assays, soluble polar ^{14}C dominated transformation in water samples. Mean rate constants (measured at 20 deg. C) in sediments collected downstream from the effluent outfall were $7.8 \times 10^{-2} \text{ hr}^{-1}$ (naphthalene), $1.6 \times 10^{-1} \text{ hr}^{-1}$ (anthracene), and $3.3 \times 10^{-3} \text{ hr}^{-1}$ (benzo(a)anthracene), which corresponded to turnover times of 13, 62, and 300 h, respectively. No unequivocal evidence for transformation of benzo(a)pyrene or dibenz(a,h)anthracene was obtained. Only naphthalene and anthracene transformations were observed in water samples: rate constants were consistently 5- and 20-fold lower, respectively, than in the corresponding sediment samples. The measured rate constants for anthracene transformation in July 1978 sediment samples were not related to total heterotroph numbers. In late July 1978, the effluent was diverted from the primary study area; however, no differences were observed either in transformation rate constants or in the downstream/upstream sediment rate constant ratio. These results are consistent with the hypothesis that continuous inputs of polycyclic aromatic hydrocarbons result in an increased ability within a microbial community to utilize certain polycyclic aromatic hydrocarbons. However, because transformation rates remained elevated for more than 1 year after removal of the polycyclic aromatic hydrocarbon source, microbial communities may shift only slowly in response to changes in polycyclic aromatic hydrocarbon concentrations.

107. Herbes, S.E. and L.R. Schwall . 1978. Microbial Transformation of Polycyclic Aromatic Hydrocarbons in Pristine and Petroleum-Contaminated Sediments. *Applied and Environmental Microbiology*, Vol. 35, No. 2, pp. 306-316.

To determine rates of microbial transformation of polycyclic aromatic hydrocarbons (PAH) in freshwater sediments, ^{14}C -labeled PAH were incubated with samples from both pristine and petroleum-contaminated streams. Evolved $^{14}\text{CO}_2$ was trapped in KOH, unaltered PAH and polar metabolic intermediate fractions were quantitated after sediment extraction and column chromatography, and bound cellular ^{14}C was measured in sediment residues. Large fractions of ^{14}C were incorporated into microbial cellular material; therefore, measurement of rates of $^{14}\text{CO}_2$ evolution alone would seriously underestimate transformation rates of [^{14}C] naphthalene and [^{14}C]

anthracene. PAH compound turnover times in petroleum-contaminated sediment increased from 7.1 h for naphthalene to 400 h for benz(a)pyrene. Turnover times in uncontaminated stream sediment were 10 to 400 times greater than in contaminated samples, while absolute rates of PAH transformation (micrograms of PAH per gram of sediment per hour) were 3,000 to 125,000 times greater in contaminated sediment. The data indicate that four- and five-ring PAH compound, several of which are carcinogenic, may persist even in sediments that have received chronic PAH inputs and that support microbial populations capable of transforming two- and three-ring PAH compounds.108. Hochman, H. Creosoted Wood in a Marine Environment - A Summary Report.

Journal of the American Wood-Preservers' Association; 1967: 138 - 150. A number of notions concerning the behavior of creosote in marine environments are examined. Among these are mechanical loss, leaching, threshold concentration, reservoir effects and bioenvironment. The relationship between these factors and the service life of creosoted wood is analyzed and the conclusion is drawn that creosote protects wood for long periods of time in cold-water harbors but not in warm-water harbors having a high population of *Limnoria tripunctata*. Suggestions are offered to increase the service life of creosoted wood in warm-water harbors.109. Hockensmith, E.H., M.L. Linn, and J.E. Waggener (Resource Consultants, Inc. 7121 CrossRoads Boulevard, P.O. Box 1848, Brentwood, TN 37024-1848). Toxicity Characteristic Leaching Procedure Testing of Railroad Crossties. Association of American Railroads, Research and Test Department, 50 F Street, N.W.,

Washington, D.C. 20001: Association of American Railroads; 1988; R-708. 49 pp. The Association of American Railroads sponsored testing of creosote treated wood crossties to determine if they would be considered hazardous waste under the EPA propose "Toxic Characteristic Leachate Procedure" (TCLP) test methodology. In accordance with the test procedure originally proposed in 1986, analyses were conducted on a new crosstie, a ten year old crosstie, and a twenty year old crosstie. Phenol levels and meta-, ortho-, para-cresol levels were determined in the test specimens. The new tie exhibited the highest levels of these substances, but no crosstie failed the test. A modified test method was proposed by EPA in 1988 and a second series of tests were conducted. Only freshly treated new crossties were tested. These crossties passed the test with a considerably higher margin than those tested under the original methodology. The results indicate that it is likely that creosote-treated crossties which are not contaminated from spillage or other sources will pass the TCLP as it was most recently proposed. New crossties and possibly those with a few years of service may approach the borderline of TCLP failure under the originally proposed test procedures.110.

Horton, D. 1984. Literature Search and Overview of Water Quality Aspects of Woodwaste Leachate. Horton Dennis and Associates, Inc. 6133 Sixth Avenue - South, Seattle, Washington 98108. Toxic strength of leachate diminishes very markedly within a few months following the start of leaching. However, different types of material within wood waste exhibit different leaching rates: bark, followed by sapwood leaches most rapidly, with heartwood showing the slowest leaching rate. Leachate from Cedar is most toxic, followed by Douglas fir, hemlock and pine. The

conclusion, therefore, is to use as little, if any, cedar or heartwood in wood waste material, particularly where it is apt to leach into an adjacent waterway. 111. Hose, J.E., J.B. Hannah, M.L. Landolt, B.S. Miller, S.P. Felton, W.T. Iwaoka.

