

Final Report
Evaluation of Polycyclic Aromatic Hydrocarbon Migration
From Railway Ties Into Ballast and Adjacent Wetlands

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**Migration of polycyclic aromatic hydrocarbons (PAH)
from new and used railway cross-ties
into ballast and adjacent wetland environments**

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Abstract

In 1996, an electric utility replaced weathered creosote treated railway ties with newly treated ties as part of a routine maintenance operation on a railway spur carrying coal through a wetland into a power generating facility. The wetland was considered important habitat to *Somatochlora hineana* an endangered dragonfly. The US Fish and Wildlife Service considered the creosote treated railway ties a threat to this endangered dragonfly and required the utility to replace the treated wood ties with steel ties and to conduct a study to determine the potential risks to wetland environments associated with the use of creosote treated railway ties.

Because there are many sources of polycyclic aromatic hydrocarbons associated with all forms of transportation, particularly railway lines carrying coal, a mesocosm study was used to determine the rate at which creosote derived PAH moves from treated ties into railway ballast and then into adjacent wetlands. This study included three cells containing newly treated ties, weathered (old) ties, and untreated red oak ties as a control. The mesocosms replicated conditions, including the wetland's hydrology, found along the actual right-of-way.

Concentrations of PAH were monitored quarterly in mesocosm ballast at distances of 5, 20 and 30 cm from the faces of all three types of railway ties and in sediments at distances of 0.0, 0.5 and 0.75 meters from the toe of the ballast for 555 days. The mesocosms were constructed without significant PAH contamination. Creosote was observed migrating from the newly treated ties into adjacent ballast to a distance of at least 30 cm during the summer of the first year following construction. A similar pulse of PAH was not observed in the weathered tie mesocosm. It appeared that this pulse of PAH was associated with warm ambient air temperatures experienced during July and August at the site and with solar insolation that may have significantly increased surface temperatures on the black colored ties, which act as a black body. Concentrations of PAH adjacent to the newly treated ties declined rapidly to low levels during the fall of the first year. This decline was likely associated with photochemical degradation in the dry ballast environment. A second pulse of PAH was not observed in any of the mesocosms during the second summer of monitoring and ballast concentrations remained low throughout the remainder of the study.

Sediment concentrations of PAH remained low until near the end of the study when a small increase in sediment PAH was observed in the new tie mesocosm. The increase in sediment PAH attributable to the creosote treated railway ties was approximately 0.3 $\mu\text{g/g}$, which was equal to the observed atmospheric PAH deposition observed in this area. However, the observed increases were not statistically significant as a function of Distance, Treatment or Day of the study. Polycyclic aromatic hydrocarbons appeared to have migrated vertically downward to a depth of approximately 60 cm in the ballast. At the end of the study, the observed ΣPAH concentration was less than 0.85 $\mu\text{g } \Sigma\text{PAH/g}$ dry ballast at any depth.

PAH were detected in one of 16 water samples. Those samples were collected on the final day of the study. However the PAH concentrations were very low and an assessment using the sum of toxic units approach indicated that none of the samples approached concentrations associated with biological stress. Likewise, the PAH concentrations observed in the two most contaminated wetland sediment samples were not predicted to be stressful using the newly developed consensus sediment benchmark methodology of Swartz (1999). No adverse biological effects to even the most sensitive organisms were predicted at the PAH concentrations observed in wetland sediments during this study.

**Migration of polycyclic aromatic hydrocarbons (PAH)
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1.0. Background. In 1996 Commonwealth Edison operated a spur rail-line crossing wetlands inhabited by the endangered Hines emerald dragonfly (*Somatochlora hineana*) in Will County, Illinois. This line, built in the 1950's, has been infrequently used in the last 30 years. In 1996, Commonwealth Edison replaced unserviceable creosote treated ties with newly treated ties raising concerns within the U.S. Fish and Wildlife Service that polycyclic aromatic hydrocarbons (PAH) associated with creosote preservative might migrate from ties, through the ballast, and into adjacent wetlands used by the endangered dragonfly. Information was not available to predict the amount of creosote that might enter the wetland. Brooks (1996) found no published literature describing the response of *Somatochlora hineana* to PAH. However, the dissolved fluoranthene concentration killing 50 percent of dragonflies in the genus *Ophiogomphus* (96-hr LC₅₀) was relatively high at 178.5 µg/L. Ultra-violet radiation enhanced PAH toxicity has been observed in several vertebrate and invertebrate species at concentrations as low as three to four µg anthracene or fluoranthene/L. However, the 96-hr LC₅₀ for photoenhanced PAH in *Ophiogomphus* was also high at 109.7 µg fluoranthene/L (U.S. EPA, 1993). The point is that *Ophiogomphus*, as a representative of the Order Odonata, to which *Somatochlora hineana* belongs is not particularly susceptible to PAH intoxication. This suggested that PAH sediment and water quality criteria designed to be protective of aquatic resources in general could be applied to this endangered species.

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 bituminous coal. 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 either fresh or seawater and new creosote oil at 38 °C has a specific gravity of between 1.08 and 1.13 when compared with distilled water at 15.5 °C (AWPA, 1996).

The preservative treatment of railway ties with creosote is accomplished in accordance with the American Wood-Preservers' Association (AWPA) Standard C2. For durability, most railway ties are cut from hardwoods, particularly red and/or white oak (*Quercus sp.*). AWPA (1996) requires an average retention of 6.0 pounds creosote per cubic foot of treated red oak with a minimum penetration depth equal to 65% of the annual rings - or to refusal. Because the cells in white oak are filled with lignin, this species is typically treated to refusal. Treatment to refusal is achieved when no more than 2% additional preservative is taken up by the wood in two consecutive half-hour periods of treatment.

Creosote treated railway ties have life expectancies that depend on rail traffic, tie placement and environmental hazard. The service life of creosote treated railway ties is typically 30 years in Southern regions; 46 years in Eastern regions; and 51 years in Western regions of the United States (Zarembski, 1990).

Brooks (1997b) reported the results of sediment PAH sampling at upstream and downstream stations in Des Plaines River wetlands adjacent to the railway right of way. Background sediment PAH concentrations upstream from the right of way were uniformly low at

$0.83 \pm 0.52 \mu\text{g } \Sigma\text{PAH}$ (sum of 16 individual PAH compounds)/g dry sediment. Sediment concentrations of PAH at the toe of the ballast on the downstream side of the right of way were slightly elevated at $2.07 \pm 1.79 \mu\text{g } \Sigma\text{PAH/g}$. Concentrations at all other distances were less than those observed at the upstream reference stations. However, four of the 35 samples collected at 0.0 meters from the toe of the ballast contained significantly elevated PAH concentrations (7.5 to 23.1 $\mu\text{g } \Sigma\text{PAH/g}$). Further investigation of the contaminated sample stations revealed a variance to mean ratio of 13 suggesting that the PAH distribution was very patchy. This observation is consistent with the *Particulate PAH Transport Hypothesis* developed by Goyette and Brooks (1998). The concentration of the ΣPAH in two of the 129 sediment samples collected in this study exceeded the Long *et al.* (1995) Apparent Effects Threshold of 13.5 $\mu\text{g } \Sigma\text{PAH/g}$ dry sediment at the observed sediment total organic carbon.

This evidence indicated that very little PAH was migrating from the railway right of way into adjacent wetlands. However, the U.S. Fish and Wildlife Service observed yellowing vegetation adjacent to several derelict creosote treated ties that had previously been taken out of service and discarded in the wetland. Based on this visual evidence, USFWS required the operator to replace the newly installed creosote treated ties with steel ties and to conduct further studies to determine the migration of PAH from railway ties into ballast and adjacent wetlands.

1.1. Soil concentrations of PAH associated with transportation systems.

Transportation systems are inherently dirty with numerous sources of contaminants, including PAH. Bradley *et al.* (1994) characterized background and urban soil concentrations of PAH in the United Kingdom and New England soils respectively. Bardley *et al.* (1994) reported significantly higher ($\alpha = 0.05$) concentrations of PAH near pavement (21.9 $\mu\text{g } \Sigma\text{PAH/g}$) when compared with areas far from pavement (8.3 $\mu\text{g } \Sigma\text{PAH/g}$).

1.2. **Fate of PAH in the environment.** Polycyclic aromatic hydrocarbons form a family of compounds whose routes of degradation and fates vary. In water, PAHs evaporate, disperse into the water column, become incorporated into bottom sediments, concentrate in aquatic biota, or experience chemical and biological degradation. Borthwick and Patrick (1982) estimated the chemical and biological half-life of the dissolved components of marine grade creosote at less than one week in laboratory experiments. More recently, Bestari *et al.* (1998a, 1998b) observed an exponential decline in creosote derived PAH released into microcosms. The concentration of PAH in these microcosms reached background levels by the end of their 84-day study.

The most important degradative processes for PAHs in aquatic environments 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 chemical and biological degradation.

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 bacteria, fungi and algae (EPA, 1980; Borthwick and Patrick, 1982; Cerniglia, 1984; Boldrin *et al.* 1993). Mueller *et al.* (1991) found that natural microbial communities mineralized 94% of the low molecular weight PAH in 14 days but only 53% of the high molecular weight PAHs

were degraded during the same period. They also noted that the most rapid biodegradation of PAHs occurred 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. Naphthalene has a short turnover time (hours to days) whereas the five ringed benzo(a)pyrene has a long turn over time (years under unfavorable conditions). However, Kanaly and Bartha (1999) demonstrated significant biodegradation of B(a)P in the presence of complex hydrocarbon mixtures. Crude oil, distillates of heating oil, jet fuel and diesel fuel supported up to 60% mineralization of 80 μg B(a)P/g soil in 40 days. Millette *et al.* (1995) also demonstrated the interdependence and cometabolism of mixtures of creosote derived PAH following an initial lag time of 5 to 7 days during which the natural microbial community was selected for those phenotypes capable of more efficiently metabolizing PAH. In this study, 60 to 75% of the phenanthrene was mineralized within 30 days. This suggests that in the presence of complex cometabolites (such as would be found in wetlands), phenanthrene, which comprises 19.4% of new creosote oil, may be rapidly lost from the matrix of PAH that move from treated wood into natural environments.

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. Neff (1979) attempted to integrate the degradative processes associated with PAH removal from aquatic environments. He concluded that the residence time of PAH in water is brief. The lower molecular weight aromatics (benzene to phenanthrene) are removed primarily by evaporation and microbial activity. Higher molecular weight PAHs 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. However, in anaerobic sediments, the heavier molecular weight PAH (4 through 7 rings) may persist for years.

1.3. Characterization of the PAH spectrum observed in environmental samples associated with different sources. Khalili *et al.* (1995), Sing *et al.* (1993), O'Malley *et al.* (1996), Dickhut and Gustafson (1995) and Bender *et al.* (1987) characterized the spectrum of PAH compounds associated with a variety of sources. Their data is combined with results presented for weathered PAH deposits in sediments adjacent to marine piling installed in a pristine marine environment by Goyette and Brooks (1998) in Figure (1).

The Midwest Generation rail line carries coal into the Will County power station. As seen in Figure (1) coal contains significant quantities of low molecular weight PAH including naphthalene, fluorene, phenanthrene, fluoranthene and pyrene. The other sources involve PAH subjected to high temperatures such as in crankcase oil, diesel exhaust and atmospheric deposition. Sediment samples collected 384 days following construction of a creosote treated dolphin (Goyette and Brooks, 1998) are presented in red columns in Figure (1). The creosote spectrum is dominated by fluoranthene and other intermediate weight PAH (phenanthrene to benzo(b or k) fluoranthene). Low molecular weight PAH represented less than two percent of the total PAH and compounds heavier than benzo(b or k)fluoranthene contributed little to the overall spectrum. In contrast, the PAH in crankcase oil are dominated by higher molecular weight compounds. The relative importance of phenanthrene and fluoranthene are reversed in highway runoff when compared with creosote. The suite of compounds associated with atmospheric deposition is similar to creosote derived PAH. However, atmospheric deposition typically results in a spatially uniform PAH distribution at levels less than 1.0 μg PAH/g.

