CREOSOTE RELEASE FROM CUT/BROKEN PILES, ASARCO SMELTER SITE

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This report was prepared by Don Weitkamp PhD and Jesse Bennett. Tim Goodman PE was the DNR project manager and Joel Breems provided review of data and the draft report. Ken Fellows PE was the Parametrix project manager for the dock demolition project.

ACRONYMS

DNR	Washington Department of Natural Resources
EPA	Environmental Protection Agency
GC/MS	gas chromatograph/mass spectrometer
PAH	polycyclic aromatic hydrocarbon
SIM	selected ion monitoring
SPMDs	semipermeable membrane sampling devices

ABSTRACT

This creosote leaching investigation was conducted to evaluate the release of creosote from freshly cut or broken pile surfaces to seawater during removal of derelict structures constructed with creosote-treated piles. The investigation employed laboratory exposure of freshly cut cubes (2 cm^3) of aged piles to artificial seawater (3 L) at temperatures of 7 and 13ºC. High concentrations of creosote components (PAHs and dibenzofuran) were measured leaching from the cubes into seawater during the first three test periods, 24 to 96 hrs. The concentrations of the several creosote components (naphthalene, 2-methylnaphtalene, benzo(a)pyrene) released during the fourth exposure period (96-334 hrs) decreased considerably. The concentrations of the other PAHs remained nearly constant or increased through the fourth exposure period. However, the leaching rate of all creosote components decreased substantially during the 336-hr laboratory exposure period.

The relative concentrations of individual PAH chemicals measured in the seawater were generally similar to previously reported creosote composition (EPA 2008) for most samples. However, cubes from one pile produced substantially different relative concentrations. Dibenzofuran, which has previously been reported as a minor component of creosote, was measured at a relatively high concentration in the leachate samples. Dibenzofuran has not been identified as specific to creosote or specific to any type of creosote.

The bioaccumulation investigation showed that the concentrations of the measured creosote components in mussels attached to the ASARCO docks were low prior to the beginning of the demolition. However, concentrations of most components had increased substantially by the interim sample collection at most locations and further increased in the mussel samples collected immediately prior to removal of the last piles. Concentrations of many of the creosote components measured in blue mussels growing on the site increased by more than an order of magnitude during dock demolition. No samples were collected following completion of demolition because the local mussel population was present on the dock piles and was removed with demolition of the docks, thereby eliminating the potential to measure the subsequent loss rate of creosote components from mussel tissue.

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INTRODUCTION

The Washington State Department of Natural Resources (DNR) retained Parametrix to conduct an investigation of the rate at which creosote components are released from freshly exposed sections of aged creosote-treated timber piles. The investigations focused on polycyclic aromatic hydrocarbons (PAHs) and a few other chemical constituents of creosote. PAH concentrations were used as an indicator of creosote because they comprise about 85% of creosote and include water soluble chemicals.

This investigation evaluated the demolition of piles broken and sheared at the ASARCO Smelter site on Commencement Bay in Puget Sound during removal of the site's three large docks. Removal of the three ASARCO docks was conducted as part of the superfund remedial action for the ASARCO Sediment Unit (OU 06). Demolition of the three docks was conducted by the DNR to remove the derelict structures and the creosote contained in their support piles, which permits completion of the site's sediment cap.

BACKGROUND

The three ASARCO docks covered approximately 1.6 acres at the former ASARCO Smelter Site (Figure 1). These docks were supported by approximately 2,300 creosote-treated piles ranging from 1 to 1.5 ft in diameter. The majority of the piles appeared to have been placed during the original construction of the docks. Based on review of historical aerial photographs, the age of the piles is estimated at 75-90 years. The Ore Dock was originally constructed in 1923 as an ore receiving dock with two large gantry cranes (Lund 1993). It appears that the Copper Dock was added sometime in the 1930s, and the Fuel Dock somewhat later, but no specific records have been found. A 1931 aerial photograph shows the Ore and Copper Docks in place (Keeney et al. 2009). Available photographs do not show the area of the Fuel Dock thereby making the time of its construction less certain. The docks are not known to have been substantially re-constructed after initial construction, although some piles have been added or replaced at later dates. The newest piles are likely in the range of 25-40 years old. No information is available on the nature of the creosote treatment applied to the ASARCO site piles.

Creosote is a complex mixture of several hundred detectable hydrocarbon chemicals. About 85% of creosote is composed of PAH chemicals. Dibenzofuran is less than 1% of creosote. The PAHs include the creosote components most likely to be detected in water exposed to freshly treated piles or freshly exposed creosote based on available information (EPA 2008). Commonly, creosote piles are treated to have creosote retention of 20-30 lbs/ft^3 of wood within that portion of the wood in which the creosote penetrates.

DOCK DEMOLITION ACTIVITIES

The docks were demolished in late 2010 between September and early December. The decks and their support structures were first removed from most of the Copper and Ore Docks. Because many of the piles had been substantially weakened by internal decay, they broke free during demolition of the decks and their support structure. The remaining stubs of broken piles were sheared near the sediment surface during cutting of the intact piles.

The piles were cut with a shear rather than pulled to maintain stability of the shoreline slope that supports the adjacent slag fill, and to minimize the potential for disturbing highly contaminated sediment under the docks. Disturbing sediment underneath the docks would potentially cause contamination of the sediment cap, constructed in 2006, that covers the adjacent offshore portion of the sediment remediation area.

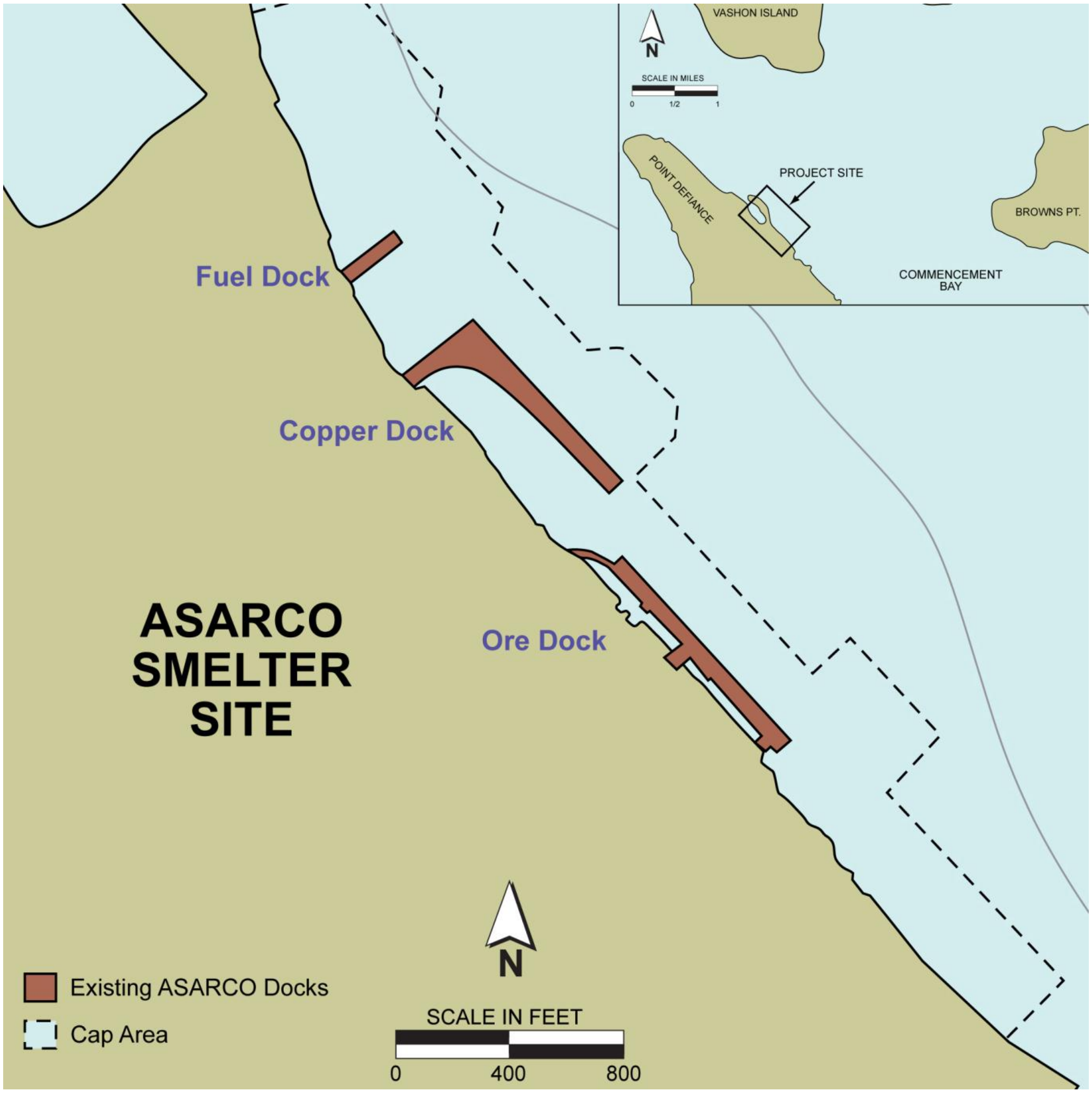

Figure 1. ASARCO Docks at the Former Smelter Site on Commencement Bay

The piles and pile stubs were removed by cutting near the sediment surface with a hydraulic shear that had two large hydraulically driven knife blades (Figure 2). The shear quickly closed to cut the piles free in less than a second. Nearly all the sheared piles had clean cuts with little or no splintering. The shear include hydraulically driven arms that grasped the pile prior to cutting and lifted the cut piles free (Figure 3) without substantial disturbance of the bottom.