Uptake of Benzo(a)Pyrene by gonadal Tissue of Flatfish (Family Pleuronectidae) and its effects on Subsequent Egg Development. *Journal of Toxicology and Environmental Health*; 1981; 7: 991 - 1000. Accumulation of benzo(a)pyrene (B[a]P) by sexually mature flatfish gonad, its transfer to developing gametes, and its subsequent effects on developing embryos were studied. Thin-layer chromatography revealed both unmetabolized B[a]P and polar metabolites in the ovary, wolffian ducts, oocytes, and semen of English sole 24 hours after ip injection with 200 microCi[3H] B[a]P. Concentrations of B[a]P and its metabolites were 3 - 11 times higher in oocytes and semen than in gonadal tissue. Fertilized eggs from flathead sole that had been fed 4.0 mg B[a]P five hours before spawning demonstrated a significantly lower ($P < 0.001$) hatching success (11.9%) than eggs from control fish (56.6%). Morphological abnormalities were found in only 1.6% of control embryos but in 5.6% of embryos from treated females.

112. Huang, X.D., D.G. Dixon and B.M.Greenberg. 1993. Impacts of UV Radiation and Photomodification on the Toxicity of PAHs To The Higher Plant *Lemna Gibba* (Duckweed). *Environmental Toxicology*. Vol. 12, pp. 1067-1077.

The toxicity of polycyclic aromatic hydrocarbons (PAHs) can be enhanced by both biotic and abiotic processes. This is exemplified by light, which, by virtue of the extensive π -orbital systems of PAHs, can be a major factor in PAH toxicity. Light activation of PAHs is known to occur via photosensitization reactions (generation of singlet oxygen and superoxide) and potentially by photomodification of the chemicals (photooxidation and/or photolysis) to more toxic species. To examine the modes of PAH action in the light and determine if the photomodified compounds are hazardous, we investigated the photoinduced toxicity of anthracene, phenanthrene and benzo[a]pyrene to the aquatic higher plant *Lemna gibba* (a duckweed). Toxicity end points were inhibition of growth and extent of chlorosis. Light did indeed activate the phytotoxicity of PAHs, with UV radiation more effective than visible light. Dose-response curves based on chemical concentration and light intensity revealed the order of phytotoxic strength to be anthracene > phenanthrene > benzo[a]pyrene. To explore whether photomodified PAHs were contributing to toxicity, the chemicals were irradiated before toxicity testing. The rates of photomodification of the three PAHs were rapid (half-lives in hours), and the relative velocities were coincident with the order of toxic strength. Furthermore, the photomodified PAHs were more hazardous to *Lemna* than the intact compounds. Because interpretations of the potential impacts of PAHs in the environment are based mostly on measurements of the structurally intact chemicals, the severity of PAH hazards is possibly underestimated.

113. Huggett, P.A., P.A. Van Veld, C.L. Smith, W.J. Hargis, and W.K. Vogelbein. 1992. The Effects of contaminated sediments in the Elizabeth River. Pp. 403-430 IN:

G.A. Burton (ed.). Sediment Toxicity Assessment. Lewis Pubs.

The Elizabeth River is a highly industrialized estuary bordered by the cities of Norfolk and Portsmouth, VA. It is located on the southern shore of the James River near its confluence with the Chesapeake Bay (Figure 1). Bottom sediments of the Elizabeth contain a record of past and present chemical discharges and spill. Particularly significant in this respect is the severe contamination of the system by creosote. Since the turn of this century there have been four or five wood treatment facilities located on the rivers' shores, treating telephone poles, railroad ties, and pilings with creosote to control fungal wet and dry rot. During this period accidental spill, point source, and chronic nonpoint inputs of the pesticide mixture have entered the river and accumulated in bottom sediments. Little attention was paid to environmental concerns before the 1970s, so few detailed records of events are available. Study of Elizabeth River sediments in midchannel shows a nearly exponential increase in sedimentary PAH content from the river mouth extending up the Southern Branch to about km 20, above which, concentrations fall off somewhat rapidly. Records show that at least two separate creosote spills occurred between 1963 and '967. There are numerous other pollutants in the Elizabeth, ranging from trace metals emanating from heavy industries to advanced primary treated sewage effluent from the city of Norfolk. Hazardous substances normally associated with municipalities and harbors enter the system from nonpoint sources. The areal distributions of these contaminants, however, are different than that of the creosote compounds, and the biological responses reported in this manuscript are best correlated with the concentration of the creosote compounds.

114. Huggett, R.J., P.O. deFur and R.H. Bieri. Organic Compounds in Chesapeake Bay Sediments. *Marine Pollution Bulletin*; 1988; 19(9): 454 - 458. The concentrations of organic compounds in bottom sediments from the main stem of the Chesapeake Bay are reviewed. In all stations listed in this paper, a few distinct polynuclear aromatic hydrocarbons (PAH) are present at much higher concentrations than other organic compounds. There is a general trend in concentrations of these PAH decreasing from north to south. This likely reflects the higher human population density in the northern region. Over the time period of 1979 to 1986, the levels of polynuclear aromatic hydrocarbons have remained relatively constant at the stations considered in this manuscript. 115. Humason, A.W. and D.F. Gadbois. Determination of Polynuclear Aromatic

Hydrocarbons. *Bull. Environm. Contam. Toxicol.*; 1982; 29: 645 - 650.

With increased offshore oil drilling along the eastern coast of the United States, the monitoring of organic contamination in this area has received greater attention. Polynuclear aromatic hydrocarbon (PAH) contamination is of particular concern, since many of these compounds are known or suspected carcinogens. Sources of PAH contamination in the marine environment other than drilling and oil spillage include creosote impregnated wooden piles, untreated sewage, and contamination with airborne particulates from the combustion of fossil fuels. These contaminants are taken up by the fish and shellfish which inhabit contaminated areas. When the fish are harvested, a human

health hazard may result.