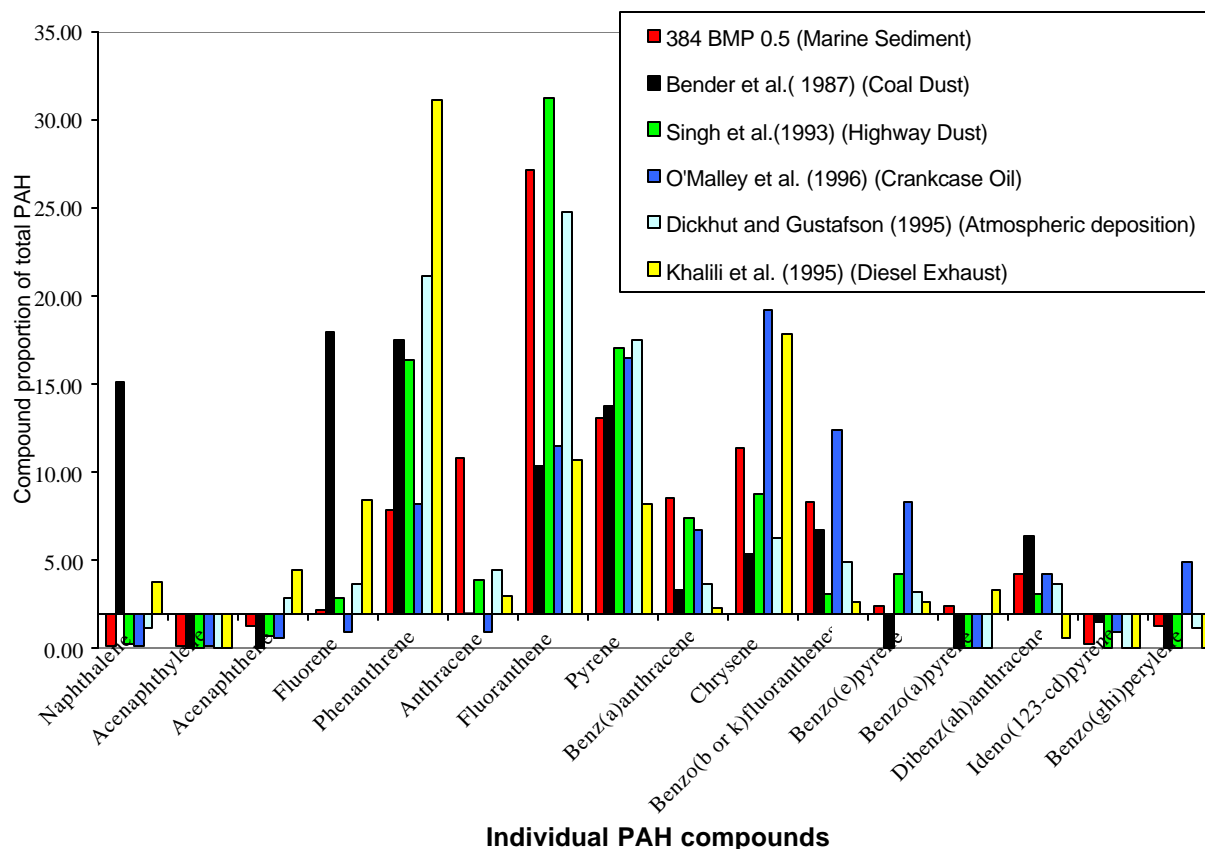


Figure 1. Polycyclic aromatic hydrocarbon profiles associated with a variety of sources.

1.4. Weathering of creosote derived PAH. Ingram *et al.* (1982) observed increasing PAH concentrations in their static leaching tests of creosote treated piling for approximately 72 hours. The concentrations then declined exponentially. The authors hypothesized that the decreases were due to photodegradation and catabolism by microbes. In a more recent article, Bestari, *et al.* (1998a 1998b) observed significant decreases in dissolved PAH concentrations in a series of static leaching tests which immersed between 0.5 and six piling in 12,000 liter microcosms. Initial concentrations as high as 97 $\mu\text{g } \Sigma\text{PAH/L}$ in these static systems decreased to less than ten $\mu\text{g } \Sigma\text{PAH/L}$ at the end of 85 days with no significant increases in sediment concentrations or uptake by the polyethylene liners used in the microcosms. Those authors also attributed the exponential declines to photodegradation and microbial catabolism. Colwell (1986) identified bacteria isolates that were responsible for the degradation of creosote derived PAH in marine environments. Since then, a rich literature has evolved describing the microbial catabolism of PAH by bacteria and fungi. Much of that literature is devoted to the growing field of biological remediation at PAH contaminated sites. For instance Mueller *et al.* (1991) described the biodegradation of creosote contaminants by methanogenic bacteria in anaerobic environments; Lamar *et al.* (1994) reported on the degradation of creosote by fungi and DeLaune *et al.* (1990) discussed the fate of hydrocarbons, including creosote, in Louisiana coastal environments. They noted that microbial degradation determines the fate of sedimented creosote more than other factors and discussed factors determining catabolic rates. The degradation of creosote by photo-oxidation and microbial catabolism is well studied and verified.

Brooks (1997a) reviewed the microbial degradation of polycyclic aromatic hydrocarbons and developed algorithms for estimating the degradation of sedimented PAH as a function of temperature and ambient oxygen levels. Goyette and Brooks (1998) reported that the proportion of low molecular weight PAH compounds decreased significantly during the creosote treating process. The PAH lost from freshly treated piling were rich in the intermediate weight compounds, particularly phenanthrene and fluoranthene. As sedimented PAH weathered, phenanthrene was reduced but remained at ca 13% of the total. Fluoranthene was degraded but at a slower rate than phenanthrene. At the end of four years (1360 days following construction), the creosote derived PAH were dominated by fluoranthene. However, phenanthrene, pyrene, benzo(a)anthracene, chrysene and benzo(b and k)fluoranthenes each represented approximately 10% of the total. PAH compounds lighter than phenanthrene were weathered to very low concentrations and those heavier than benzo(b and k) fluoranthene remained at low concentrations similar to those found in the raw oil and/or newly treated wood. These results are summarized in Figure (2).

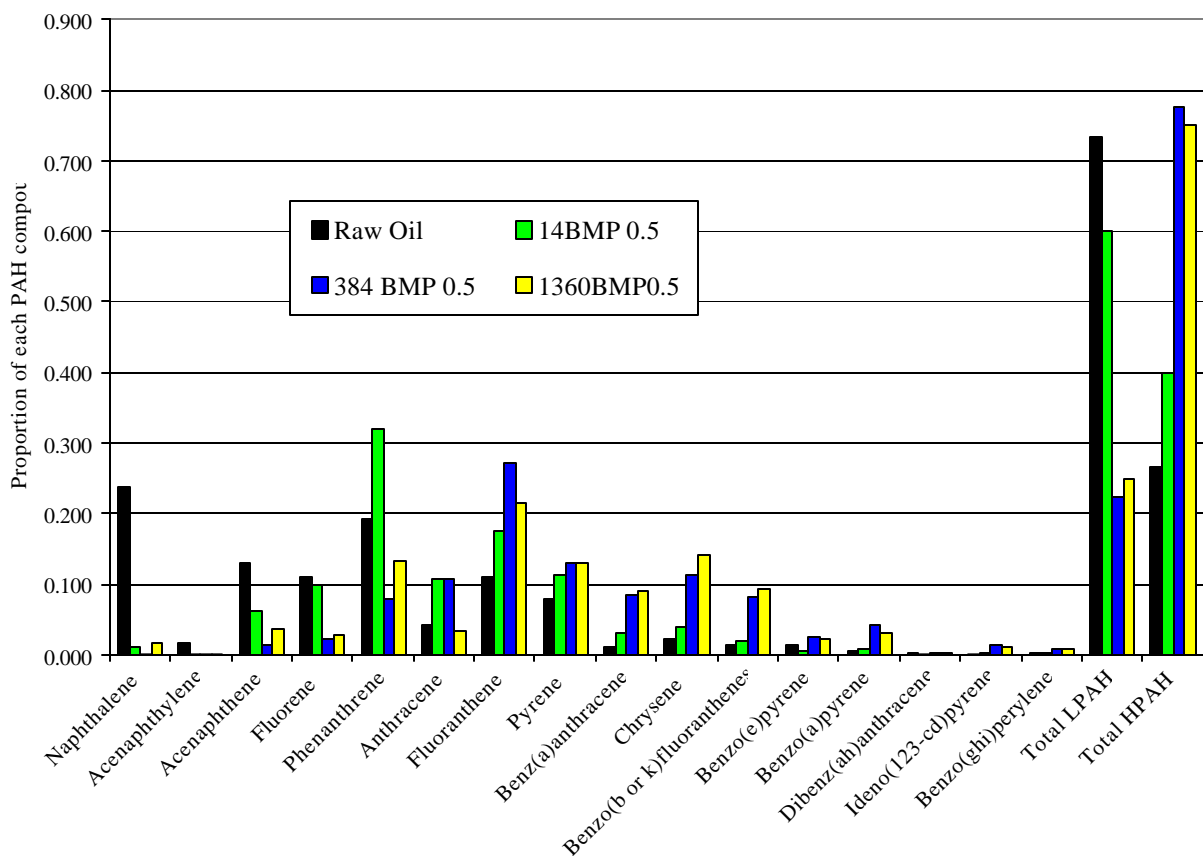


Figure 2. Changing composition of weathering creosote in marine sediments.

Bestari *et al.* (1998a, 1998b) observed similar results in microcosm studies with either unused creosote oil or pressure treated piling. In their studies, the PAH spectrum also shifted from low to heavier weight compounds. At the end of 84 days, sediments contaminated with liquid creosote by Bestari *et al.* (1998a) were dominated by phenanthrene, fluoranthene, pyrene and chrysene with very low concentrations of other compounds. Bestari *et al.* (1998b) observed

a similar PAH distribution at the end of 68 days in microcosms containing piling freshly treated with creosote.

Burns *et al.* (1997) fingerprinted 18 possible sources of PAH in association with the Exxon Valdez oil spill in Alaska. They also found that the suite of PAH in sediments next to creosote treated piling in Crab Bay were dominated by phenanthrene, fluoranthene, pyrene and chrysene. All of these studies found very low proportions of PAH compounds heavier than benzo(b or k)fluoranthene.

Wan (1991) and Ernst (1994) examined sediments adjacent to operating railway rights of way in British Columbia and adjacent to a creosoted wharf structure in Nova Scotia. The spectra are similar except that more naphthalene was found adjacent to the railway rights of way than adjacent to the creosote treated structures located in marine environments. That is likely due to the presence of diesel fuel and coal dust, both of which contain higher proportions of the lower molecular weight PAH and are associated with rail lines in the lower mainland of British Columbia.

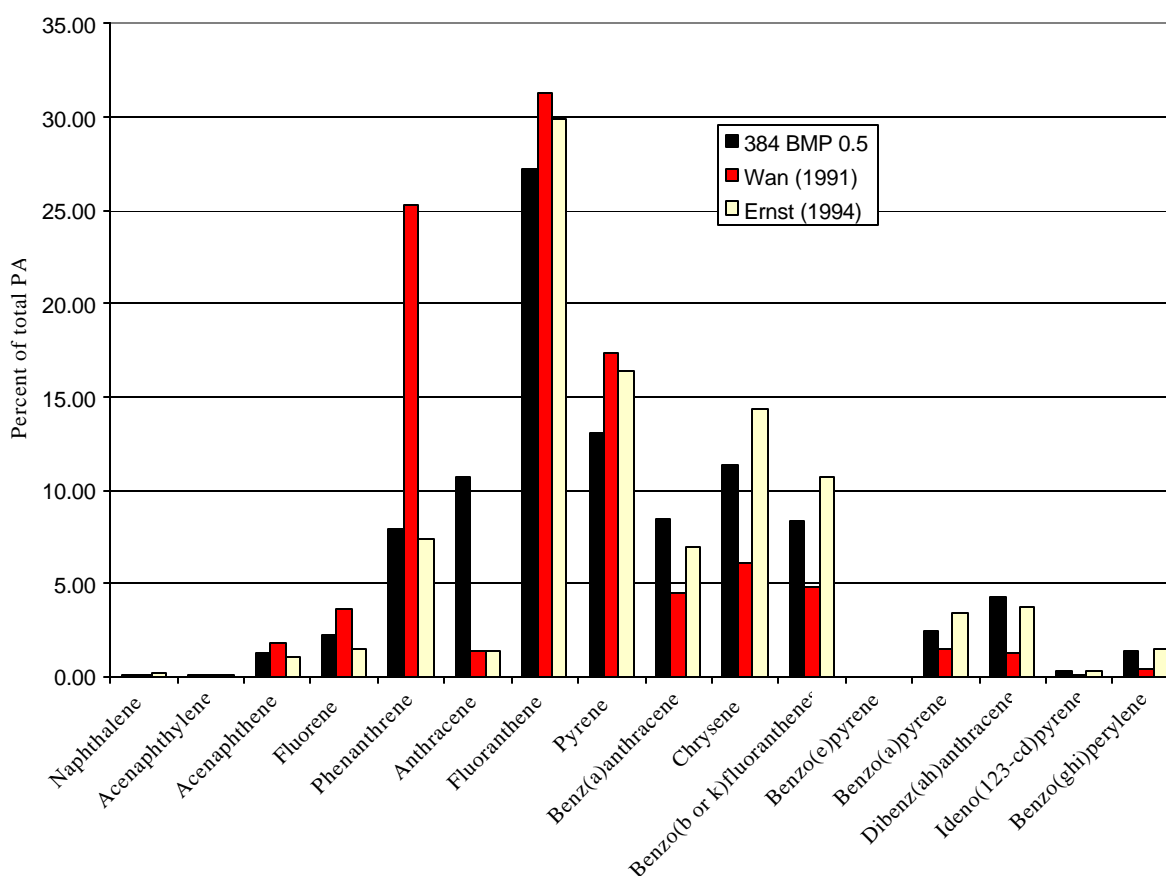


Figure 3. Proportion of PAH compounds associated with creosote treated piling (384 BMP 0.5) and railway rights-of-way in the lower mainland of British Columbia (Wan, 1991) with sedimented PAH adjacent to a creosote wharf structure in Nova Scotia (Ernst, 1994)

The preceding discussion is important in that it clearly demonstrates that the suite of PAH associated with recent (<4 year old) losses from creosote treated wood are dominated by phenanthrene, fluoranthene, pyrene and chrysene with lesser amounts of benzo(a)anthracene and benzo(b or k) fluoranthene. Other compounds are found only at very low concentrations.