Figure 2. Shear Used to Cut ASARCO Docks Piles

Figure 3. Sheared Copper Dock Pile Being Removed

Freshly cut surfaces of the creosote-treated piles were expected to release some creosote, and thus PAHs, into water from broken and cut piles. The release rate was expected to have a declining rate with time. This expectation was based on available information that previously demonstrated that treated piles release many PAHs and dibenzofuran into estuarine water (Ingram et al. 1982). The large number of piles that broke during demolition was not anticipated. The broken piles exposed substantially larger amounts of fresh creosote-treated surfaces than shearing.

The area under the docks was generally covered with shell debris produced by organisms that grew on the piles over many decades since the 1930s. This shell hash armored the bottom under the docks helping to minimize disturbance of the contaminated sediment. However, the action of broken piles dropping during deck demolition and the action of the shear did cause some disturbance of the fine silt within the shell hash.

Splintering of numerous piles occurred when piles broke during deck demolition. The splintering occurred at places in the piles where the pile’s untreated interior had severely decayed. An unknown amount of splintered wood from the pile's heavy creosote-treated exterior remained extending from the broken pile stubs or sunk to the bottom and was later identified by divers for removal if it protruded well above the bottom or was large enough to be recovered.

The last stage of dock removal project was to place a 2-ft thick sand cap over the bottom within the footprints of the three docks. All dock materials resulting from dock demolition were disposed of at a permitted Subtitle D landfill.

SEDIMENT AND WATER MONITORING DURING DOCK DEMOLITION

Surface sediment grab samples were collected from the 2006 sediment cap before, during, and following demolition work to assess the spread of contaminants to the cap as a result of dock demolition activities (Parametrix 2011b). A clear creosote odor was detected in a substantial number of the interim (09/30/2010) sediment samples (analyzed for metals) collected in surface grabs from areas of the 2006 sediment cap adjacent to the docks. The creosote odor was not present in surface sediment samples collected from the sediment cap prior to initiation of demolition. A distinct creosote odor was detected again in many of the surface sediment grab samples collected from the sediment cap adjacent to the docks following demolition.

Pre- and post-demolition (but not interim) surface sediment grab samples were collected on the 2006 sediment cap to assess the spread of PAH contaminants to the cap as a result of dock demolition activities. The surface of the 2006 sediment cap was sampled prior to dock demolition and was found to have generally low concentrations of creosote PAHs prior to dock demolition. Interim sediment samples collected, but were not analyzed for PAHs. At completion of demolition, most areas of the 2006 sediment cap exhibited increased PAHs concentrations in 0-2 cm and 0-10 cm surface grab samples as compared to pre-demolition samples collected at the same locations. Approximately 1.8 acres of the 2006 sediment cap, mostly located offshore of the Copper Dock and between the Copper and Fuel Docks, were found to have PAH concentrations exceeding SMS in 0-2 cm surface sediment grab samples. These areas were subsequently capped with an additional 0.5 ft of clean sand cap. See Parametrix (2011b) for a detailed discussion of the sediment sampling and the probable source of the creosote that appeared to be released by broken piles.

Turbidity and dissolved oxygen were monitored regularly during dock demolition. The results indicated compliance with water quality criteria, except for infrequent turbidity exceedances and low dissolved oxygen values. Water quality monitoring during demolition did not include chemical analyses.

STUDY OBJECTIVES

This investigation was conducted to examine both the potential and the actual creosote release that may have occurred during removal of the three docks. The basic objective was to develop information that would monitor the release of creosote from freshly cut piles in an estuarine environment.

Thus, the investigation includes two independent studies to evaluate the release of creosote:

1. **Creosote Leaching**: Determine the rate of PAH leaching into the surrounding water by measuring the release of PAHs from a specific area of creosote-treated surface placed in a static volume of artificial seawater during specific exposure periods following cutting of the pile section.
2. **Biological Accumulation**: Determine the rate of PAH accumulation by an *in situ* organism in close proximity to docks. This was accomplished by analysis of PAHs in tissues of mussels (*Mytilus trossulus*) collected from adjacent piles immediately preceding and during demolition, and immediately prior to removal of the last piles.

The leaching investigation attempted to measure the “maximum” rate of PAH leaching into a small volume of surrounding water under laboratory conditions. The bioaccumulation study measured the actual PAH accumulation by an *in situ* organism in close proximity to the broken and cut piles during removal of the three ASARCO Docks. Mussels were selected as the bioaccumulation organism because they have been found to rapidly and effectively accumulate PAHs (McLeese and Burridge 1987). Boehm et al. (2005) concluded that mussels are the preferred monitoring tool for assessing PAHs effects on the food-chain. Neff and Burns (1996) found that mussel tissue concentrations were 5-10 times that of average PAH concentrations in water samples.

The biological accumulation investigation changed during the project as a result of the nature of demolition. The original objective was to evaluate bioaccumulation resulting from sheared piles. However, the breakage of large numbers of deteriorated piles during deck removal produced large amounts of freshly exposed surfaces of creosote-treated wood at both of the larger docks prior to any pile shearing. This altered the nature of the study from specifically evaluating creosote release from relatively small surfaces exposed by shearing to evaluating exposure of large amounts of creosote-treated wood produced by breaking piles.

A project Sampling and Analysis Plan and Quality Assurance Plan was prepared (Parametrix 2010). Sample collection, handling, and analyses were conducted in accordance with the plan with no substantive deviations.

CREOSOTE LEACHING METHODS

This section describes the laboratory study conducted to determine the maximum leaching rate and short-term changes in the leaching rate of PAHs and dibenzofuran from freshly cut sections of the aged piles under average ambient temperature and salinity conditions.

PILE SECTION COLLECTION

Sections of the creosote-treated piles were collected on-site during the initial stages of shearing the Copper Dock piles. Sections approximately 10-15 cm thick were cut from near the bottom of the subtidal portion of each of five piles (Figures 4 and 5).

Each section was cut from a separate pile sheared less than 24 hrs prior to sample collection. Sections taken from the five piles were shipped to a bioassay laboratory for processing. Photographs were taken of the pile sections prior to transport. Each pile section was placed in a doubled plastic bag. The plastic bags were packed in transport coolers. Sufficient ice was sealed in plastic bags and packed in the coolers to maintain samples at approximately 4°C. Sample labeling and Chain-of-Custody protocols were followed as specified by the project Sampling and Analysis Plan and Quality Assurance Plan. Pile section samples were shipped to a bioassay laboratory for processing within 24 hrs following their collection at the demolition site.

Figure 4. Cutting Lower Portion of Copper Dock Pile for Test Sections

Figure 5. Sections of Two Piles Cut for Laboratory Testing

LABORATORY TEST CONDITIONS

At the bioassay laboratory, 2 cm cubes were cut from the creosote-treated periphery (outer 3-5 cm) of freshly cut pile sections, thereby providing freshly cut total surface areas of 24 cm^2 per cube. Prior to cutting the cubes, the slabs were rinsed with artificial seawater to remove sawdust produced during the initial section cutting. The cubes were then cut from within the creosote-treated portion of the pile sections (outer ring). These cubes excluded the weathered exterior pile surface and the interior edge of the creosote-treated area. Additional cubes were cut for creosote bulk and PAH analysis that were 3 cm per side to provide adequate quantity for analyses.

Although the interior of the aged piles was commonly degraded, the exterior creosote-treated layer of each pile was commonly intact with the exception of cracks. No boring organisms were detected in the creosote-treated outer ring of the piles. The cubes cut from the creosote-treated layer avoided cracked areas to produce intact uniform blocks of creosote-treated wood that visually had the appearance of freshly treated wood.

The leachate cubes were exposed to artificial seawater (controlled conditions with no biological component) for various periods of time, with complete changes of water and containers at the end of each test period. The water and containers were changed at the end of each exposure period to avoid transfer of previously leached PAHs to the water of the subsequent leaching period. This precaution was based on the literature information that indicates initial creosote leaching rate can decline rapidly. Leaving the pile cubes in the same water with periodic sampling might have made it difficult to distinguish differences in cumulative concentrations during the subsequent test period. Brooks (1997) used an average leaching rate of 17.3 µg creosote/cm^2/day at 12ºC with a salinity of 30[1], but various other investigations indicate that the release of creosote diminishes rapidly with time.

The following test conditions were employed to represent general ambient conditions for Puget Sound with worst case limitations for dispersal, diffusion, and degradation of leached PAHs:

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[1] Although salinity has been commonly expressed as ‰ or ppt, it is technically a conductivity ratio that does not have physical units.

- 2 cm cubes, 24 cm^2 surface area cut from creosote-treated periphery (3-5 cm) of pile sections
- 3 L test containers (substantial water volume to creosote surface ratio)
- Artificial seawater (no biological component)
- Water temperatures of 7 and 13°C (range of average Puget Sound temperatures)
- Salinity 30
- No circulation or aeration (to limit creosote degradation and evaporation)
- Test periods: 0-24 hrs, 24-48 hrs, 48-96 hrs, 96-336 hrs

PILE SAMPLE PREPARATION AND TESTING

Creosote-treated portions of the pile sections were cut into 2 cm cubes within 12 hrs of receipt by the bioassay laboratory. The freshly cut cubes were then immersed in the seawater test containers within 1hr of cube preparation.