The National Marine Fisheries Service, Gloucester laboratory, has undertaken a study of PAH levels in specimens found in the New York Bight and Long Island Sound region for comparison with future levels. Samples of winter flounder, windowpane, red hake, rock crab, lobster, and sea scallops were collected from 25 sites by the Kelez Research Vessel during the Kelez-8008 cruise of July through August, 1980. The samples of five animals were collected by standard otter trawl, wrapped in pre-washed aluminum foil, and stored at -30 deg. C for future analysis. These specimens have been analyzed quantitatively for the presence of 15 PAHs. 116. Ingram, L.L. Jr., G.D. McGinnis, S.E. Prince, L.R. Gjovik and D.A. Webb. The

Effects of Temperature, Air Flow Rates, and Coatings Systems on the Vaporization of Creosote Components from Treated Wood. *Journal of the American Wood-Preservers' Association*; 1984: 1 - 8. In studies with treated specimens of southern pine (3/4" x 3" x 11"), the concentrations of the observed components increased exponentially with an increase in temperature. Results from these experiments indicated that the vapor pressure and the amounts of the component present in treated wood were both related to the measured air levels. The air concentrations of indene, naphthalene, and the methylnaphthalenes increased as the air flow rate was decreased from 1.25 l/min to 0.25 l/min. The air concentrations of biphenyl, acenaphthene, dibenzofuran, fluorene and phenanthrene were not affected by the air flow rates. In the range of air flow rates studied, the change in rates of vaporization for the latter group of compounds was almost linear with the change in air flow. Relative humidity had little or no effect on vaporization for the latter group of compounds was almost linear with the change in air flow. Relative humidity had little or no effect on vaporization rates.

The effect of selected coating systems on creosote vaporization was studied with specimens of wood floor blocking (Southern pine, 5.75" x 3.75" x 2.4") that had been treated with creosote to a retention of approximately 2 pounds/cu.ft. The major components of creosote and average air levels (mg/m³) found with uncoated specimens of floor blocking were as follows: naphthalene (31.), 2-methylnaphthalene (3.5), 1-methylnaphthalene (1.8), biphenyl (0.38), acenaphthene (2.1), dibenzofuran (0.82) and fluorene (0.51). Phenanthrene, fluoranthene, and pyrene were detected by gas chromatography-mass spectrometry (GC/MS) analysis.

The average effectiveness of the coatings evaluated ranged from 81 to 99 percent. The effectiveness of pitch (86 to 99 percent) may have been due to the thickness of the coating rather than its impermeability to creosote vapors. Most coatings were greater than 90 percent effective. 117. Ingram, L.L., G.D. McGinnis, L.R. Gjovik and G.

Roberson. Migration of Creosote

and its Components from Treated Piling Sections in a Marine Environment.

Journal of the American Wood-Preservers' Association; 1982: 1 - 8. The migration of 16 polycyclic aromatic hydrocarbons (PAH) into fresh and sea water was investigated in a series of experiments that involved as variables: vessel size, temperature, piling age, and exposure period. The major components that migrated into water was naphthalene, phenanthrene, acenaphthene, dibenzofuran, fluorine, and 2-methylnaphthlene.

However, all of the PAHs present in the wood, except chrysene, migrated into water. Rate of migration increased significantly with increasing temperatures within the range of 20 to 40 degrees C; it was lower for 12-year-old aged pilings sections than for freshly treated sections, although the aged sections contained the higher creosote retentions. The concentration of PAHs in a 300-gallon vessel containing sea water reached a maximum within 24 to 48 hours, then decreased during the remainder of the exposure period. These reductions are thought to have been caused by biological activity. A similar trend in concentration was not observed when 4-liter vessels were used.

118. Jensen, K. Atmospheric Fallout of Polycyclic Aromatic Hydrocarbons in a Marine Coastal Area. Rep. Mar. Pollut. Lab.; 1983; 6: 1 - 5. 16 polycyclic aromatic hydrocarbons (PAH) have been sampled at two stations on the coast of a Danish Inlet and analysed by HPLC. The yearly deposition has been estimated and the possible sources are being discussed. 119. Johnson, A.C., P.F. Larsen, D.F. Gadbois and A.W. Humason. The Distribution of Polycyclic Aromatic Hydrocarbons in the Surficial Sediments of Penobscot Bay

(Maine, USA) in Relation to Possible Sources and to Other Sites

Worldwide. Marine Environmental Research; 1985; 15: 1 - 16. Sediments from the Penobscot Bay region of the Gulf of Maine were analyzed by HPLC and GC-MS for polycyclic aromatic hydrocarbons (PAHs). Total PAH concentrations ranged from 286 to 8794 ppb (dry weight) and formed a distinct gradient decreasing seaward from the head. Gradients of decreasing concentration were also measured in the various harbors in the bay. PAH composition was uniform throughout Penobscot Bay. Atmospherically transported particulate combustion products are hypothesized as a major source of PAH contamination. Sedimentary PAH concentrations from around the world which have been reported in the literature are compiled in a Table. PAH levels in Penobscot Bay sediments fall within the range found in industrialized regions throughout the world and are significantly higher than would be expected for an area previously considered to be uncontaminated.

120. Johnston, E.P., and P.C. Baumann. 1989. Analysis of fish bile with HPLC-fluorescence to determine environmental exposure to benzo(a)pyrene. Hydrobiologia. 188/189/ pp. 561-566.

Brown bullhead from the Black River, Ohio, have a high incidence of liver neoplasia which is associated with elevated concentrations of polynuclear aromatic hydrocarbons (PAHs) in the sediment. We evaluated the use of biliary concentrations of benzo(a)pyrene [B(a)P] equivalents as a means for determining PAH exposure. Bile was collected from 16 brown bullheads and 8 common carp taken from each of two Lake Erie tributaries in Ohio, the industrialized Black River and the non-industrialized Old Woman Creek. Hatchery bullhead (n = 8) were used to determine base levels of PAHs. A high performance liquid chromatography (HPLC) – fluorescence technique was used to determine the concentration of B(a)P equivalents in the bile samples. The area of all peaks fluorescing at 380/430 nm was summed to give a single value for B(a)P equivalents

in each sample. Concentrations of B(a)P equivalents generally reflected concentrations of PAH in sediment where fish were collected. Bile taken from Black River carp contained the highest concentration of B(a)P equivalents and was significantly different from all other groups. The value obtained for Black River bullhead was also high and was found to be significantly different from hatchery bullhead. B(a)P equivalents varied between carp and bullhead from the same habitat possibly because of differing food habits or metabolic pathways. However, our results indicate that relative levels of B(a)P equivalents in the bile of fish correspond well to B(a)P levels in sediment and may offer a means of determining environmental exposure of fish to the parent compound.