1.6. PAH toxicity in freshwater. Because PAH heavier than naphthalene are so hydrophobic, they are generally found at extremely low concentrations in freshwater and have little potential to create acute or chronic stress in aquatic communities. Suter and Tsao (1996) and Swartz (1999) summarized conventional benchmarks for priority contaminants in freshwater. These values are summarized in $\mu\text{g/L}$ in Table (1). Because daphnids and dragonflies (Odonata) are both arthropods, the lowest daphnid chronic values are presented from Suter and Tsao (1996).

Table 1. Summary of consensus LC₅₀ values for sediment PAH compounds from Swartz (1999) and lowest daphnid dissolved PAH chronic values reported by Suter and Tsao (1996).

Compound	Swartz (1999) LC ₅₀ ($\mu\text{g/g}$)	Suter & Tsao (1996) lowest daphnid chronic value ($\mu\text{g/L}$)
Naphthalene	71	1,163
Acenaphthylene	15	Not Given
Acenaphthene	23	6,646
Fluorene	90	Not Given
Phenanthrene	155	200
Anthracene	114	<2.1
Fluoranthene	371	15
Pyrene	481	Not Given
Benz(a)anthracene	111	0.65
Chrysene	169	Not Given
Benzo(b)fluoranthene	180	Not Given
Benzo(k)fluoranthene	155	Not Given
Benzo(a)pyrene	179	0.30
Low molecular weight PAH	468	
High molecular weight PAH	1646	
Total PAH	2114	

The data presented in U.S. EPA (1993) suggests that at least some odonates are not particularly susceptible to polycyclic aromatic hydrocarbon intoxication. As an example, *Ophiogomphus sp.* has a UV photoenhanced fluoranthene LC₅₀ of 109.7 $\mu\text{g/L}$. This UV exposed acute value is much higher than the values of 1.0 to 3.0 μg UV enhanced anthracene or fluoranthene/L observed to cause mortality in other organisms. The point is that the available evidence suggests that this order may be more robust to PAH contamination than are other, more sensitive, species.

Toxicity associated with mixtures of compounds can be additive, antagonistic or synergistic. This is true of mixtures of PAH, which appear to have slightly less than additive toxicity. For instance, the LC₅₀ for rainbow trout (*Oncorhynchus mykiss*) associated with fluoranthene is >90.5 $\mu\text{g/L}$. The LC₅₀ for rainbow trout subjected to whole creosote oil is nearly ten times as high at 880 $\mu\text{g/L}$ (Polisini, 1994). Padma *et al.* (1998) examined the toxicity of the water soluble fraction of creosote to the mysid (*Mysidopsis bahia*) and found median lethal concentrations (expressed as total identified aromatic hydrocarbons) of 180 $\mu\text{g/L}$. For purposes of evaluating dissolved PAH, this study will use the ΣPAH model of Swartz *et al.* (1995), which assumes additive toxicity. This discussion suggests that this is likely an overly conservative assumption for creosote.

1.7. PAH toxicity summary. The low molecular weight PAHs such as naphthalene and acenaphthene produce acute toxic effects in aquatic organisms because they are more soluble than the higher molecular weight compounds. Acute intoxication in the sensitive larval stages of marine invertebrates may occur at water column concentrations as low as 8 to 10 $\mu\text{g/L}$. However, for most species, the literature suggests that water column concentrations of greater than 20 $\mu\text{g/L}$ are required for significant responses. Low molecular weight PAHs are more soluble than the high molecular weight compounds and bacteria and other aquatic organisms more rapidly metabolize them. The potential for their accumulation to toxic levels is 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 $\mu\text{g}\cdot\text{L}^{-1}$ in the water column.

Because of their decreased 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 $\text{mg}\cdot\text{kg}^{-1}$ have been shown to cause significant impacts on populations of the most sensitive taxa (Tagatz *et al.*, 1983). 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. The literature suggests that chronic stress can occur in organisms, including bivalves at concentrations as low as 30 to 40 $\mu\text{g}\Sigma\text{PAH/L}$. 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 PAH (particularly B[a]P) to form carcinogenic, mutagenic and teratogenic compounds during metabolism by crustaceans and vertebrates. Neff (1979) summarized 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 studies describe increases in the number of hepatic lesions and carcinomas with sediment ΣPAH burdens as low as seven to 10 $\text{mg}\cdot\text{kg}^{-1}$.

Goyette and Brooks (1998) hypothesized that PAH are transported to sediments in micro particles or micro liter size droplets. Preliminary laboratory studies (Brooks, unpublished data) have substantiated this hypothesis. Micro liter quantities of PAH released beneath the air-water interface settled to the bottom of graduated cylinders with speeds that appear consistent with those predicted by Stokes' equation. Furthermore, the particles settled into either quartz sand or crushed oyster shell substrates and remained intact for at least two years. Small quantities of creosote oil injected above the air-water interface formed sheens on the water's surface. These sheens remained intact until the water was disturbed as would be created by waves. The sheen then broke up into small, irregularly shaped, particles that settled to the bottom and worked their way into the sediments. Milliliter quantities of creosote oil injected under the air-water interface settled to the bottom of glass vials where they retained their ellipsoidal shape for periods of up to two years. If the vials were vigorously shaken, the larger droplets broke up into smaller particles – some of which adhered to the sides of the vials. These studies used distilled water and sterilized substrates to prevent bacterial degradation of the creosote particles.

This hypothesis, if substantiated, will significantly change science's approach to assessing the toxicity of creosote-contaminated sediments. Infauna, rather than being subjected

to an environment that is uniformly contaminated by a diffuse pattern of PAH would be confronted with an environment that is dominantly uncontaminated with foci of high contamination. In this scenario, exposure is best described stochastically with consideration for possible avoidance or attraction to the PAH foci by various organisms. This hypothesis would explain the extreme patchiness of PAH concentrations found in associated with PAH contaminated sediments. It would also help explain why mixtures of PAH, like creosote, are found to be less toxic than an additive toxicity assumption would predict (Tagatz *et al.* 1983; California EPA, 1994). Lastly, this hypothesis would explain the presence of cm^2 sized microspheres observed to depths of 4 cm in creosote-contaminated sediments at Sooke Basin (Goyette and Brooks, 1998).

1.8. Recommended numerical benchmarks for evaluating the environmental risks associated with PAH. Numerous jurisdictions have established benchmarks for evaluating the human health and environmental risks associated with polycyclic aromatic hydrocarbons in aquatic environments. Washington State (WAC 173-204) has published sediment quality standards for individual PAH and for the sum of low and high molecular weight compounds. In addition, the U.S. EPA has proposed, but not adopted, freshwater criteria for acenaphthene, phenanthrene and fluoranthene. This review did not reveal any final freshwater sediment quality criteria for individual PAH compounds or their mixtures. There are numerous proposals based on the lowest levels at which adverse effects are observed in consolidated databases representing a broad spectrum of environments. The broad application of criteria based on the observance of effects in worst-case environments results in very conservative assessments in those environments not representative of the worst case. In addition, the following discussion assumes that the toxicity of mixtures of PAH is additive. As previously discussed, it appears that toxicity associated with the mixture of PAHs called creosote is significantly less than additive – thereby adding to the conservativeness of the following proposed benchmarks.

1.8.1. Benchmarks for assessing the risk of dissolved PAH. The ΣPAH model in Swartz *et al.* (1995) assigns a <5% probability of mortality greater than 24% for all samples with $\Sigma\text{TU}_i < 0.186$. Swartz *et al.* (1995) stated that, “The ΣPAH Threshold of Acute Toxicity ($\Sigma\text{TU}_i = 0.186, p_{>24} = 0.05$) is the toxic-unit concentration below which mixtures of PAHs are unlikely to contribute to sediment toxicity and above which PAH mixtures increase $p_{>24}$ over background conditions.” Swartz *et al.* (1995) did not distinguish between chronic and acute toxicity in stating that $\Sigma\text{TU} = 0.186$ is an appropriately protective benchmark. The Swartz *et al.* (1995) model was developed, based on equilibrium partitioning, to estimate sediment toxicity for infauna. More importantly, Swartz *et al.* (1995) compared the ΣPAH model with other PAH benchmarks and found that $\Sigma\text{TU} = 0.186$ was equivalent to both the Screening Level Concentration and NOAA’s Effects Range-Low (ER-L). Both the SLC and ER-L are sediment benchmarks below which adverse effects (including chronic effects) are rarely observed (lower 10th percentile of the effects database). The SLC and ER-L are frequently used as benchmarks to determine if sediments require further investigation. Contaminant levels at or below the ER-L or SLC are not considered biologically stressful and generally require no further evaluation.

Swartz *et al.* (1995) assumed additive toxicity for suites of PAH compounds such as found in creosote. However, there is evidence indicating that the PAH in creosote are less than additive in their cumulative toxicity. The California Environmental Protection Agency (California EPA, 1994) determined 96-hr LC_{50} ‘s of 990 $\mu\text{g/L}$ for bluegill (*Lepomis macrochirus*)

and 880 µg/L for rainbow trout (*Oncorhynchus mykiss*) exposed to whole creosote oil. Assuming that the creosote components were present in the bioassay in proportion to that found in whole creosote oil, these LC₅₀'s represent approximately 112 toxic units. Munoz and Tarazona (1993) noted that “when the sum of individual compounds have to be used, the differences in acute toxicities between individual chemicals (and their cumulative action) could be higher than an order of magnitude.”

Application of a 0.1 factor to convert the 96-hr LC₅₀ of 880 µg creosote/L for rainbow trout to a chronic value suggests that 11.2 TU would be a defensible benchmark for creosote. However, the 0.186 TU benchmark suggested by Swartz *et al.* (1995) provides a very conservative value for use in evaluating the risks associated with dissolved PAH. The TU approach is adopted in this assessment because the combined stresses of multiple contaminants may cause environmental effects that would not be expected if the risk of each contaminant were evaluated separately. However, previous cautions regarding the conservative nature of assuming additive toxicity for creosote may make this unnecessarily conservative.

1.8.2. Sediment quality benchmarks for polycyclic aromatic hydrocarbons in aquatic environments. Swartz (1999) examined existing and proposed sediment quality guidelines and proposed *Consensus Guidelines* that appear to resolve some of the current inconsistencies. He described a ΣPAH toxicity threshold that is consistent with the Effects Range Low (ER-L) of Long *et al.*, 1995) and a ΣPAH mixture LC₅₀ that is similar to the Effects Range Median (ER-M) described by the same authors. In this report, sediment concentrations of PAH will be compared with the ΣPAH Toxicity Threshold, the ΣPAH Mixture LC₅₀ and the mean of these two values in predicting biological risk associated with creosote derived PAH. Table (2) summarizes these benchmarks.

Table 2. Summary of the ΣPAH Toxicity Threshold, ΣPAH Mixture LC₅₀ and the mean of these two values for 17 parental PAH. All values are mg·g⁻¹ organic carbon. Values, excepting the mean, are from Swartz (1999).

PAH Compound	Σ PAH Toxicity Threshold	ΣPAH Mixture LC ₅₀	Mean
Naphthalene	13	71	42.0
Acenaphthylene	3	15	9.0
Acenaphthene	4	23	13.5
Fluorene	17	90	48.5
Phenanthrene	29	155	92.0
Anthracene	21	114	67.5
Fluoranthene	69	371	220.0
Pyrene	90	481	285.5
Benz(a)anthracene	21	111	66.0
Chrysene	31	169	100.0
Benzo(b)fluoranthene	33	180	106.5
Benzo(k)fluoranthene	29	155	92.0
Benzo(a)pyrene	33	179	106.0
Low molecular weight PAH	87	468	277.5
High molecular weight PAH	306	1646	976.0
Total PAH	393	2114	1253.5

It should be emphasized that the benchmarks given in Table (2) are not enforceable sediment quality standards. They are simply guideposts for evaluating the effects of contaminants in sediments. Washington State (WAC 173-204) has developed enforceable sediment quality standards (SQS) for marine environments. Draft Rule Amendments to these standards were distributed in June of 1999. The new standards include an increase in the low molecular weight PAH standard from 370 mg/kg OC to 593 mg/kg OC and a decrease in the high molecular weight PAH standard from 960 mg/kg OC to 900 mg/kg OC. The sum of these two classes of PAH is proposed to increase from 1330 mg Σ PAH/kg OC to 1493 mg Σ PAH/kg OC.

4.0. Materials and methods. There are many potential sources of PAH associated with railway rights of way (Wan, 1991). These include coal and coal dust from cargo entering a coal-fired plant, herbicides used to control vegetation along rights of way, diesel exhaust from diesel-electric locomotives and heated lubricating oils and greases. These confounding sources of PAH make it very difficult to determine the contribution from creosote treated railway ties along actual rights-of-way. Wan (1991) reported an average PAH concentration of 18.07 g/m² in railway right-of-way ballast. He noted that creosote treated ties, herbicides and locomotive exhaust were likely sources, but did not attempt to partition the observed PAH concentrations into source compartments.