Each cube was suspended within a 3 L test container by a stainless steel wire cradle to provide exposure of all sides of the cube to the test water (Figure 6). The exposure water was not mixed or aerated to minimize evaporation of volatile creosote chemicals. Water samples for analysis were withdrawn by siphon from below the surface of the exposure water at the end of each exposure period immediately following transfer of the cube to the next exposure container (Figure 6). Water samples were held in sealed jars at approximately 4°C until they are received by the analytical laboratory.

Figure 6. Leachate Cube Testing Apparatus

At the end of each test period, the cube and wire cradle were transferred to a fresh container with fresh seawater. The cube and cradle were rinsed with clean seawater during the transfer to avoid contamination of the subsequent test water by water from the preceding test period. Test containers were cleaned prior to initiation of the leaching study and between test periods if reused.

Laboratory information recorded on log sheets and recorded significant events included the following information:

- Date and time of sampling or observations
- Names of all personnel involved in sampling
- Cube and exposure period identification number
- Relevant details, if any, of sampling and deviations from established procedures
- Observations and measurements.

Pile sections were transferred to the bioassay laboratory within 12 hrs of cutting at the ASARCO site. All pile samples transported in coolers with sufficient ice to maintain a temperature of approximately 4°C until they were received by the bioassay laboratory. Two cubes were cut from each pile sample for leach testing, one for each temperature condition. Additional cubes were cut from three pile samples for creosote analysis. Leach testing and chemical analysis proceeded as soon as practical following sample collection (1-5 days). The project Sampling and Analysis Plan and Quality Assurance Plan procedures were followed for all samples. Representative creosote chemicals assessed in the water samples were identified from the EPA (2008) ecological hazard and environmental risk assessment as shown in Table 1.

Table 1. PAHs Used in EPA Ecological Hazard and Environmental Risk Assessment (EPA 2008), Other PAHs and Dibenzofuran Measured in Pile Leachate Samples

CHEMICAL	% of Creosote
PRIMARY	
Anthracene	11
2-Methylnaphthalene	11
Naphthalene	11
Phenanthrene	11
Fluorene	7
Acenaphthene	3
Fluoranthene	3
Chrysene	2
Pyrene	2
OTHER <2%	
Acenaphthylene	
Benz(a)anthracene	
Benzo(a)pyrene	
Benzo(b)fluoranthene	
Benzo(g,h,i)perylene	
Benzo(k)fluoranthene	
Dibenz(a,h)anthracene	
Indeno(1,2,3-cd)pyrene	
Dibenzofuran	<1

CREOSOTE ANALYSIS

To determine the concentrations of creosote released from each cube, water samples were analyzed for PAHs and dibenzofuran by GC/MS SIM Ultra Low Level - 8270C SIM (see Table 1).

Three cubes, cut from the same pile sections as the leaching study samples, were analyzed for:

- PAH and dibenzofuran concentrations
- Bulk density
- Moisture content
- Bulk creosote content

BIOLOGICAL ACCUMULATION

In general, mussels are useful as the bioaccumulation indicator organism because they have been found to rapidly and effectively accumulate PAHs (McLeese and Burridge 1987). Boehm et al. (2005) concluded that mussels are the preferred monitoring tool for the assessment of PAHs in food-web effects investigations. Neff and Burns (1996) found that mussel tissue PAH concentrations were 5-10 times greater than those of average water samples.

Blue mussels (*Mytilus trossulus*) were selected as an indicator organism because they are likely to accumulate released PAHs and dibenzofuran and because they occur naturally at the site. Blue mussels have been demonstrated to accumulate essentially the same PAH chemicals at essentially the same rates as semipermeable membrane sampling devices (SPMDs) (Eaton and Zitko 1978, Baussant et al. 2001, Boehm et al. 2005). We assumed that lower molecular weight PAHs are likely to be released into the surrounding water to a greater degree than higher molecular weight PAHs. However, the higher molecular weight PAHs have been shown to accumulate in mussels at a higher rate than in SPMDs (Boehm et al. 2005). Dibenzofuran is a relatively minor creosote component, but one that has been shown to migrate into water from treated wood (Ingram et al. 1982) and was detected in the leachate samples.

Thus, existing mussel populations in the immediate vicinity of the ASARCO docks were expected to accumulate any PAHs released from the freshly exposed surfaces of cut piles. As filter feeders, collecting plankton and detritus from the water column, the mussels in the immediate vicinity of the broken and cut piles provided a sensitive ambient monitoring device for released PAHs. The mussels filter substantial volumes of the water over their gill surfaces as they capture food providing a means of high exposure relative to most other marine invertebrates present at the site. Mussels suspended within the water column in close proximity to the cut piles provided maximum exposure to water born PAHs.

The predominant long-shore currents at the site tend to move water along the shoreline in either direction parallel to the shoreline depending on flood and ebb tides. These currents carried potentially contaminated water directly from the broken and cut piles to mussels living on piles in the areas adjacent to either end of the active demolition area. The mussels were also short distances from the demolition work. Thus, these populations most likely were exposed to the highest concentrations of creosote released from the freshly exposed treated wood surfaces at the site.

The strong odor of pile sections and visual observations indicated that some creosote components were released from the freshly cut pile surfaces. Thus, it is likely that some creosote components (PAHs) were released to the water column at the site from the freshly cut or broken pile surfaces and potentially accumulated by biota inhabiting the site. Breaking of numerous piles during demolition resulted in exposure of much larger amounts of fresh creosote surfaces than was anticipated to be produced by shearing of piles. Splintering of the piles produced both irregular surfaces and large elongated splinters of creosote-treated wood.

MUSSEL COLLECTION

The bioaccumulation study followed a before and after exposure approach conducted to monitor concentrations of creosote chemicals in the mussels at the site. Analyses of mussel tissue were conducted for those PAH and other chemicals that are most indicative of creosote (see Table 1).

Baseline sampling of mussels from piles at and adjacent to the Copper and Ore Docks occurred (8/26/2010) at the beginning of deck removal at the Copper Dock. The interim mussel sampling was conducted 10/26/2010 near the end of the first stage of shearing when about two-thirds of the Copper Dock piles had been cut. Prior to this interim sampling many of the Copper Dock and Ore Dock piles had broken off during removal of the decks resulting in exposing substantial amounts of creosote-treated surfaces on the remaining pile splinters and debris. There were no means to determine the amount of freshly exposed creosote-treated surface area from the splintered piles and debris as the surfaces were highly irregular with an unknown number of stubs and an unknown amount of debris present on the bottom. The final set of mussel samples was collected when only a few piles remained (11/11/2010).

The interim and final mussel samples collected during and near the end of pile removal did not include samples from each of the locations sampled prior to pile removal due to removal of all piles from several of the baseline sample areas. There were insufficient quantities of mussels on the slag shoreline in the vicinity of the original sample locations to provide adequate samples. Due to the modest size of the mussels present on the site it was necessary to collect large numbers (~100) to provide adequate quantities of flesh for each sample. The mussels collected at the end of the project were smaller than those collected initially.

Figure 7 shows the general locations from which baseline mussel samples were collected. These include two at the Fuel Dock, two from either end of the outside edge of the Copper Dock and two from either end of the outside edge of the Ore Dock. All mussel samples were collected during low tide periods that exposed the mussels growing naturally on the sites piles. Parametrix sampled the mussel populations growing the Ore and Fuel Docks and at either end of the central Copper Dock, which was the first dock to be demolished. The baseline samples provided an initial reference before any piles were broken or sheared. The sampled mussels had set and grown on site piles, and therefore provide the background PAH concentrations prior to exposure to any fresh creosote surfaces. These baseline PAH concentrations represent an equilibrium with exposures to on-going leaching of PAHs from aged piling prior to dock demolition.

The second set of mussel samples was collected immediately following approximately three weeks exposure to the fresh creosote surfaces of numerous broken piles and several weeks of pile shearing. The third set of mussel samples was collected from a few remaining piles near the end of pile shearing. Mussels collected near the end of pile removal likely received maximum exposure to released PAHs. The contractor left small numbers of piles near either end of the site until the end of demolition to accommodate mussel sampling. The sparse abundance of mussels on the slag and riprap shoreline required that mussel samples be collected from the piles.

The second and third sets of mussel samples did not include all the locations shown on Figure 7 due to removal of all piles at the central sample locations. These later mussel samples were collected from essentially the same locations that still had piles present during demolition.

The schedule for the post-cutting mussel collection was determined by the contractor's progress in removing the docks and the deteriorated condition of the docks. The original schedule was to collect the second set of mussel samples following cutting of nearly all the Copper Dock piles. However, dock demolition did not proceed in the planned sequence. It became necessary to retain approximately one third of the Copper Dock to unload the debris barge because of the structural weakness of the Fuel Dock. Also some of the piles broke during removal of the Copper Dock deck, and many piles broke at the Ore Dock during demolition of its deck. Thus, the second collection of mussels occurred at the end of pile cutting for the first portion of the Copper

Dock and a portion of the Ore Dock. At that time about ⅔ of the Copper Dock piles had been cut or broken, and most of the Ore Dock piles were broken or cut.