121. Johnson, L.L., M.S. Myers, D. Goyette, and R F. Addison. 1994. Toxic Chemicals and Fish Health in Puget Sound and the Strait of Georgia. Symposium on the Marine Environment. Pp. 304-329.

Exposure to anthropogenic contaminants in the marine environment has been associated with a variety of detrimental health effects in fish from urban areas in Puget Sound and Strait of Georgia. These include elevated levels of such chemicals as chlorinated and aromatic hydrocarbons in tissue and body fluids, elevated activities of hepatic xenobiotic metabolizing enzymes, binding of chemical carcinogens to DNA in liver, and pathological conditions such as liver disease. These conditions are more common in bottomfish from heavily polluted sites, but are also observed in fish from moderately contaminated sites with total aromatic hydrocarbon concentrations in sediment of approximately 1ppm. Generally, however, fish from transboundary sites located in non-urban areas show minimal effect of contaminants. Transient species such as outmigrating juvenile salmon may also accumulate detectable levels of contaminants as they migrate through urban estuaries, and these contaminants may be linked to impaired growth and dysfunction of the immune system. The long-term impact that toxicopathic disease and reproductive impairment have on the survival and abundance of affected fish is not known, but preliminary population modeling studies suggest that contaminant-related declines in reproductive output may have the potential to reduce the growth rate of certain sub-populations of sole from contaminated area. Sediment contaminant levels and disease prevalences in fish from heavily contaminated sites in Puget Sound are still among the highest in sewage treatment, regulation of toxic chemicals, and remediation efforts. However, as a consequence of increased urban development throughout the Pacific Northwest, the number of sites with sediment contaminant levels high enough to induce mild toxicopathic effects in fish may increase.

122. Kailin, E. 1989. Memorandum to Watershed Management Committee. 23 March 1989. Protect the Peninsula's Future, P.O. Box 1677, Sequim, WA, 98382.

This memorandum to the Watershed Management Committee addresses the toxic problem with new creosoted pilings. Data from sediment traps in John Wayne Marina

are compared with sediments from Eagle Harbor where severe damage to sealife, including liver tumors in fish are found.

123. Karlehagen, S., A. Andersen, and C.G. Ohlson. Cancer incidence among creosote-exposed workers. *SCAND. J. WORK ENVIRON. HEALTH*; 1992; vol. 18, no. 1: 26-29.

Cancer incidence was studied among 922 creosote-exposed impregnators at 13 plants in Sweden and Norway. The subjects had been impregnating wood (eg, railroad cross-ries and telegraph poles), but no data on individual exposures were available. The study population was restricted to men employed during the period of 1950-1975, and their cancer morbidity was checked through the cancer registries. The total cancer incidence was somewhat lower than expected, 129 cases versus 137 expected [standardized incidence ratio (SIR 1.9, 95% CI 0.81-5.83), skin cancer (SIR 2.37, 95% CI 1.08-4.50), and malignant lymphoma (SIR 1.9, 95% CI 0.83-3.78). Exposure to sunlight may have contributed to the risk of lip and skin cancer. The small number of cancer cases does not permit valid conclusions. The findings indicate that impregnating wood with creosote in earlier decades increased the risk of skin cancer.

124. Kelso, W.C. and E.A. Behr. Depletion of Preservatives from Round Southern Pine in Fresh Water. *Journal of the American Wood-Preservers' Association*; 1977: 135-141. Green southern pine pole sections were empty-cell treated with

pentachlorophenol and a heavy aromatic oil or coal tar creosote. They were exposed by submerging them in fresh water for 5.5 to 13 months followed by a period out of water. analysis of half to one inch zones before and after exposure indicated greatest losses for both preservatives from the outer half inch of wood with no or smaller losses from inner zones.

125. Kenaga, E.E. Predicted Bioconcentration Factors and Soil Sorption coefficients of

Pesticides and Other Chemicals. *Ecotoxicology and Environmental Safety*; 1980;

4: 26 - 38. Equations were used to calculate soil sorption coefficients (K_{oc}) and bioconcentrations factors (BCF) for 358 compounds, mostly pesticides, from known water solubility values. Bioconcentration factor (BCF) values were also calculated from K_{oc} values. comparisons were made between calculated and actual values where possible. The highest experimental BCF values were associated with persistent chemicals having water solubility's below 0.1 ppm. With some exceptions, such as certain ionic compounds, the highest K_{oc} values were also associated with low water solubility.

Calculated values for BCF or K_{oc} in excess of 1000 should be experimentally confirmed in order to be certain of their environmental significance. Of the values calculated from water solubility, 10% of the BCF values were over 1000 and 30% of the k_{oc} values were over 1000. BCF and K_{oc} values are simple to calculate from water solubility and are useful for estimation of partitioning in soil, and in animal tissues for contributing to early assessment of potential hazard. Low water solubility is not a good indicator for

differentiating between insecticides, fungicides, and herbicides.

126. Kennicutt, M.C., T.J. McDonald, G.J. Denoux and S.J. McDonald. Hydrocarbon Contamination on the Antarctic Peninsula. *Marine Pollution Bulletin*; 1992;

24(10): 506-511. Accidental and operational releases of hydrocarbons during activities in support of scientific bases in the Antarctic can contaminate organisms in close proximity to these locations. Intertidal and subtidal limpets in Arthur harbor were found to contain elevated levels of polynuclear aromatic hydrocarbons near Palmer and Old Palmer Stations. Contamination was highest in the intertidal and decreased with increasing water depth in the subtidal. The highest concentrations of tissue contamination were found in intertidal areas associated with high levels of onshore soil contamination. Limpets (*Nacella concinna*) preferentially incorporated the more water soluble aromatic compounds suggesting exposure to dissolved contaminants in run-off rather than particulates or slicks. This was in contrast to subtidal sediments that were primarily contaminated with freshly spilled diesel fuel. While contamination was present near stations, the concentrations observed are 1-2 orders of magnitude lower than the initial contamination caused by the Bahia Paraiso diesel fuel spill in 1989.