Brooks (1997c) proposed a mesocosm study to examine the migration of creosote from railway rights of way into ballast and adjacent wetlands. A mesocosm design was chosen in an attempt to minimize the other sources of PAH and to focus on those released from new and used creosote treated railway ties. The mesocosm design was designed to closely mimic the railway passing through the Des Plaines River wetland. This study analyzed PAH in ballast, adjacent wetland soils, shallow groundwater and stormwater at quarterly or annual intervals, depending on the type of railway tie treatment, for two years. The U.S. Fish and Wildlife Service and Corps of Engineers reviewed and approved the proposal with minor modification.

4.1. Understanding of the project. The question being asked in this study is, "To what extent do polycyclic aromatic hydrocarbons migrate from creosote treated railway ties into adjacent environments?"

4.2. Mesocosm site selection. An upland site, identified in Figure (4), was chosen for this study. This site was located in a relatively undisturbed area. It lies at an elevation of approximately 28.5' above the Des Plaines River wetland. Wetland soils were excavated (with an appropriate Corps of Engineers Section 404 permit) from the area marked in Figure (4). These wetland soils were 316 (Romeo Silty Clay Loam) as listed in the Soil Conservation Service Soils Inventory for Will County.

Three random surficial soil samples were collected at the mesocosm site on May 6, 1997 and submitted to National Environmental Testing for polycyclic aromatic hydrocarbon (PAH) analysis using EPA Method 8310 following Soxhlet extraction. Harkey and Young (2000) have suggested that Soxhlet extraction overestimates biological effects because aromatic compounds are released from sediments that would not normally be bioavailable. They recommended a supercritical fluid extraction as more representative of actual toxicity. To be conservative, and in light of its long use, Soxhlet extraction was used throughout these studies.

4.3. **Mesocosm design and construction.** A plan view of the mesocosm is provided in Figure (5) and a cross-sectional view in Figure (6). The Corps of Engineer's permit condition required only a comparison of used railway ties with untreated ties. However, a third mesocosm containing new creosote treated cross ties was also evaluated.

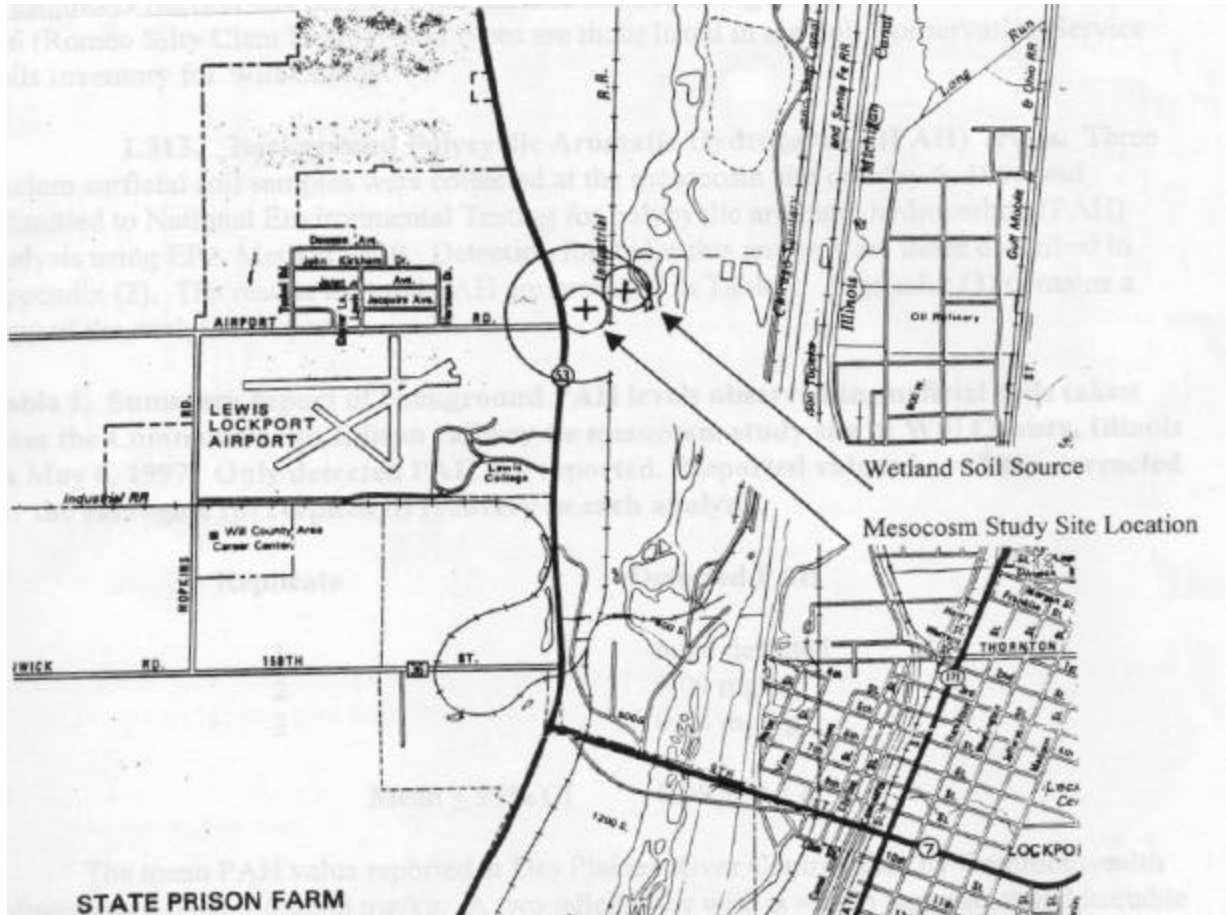


Figure 4. Site plan describing the location of the mesocosms used to evaluate the migration of creosote from new and used railway ties into adjacent ballast, wetland soils, and groundwater.

4.3.1. **Mesocosm liners and subsurface irrigation system** Each mesocosm was isolated from the native soils with a 6 ml polypropylene liner with welded seams to insure that PAHs in water percolating down through the mesocosm were contained. This allowed for an understanding of the bulk loss of PAH from the railway ties to underlying groundwater. In addition, the impermeable membrane prevented shallow groundwater, or stormwater, from transporting PAH laterally out of the mesocosms. The liner was bedded in sand to prevent underlying rocks from compromising it. The impermeable membrane also helped to retain natural rainfall – maintaining wetland hydrology. Additional water was made available through an underground delivery system mimicking ground water that flows in fractured limestone under the Des Plaines River wetland. To accomplish this, the design included a 1,000 gallon water tank, supply lines and float valves to maintain soil moisture at a level mimicking that found in the wetland adjacent to the actual rail line.

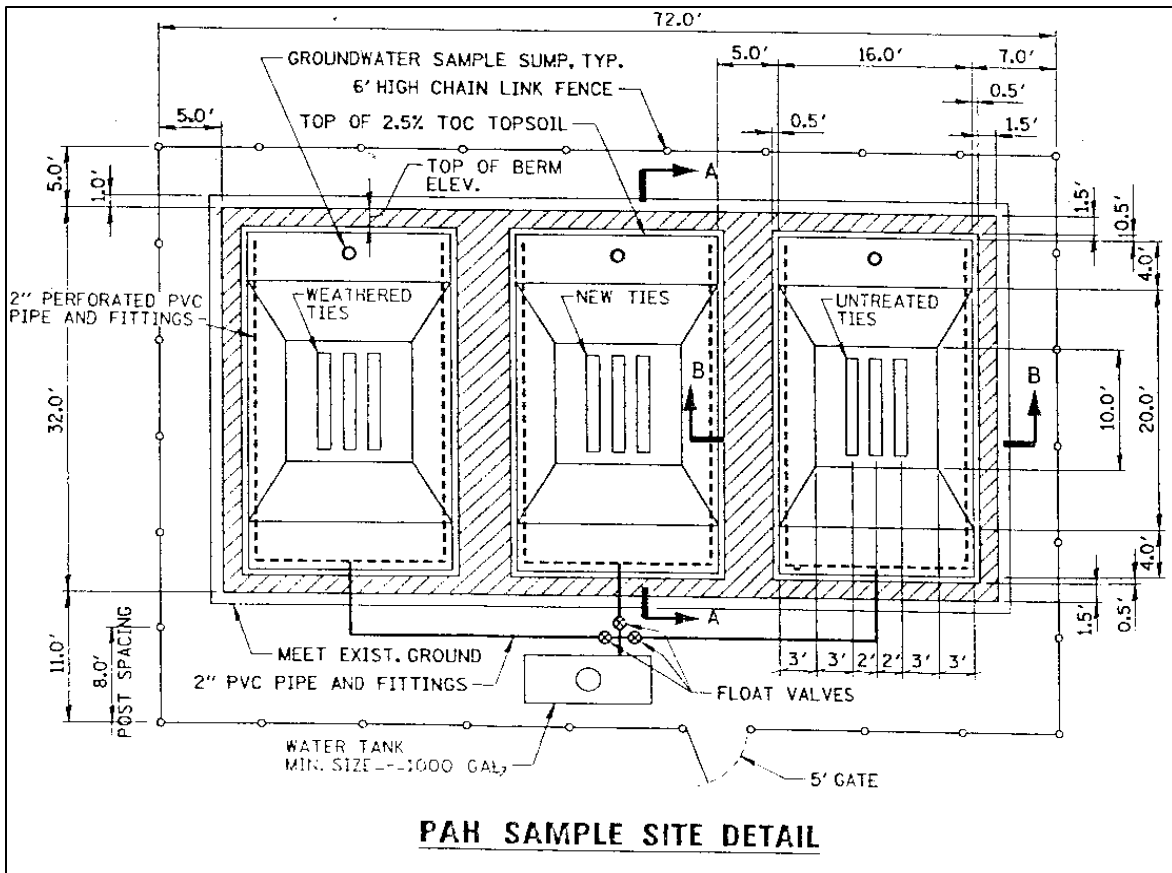


Figure 5. Plan view of the mesocosm used to examine PAH migration from used and new creosote treated railway ties and from untreated controls.

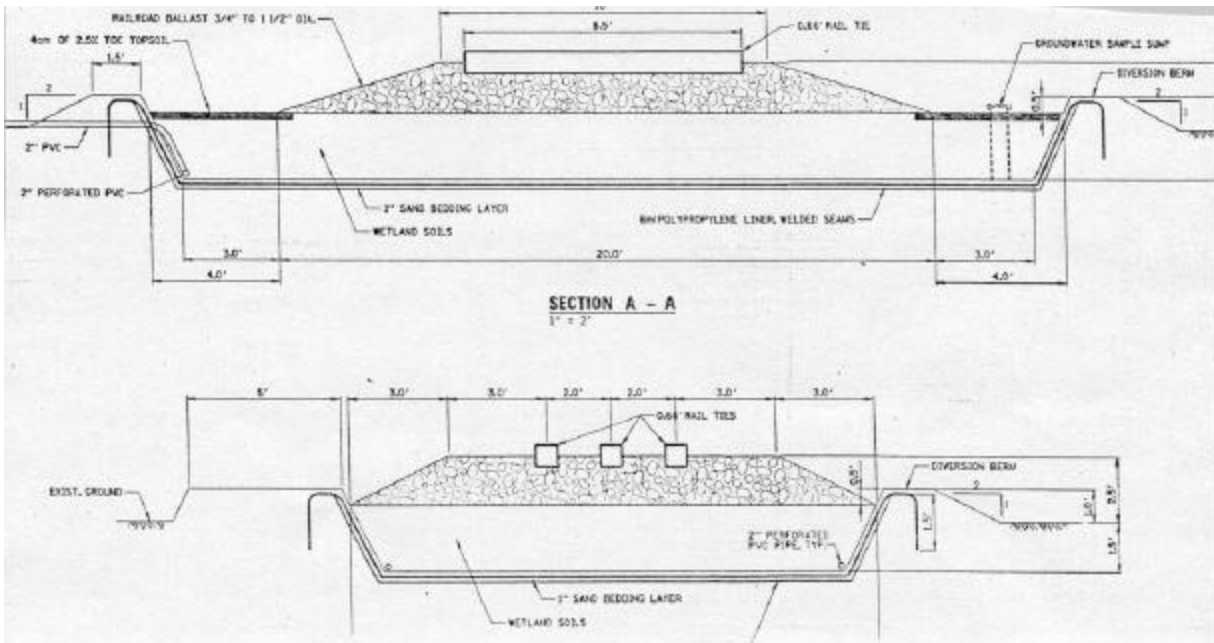


Figure 6. Cross-sectional view of one of three mesocosm compartments used to examine PAH migration from used and new creosote treated railway ties and from untreated controls.

Following installation of the liner and subsurface irrigation system, each mesocosm was filled to a depth of 60 cm with native wetland soil, excavated from the area identified in Figure (4). Broken limestone ballast (0.75” to 1.5”) was added to the mesocosms.

Newly treated and weathered ties, removed from the Commonwealth Edison spur, were installed in two of the mesocosms. Untreated hardwood ties, of the same tree species (red oak) were placed in the third mesocosm as a control. The weathered ties were cut to the same length as the new ties and the untreated ties prior to installation. Each mesocosm contained three standard sized crossties placed in a fashion identical to the actual right of way. Each tie was identified with a plastic label. Day (0) samples were collected on the day the ties were placed in the ballast. Figure (7) is a photograph of the mesocosms taken in the fall of 1998.