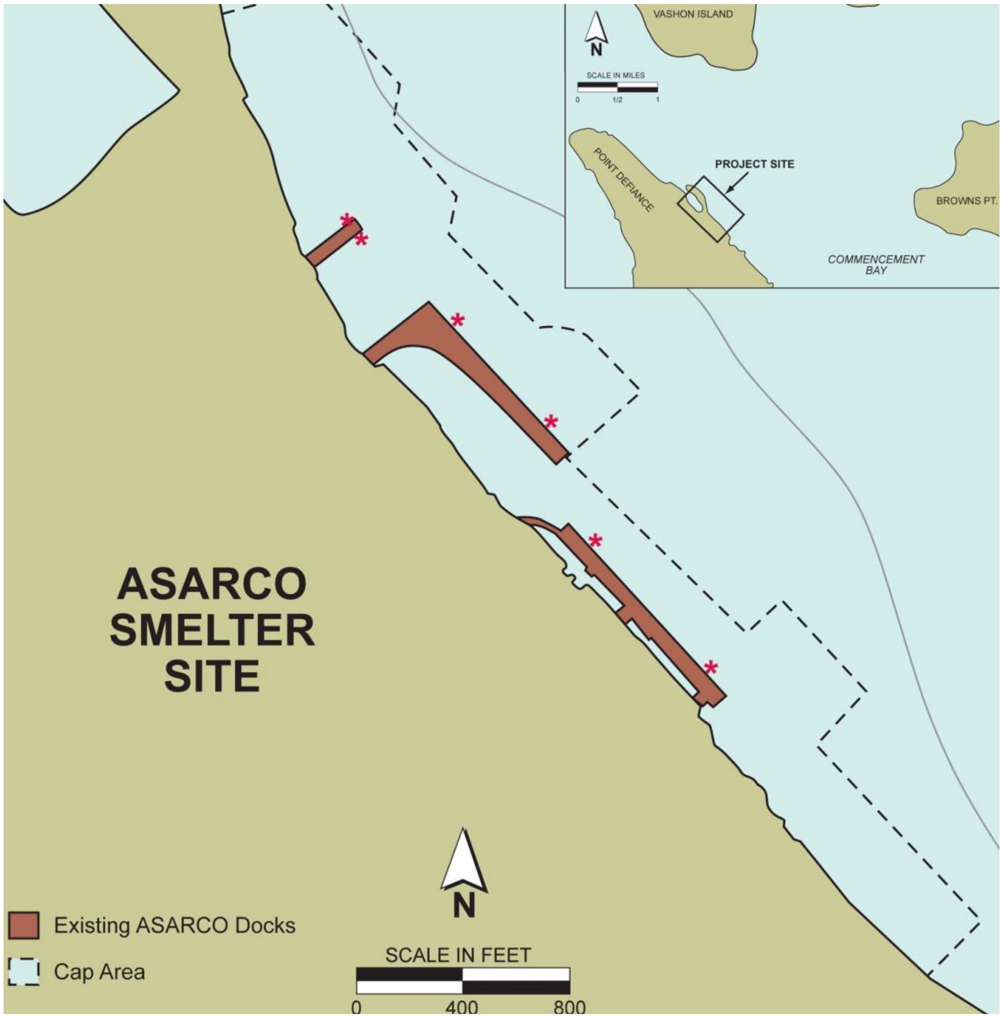

Figure 7. Mussel Sample Locations, Aug. 23, 2010

Mussel Collection Methods

All mussel samples were collected during low tide periods that exposed the mussels growing naturally on the dock piles. Mussels were collected by hand pulling and scraping from each collection site. The collected mussels were immediately rinsed with clean seawater and placed in burlap bags wetted with site seawater. Approximately 100 mussels of various sizes were collected for each sample to ensure adequate tissue was available for analysis. Labels identifying the location and date of collection were inserted in the bags. The bagged mussels were placed in a cooler containing sealed bags of ice for transport to the analytical laboratory within 24 hrs. Mussel sample tracking and chain of custody procedures were the same as for the pile samples.

TISSUE ANALYSIS

The intact mussels were rinsed with clean water prior to removal of tissue from the shells. The tissue from all mussels collected at a sample location was combined and freeze dried, prior to homogenization for chemical analysis.

Each tissue sample was analyzed for PAHs by GC/MS SIM Ultra Low Level - 8270C SIM. Mussel tissue samples were also analyzed for lipid and moisture content.

RESULTS

The complete data produced by the Creosote Leaching and Bioaccumulation investigations are provided in separate data reports. Each data report includes complete laboratory data packages, quality assurance reviews, copies of field logs and/or sample logs, and copies of Chain of Custody forms. Summaries of these data are provided below.

CREOSOTE LEACHING

During testing, laboratory staff reported strong creosote odors from both the pile cubes and the water in which they were immersed, indicating that initially the samples were releasing substantial creosote concentrations. Figure 8 shows the general changes in the mean concentrations of creosote components within the first 14 days following exposure (13 ºC) of fresh surfaces of creosote treated wood from the ~60-year old piles.

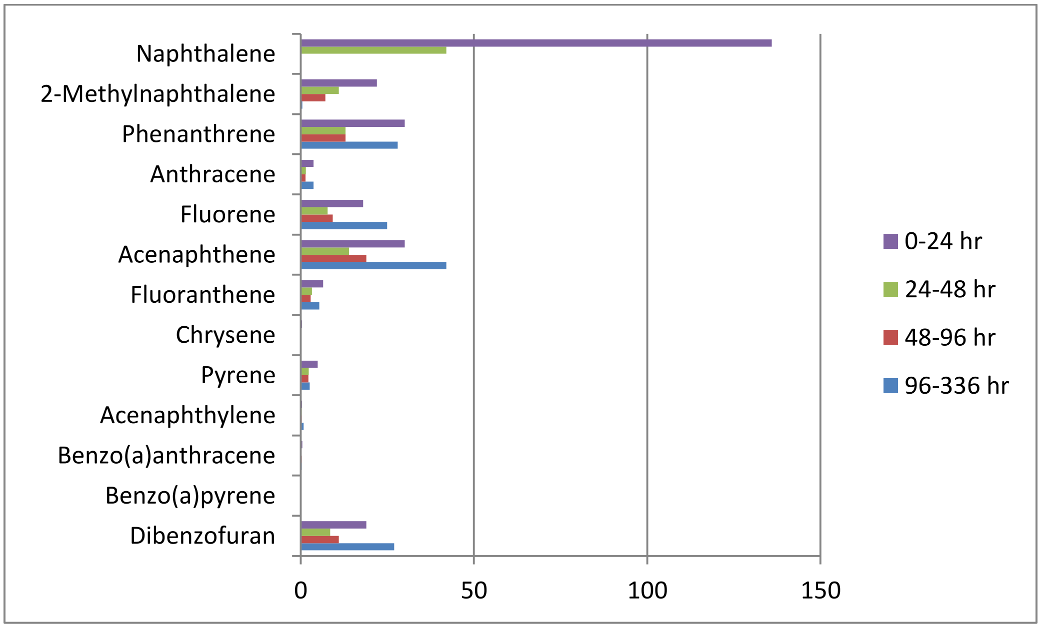

Figure 8. Mean Seawater (13 ºC) Concentrations (µg/kg dry weigh) from Freshly Exposed Creosote Treated Pile Surfaces

Figure 9 shows the general changes in the mean concentrations of creosote components within the first 14 days following exposure to fresh creosote surfaces at 7 ºC.

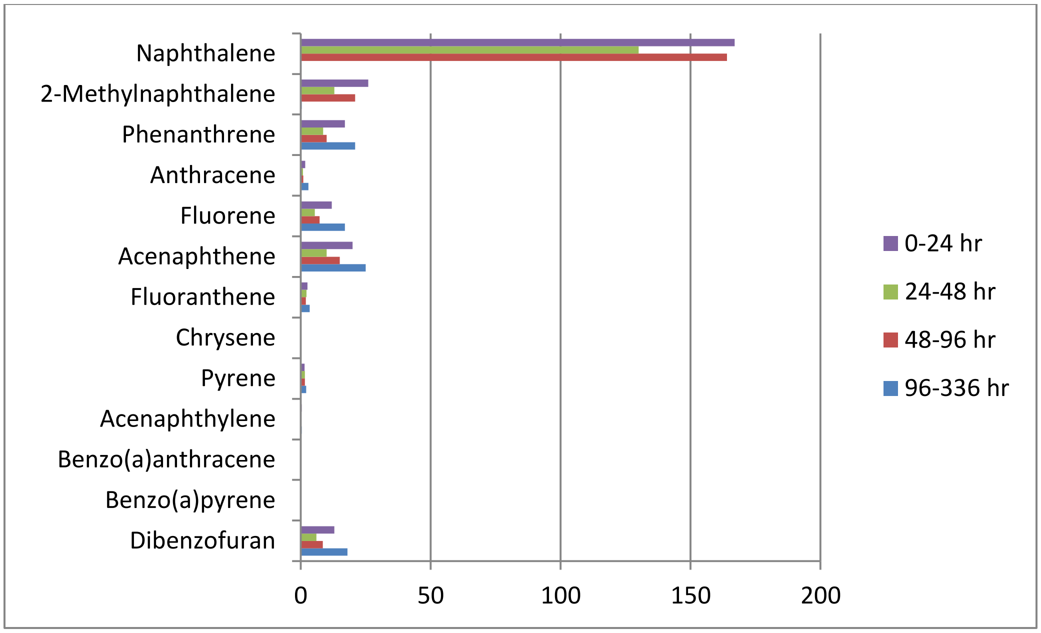

Figure 9. Mean Seawater (7 °C) Concentrations (µg/kg dry weigh) from Freshly Exposed Creosote Treated Pile Surfaces

Table 2 summarizes the creosote component concentrations (average and range) measured in water at the end of each laboratory exposure period produced by five sample freshly cut cubes (2 cm) immersed in 3 L each of artificial seawater at 13°C.