127. King, P.J. An Assessment of the Potential Carcinogenic Hazard of Petroleum Hydrocarbons in the Marine Environment. Rapp. P.-v. Reun. Cons. int. Explor.

Mer; 1977; 171: 202- 211. Crude petroleum is known to contain low concentrations of a number of substances mainly of the polycyclic aromatic hydrocarbon type, which can, on prolonged intimate contact, cause skin cancer in man. Similar substances are present in the environment as byproducts of pyrolysis etc. and as natural constituents of certain vegetable foodstuffs. These substances have only a

very limited solubility in water and at such low concentrations should cause little hazard, but there is a possibility of their concentration in the food chain. This paper attempts to examine all aspects of this problem in the light of published research in a variety of disciplines.

128. King, T.L., J.F. Uthe, and C.J. Musial. Polycyclic Aromatic Hydrocarbons in the Digestive Glands of the American Lobster, *Homarus americanus*, Captured in the Proximity of a Coal-Coking Plant. Bull. Environ. Contam. Toxicol.; 1993; 50:

907-914. For many years two coal-coking plants on the shoreline of Sydney Harbor, Nova Scotia, discharged their liquid effluents through a pond into the south Arm of the harbor. One plant was shut down in 1981 and the second in 1983. In 1982 the South Arm of Sydney Harbor was closed to commercial lobster fishing due to elevated polycyclic aromatic hydrocarbon (PAH) concentrations in the digestive glands (hepatopancreas) of American lobsters (*Homarus americanus*). A study in 1984 supported the continuation of the closure. Our results from the

South Arm of Sydney Harbor confirm the accumulation of high PAH and HAC levels in lobsters. It is probable that the South Arm of Sydney Harbor will remain closed to commercial fisheries for a long time, at least until the action to clean up the PAH contamination is completed.

129. Kocan, R.M. (School of fisheries, University of Washington). Review of Possible

Threat to Aquatic Organisms by Creosote Treated Piles. Seattle, Washington:

Mr. W. Legg, L.E.C.O. Marine, Seattle, Washington; unknown. 7 pp.

Cursory review of the risks associated with the use of creosote in marine environments Concludes that there are no risks.

130. Klaunig, J.E., R.J. Ruch and P.J. Goldblatt. 1985. Trout Hepatocyte Culture: Isolation and Primary Culture. *In Vitro Cellular & Developmental Biology*. Vol 21. No. 4: 221-228.

Rainbow trout (*Salmo gairdneri*) hepatocytes were isolated using a two-step perfusion through the portal vein. A typical perfusion yielded 2.92×10^6 liver cells with a mean viability of 96.3%. Hepatocytes comprised 93.4% of the total cell isolate. Survival of hepatocytes in suspension culture was dependent on fetal bovine serum concentration and temperature of incubation. Serum concentrations of 5, 10, and 20% produced the highest survival during primary culture. Hepatocyte survival was in inverse proportion to the incubation temperature. Trout hepatocyte DNA synthesis and mitosis decreased during the culture period. Cytochrome P₄₅₀ activity decreased rapidly during the first 2 d of culture and then remained low but measurable during the remaining 8 d of culture. Culture temperature also influenced the P₄₅₀ activity with lower temperatures producing greater activity. Morphologic changes occurred in the cells during culture. Isolated hepatocytes self-aggregated, forming strands and clumps that increased in size with time in culture. Junctional complexes between cells were evident within the aggregates. Nuclear atypia, increases in size and number of autophagic vacuoles, and the appearance of bundles of intermediate filaments also were observed with increased time in culture.

131. Konasewich, D.E. and F.A. Henning. Creosote Wood Preservation facilities: Recommendations for Design and Operation. Minister of Supply and Services Canada, 1988.

This is an EPS Report produced by Environment Canada which established the Wood Preservation Industry Technical Steering Committee to develop technical recommendations for wood preservation facility design and for operational measures. A draft of technical recommendations was developed. These recommendations reflect the intent of the Federal Fisheries Act, and the intent of provincial environmental and worker health and safety legislation and regulations.

The Steering Committee recommends that new creosote pressure treatment facilities comply with the objectives in this technical recommendations document and that existing facilities make all practicable modifications necessary to meet the recommendations. Site-specific circumstances will influence the applicability and implementation of specific measures at both new and existing facilities. However, the authors recommend a definitive periodic review of these recommendations.

It is the belief of the Technical Steering Committee believes that the proper implementation of the recommendations will allow the continued beneficial use of

creosote as a wood preservative and will protect both the environment and workers from potential harmful effects.

132. Landahl, J.T., B.B. McCain, M.S. Myers, L.D. Rhodes and D.W. Brown. Consistent Associations between hepatic Lesions in English Sole (*Parophrys vetulus*) and Polycyclic Aromatic Hydrocarbons in Bottom Sediment. *Environmental Health Perspectives*; 1990; 89: 195-203. A consistent and statistically significant association between prevalence of hepatic neoplasms in free-living sole (*parophrys vetulus*) and levels of anthropogenic polycyclic aromatic hydrocarbons in bottom sediment from sites of fish capture was documented in a series of studies conducted over a period of 7 years in Puget Sound, Washington. This result strengthens the evidence supporting a causal relationship between exposure to sediment-associated hydrocarbons and development of hepatic neoplasms in this bottom-dwelling marine fish species. Prevalences of two other distinct categories of idiopathic hepatic lesions - megalocytic hepatitis and steatosis/hemosiderosis-also showed consistent, statistically significant associations with polycyclic aromatic hydrocarbon concentrations in bottom sediment, and association with prevalence of a third category (putatively preneoplastic foci of cellular alteration) approached statistical significance. On the basis of other studies, megalocytic hepatitis and foci of cellular alteration are both considered to be important precursor lesions in the stepwise histogenesis of hepatic neoplasms.
133. Landrum, P.F., B.J. Eadie and W.R. Faust. 1991. Toxicokinetics and Toxicity of a Mixture of Sediment-Associated Polycyclic Aromatic Hydrocarbons to the Amphipod *Diporeia* Sp.