Figure 7. Commonwealth Edison railway tie mesocosm study site in the Fall of 1998, approximately six months following construction.

Actual creosote retention in the new and old ties was determined by Kerr MaGee – the producer of the newly treated ties. Twelve cores measuring three inches long were taken from each tie (three per longitudinal surface). The mean retention for the three new ties (2.68 pcf) was less than the mean for the three old ties (3.75 pcf), but the differences were not statistically significant at $\alpha = 0.05$ ($t_{crit} = 2.78$ and $t_{calc} = 1.09$).

4.3.2. Volunteer mesocosm vegetation. Mesocosm vegetation was inventoried by Christopher B. Burke Engineering Ltd. on June 29, 1999. Vegetation grew in wetland areas of the mesocosm located on either side of the ballast. The plants growing within each cell were identified and assigned wetland indicator values (W) given in Swink and Wilhelm (1994). These

values range from $W = -5$, indicative of obligate wetland species occurring in wetlands with a probability of >99% to $W = 5$, representing species that are obligate upland species with a probability of being found in wetland areas of <1%. Wetland indicator values ranged between -0.9 and -1.0 in the three mesocosms confirming the wetland environment.

4.3.3. Groundwater sampling. Water did not migrate vertically in these Des Plaines River wetland soils and the sumps collected insufficient amounts of water for sampling during this study – even though the soils remained saturated during the entire study and wetland portions of the mesocosms were periodically inundated during periods of heavy rainfall. Beginning in the summer of 1998, stormwater was collected in deep Pyrex™ beakers inserted into the wetland soils with their tops flush with the surrounding wetland soils.

4.4. Sample collection, schedule and location. Brooks (1997c), provided detailed monitoring protocols for this study taken from PSEP (1996). The following types of samples were collected.

4.4.1. Stormwater. Three stormwater samples were collected from the untreated mesocosm and five samples each from the untreated and weathered tie mesocosms were collected during this study to evaluate the migration of PAH from ballast in surface flows using GC/MS; EPA Method 625. A total of 13 stormwater samples were analyzed for PAH.

4.5.2. Sediment samples for PAH analysis in mesocosm wetland soils at distances of 0.0, 0.25, 0.50 and 0.75 meters from the edge of the ballast along three transects in each mesocosm (HPLC; EPA Method 8310). A total of 229 surficial wetland sediment samples (upper 2 cm) were collected and analyzed for 16 priority PAH.

4.5.3. Ballast rock was collected for PAH analysis at distances of 5, 20 and 30 cm from the east or west face of each tie (HPLC; Modified EPA Method 8310). One hundred seventy-four ballast samples were collected and analyzed.

4.5.4. Core samples were collected at 10 cm intervals to the full depth of the ballast and wetland sediments at the end of the study. These core sections were analyzed individually for PAH to determine the potential for vertical migration (HPLC; EPA Method 8310). Thirty-six ballast core samples were collected from two locations in each mesocosm and 11 wetland sediment core samples were collected at the zero station in the New Tie Mesocosm.

4.5.5. Stormwater and ground water sampling. A field (battery operated) peristaltic pump was used for all water sampling. All tubing, excepting a short section of tubing for the pump was made of Teflon or glass. Separate tubing was used for each mesocosm ground water sample and for each stormwater sample. Replicate samples within the same mesocosm were obtained using the same tubing.

4.5.6. Laboratory QA/QC. National Environmental Testing is an Illinois State Accredited Laboratory. All of the detection limits provided by NET were less than, or equal to, the recommended detection limits (0.020 to 0.100 µg/g) defined in PSEP (1996). Most QC requirements were met using standard protocols. However, the matrix spike of ballast (3/4” to

1.5” stones) is an unusual requirement. National Environmental Testing verified their extraction procedures for ballast using spiked samples prior to evaluating samples collected from the mesocosms during the baseline evaluation. The following QA program was required for each batch of PAH analyses (batches not to exceed 20 samples). Quality assurance results will be discussed in a later section of this report

QC Requirement	Data Qualifier Criteria
Method Blank (1 per batch)	None detected in blanks
Replicates (1 per batch)	$\leq 100\%$ Relative percent difference
Matrix Spike (1 per batch)	50 to 150 % matrix spike recovery
Surrogate in all samples and QC samples	$\pm 95\%$ Confidence Interval

4.5.7. **Field QA/QC.** One randomly chosen field replicate for ground water sampling in each mesocosm and one random field replicate for the wetland soil sampling was required during each sample period. No field replicates were collected for the ballast samples because this would use too many sample locations requiring resampling of the same location during the study. Container Blanks, Field Blanks, Preservation Blanks, Rinsate Blanks and Trip Blanks were not required for this study. A temperature blank was included in each cooler and the temperature of the cooler determined on receipt at NET.

5.0. Physicochemical results. The mesocosms were constructed without significant PAH contamination. In other words, this study started with a relatively clean PAH slate. Polycyclic aromatic hydrocarbons, in a profile characteristic of creosote, were observed in ballast immediately adjacent to the newly treated ties within ten days. A single sample of ballast from the untreated tie mesocosm also contained significantly elevated levels of PAH on August 18, 1998. Since there were no known sources of PAH in the untreated tie mesocosm, this suggested that care must be taken in evaluating PAH data to not give too much weight to single samples that are different from trends or other replicates.

5.1. **Data quality assurance.** Five of the 450 PAH analyses (1.1%) were excluded from the database because the observed distribution of individual compounds was not characteristic of the suite of PAH compounds observed in association with creosote treated wood products. One sediment sample in the Untreated Tie mesocosm contained 35 μg naphthalene/g dry sediment with no other PAH observed. This sample was likely contaminated during collection or analysis. The spectra of PAH compounds observed in the other four excluded samples is compared with the suite of PAH observed in several year old aged creosote deposits in Figure (8). Three of the remaining four samples were collected in the Weathered Tie mesocosm and one sample was collected in the New Tie mesocosm. Dominant compounds in creosote, including phenanthrene, anthracene and fluoranthene were either absent or detected at low levels in these samples. The spectrum of PAH in the excluded samples was dominated by benz(a)anthracene, chrysene, benzo(b or k)fluoranthene, benzo(a or e)pyrene and/or benzo(ghi)perylene. As noted in Sections 1.4 and 1.5, this spectrum is more likely associated with crankcase oil or with very old (>5 to 10 years) creosote derived PAH. They are not associated with one to three year old creosote deposits. The remainder of this analysis excludes these five samples.

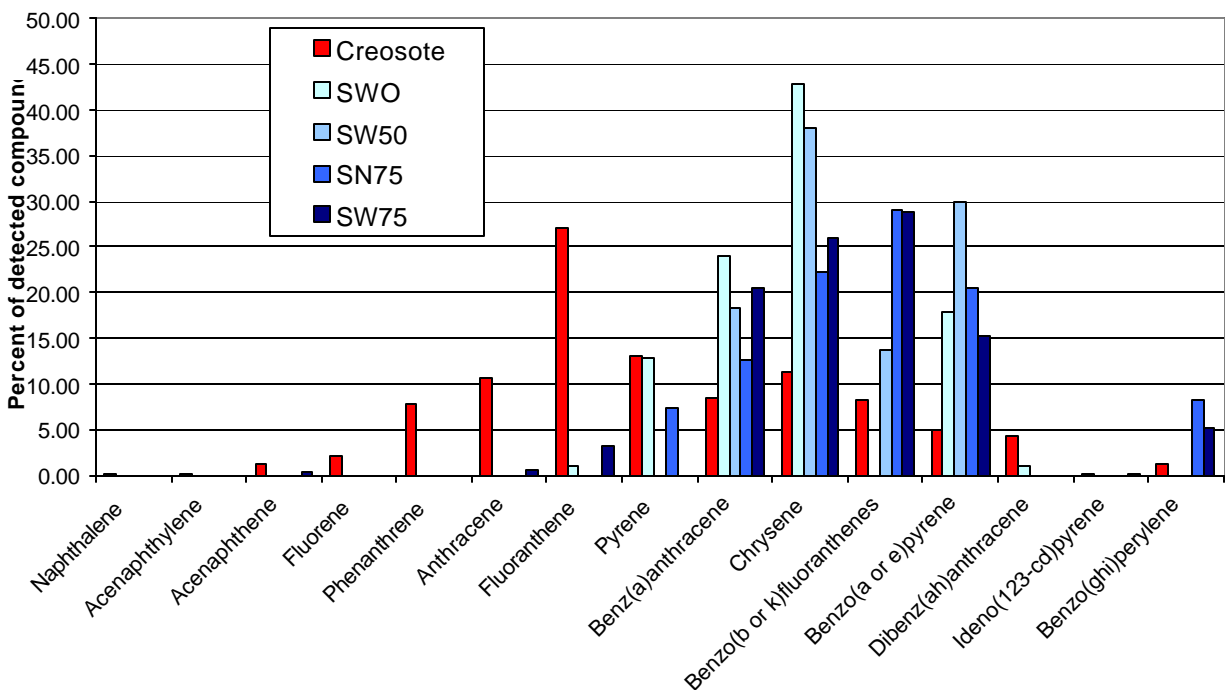


Figure 8. Comparison of 1320 day aged creosote derived mixtures of PAH in sediments with the PAH spectrum observed in samples excluded from the mesocosm study database.

5.2. Polycyclic aromatic hydrocarbons in ballast. Polycyclic aromatic hydrocarbons appeared to migrate from the new creosote treated ties into adjacent ballast during the first summer following placement. The maximum concentration in ballast reached ca. 1000 μg $\Sigma\text{PAH/g}$ dry ballast within 5 cm of the face of newly treated ties on August 18, 1998. Concentrations declined with distance but remained high at 20 cm. The initially high ballast PAH concentrations declined significantly during the remainder of the study. A second pulse of PAH was not observed during the second summer of this study and significant PAH loss from the ties appeared restricted to the first period of high temperatures. Creosote treated wood is black and is expected to behave much like a black body – absorbing a broad spectrum of solar radiation. The thermal expansion may have brought creosote oil to the surface where it was more available to migrate into the ballast. Polycyclic aromatic hydrocarbons migrating into the crushed limestone ballast would most likely evaporate and be chemically and photochemically degraded in the dry, porous ballast environment. Little microbial degradation was expected in ballast. Figure (9) is a three dimensional contour plot constructed using a distance weighted least squares algorithm. It describes the spatial and temporal distribution of PAH in limestone ballast supporting newly treated railway ties during the 555 days of this study.

Other than one sample, significantly elevated concentrations of PAH were not observed in the Untreated tie Mesocosm. As described in Figure (10), a small pulse of PAH was also observed in ballast immediately adjacent to the Weathered Ties during the first summer. However, the PAH concentrations were low with a maximum observed mean concentration of $1.489 \pm 2.918 \mu\text{g} \Sigma\text{PAH/g}$ ballast.

PAH in ballast next to newly treated ties

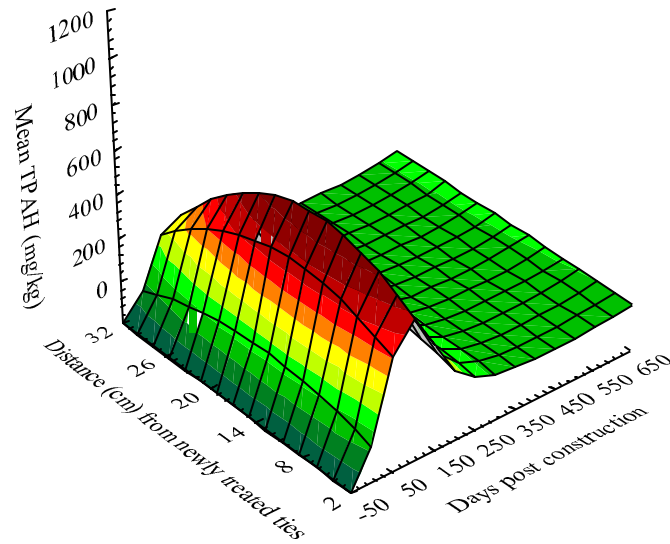


Figure 9. Spatial and temporal trends in the concentration of polycyclic aromatic hydrocarbons observed in ballast adjacent to newly treated railway ties during the first 555 days following construction.

3D Surface Plot of PAH in ballast next to old ties

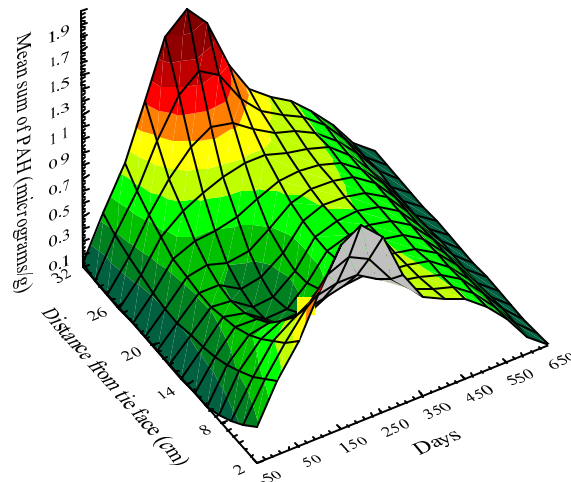


Figure 10. Spatial and temporal trends in the concentration of polycyclic aromatic hydrocarbons observed in ballast adjacent to old, weathered railway ties during the first 555 days following construction.