Table 2. Creosote Leachate Concentrations at 13°C, Mean (Range) Each Exposure Period

Chemical	Concentration (µg/mL) / time period			
	0-24 hr Mean (range)	**24-48 hr** Mean (range)	**48-96 hr** Mean (range)	**96-336 hr** Mean (range)
Naphthalene	136 (0.019 - 380)	42 (0.0094 - 120)	0.022 (0.016 - 0.025)	0.014 (0.006 - 0.033)[a]
2-Methylnaphthalene	22 (0.23 - 54)	11 (0.029 - 28)	7.1 (0.004 - 19)	0.481 (0.002 - 1.2)[a]
Phenanthrene	30 (16 - 49)	13 (1.6 - 22)	13 (0.021 - 22)	28 (0.73 - 71)[a]
Anthracene	3.7 (1.9 - 6.2)	1.5 (0.79 - 2.3)	1.4 (0.125 - 2.4)[a]	3.7 (0.24 - 8.7)[a]
Fluorene	18 (9.2 - 23)	7.8 (3.1 - 10)	9.3 (0.14 - 13)	25 (0.0017 - 59)[a]
Acenaphthene	30 (12 - 57)	14 (5.3 - 28)	19 (8.3 - 36)	42 (0.025 - 110)[a]
Fluoranthene	6.5 (3.4 - 13)	3.3 (1.5 - 5.8)	2.9 (0.96 - 5.7)	5.4 (1.4 - 11)
Chrysene	0.40 (0.17 - 0.84)	0.15 (0.12 - 0.23)	0.190 (0.065 - 0.040)	0.230 (0.059 - 0.350)
Pyrene	4.9 (2.8 - 8.3)	2.3 (1.1 - 3.6)	2.2 (0.52 - 3.9)	2.6 (0.009 - 6.9)
Acenaphthylene	0.38 (0.13 - 0.85)	0.277 (0.063 - 0.650)	0.31 (0.10 - 0.62)	0.8951 (0.006 - 1.8)[a]
Benzo(a)anthracene	0.54 (0.25 - 0.54)	0.24 (0.16 - 0.31)	0.280 (0.072 - 0.540)	0.30 (0.04 - 0.55)
Benzo(a)pyrene	0.115 (0.033 - 0.220)	0.031 (0.018 - 0.052)[a]	0.036 (0.014 - 0.058)	0.047 (0.012 - 0.08)
Dibenzofuran	19 (8.1 - 28)	8.5 (3.4 - 11)	11 (2.8 - 17)	27 (0.0017 - 73)[a]

[a] Some undetected at reported minimum detection limit, ½ MDLs used for undetected values.

The leach test periods were 24, 24, 48, and 230 hrs to accommodate anticipated decreases in leaching rates with increasing time immediately following exposer of the freshly cut surfaces. The observed changes in leached concentrations of creosote components varied over time among the different components. At 13°C (Table 2) the average leaching rate of several components (naphthalene, 2-methylnaphthalene, and pyrene) decreased rapidly during the first two days, indicating that little was available for release after a short time. Most components [phenanthrene, anthracene, fluoranthene, chrysene, benzo(a)anthracene, benzo(a)pyrene] showed rapid, but more gradual decreases in leaching rates with lower total concentrations at 14 days (96-336 hr leaching) than following the initial 24 hr leaching period. Other components (fluorene, acenaphthene, acenaphthylene, and dibenzofuran) showed a slower decrease in leaching rates with leached concentrations at 336 hr exceeding the concentrations measured at 24 hr. Examples of the three conditions are shown in Figure 10. However, as these examples indicate, all creosote components showed a substantial decrease in leaching rates during the 336 hr exposure periods. The changes in leaching rates over time at 7°C showed similar but somewhat different trends.

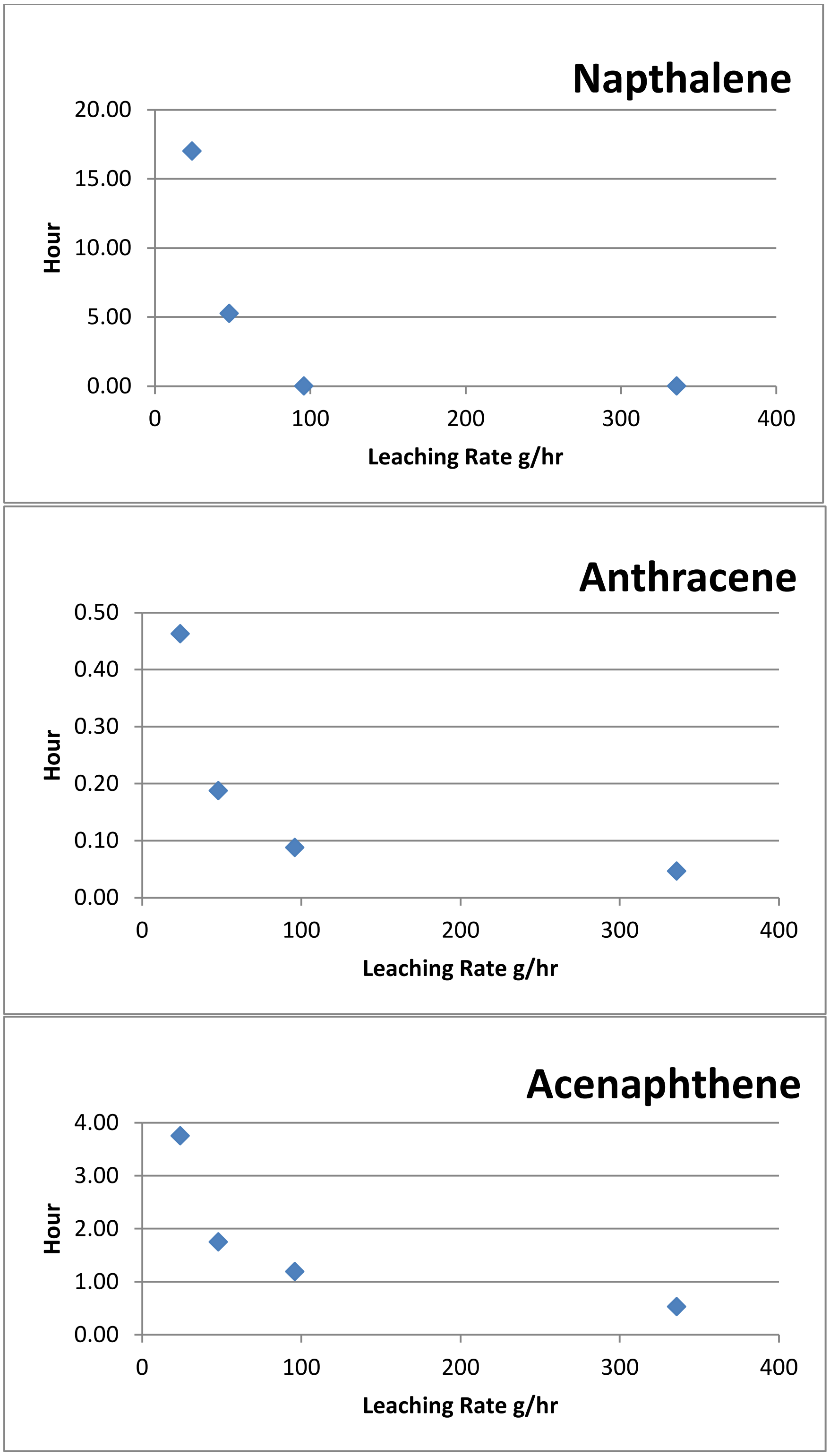

Figure 10. Leaching Rate Changes of Three Creosote Components During 336 hr Exposure (13ºC).

Table 3 summarizes the creosote component concentrations in water at the end of the 7°C laboratory exposures for five pile samples. The samples leached at 7°C resulted in higher concentrations at 48-96 hr for a number of PAHs than the samples leached at 13°C.

Table 3. Creosote Leachate Concentrations at 7°C, Mean (Range), Each Exposure Period

Chemical	Concentration (μg/mL) / time period			
	0-24 hr Mean (range)	**24-48 hr** Mean (range)	**48-96 hr** Mean (range)	**96-336 hr** Mean (range)
Naphthalene	167 (0.012 - 280)	130 (0.13 - 180)	164 (0.02 - 230)	0.021 (0.015 - 0.028)
2-Methylnaphthalene	26 (4.6 - 49)	13 (3.0 - 18)	21 (2.3 - 33)	0.40 (0.11 - 0.86)
Phenanthrene	17 (9.1 - 24)	8.7 (3.7 - 14)	9.8 (5.7 - 15)	21 (9 - 27)
Anthracene	1.7 (1.1 - 2.8)	0.85 (0.44 - 1.3)	0.98 (0.59 - 1.3)	3.0 (1.6 - 3.6)
Fluorene	12 (5.6 - 19)	5.4 (2.7 - 6.7)	7.3 (4.3 - 9.2)	17 (8.9 - 20)
Acenaphthene	20 (8.2 - 29)	10 (4.4 - 17)	15 (6.7 - 26)	25 (11 - 44)
Fluoranthene	2.6 (1.7 - 3.7)	2.3 (0.73 - 5.6)	2 (0.77 - 4.4)	3.5 (2.0 - 5.6)
Chrysene	0.137 (0.096 - 0.180)	0.175 (0.062 - 0.550)	0.089 (0.049 - 0.120)	0.164 (0.081 - 0.220)
Pyrene	1.5 (1.0 - 1.9)	1.6 (0.44 - 4.1)	1.6 (0.46 - 3.7)	2.1 (1.1 - 3.7)
Acenaphthylene	0.36 (0.12 - 0.77)	0.224 (0.061 - 0.420)	0.333 (0.096 - 0.570)	0.4 (0.18 - 0.56)
Benzo(a)anthracene	0.18 (0.15 - 0.23)	0.229 (0.075 - 0.680)	0.161 (0.056 - 0.310)	0.24 (0.10 - 0.40)
Benzo(a)pyrene	0.033 (0.027 - 0.043)	0.062 (0.010 - 0.220)[a]	0.013 (0.007 - 0.017)[a]	0.028 (0.015 - 0.048)
Dibenzofuran	13 (7.4 - 19)	6.1 (2.7 - 8.4)	8.5 (4.3 - 12)	18 (8.3 - 23)

Note: Sample size = 5

[a] Some undetected at reported minimum detection limit, ½ MDLs used for undetected values.