Amphipods, *Diporeia* sp., were exposed to a reference sediment dosed with two radiolabeled polycyclic aromatic hydrocarbons (PAHs) and sediments dosed with a mixture of PAHs at four concentrations: 21.4, 41.0, 119.6, and 327.0 nmol g⁻¹ dry sediment as the molar sum of the PAHs. *Diporeia* sp. Were sampled for mortality and toxicokinetics for up to 26 d. Significant sediment avoidance was observed at the highest dose out to 6 d of exposure. The toxicity for the mixture was 38 ± 3% after 19 d of exposure at the highest dose, 327 nmol g⁻¹ dry sediment as the molar sum of the PAHs. The measured organism concentration required to produce the mortality at day 19 was 2.9 µg g⁻¹ as the sum of the bioaccumulated PAHs. The uptake clearance (g dry sediment g⁻¹ organism h⁻¹) from sediments for the radiotracers increased with dose to an apparent plateau. Uptake clearance is the conditional constant relating the contaminant flux into the organism to the contaminant concentration in the referenced environmental compartment, in this case the sediment. This enhanced bioavailability with dose occurred even in the absence of over effects and in the absence of changes in the measured partition coefficients for phenanthrene (273 ± 98) and pyrene (540 ± 212), between the freely dissolved radiotracers in interstitial water and the sediment particles. These changes in bioavailability with changes in PAH concentration suggest that predictions of bioaccumulation of PAH congeners from sediments under different field concentration

conditions will not be possible with standard partitioning relationships. 134. Landrum, P.F., J.P. Giesy, J.T. Oris, and P.M. Allred. 1987. Photoinduced toxicity of polycyclic aromatic hydrocarbons to aquatic organisms. In J.H. Vandermeulen and S. Hrudy, Eds., *Oil in Freshwater: Chemistry, Biology, Countermeasure Technology*. Pergamon Press, Elmsford, NY, pp. 304-318.

Polycyclic aromatic hydrocarbons (PAH) such as anthracene are ubiquitous pollutants that are normally not considered acutely toxic to aquatic organisms because they are only sparingly soluble in water. Thus, bioassays conducted under the usual laboratory conditions have resulted in estimates of acute toxicity that exceed the aqueous solubilities of PAH. However, these studies are usually conducted under conditions that minimize photodegradation, and therefore the potential to observe ecologically relevant photoinduced toxicity is eliminated.

Studies under more ecologically relevant conditions in an illuminated artificial stream microcosm have demonstrated that anthracene is acutely toxic (100% mortality) to juvenile bluegill sunfish at $12 \mu\text{g}_\text{L}^{-1}$ in less than 9 h. This toxicity is more than 400 times greater than previously reported no-effect concentrations. *Daphnia pulex* are even more sensitive (LT_{50} , time to 50% immobilization – 13 min at $1.2 \mu\text{g}_\text{L}^{-1}$). These dramatic effects occur as a result of the interaction of bioaccumulated parent PAH and light, not the action of externally formed photodegradation products. Preliminary screening has indicated that benzo(a)pyrene is even more toxic than anthracene. We predict that 50% of the aquatic organisms in a lake will be immobilized at a depth of 7.25 m with a $1.2 \mu\text{g}_\text{L}^{-1}$ anthracene concentration based on the use of the Bunsen-Roscoe Law of Reciprocity, the measured extinction coefficient for UV-B in Lake Michigan (0.575 m^{-1}), an average summer day length of 14 h, and the LT_{50} for *Daphnia pulex*.

These effects, the depths at which they may be occurring, and the concentrations of PAH in the Great Lakes indicate that acute effects could be occurring at present in the Lakes. With expected increases in PAH load due to increased coal usage and increased ambient levels of solar UV due to depletion of the ozone layer, the potential exists for large effects in the Great Lakes and other aquatic systems.

135. Larsen, P.F., D.F. Gadbois and A.C. Johnson. Polycyclic Aromatic Hydrocarbons in

Gulf of Maine Sediments: Distributions and Mode of Transport. *Marine Environmental Research*; 1986; 18: 231-244. Sediments from 19 stations in the Gulf of Maine were analyzed for 16 priority polycyclic aromatic hydrocarbon (PAH) compounds in 1983. Thirteen of the compounds were distributed widely with total concentrations ranging from 10 - 512 ppb (dry wt). These values are an order of magnitude lower than those observed in the coastal zone but higher than those on Georges Bank. PAH concentration was directly related to grain size, total organic carbon (TOC) and distance from source. PAHs appear to be accumulating in Wilkinson and Jordan Basins but not in Georges Basin. Observed PAH distributions support the conclusion that the principal transport mechanism is through the atmosphere with localized augmentation by sediment resuspension and transport from coastal embayments.

136. Leach, C.W. and J.R. Weinert (AWPI). Migration of Creosote Through Pressure Treated Wood. AWPI: AWPI; 1976; A Report to the Environmental Program Task Group, Sub-Group No. 5 (Creosote) of the American Wood Preservers Institute. 12 pp. plus appendices. This paper provides an analysis of the inter-relating environmental and processing factors that effect the leaching of creosote from pressure treated wood.

137. Lebow, S.T. and J.J. Morrell. Exposure of creosoted Douglas-fir panels in Oregon coastal waters: a preliminary report. *Forest Products Journal*; 1988; 38(5): 25-32.