5.3. Polycyclic aromatic hydrocarbons in wetland sediments. Concentrations of the Σ PAH varied with time and distance in all three mesocosms. The Σ PAH values used in this analysis assumes that undetected compounds were present at the detection limit. That assumption is likely overly conservative and will be discussed in a subsequent section of this report. The spatial and temporal profiles associated with PAH in wetland sediments are described in Figure (11) for the untreated and weathered tie mesocosms and in Figure (12) for the newly treated tie mesocosm. In general, the concentration of PAH increased during the summer of the second year of the study. Wetland sediment concentrations then declined in the New Tie and Untreated Tie mesocosms but remained slightly elevated at the zero meter ($1.708 \pm 0.421 \mu\text{g } \Sigma\text{PAH/g}$) and 0.75 meter ($3.435 \pm 2.860 \mu\text{g } \Sigma\text{PAH/g}$) stations. Values are mean \pm 95% confidence intervals.

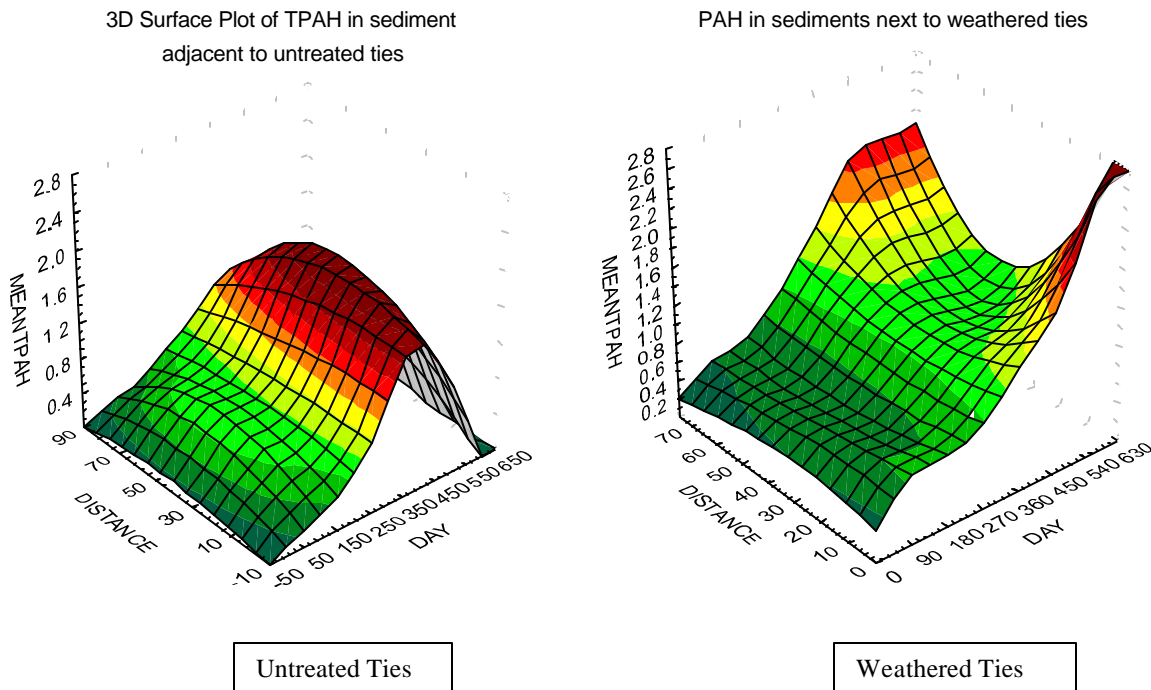


Figure 11. Spatial and temporal distribution of the SPAH observed in sediments from the Untreated Tie Mesocosm and the Weathered Tie Mesocosm.

The highest concentration of sedimented PAH ($3.945 \mu\text{g } \Sigma\text{PAH/g}$) was observed in the Newly Treated Tie mesocosm on August 24, 1999 at the furthest station from the ballast (75 cm). The variance to mean ratio for these three samples was 1.46 suggesting a slightly more patchy distribution than would be expected from a randomly distributed variable. Sediment concentrations declined in November 1999 to between 0.209 and $1.357 \mu\text{g } \Sigma\text{PAH/g}$ dry sediment. November 1999 sediment PAH concentrations observed in the New Tie Mesocosm were less than those observed in the Untreated Tie Mesocosm (0.486 to 1.541). However, the difference was not significant at $\alpha = 0.05$.

Goyette and Brooks (1998) presented evidence suggesting that creosote remains in a particulate form in sediments and that these particles gradually work their way downward – or that they adhere to inorganic and organic surfaces such as algae and cobbles or gravel. Brooks (unpublished data) has observed that microspheres or particles of creosote oil remain intact in sterile substrates for periods up to two years. The patchy distribution of PAH observed in this

study (variance to mean ratios $\gg 1$) is consistent with observations in Sooke Basin and supports the particulate transport hypothesis for creosote derived PAH.

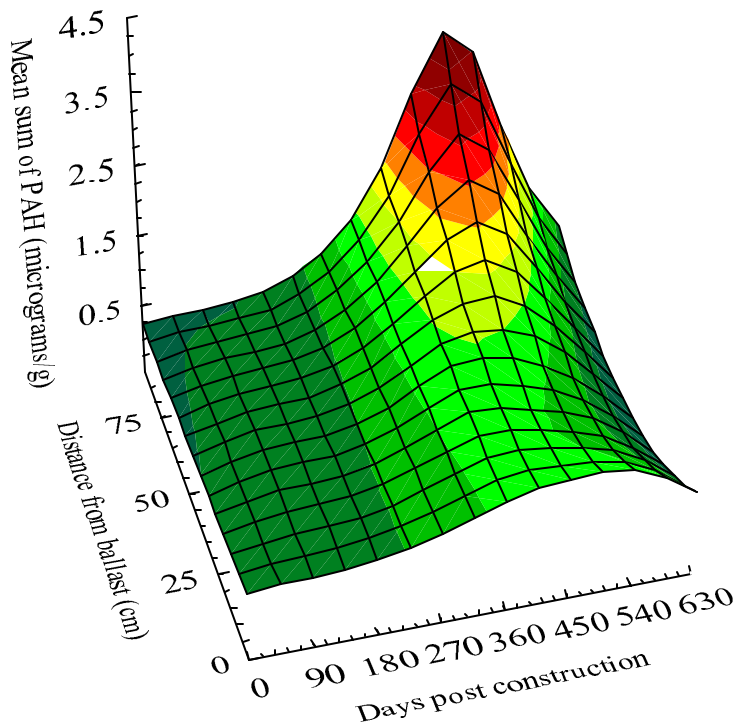


Figure 12. Spatial and temporal distribution of the SPAH observed in sediments from the Newly Treated Tie mesocosm.

Observed differences in mean Σ PAH values were not significantly different as a function of the sample's distance from the face of the tie (ANOVA, $F = 0.33$, $p = 0.96$). These relationships are described in Figure (13). Mean Σ PAH values were also not significantly different between Treatments (ANOVA, $F = 0.76$, $p = 0.72$). However, these differences were significantly different as a function of Day (ANOVA, $F = 12.46$, $p = 0.000$). These differences are described in Figure (14) using box and whisker plots for each treatment as a function of time. This suggests that seasonal changes in wetland sediment concentrations of PAH were not associated with the presence of the ties but rather with atmospheric deposition, which would affect all of the mesocosm treatments and all distances equally – as was observed.

The preceding summary was based on the conservative assumption that undetected PAH compounds were present at the analytical detection limit. Figure (15) describes the relationship between the reported Σ PAH concentrations and only the detected PAH. The apparent seasonal trend in observed differences may be associated with the proportion solids in the samples, which changes with water content and therefore with season. This analytical phenomenon was not investigated as part of the study. Each value is the mean for all treatments and distances on each day. This is considered a valid grouping because significant differences were not observed as a function of either treatment or distance.

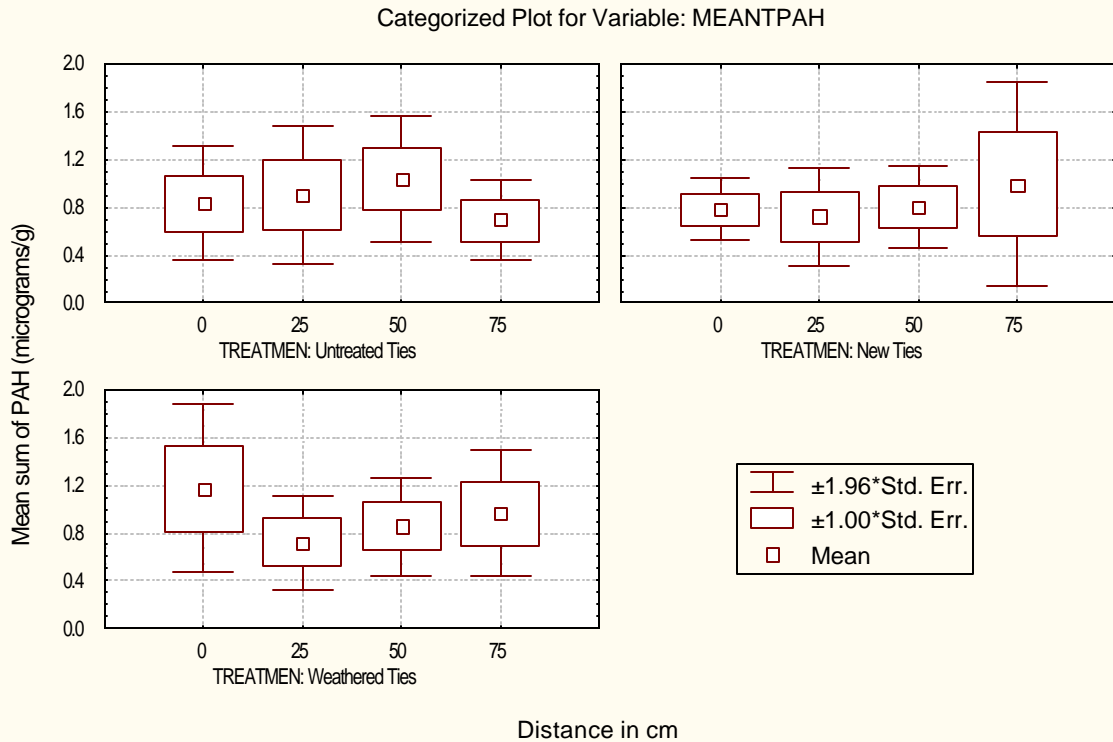


Figure 13. Box and whisker plots describing the non-significant differences in mean SPAH concentrations in sediments as a function of distance from railway tie faces and tie treatment.

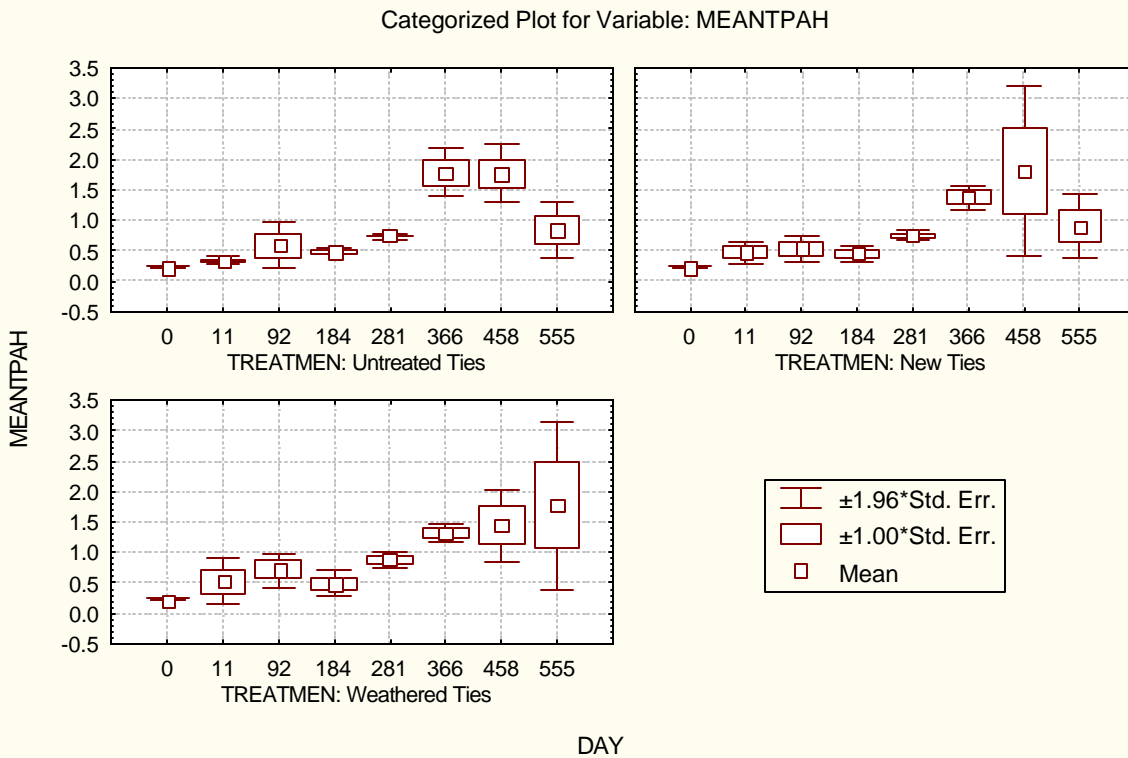


Figure 14. Box and whisker plots describing the significant (Anova, $p = 0.000$) differences in mean SPAH concentrations in sediments as a function of time following placement of untreated oak ties and newly treated or weathered oak ties preserved with creosote.