The PAHs measured at high concentrations in the initial leaching samples included those previously identified to be present in the highest concentrations in creosote (EPA 2008). These PAHs were: naphthalene, phenanthrene, 2-methylnaphthalene, anthracene, fluorene, acenaphthene, fluoranthene, chrysene, and pyrene.

The PAHs released by the five pile samples varied substantially with one pile releasing obviously different concentrations of some PAH chemicals than the other four pile samples (Appendix B). Naphthalene was a dominant chemical released by four of the samples, but was a minor component released from the one pile sample. Naphthalene is a relatively low molecular weight aromatic hydrocarbon with a structure of two fused benzene rings (Appendix A). It is the white crystalline chemical that is the common ingredient of moth repellants.

Dibenzofuran is an O-heterocyclic/furan that is a relatively minor creosote component (see Table 1). However, dibenzofuran is released to water from treated wood (Ingram et al. 1982) and was measured as one of the dominant creosote components in leachate from the ASARCO docks pile samples.

As part of the leachate investigation, the creosote content of the treated wood was analyzed to assess the source concentrations of the chemicals leaching into the seawater. Three pile samples analyzed to determine their total creosote content (Table 4) demonstrated a substantial variation in the amount of creosote present in the piles, from 12 to 28 lb/ft^3. Differences in the densities of the three samples demonstrate how the creosote treatment increases the density of wood resulting in treated wood having a higher density than water.

Table 4. Creosote Bulk Chemistry, Three Pile Samples

Pile	Bulk Density (g/cm^3)	Creosote (lb/ft^3)	Total Moisture (%)
Pile 1	1.09	27.6	20.1
Pile 3	1.01	12.3	16.7
Pile 5	1.06	22.3	17.5

Table 5 provides the results of analysis of the selected chemicals in three samples of creosote-treated wood cut from the same pile sections as the leachate samples. Despite differences in the total creosote content of the samples (Table 4) the concentrations of the specific chemicals were found to be very similar (Table 5).

Table 5. Creosote Chemical Concentrations, Three Pile Samples

CHEMICAL	Concentration (µg/g dw)		
	Pile 1	Pile 3	Pile 5
Naphthalene	30,000	36,000	27,000
2-Methylnaphthalene	16,000	14,000	14,000
Phenanthrene	36,000	42,000	32,000
Anthracene	7,000	7,400	3,900
Fluorene	15,000	15,000	12,000
Acenaphthene	15,000	15,000	13,000
Fluoranthene	12,000	16,000	11,000
Chrysene	1,300	1,500	1,200
Pyrene	9,700	11,000	8,900
Acenaphthylene	300	130	230
Benz(a)anthracene	1,600	1,800	1,400
Benzo(a)pyrene	400	410	340
Dibenzofuran	11,000	12,000	9,900

CREOSOTE CHEMICAL BIOACCUMULATION

Mussel samples collected prior to, during, and at the end of pile removal did not exhibit visual or odor evidence of creosote in their flesh.

Figure 11 shows the considerable increase in most of the measured PAHs during demolition of the three ASARCO Docks.

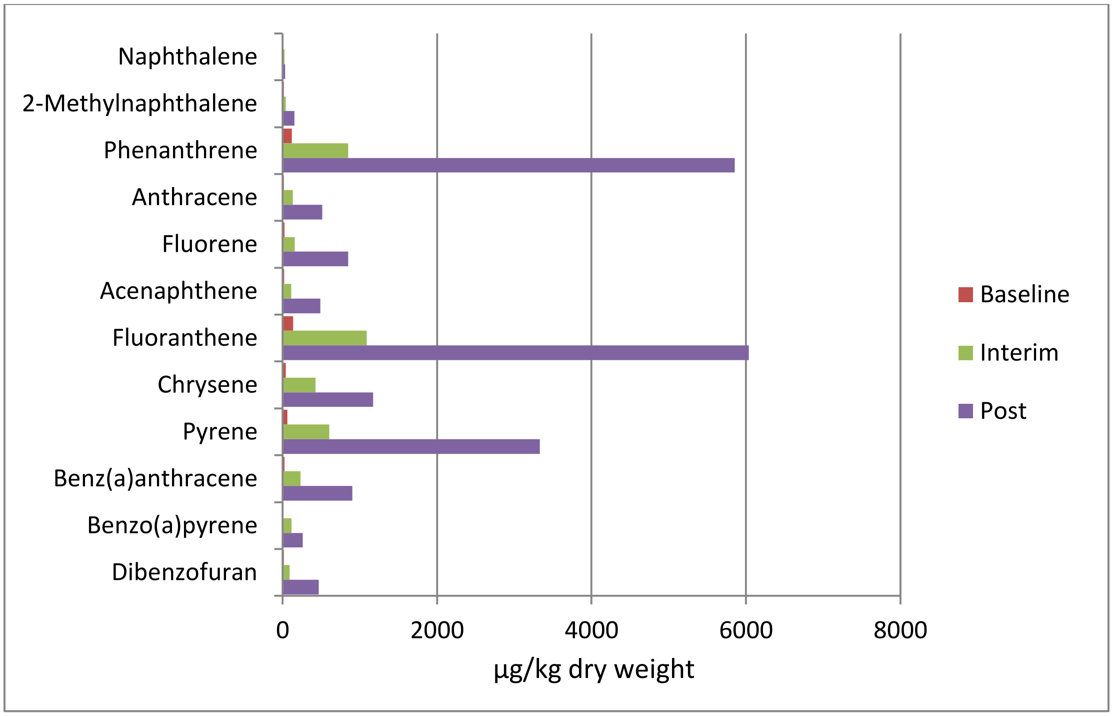

Figure 11. Mussel Tissue PAH and Dibenzofuran Concentrations during ASARCO Docks Demolition

Table 6 provides the actual concentrations of the selected PAHs and dibenzofuran in mussel tissue collected during each of the three sampling events. No mussels remained at a number of locations during the interim and post-demolition sampling events making it impossible to resample at these locations. The Table 6 data show an obvious increase in the tissue concentrations during the docks demolition, with the highest concentrations occurring near the end of the demolition.

Table 6. Mussel Tissue Concentrations of Specific Creosote Chemicals

PAH	**Concentration (µg/kg dw) / Location**[b]					
	Fuel Dock		**Copper Dock**		**Ore Dock**	
	NW	SE	NW	SE	NW	SE
Naphthalene						
Baseline	8	7[a]	7	7	8	8
Interim	25	14	NA	NA	12	15
Post	32	NA	NA	NA	17	NA
2-Methylnaphthalene						
Baseline	15	10	14	16	15	16
Interim	42	35	NA	NA	33	20
Post	153	NA	NA	NA	53	NA
Phenanthrene						
Baseline	118	88	147	177	142	177
Interim	849	778	NA	NA	1152	765
Post	5856	NA	NA	NA	2368	NA
Anthracene						
Baseline	17	13	20	20	24	39
Interim	133	132	NA	NA	230	212
Post	514	NA	NA	NA	237	NA
Fluorene						
Baseline	25	16	26	30	21	36
Interim	158	144	NA	NA	152	106
Post	847	NA	NA	NA	386	NA
Acenaphthene						
Baseline	19	12	20	22	16	26
Interim	109	109	NA	NA	85	71
Post	487	NA	NA	NA	202	NA
Fluoranthene						
Baseline	137	95	223	265	432	222
Interim	1091	958	NA	NA	2061	1588
Post	6036	NA	NA	NA	2193	NA
Chrysene						
Baseline	42	35	56	72	96	64
Interim	424	323	NA	NA	552	588
Post	1171	NA	NA	NA	333	NA
Pyrene						
Baseline	62	44	107	111	203	79
Interim	606	539	NA	NA	1333	941
Post	3333	NA	NA	NA	1228	NA
Benz(a)anthracene						
Baseline	24	21	40	23	61	36
Interim	230	200	NA	NA	424.2	376
Post	901	261	NA	NA	324.6	NA
Benzo(a)pyrene						
Baseline	10	6	11.0	10	20	17
Interim	115	73	NA	NA	182	176
Post	261	NA	NA	NA	83	NA
Dibenzofuran						
Baseline	17	12	20	23	19	24
Interim	91	90	NA	NA	79	57
Post	469	NA	NA	NA	219	NA

[a] Undetected at this method detection limit.

[b] Piles removed, no mussels available at this location.

The total solids and lipid content (percent) of the mussel tissue sampled was not the same during the three sample periods (Table 7). The baseline and interim samples had similar total solids and lipids content. However, the post demolition mussel samples had lower total solids and lipids content than the previous two sample sets. This may have been due in part to the smaller size of mussels in the last set as compared to those collected for the first two sets. The mussels remaining at the end of dock removal were a peripheral portion of the original population that appeared to have experience less favorable growing conditions than the mussels previously sampled. The lower lipid content of the smaller mussels appears to reflect the poorer rearing conditions. However, the PAH concentrations within the smaller mussels lipids were the highest measured indicating that their lower lipid content did not substantially reduce their capacity to accumulate PAHs released exposed creosote.