Douglas-fir test panels were treated with creosote at one of five retention levels and immersed at three locations along the Oregon coast. After 2 years, panels with a retention of 321 kg/m³ (20 lb./ft³), as specified by AWPA, effectively repelled attack by marine borers (*Limnoria* spp.), but several panels with a retention of 160 kg/m³ (10 lb./ft³) were attacked internally by shipworms (*Bankia setacea*). Although *Limnoria tripunctata* lightly attacked some creosoted panels, its attack of untreated controls was significant at only one site. Gas chromatographic analyses revealed an absence of significant migration of creosote components from the panels after 2 years. However, components with low boiling points had much lower concentrations in wood that had been immersed than in the original creosote. The study is continuing.

138. Lee, R.F., W.S> Gardner, J.W. Anderson, J.W. Blaylock, and L. Barwell-Clarke. 1978. Fate of polycyclic aromatic hydrocarbons in controlled ecosystem enclosures. *Environ. Sci. Technol.* 7, 832-838.

This paper summarizes an experimental study of the fate of a number of polycyclic aromatic hydrocarbons of increasing molecular weight in a controlled ecosystem enclosure. The hydrocarbons included naphthalene, methylnaphthalenes, dimethylnaphthalenes, anthracene, fluoranthene, benzo(a)anthracene, and benzo(a)pyrene. Prudhoe crude oil was enriched with these aromatics and added as a dispersion to a quarter-scale enclosure (ca. 2 m diameter and 15 m deep—60000 L). After oil addition, water, sediment, zooplankton, and oysters in the enclosures were analyzed for the various hydrocarbons. A second experiment involved adding radiolabeled benzo(a)pyrene to an enclosure to allow quantification of hydrocarbon products.

The changes in the concentration of the different hydrocarbons in water are a reflection of the action of evaporation, biological degradation, photochemical oxidation, and adsorption to living or dead particles with subsequent sedimentation. Using the results of our experiments we have attempted to evaluate the importance of these processes as it affects different types of aromatic hydrocarbons.

139. Lefkovitz, L.F., E.A. Creelius, J.L. Licker, and T.J. Gilfoil. 1994. The Use of Semipermeable Membrane Devices to Predict Bioaccumulation of Hydrophobic Organic Contaminants. Marine Sciences Laboratory, 1529 West Sequim Bay Road, Sequim, WA 98382.

One means of predicting bioaccumulation of hydrophobic organic compounds (HOC) is to measure the bioavailability of these constituents from water and sediment. This is currently performed in the laboratory using live organisms. A semipermeable membrane device (SPMD) filled with a small amount of synthetic lipid (triolein) simulated bioconcentration of HOCs. Polyethylene alone (polyfilm) may also be a good predictor of bioaccumulation. SPMDs containing the lipid and the polyethylene alone were used to determine the rate of uptake of PAHs from a sediment-water slurry. Sediment from two different locations were used. Equilibrium was approached within one week to several weeks, depending upon the type of SPMD and the octanol-water partitioning coefficient (K_{ow}) of the chemical. SPMD concentrations of selected chemicals were compared to those of organisms which had been subjected to the same sediments during a 28-day bioaccumulation study. Similar trends in concentrations did appear to occur in both the organisms and the SPMDs. Equilibrium was not reached for all compounds. Equilibrium was approached earlier using the polyethylene alone and concentrations in the polyfilm were lower than in the SPMDs. For some of the high molecular weight PAH compounds, uptake rates into the polyfilm and the SPMD were almost identical and suggests that uptake is controlled in part by the release rate of the HOCs from the sediment.

140. Lefkovitz L., E. Creelius, N. McElroy. Unknown. The Use of Polyethylene Alone to Predict Dissolved-Phase Organics in the Columbia River. Battelle Marine Sciences Laboratory, Sequim, WA 98382.

Semipermeable membrane devices (SPMDs) filled with a small amount of synthetic lipid (triolein) have been shown to concentrate hydrophobic contaminants (HOCs) from water in a predictable way. Polyethylene alone (polysheets) has also been shown to be a good predictor of trace HOC concentrations in water. A recent survey of a number of HOCs was performed by the Battelle in the Columbia River using SPMDs, both lipid-filled and polyfilm only. Dissolved-phase concentrations of 16 chlorinated pesticides and over 30 PCB congeners were measured at 10 sites in the Columbia River and its tributaries by analyzing the deployed SPMDs. Concentrations of these chemicals were estimated using uptake rates, determined by J. Huckins of the National Biological Survey in Columbia, Missouri. Water concentrations determined from the polyethylene sheets were calculated using polyethylene-water partition coefficients determined by Battelle. Concentrations from both devices were in close agreement.

141. Licht, D., B.K. Ahring and E. Arvin. 1996. Effects of electron acceptors, reducing agents, and toxic metabolites on anaerobic degradation of heterocyclic compounds. *Biodegradation*. Vol. 7, no.1, pp. 83-90.

Degradation of four heterocyclic compounds was examined under nitrate-reducing, sulphate-reducing and methanogenic conditions. Soil samples from a creosote-polluted

site in Denmark were used as inoculum. Indole and quinoline were degraded under all redox conditions with the highest degradation rates obtained under sulphate-reducing conditions. Benzothiophene and benzofuran were not degraded during the observation period of 100 days under any of the redox conditions. Indole and quinoline degrading cultures could be repeatedly transferred under all redox conditions, except for degradation of quinoline under sulphate-reducing conditions, which was inhibited by sulphide at concentrations above 0.8 mM. Degradation of quinoline under methanogenic conditions was also inhibited by 3.2 mM sulphide used as a reducing agent, but sulphide had no inhibitory effect on the degradation of indole in methanogenic and sulphate-reducing soil slurries.