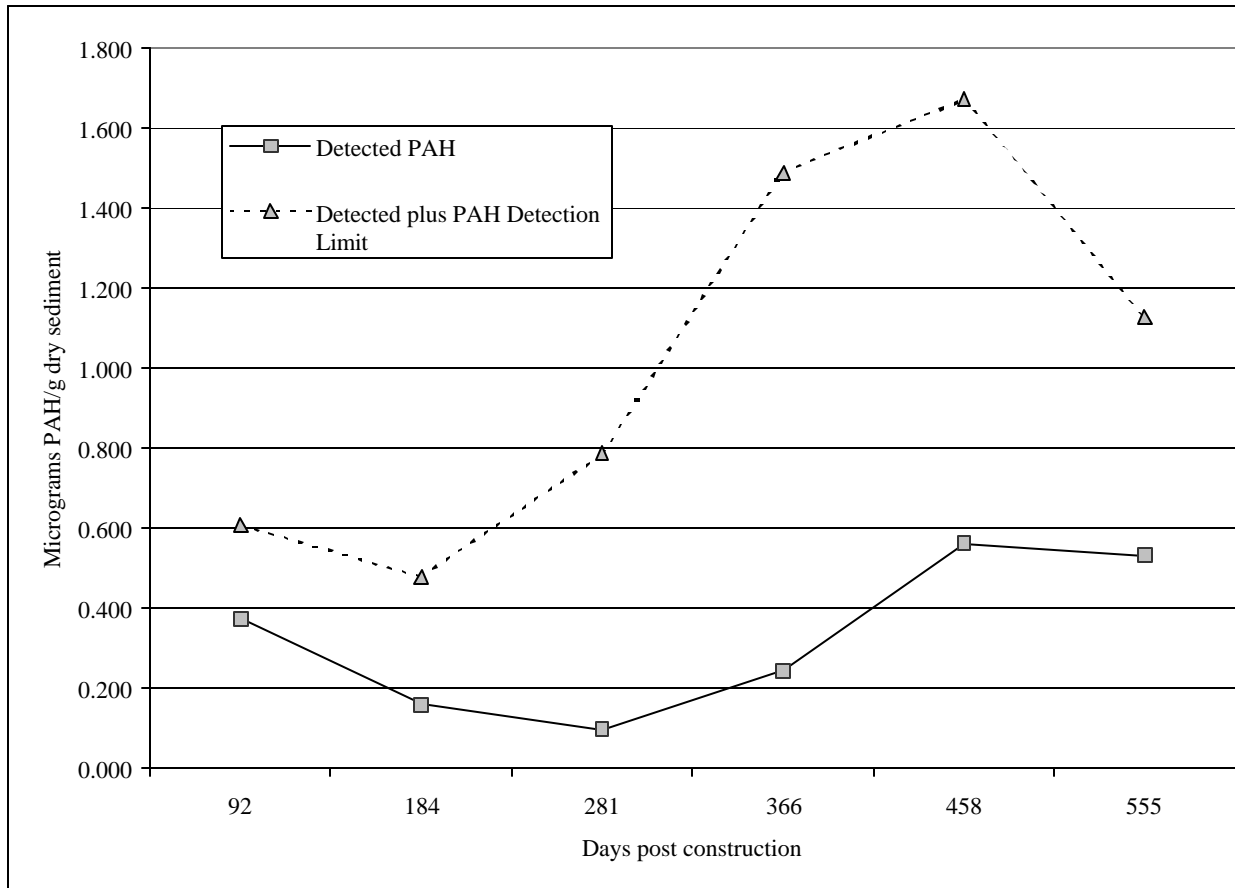


Figure 15. Relationship between the sum of the detected PAH and the detected PAH plus the analytical detection limit for each compound. Each value is the mean of for all treatments and distances on a particular day in the study.

These results strongly suggest that seasonally varying atmospheric PAH deposition is a major source of the observed low levels of PAH. The question remains, “Do the creosote treated railway ties contribute PAH to adjacent wetlands?” This question is explored in Figure (16) which summarizes the mean concentrations of the sum of PAHs observed in the Weathered and New Tie mesocosms less the mean observed in the Untreated Tie mesocosm. This summary suggests that the concentrations of PAH in treated tie mesocosm sediments were not elevated above that observed in the untreated tie mesocosm during the first 281 days of the study. However, it also appears that during the last three sample periods, the concentrations of detected PAH were elevated by ca. 0.35 μg PAH/g dry sediment in the mesocosms containing creosote treated ties when compared with the untreated mesocosm. The significance of these increases was investigated using a new variable equal to the detected PAH in creosote treated wood mesocosm samples less the mean detected PAH concentration observed in sediment samples collected from the untreated mesocosm on the same day. This variable was subjected to analysis of variance using a nested design with Treatment, Day and Distance as independent variables. Increases in detected PAH observed in the Weathered and New Tie mesocosms were not significantly different as a function of Treatment ($p = 0.47$), Day ($p = 0.10$) or Distance ($p = 0.86$). Note that increases in the ΣPAH would have been significant for Day at $\alpha = 0.10$.

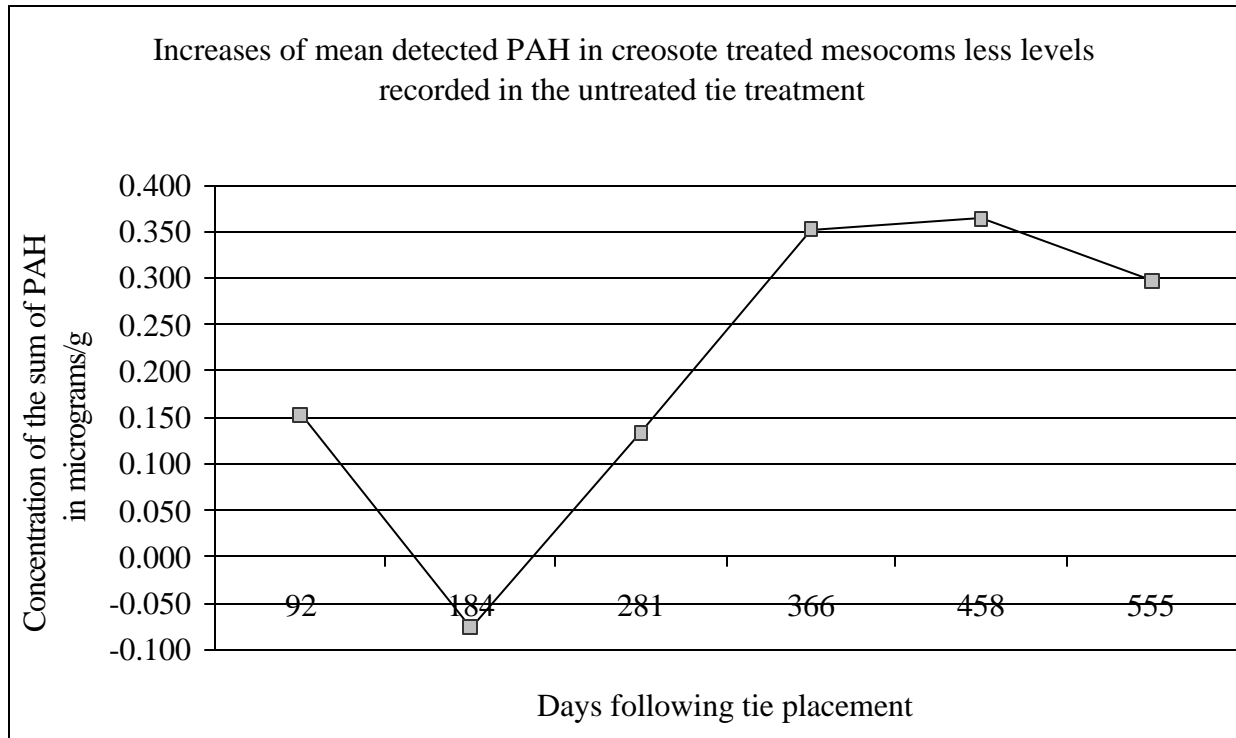


Figure 16. Differences in detected PAH between mesocosms containing creosote treated railway ties and a reference mesocosm containing identical untreated oak ties.

5.5. Biological assessment. Much of the preceding discussion focused on the migration of PAH from creosote treated railway ties into supporting ballast and from the ballast into the adjacent wetland environment. Regardless of the source of PAH, it is the cumulative effect of all observed PAH that contribute to potential stress and at low concentrations to chronic toxicity. The following assessment will assume that individual PAH compounds were present at the analytical detection limit when they were not detected. This is a very conservative assessment, which likely overestimates the potential for adverse effects.

As previously discussed, PAH were only observed in stormwater on the final day of sampling. These compounds were observed in all three mesocosms on that day at levels below the sum of toxic unit threshold defined by Swartz *et al.* (1995). Biological stress, including that associated with photoenhanced PAH toxicity, cannot reasonably be predicted at the observed concentrations. Brooks (1994) has argued that dissolved concentrations of PAH found in association with creosote treated wood are not expected to create environmental stress. It is sedimented PAH that must be managed to insure the integrity of plants and animals living in the vicinity of treated wood. The recently published Consensus Sediment Quality Benchmarks recommended by Swartz (1999) were chosen as a conservative benchmark for use in evaluating the biological response to sedimented PAH in this study.

Polycyclic aromatic hydrocarbons are hydrophobic and bind with organic molecules in aquatic environments. This reduces their bioavailability and potential toxicity. In recognition of this, most organic contaminant benchmarks are based on the concentration of the contaminant expressed in micrograms of contaminant per gram of organic carbon. Des Plaines River wetland sediments used in this study were analyzed for Total Organic Carbon (TOC) and/or Total

Volatile Solids (TVS) at the beginning and end of the study. A mean TOC value of 11.91% was determined.

Figure (17) is a histogram describing the number of sediment samples in categories described by the sum of PAH (including the detection limit for undetected compounds). One hundred and forty of the 234 samples contained PAH concentrations less than

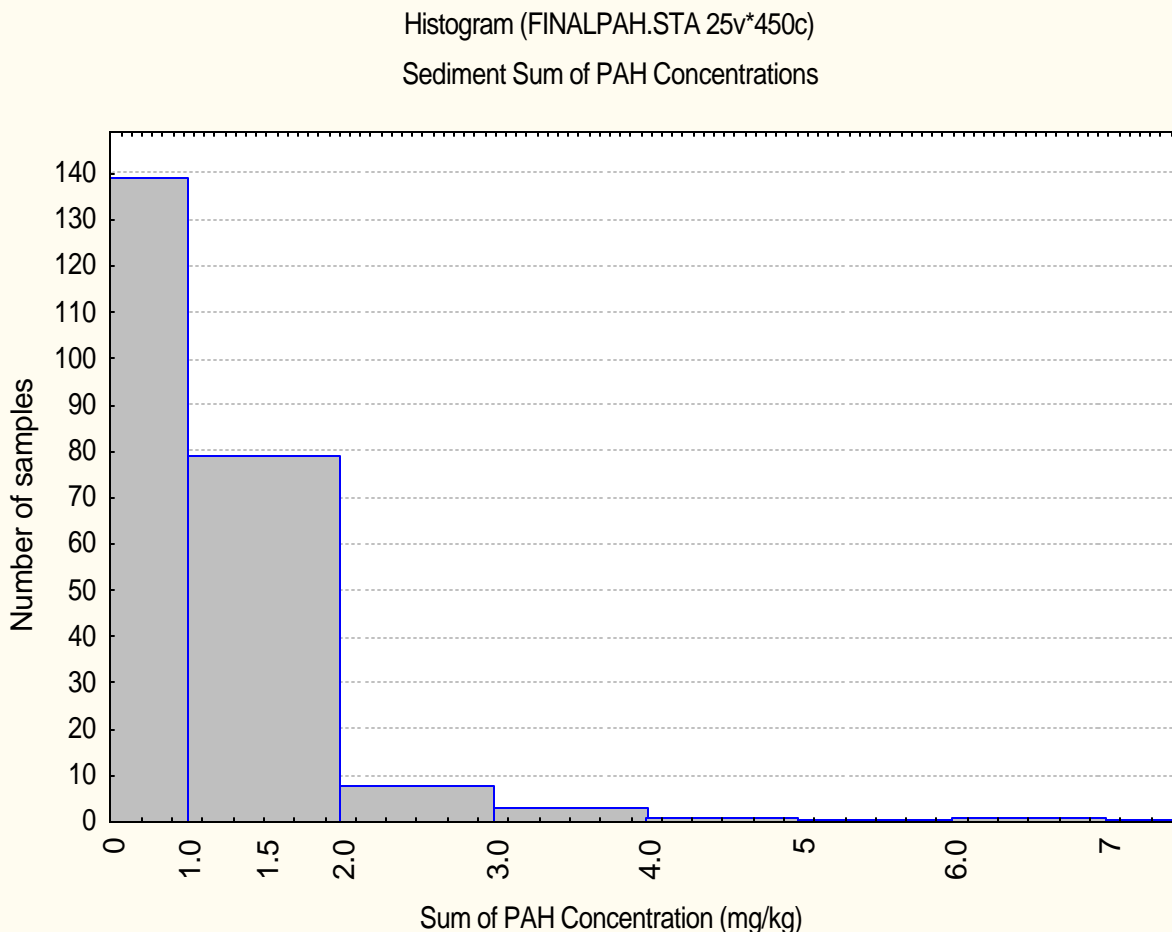


Figure 17. Histogram describing the number of mesocosm sediment samples as a function of the observed ΣPAH in the sample.