Table 7. Mussel Tissue Total Solids and Lipids Content

SAMPLE PERIOD	Total Solids %	Lipids %
Baseline	15-20	1.0-3.3
Interim	17	1.2-1.4
Post	11-12	0.5-0.7

DISCUSSION

Demolition of the three large docks at the ASARCO Smelter site on Commencement Bay in southern Puget Sound resulted in exposure of large amounts of creosote-treated pile surfaces within the water column. During removal of the dock's decks, substantial numbers of decayed piles broke beneath the water surface exposing fresh, long, and irregular surfaces of creosote-treated wood to the water moving through the site. These broken piles produced freshly exposed creosote-treated surfaces that apparently released substantial quantities of creosote chemicals into the water column, which were subsequently accumulated by mussels growing on nearby piles. Laboratory investigation of freshly exposed surfaces of the creosote-treated wood also demonstrated the substantial amounts of various creosote chemicals are released to the surrounding seawater in the days and weeks immediately following exposure.

The aged piles had dense populations of benthic invertebrates growing on their lower intertidal and subtidal surfaces, as is commonly observed on aged creosote-treated wood in marine conditions. These communities of sessile invertebrates indicate that the toxic components of creosote are no longer released from the surface of the wood after some uncertain time in the water, as their relatively sensitive larvae have settled and grown on the treated pile surface. The baseline condition of the mussels, which were collected from aged creosote surfaces, demonstrated low tissue concentrations of the creosote chemicals. However, visual, odor, and chemical analysis indicates that the treated wood beneath the aged surface retains potentially mobile chemicals.

The treated wood below the surface of the aged piles was exposed during demolition of the docks both by piles breaking and by shearing of piles. The amount of creosote treated wood surface exposed by breaking piles appeared to be much greater than the surface exposed by cutting piles. These freshly exposed surfaces released at least some of the creosote chemicals to the water flowing through the site, resulting in the elevated levels measured in the mussels sampled during demolition.

Pile stubs remaining from shearing both the intact piles and the broken pile stubs produced small amounts of freshly exposed creosote-treated surfaces. For most piles, the outer 3-5 cm (1.5-2 inches) of wood was penetrated with visible creosote (black to brown discoloration). The interior of the piles had a natural wood color with a few to numerous boring mollusk holes. In many piles the interior wood was completely missing from substantial portions of the piles between the lower intertidal level and the sediment surface.

Breaking and cutting the piles during demolition produced exposure of substantial fresh pile surfaces that apparently released creosote components to the surrounding water. Based on visual observations and a strong creosote odor, these freshly exposed surfaces appeared similar to the surface of newly treated piles. The two creosote leaching studies described in this report are an attempt to evaluate the nature and result of creosote that initially leached from the freshly exposed surfaces of aged piles. In these investigations creosote was assessed by measuring concentrations of PAHs, which are approximately 85% of the complex mixture of creosote chemicals.

CREOSOTE LEACHING

Initial visual and odor observations indicated that a substantial amount of at least some creosote chemicals were released from the freshly exposed surface of the aged piles. Although the interior of the aged piles was commonly severely degraded, the exterior creosote-treated layer of each pile was commonly intact with the exception of cracks. No boring organisms were detected in the creosote-treated outer ring of the piles. Apparently the aged creosote remained sufficiently toxic to prevent boring organisms from living within the creosote treated outer ring.

The creosote leaching study attempts to characterize the nature and rate of release of creosote chemicals into the surrounding seawater. The laboratory conditions were established to provide steady-state conditions that minimize dispersal, diffusion, and degradation of leached creosote chemicals. The limited water volume, absence of circulation (minimum surface loss), and lack of biological degradation of leached creosote chemicals provided maximum water concentrations in a short time, whereas the ambient site conditions provided a large water volume, continuous flushing produced by tidal currents, and probable biological degradation that minimized ambient water concentrations of the creosote chemicals and maximized the loss of the more volatile chemicals. However, the high concentrations accumulated by the mussels sampled from the site provide evidence that sufficient water concentrations occurred at the demolition site to produce rapid and considerable bioaccumulation.

The leaching rates of the creosote components decreased rapidly within the 336-hr test period measured in the laboratory tests. Leaching of some components decreased to very low levels within 48 hr, while others maintained reduced but substantial leaching into the 96-336-hr test period.

The creosote chemicals measured at high concentrations in the initial leaching samples included those previously identified to be present in the highest concentrations in creosote (EPA 2008). These creosote chemicals were: naphthalene, phenanthrene, 2-methylnaphthalene, anthracene, fluorene, acenaphthene, fluoranthene, chrysene, and pyrene. However, dibenzofuran was also prevalent in leachate samples from four of the five piles, but not in one sample.

The concentrations of PAHs leached from the pile samples showed substantial variability. Samples from pile 2 were substantially different than the other four piles. Likewise, different samples from the same pile (pile 3) produced different PAH concentrations in the seawater.

Naphthalene and dibenzofuran are relatively low molecular weight hydrocarbons that are likely to be readily released by freshly exposed creosote surfaces if they are present. Naphthalene was expected to be prevalent in the leaching investigation as it is a major component of creosote and relatively soluble in water (EPA 2008). However, dibenzofuran was not expected to be prevalent at a high concentration as it has not been reported as one of the major creosote components. The absence of any information on the nature of the creosote used to treat the ASARCO Dock piles prevents us from making any useful comparisons to other available information.

These laboratory concentrations do not demonstrate the concentrations of PAHs that occurred in the ambient water during removal of the ASARCO docks or will occur at other sites. The laboratory study was designed to produce worst case conditions. The *in-situ* conditions at the ASARCO site were highly variable during continuously changing tidal cycles and among locations within the pile fields. It was not practical to attempt to reproduce these highly variable conditions with the limited laboratory study. The PAH concentrations would be much lower with pile shearing than with substantial amounts of new creosote-treated wood due to the small amount of exposed surface area of sheared piles.

Goyette and Brooks (1998) measured PAH concentrations in water within 25 cm of new piles placed within six months prior to the measurement (Table 8). The concentrations measured by

Goyette and Brooks (1998) are much lower than our laboratory measurements, and the implications of our mussel bioaccumulation samples. We would not expect even the initial real world conditions to produce concentrations near those measured in our laboratory study. Also the concentrations measured after 6 months may have decreased substantially from higher initial levels as the creosote-treated wood surface aged. Aging apparently reduces the release of creosote chemicals, thereby allowing settlement of larvae and development of sessile invertebrate populations that become abundant on estuarine piles.

Table 8. PAH Concentration in the Water Column within 25 cm of New Creosote-Treated Piles at Sooke Basin 6 Months Post Installation (from Goyette and Brooks 1998)

PAH	Concentration (µg/L)
Acenaphthene	0.007
Naphthalene	0.007
Phenanthrene	0.006
Fluorene	0.005
Fluoranthene	0.004
Chrysene	<0.001
Pyrene	<0.001
Anthracene	<0.001
Others	<0.001
Total PAH	0.031

BIOACCUMULATION

The mussels growing on piles adjacent to the freshly exposed creosote surfaces of cut and broken piles offer the best on-site monitoring of maximum biological accumulation of the released PAHs. These filter feeding blue mussels are continuously exposed to creosote components in the water during feeding that passes large volumes of water over their gills. The large surface of their gills provides a thin membrane through which PAHs can be accumulated. Previous research (Eaton and Zitko 1978, Baussant et al. 2001, Boehm et al. 2005) has shown that blue mussels accumulate essentially the same PAH chemicals at essentially the same rates as semipermeable membrane sampling devices (SPMDs) that are often used to monitor organic chemicals in ambient water. The mussels growing on the ASARCO docks site appear to have provided a reliable sampling device already established on site and acclimated to ambient conditions.

The initial concentrations of PAHs in the mussel's tissues were found to be low as shown in Table 6. However, the concentrations of many creosote components increased substantially during dock demolition. A few of the creosote components at some locations were at or near their peak concentrations when sampled at the interim event. However, most creosote components continued to increase at most locations throughout dock demolition reaching high concentrations near the end of demolition.

Following exposure of freshly broken and cut piles surfaces, the concentrations of PAHs in the mussel's tissues were found to be considerably elevated as shown in Table 6. Essentially all the measured PAHs (except naphthalene) and dibenzofuran increased by an order of magnitude or more in the tissue of mussels remaining on site during dock demolition.

Given the estimated half-life of the PAHs in water (Table 9), the continuous increase in mussel tissue concentrations provides an indication that creosote chemicals were continuously released during dock demolition.

Table 9. Estimated Half-lives of PAHs in Various Environmental Media (EPA 2008)

PAH	No. Aromatic Rings	Molecular wt.	Est. Half-Life (weeks)			K_{ow}
			Water	Soil	Sediment	
Naphthalene	2	128	1	8	32	3.37
Acenaphthene	3	152	3	32	104	4.03
Fluorene	3	166	3	32	104	4.12
Phenanthrene	3	178	3	32	104	4.57
Anthracene	3	178	3	32	104	4.54
Fluoranthene	4	202	8	104	312	5.22
Pyrene	4	202	8	104	312	5.18
Chrysene	4	228	8	104	312	5.91
Benz(a)anthracene	4	228	8	104	312	5.91
Benzo(a)pyrene	5	252	8	104	312	6.04

Bioaccumulation by on-site mussels was evaluated during docks removal but evaluating depuration of the mussels following completion of the demolition was not possible. There were no remaining mussel populations present following dock demolition to track the decline in creosote components in mussel tissue in the months following dock removal and sediment capping. The results of other investigations imply that the PAHs would likely be rapidly lost from the mussels following removal of the source of contamination.