142. Lindmark, D.G. Activation of Polynuclear Aromatic Hydrocarbons to Mutagens by the Marine Ciliate *Paraurionema acutum*. *Applied and Environmental Microbiology*; 1981; 41(5): 1238 - 1242. The marine ciliate *Paraurionema acutum* converted 2-aminofluorene and 2-acetylaminofluorene to compounds with mutagenic activity in the Ames Salmonella test. The ciliate, however, did not activate benzo(a)pyrene or benzanthracene or destroy the mutagenic properties of nitrosoguanidine. Homogenates, when substituted for the liver S-9 fraction in the Salmonella/microsome test activated 2-aminofluorene and 2-acetylaminofluorene to mutagens. Benzo(a)pyrene and benzanthracene were not activated, nor was nitrosoguanidine inactivated. Phenobarbitol did not induce or increase the amount of activating activity. The activation showed no requirement for the reduced nicotinamide adenine dinucleotide phosphate-regenerating system required by liver P-450 cytochromes. Upon differential sedimentation of a cell homogenate, the majority of the activity sedimented with a small-particle fraction with sedimentation properties like those of microsomes from higher eucaryotes. Benzo(a)pyrene, although not metabolized, was accumulated by cultures of *P. acutum* at a linear rate and was not appreciably released (10%) after removal of benzo(a)pyrene from the incubation medium. Hence, this ciliate could convert certain polynuclear aromatic hydrocarbons to mutagens and accumulate others.

143. Lippiatou and A. Saliot. Fluxes and transport of anthropogenic and natural polycyclic aromatic hydrocarbons in the western Mediterranean Sea. *Marine Chemistry*; 1991; 32: 51-71. Surface sediments were collected in the Gulf of Lions and in the Rhone delta and analyzed for composition of polycyclic aromatic hydrocarbons (PAH). After isolation of lipids, the hydrocarbons were separated into fractions by high-performance liquid chromatography (HPLC) and fractions were analyzed by gas chromatography (GC) and gas chromatography/mass spectrometry (GC/MS). Annual PAH fluxes were calculated for the northwestern Mediterranean basin. The fluxes of open-sea sediments varied from 164 micrograms/m²/year, for a station located far from the coast and influenced by atmospheric deposition, up to 1420 micrograms/m²/year for stations directly influenced by the Rhone river inputs, whereas stations located in the Rhone delta were characterized by higher fluxes, up to 12,250 micrograms/m²/year. PAH concentrations decreased significantly with distance from the river mouth. Detailed

analysis of PAH revealed the presence of anthropogenic compounds, pyrolytic and petrogenic, and naturally derived compounds. The distribution and ratios of specific compounds of PAH are discussed as a function of morphological and sedimentological features to evaluate and characterize the respective importance of atmospheric and Rhone-derived river inputs. Pyrolytic inputs from anthropogenic combustion processes were predominant at all studied stations. Compounds of natural origin were quantified, such as retene and related abietic acid precursors, and pentacyclic triterpenes derived from alpha- and beta-amyrins. Anthropogenic PAH fluxes, determined for an open-sea sediment corresponding to the end of the nineteenth century (about 100 years ago), were three to four times less than the current flux; however, the retene flux was equal to or higher than that of today. sediments, Rhone delta, PAH, sources, Mediterranean, anthropogenic, natural.

144. Lipiatou, E. and A. Saliot. Hydrocarbon Contamination of the Rhone Delta and Western Mediterranean. *Marine Pollution Bulletin*; 1991; 22(6): 297-304. The distribution and origin of non-aromatic hydrocarbons (NAH) and polycyclic aromatic hydrocarbons (PAH) were investigated in superficial sediments from the Rhone delta and from the open Western Mediterranean Sea. Hydrocarbons extracted from sediments were fractionated by high performance liquid chromatography and analysed by gas chromatography and GC/mass spectrometry. NAH concentrations ranged 6.5 to 348.9 micrograms/gram of dry sediment and from 1.7 to 20.2 mg/gram of organic carbon (OC) in sediment. PAH concentrations ranged from 179 - 2427 ng/g and 43.8 to 237.9 microgram/g OC, respectively. Higher concentrations were observed at stations close to the river mouth and in the Gulf of Fos. Lower background levels of hydrocarbons were found in deep sediments from the north and central western Mediterranean. Different diagnostic criteria, such as unresolved/resolved compounds ratio, carbon preference index of n-alkanes, pristane/n-C17 ratio, and distribution patterns of PAH were used to distinguish between natural and mixed anthropogenic inputs, underlining the utility of a multi-diagnostic criteria approach. The amount of hydrocarbons deposited in this part of the Mediterranean Sea is estimated at 416 tons/yr. 145. Lipkin, R. Cosmic dust can ferry in organic molecules. *Science News*; 1993; 144(18): 278. Simon J. Clemett, a chemist at Stanford University, and his colleagues report in the Oct. 29 *Science* the detection of polycyclic aromatic hydrocarbons (PAHs) on interplanetary dust. The PAHs bear unusual features that distinguish them from similar molecules found on terrestrial particles and meteorites.

146. Lipovsky, S.J. 1995 Proposal For Field Investigation of Creosote Treated Wood Impacts and Fuidelines Project. Submitted To: Scott Christie, Foreshore Technologies Incorporated, 118 Garden Avenue, North Vancouver, BC V7P 3H2. 147. Lonning, L. Unknown. *American Wood Preservers Association Standards and Quality Control. LDLC (AWPA-QC)*. Unknown. pp. 1-4.

This article addresses the American Wood Preservers Association Standards and Quality Control.¹⁴⁸ Luoma, S.N. and D.J.H. Phillips. Distribution, Variability, and Impacts of Trace Elements in San Francisco Bay. *Marine Pollution Bulletin*; 1988; 19(9): 413-425. Studies conducted to date in San Francisco Bay suggest that the trace elements of greatest concern are Ag, Cu, Se, Cd, and perhaps Hg. The distributions of these elements in the Bay are complex, as are temporal trends. Neither spatial nor temporal variability are fully documented. However, certain locations are considerably metal-enriched, coincident with locations of anthropogenic element input. Some evidence suggests that trace elements may exert detrimental impacts on benthic species in contaminated localities. Broad scale impacts will be difficult to determine without a fundamental understanding of ecological processes and a systematic description of the frequency of patches of metal disturbance in the Bay.

149. BLANK