1.0 $\mu\text{g } \Sigma\text{PAH/g}$. Concentrations in an additional 80 samples were between 1.0 and 2.0 $\mu\text{g } \Sigma\text{PAH/g}$. Only two of the 234 sediment samples exceeded the 3.93 $\mu\text{g } \Sigma\text{PAH/g}$ Toxic Effects Threshold (TEL) for ΣPAH given by Swartz (1999) in one percent TOC sediments. None of the samples exceeded the Swartz (1999) benchmark for ΣPAH in 11.9% TOC sediments. The two samples containing more than 3.93 $\mu\text{g } \Sigma\text{PAH/g}$ were chosen for an evaluation of individual compounds because one was from the Weathered Tie mesocosm (6.26 $\mu\text{g } \Sigma\text{PAH/g}$) and the other from the Newly Treated Tie mesocosm (9.83 $\mu\text{g } \Sigma\text{PAH/g}$). The results of computing the sum of toxic units at the mean sediment TOC are presented in Table (3). Three benchmarks were presented for each compound in the analysis. However, in this case, the observed PAH levels were so low that the toxic unit calculations are compared only with the TEL. Recall that this is the value below which adverse biological affects should not be anticipated in any species. The LC_{50} value represented the concentration above which significant adverse affects should always

be anticipated and the mean of these two values was suggested as representative of the concentration above which adverse affects were likely to be observed in sensitive species. In sediments containing 11.9% TOC, the Σ PAH Mixture LC₅₀ is 251.8 μ g Σ PAH/g dry sediment and the mean value is 149.3 μ g Σ PAH/g. The sediment PAH concentrations observed in this study were between one and two orders of magnitude lower than these levels. Tables (3) and (4) compare the observed sediment concentrations of PAH in the highest newly treated and weathered tie mesocosms with their respective toxicity thresholds.

Table 3. Summary of the Σ PAH Toxicity Threshold and the observed concentration of PAH compounds and classes of compounds in the newly treated tie mesocosm sample with the highest concentration of PAH. The number of toxic units (Swartz, 1999) associated with each compound is provided in the last column. These sediments contained a mean of 11.9% total organic carbon.

PAH Compound	Σ PAH Toxicity Threshold (μ g PAH/g dry sediment)	Observed Concentration (μ g PAH/g dry sediment)	Toxic Units
Naphthalene	1.548	0.062	0.040
Acenaphthylene	0.357	0.062	0.174
Acenaphthene	0.476	0.150	0.315
Fluorene	2.025	0.220	0.109
Phenanthrene	3.454	2.270	0.657
Anthracene	2.501	0.450	0.180
Fluoranthene	8.218	2.220	0.270
Pyrene	10.719	1.400	0.131
Benz(a)anthracene	2.501	0.680	0.272
Chrysene	3.692	0.630	0.171
Benzo(b)fluoranthene	3.930	0.350	0.089
Benzo(k)fluoranthene	3.454	0.340	0.098
Benzo(a)pyrene	3.930	0.430	0.109
Low molecular weight PAH	10.362	3.214	0.310
High molecular weight PAH	36.445	6.050	0.166
Total PAH	46.806	9.264	0.198

None of the PAH compounds exceeded their toxic threshold, nor did any of the classes of mixtures. No toxicity could be expected in association with either of these two highest samples and therefore, no toxicity can reasonably be expected with the several hundred samples in which the Σ PAH compounds was in the range of zero to two μ g Σ PAH/g dry sediment. Aside from the lack of evidence of toxicity, there are several interesting points in Figures (3) and (4).

- Consistent with the Sooke Basin study (Goyette and Brooks, 1998), phenanthrene was the most problematic compound associated with the new tie mesocosm. The phenanthrene concentration in the single highest sample collected from the New Tie mesocosm represented 0.657 toxicity threshold units.

Table 4. Summary of the Σ PAH Toxicity Threshold and the observed concentration of PAH compounds and classes of compounds in the weathered tie mesocosm sample with the highest concentration of PAH. The number of toxic units (Swartz, 1999) associated with each compound is provided in the last column. These sediments contained a mean of 11.9% total organic carbon.

PAH Compound	Σ PAH Toxicity Threshold ($\mu\text{g PAH/g dry sediment}$)	Observed Concentration ($\mu\text{g PAH/g dry sediment}$)	Toxic Units
Naphthalene	1.548	0.037	0.024
Acenaphthylene	0.357	0.089	0.249
Acenaphthene	0.476	0.030	0.063
Fluorene	2.025	0.100	0.049
Phenanthrene	3.454	0.410	0.119
Anthracene	2.501	0.059	0.024
Fluoranthene	8.218	0.190	0.023
Pyrene	10.719	0.430	0.040
Benz(a)anthracene	2.501	0.990	0.396
Chrysene	3.692	1.300	0.352
Benzo(b)fluoranthene	3.930	0.500	0.127
Benzo(k)fluoranthene	3.454	0.650	0.188
Benzo(a)pyrene	3.930	0.930	0.237
Low molecular weight PAH	10.362	0.725	0.070
High molecular weight PAH	36.445	4.990	0.137
Total PAH	46.806	5.715 ¹	0.122

Note. 1) The Σ PAH for these samples given in Tables (3) and (4) is slightly lower than determined in this study because the model of Swartz (1999) considers only 13 PAH compounds and 16 PAH compounds were evaluated in this study. This is not considered a significant flaw in the analysis because the PAH not considered by Swartz (1999) were not detected or detected at low levels in these samples.

- Low molecular weight PAH compounds made up 34.7% of the observed PAH in the highest Newly Treated Tie mesocosm sediment sample but only 14.5% of the PAH in the highest sediment sample from the Weathered Tie mesocosm. This is consistent with the preferential loss of low molecular weight compounds as creosote treated wood ages.

- Similarly, the low molecular weight compounds resulted in a higher toxic unit value (0.310 TU) than did the high molecular weight compounds (0.166 TU) in the New Tie mesocosm sample. In contrast, the low molecular weight compounds were represented by a very low toxic unit value (0.070 TU) in comparison with the high molecular weight compounds (0.122 TU) in the Weathered Tie mesocosm.

This discussion should not be misunderstood. The preceding analysis focuses on the two sediment samples with the highest PAH concentrations in a dataset consisting of 234 samples, most of which contained less than 2.0 $\mu\text{g } \Sigma\text{PAH/g dry sediment}$. The reason for belaboring these two samples is that they show spectra similar to that expected from creosote and to demonstrate the lack of toxicity in even the highest samples. The bottom line is that there is no indication in

this study that PAH lost from either the Newly Treated or Weathered Ties presents any potential stress for dragonflies or any other more sensitive species in this wetland.

6.0. Conclusions. Brooks (1996) assessed the potential impact of this railway right of way on Hines emerald dragonfly (*Somatochlora hineana*) and concluded that, based on the limited data available at that time, “There was no indication that the past use of creosote ties, or their current replacement (new ties) had compromised the biological integrity of wetland plants or animals (including *Somatochlora hineana*). The completion of the River South PAH study (Brooks, 1997b) and these results have added significantly to the database upon which biological effects associated with creosote treated railway ties can be evaluated. The following conclusions are substantiated by the results presented herein:

- The PAH spectrum associated with creosote changes with time. The proportion of high molecular weight compounds increases as the low molecular weight compounds are degraded and or evaporate. However, creosote derived PAH mixtures are dominated by phenanthrene and fluoranthene for at least the first two to three years following migration from the wood. The PAH spectra provided in this report give insight into discriminating sources of PAH. However, mixtures of PAH derived from creosote plus other sources may not be as amenable to simple analysis.
- Creosote derived PAH will likely migrate from newly treated railway crossties into supporting ballast during the summer of the first year. In this study, this pulse was not observed during the second summer. However, other site-specific behavior will depend on the wood species, creosote retention, solar insolation and ambient air temperatures.
- Creosote oil, containing PAH, is heated during the summer. The black surface of the railway ties acts as a black body. Creosote treated wood surface temperatures have not been measured. However, the dark color likely acts as a black body and high temperatures are quite possible.
- At sufficiently high temperatures, the expansion of the wood forces creosote oil to the surface where it coalesces to form droplets that may run down the face of the treated wood into ballast. Alternately, these droplets may form blisters that burst – projecting minute particles of creosote an unknown distance (likely a few tens of centimeters).
- Polycyclic aromatic hydrocarbons, particularly the intermediate and high molecular weight compounds, are hydrophobic with solubility’s ranging from 0.07 mg/l for anthracene to 0.00026 mg/L for benzo(g,h,i)perylene. They adhere to most dry surfaces (like ballast rocks) and are immobilized.
- Railway ballast contains little organic material and it is unlikely that bacterial communities capable of metabolizing PAH would thrive in this environment. However, PAH are degraded by photo- and chemical oxidation (weathering) and these processes likely represent the primary degradative pathways of creosote derived PAH in railway ballast.
- A small portion of these PAH appeared to have moved vertically down into the ballast to a depth of approximately 60 cm. The observed Σ PAH concentrations, including the value

of the detection limit for undetected compounds was less than 0.85 $\mu\text{g } \Sigma\text{PAH/g}$ dry ballast.

- It appears that atmospheric deposition of PAH contributes much of the observed background to Des Plaines River wetland sediments.
- Small amounts of PAH may have migrated from the ballast into adjacent wetlands during the summer of the second year of this study. The PAH spectrum in these samples and a comparison of PAH concentrations in the untreated mesocosm with the creosote treatments suggests that these increases ($\sim 0.3 \mu\text{g } \Sigma\text{PAH/g}$) were real. However, the observed increases were not statistically significant as a function of distance, treatment or day of the study.
- PAH were detected in one of 16 water samples. Those samples were collected on the final day of the study. Benzo(a)anthracene was observed in the untreated and new tie mesocosms. Phenanthrene was detected in the new tie mesocosm and fluoranthene, phenanthrene and pyrene were detected in stormwater from the weathered tie mesocosm. The PAH concentrations were all very low and an assessment using the sum of toxic units described by Swartz *et al.* (1995) indicated that none of the samples approached the benchmark recommended by those authors for the protection of aquatic life.
- The PAH concentrations observed in the highest samples collected in the Newly Treated Tie or Weathered Tie mesocosms are not predicted to be stressful using the consensus sediment benchmark methodology of Swartz (1999). No adverse biological effects can reasonably be predicted at the observed levels of PAH. It should be emphasized that this assessment assumed that undetected PAH compounds were present at the analytical detection limit. This makes this assessment, particularly the biological assessment, very conservative because the reported ΣPAH concentrations likely overestimate those present.

As discussed in the introduction to this study, there are many sources of PAH associated with railway transportation systems. These include diesel exhaust, lubricating oils, cargo (coal and oil) and herbicides. A mesocosm study was designed to minimize these confounding sources of PAH and to focus on those associated with creosote treated railway ties. These results suggest that seasonally variable atmospheric deposition of PAH contributes a significant portion of the background observed throughout the Des Plaines River wetland. It also appears that on average, the use of creosote treated railway ties may add an additional $0.3 \mu\text{g } \Sigma\text{PAH/g}$ dry sediment within half a meter of the toe of the ballast. Even the two highest observed PAH concentrations did not reach toxic threshold levels in these wetland sediments.

7.0. Recommendations. This study suggests that newly treated railway ties pose minimal environmental risk - even in sensitive wetland environments. However, experience from this study suggests the following three management practices to insure that risks are minimized:

- 7.1. Numerous derelict railway crossties were observed after having been discarded along side this right of way in the Des Plaines River wetland. Ties taken out of service should be properly disposed of.

- 7.2. The early loss of creosote from treated wood during first exposure to summer heat was observed in this study and has been reported by Brooks (2000) in association with creosote treated timber bridges. The temporary storage of newly treated railway crossties in sensitive environments while awaiting installation should be avoided. Ties should be stored on the ballast or on railway cars.
- 7.3.
- 7.4. Railway ties should be produced using management practices that reduce the probability of significant creosote loss from deep checks in the wood or from excess surface deposits. The ties used in this study were randomly selected. They were relatively clean and free from surface creosote deposits.

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