The EPA (2008) data provided in Table 10 indicate the potential loss of the accumulated creosote chemicals from mussel tissue following removal of the creosote source. This information indicates that PAH concentrations in the mussels would have approached background concentrations within a few weeks after the creosote in the water column was eliminated.

Table10. Estimated Half-Lives of PAHs in Mussels (EPA 2008)

PAH	Estimated Half Life (days)
anthracene	1.9
naphthalene	2
phenanthrene	1.9-2.2
fluoranthene	2.0-11.1
pyrene	4.1-5.5
chrysene	5.0-14.2
fluoranthene	29.8

PILE CREOSOTE CONTENT

No information is available on the original treatment of the piles removed at the ASARCO Smelter site. The two larger docks (Ore and Copper Docks) were constructed between 1923 and 1931. The Fuel Dock was constructed at an unknown later date. To evaluate the nature of the creosote contained in the piles, three samples were analyzed for total creosote content.

Three pile samples analyzed to determine their total creosote content (see Table 4) demonstrated a substantial variation in the amount of creosote present in the piles from 12 to 28 lb/ft^3. The densities of the three samples demonstrate how the creosote treatment increases the density of wood resulting in treated wood having a higher density than water.

The results of analysis of the selected chemicals in three samples of creosote-treated wood cut from the same pile sections as the leachate samples (see Table 5) indicate considerable concentrations of creosote chemicals remain in the treated portions of the approximately 80-year old piles. Despite differences in the total creosote content of the three samples (see Table 4), the concentrations of the specific chemicals were found to be similar. These concentrations of creosote chemicals are sufficiently high to produce the substantial leaching and bioaccumulation measured by this investigation.

CONCLUSIONS

The laboratory investigation of creosote leaching demonstrated that substantial amounts of some creosote chemicals leach from freshly exposed creosote-treated surfaces of aged timber piles. Samples of artificial seawater in which 2-cm cubes of creosote-treated piles were immersed had elevated levels of creosote components within 24 hours. The rapid release of creosote components was similar to the observations of Bestari et al. (1988a) in freshwater microcosms. The creosote components also appear to break down or are released rapidly from water. Bestari et al. (1988a) observed post-treatment concentrations of PAHs in water decreased exponentially with time in the microcosms. In a subsequent investigation Bestari et al. (1988b) determined that creosote was primarily lost from water via degradation pathways such as photolysis and microbial decomposition. The cube leaching study also showed a substantial variability in the concentrations of chemicals released from different piles and duplicate samples of one pile.

The concentrations of creosote chemicals in tissue of mussels collected from ASARCO Dock piles prior to demolition (baseline) were low (see Table 4) similar to the findings of Goyette and Brooks 2001. The creosote chemical concentrations in the site's mussels increased substantially during dock demolition, with increases exceeding an order of magnitude at completion of the demolition for most chemicals measured. It appears that the creosote chemicals were derived from freshly exposed surfaces of treated piles that were produced when piles broke or were sheared. Breaking piles appear to have produced larger amounts of freshly exposed surface area due to the irregular nature of the breaks compared to the flat cross section produced by shearing. Similar results were found in the surface of clean sediment adjacent to the demolished docks, with most creosote chemicals increasing substantially in the sediment immediately adjacent to the docks (Parametrix 2011b).

Following removal of the docks there were no mussel populations remaining on the site with sufficient numbers to provide adequate samples for analysis. Based on the decline of PAHs in Prince William Sound mussels following the EXXON Valdez oil spill (Page et al. 2005), it is likely the PAH concentrations of the sites biota have diminished and will continue to do so rapidly since the creosote source has been removed or isolated, based on the estimated half-life of PAHs in mussels (EPA 2008). McLeese and Burridge (1987) found PAH concentrations in mussels decreased by 25-100% in a 14-day post exposure period.

The mussels and other biota at the docks' demolition site experienced an acute exposure of up to 90 days to variable and unknown concentrations of PAHs in the water at the site. There was no observed effect to the mussels, other than the substantial increases in tissue concentrations of the monitored PAHs. It is likely that the PAH concentrations released to the surrounding water from the broken and cut piles were similar to or less than those occurring with the installation of new piles. Goyette and Brooks (2001) found that mussels held in cages adjacent to newly installed piles in Sooke Harbor did not show any adverse effect on survival. However, mussels held within 15-30 cm of new creosote treated piles grew more slowly than did mussels held at greater distances. Donkin et al. (1991) reported 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. They found hydrocarbons with aqueous solubility's >70 $\mu g/cm^3$ were toxic to feeding activity of mussels when bioaccumulated to similar concentrations, whereas compounds of lower solubility were less toxic. However, they observed that the polyaromatic hydrocarbons pyrene and fluoranthene were less toxic than predicted based on the chemicals solubility.

This study demonstrates that demolition of aged creosote-treated wood structures has the potential to release substantial quantities of creosote chemicals that may impact the adjacent biota and sediment. Freshly broken or cut pile surfaces can leach substantial quantities of creosote chemicals to the water column at a project site. These releases are likely to produce variable concentrations of PAHs in the water column depending on site conditions. However, these releases are likely to be of relatively short duration, extending no longer than the time that the freshly exposed creosote treated surfaces are present.

Sampling of sediment adjacent to the ASARCO Docks indicated that increased concentrations of PAHs occurred in close proximity to the demolished docks (Parametrix 2011b). However, there was no evidence that water concentrations resulted in a wide distribution of PAHs in the surrounding sediment.

It is desirable to anticipate potential adverse impacts associated with creosote release for projects that propose to remove deteriorated piles. Aged piles may potentially break during removal with demolition of dock superstructures. It may be appropriate to consider corrective action measures such as detailed debris cleanup from the bottom and enhanced natural recovery by placing a thin layer of sand cap material following pile removal. Monitoring during demolition will aid in assessing impacts and the need for corrective action.

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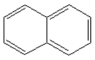
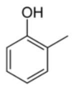
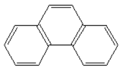
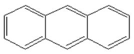
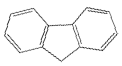
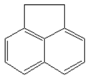
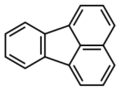
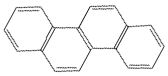
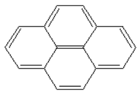
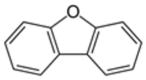
APPENDIX A

Creosote PAH Characteristics

Table A1. Creosote Chemical and Physical Characteristics (from EPA 2008, National Library of Medicine-TOXNET, Howard et al. 1991)

Chemical	Chemical Structure	Formula	Mol. Wt.	~ % of Creosote	Water Solubility at 25°C (mg/L)[a]	Log K_{ow} at 25°C (K_{ow})[1]	Photolysis half-life (days)[1]	Henry's Law Constant at 25°C (Pa m^3/mol)
Naphthalene		$C_{10}H_8$	128.2	11	3.1×10^{-2}	3.37 (2344)	2.96	43.01
2-Methylphenol		C_7H_8O	108.1	11	2.5×10^{-2}	1.95	1-7	1.20
Phenanthrene		$C_{14}H_{10}$	178.2	11	1.1×10^{-3}	4.57 (37153)	2	3.24
Anthracene		$C_{14}H_{10}$	178.2	11	4.5×10^{-5}	4.54 (34673)	0.34	3.96
Fluorene		$C_{13}H_{10}$	166.2	7	1.9×10^{-3}	4.18 (15136)	4.6	7.87
Acenaphthene		$C_{12}H_{10}$	154.2	3	3.8×10^{-3}	3.92 (8318)	1	12.17
Fluoranthene		$C_{16}H_{10}$	202.3	3	2.6×10^{-4}	5.22 (165958)	0.88	1.037
Chrysene		$C_{18}H_{12}$	228.3	2	1.3×10^{-5} 2×10^{-3}	1.65 (44.7)	4.2	5.23
Pyrene		$C_{16}H_{10}$	202.3	2	1.3×10^{-4}	5.18 (151356)	<1	0.92
Dibenzofuran		$C_{12}H_8O$	168.2	<1	3.1×10^{-7}	3.2 - 4.1	7-28	2.13

[a] Various sources provide substantially different values.

APPENDIX B

Creosote Chemical Leaching Data

Table B1. Creosote Chemicals Measured in Leach Water 13ºC

	Pile Sample Concentration (ng/mL)				
Analyte	P1	P2	P3	P4	P5
24 hr Leaching Period					
Naphthalene	380	0.019	0.024	300	0.063
2-Methylnaphthalene	54	0.23	6.8	36	12
Phenanthrene	30	16	18	39	49
Anthracene	3.4	2.8	1.9	4	6.2
Fluorene	22	9.2	13	23	23
Acenaphthene	33	12	18	57	29
Fluoranthene	3.9	4.7	3.4	7.7	13
Chrysene	0.17	0.38	0.25	0.38	0.84
Pyrene	3.3	3.6	2.8	6.5	8.3
Acenaphthylene	0.85	0.13	0.4	0.26	0.27
Benz(a)anthracene	0.25	0.45	0.33	0.56	1.1
Benzo(a)pyrene	0.033	0.11	0.064	0.15	0.22
Dibenzofuran	22	8.1	13	28	22
48 hr Leaching Period					
Naphthalene	89	0.009	0.012	120	0.014
2-Methylnaphthalene	28	0.029	5	18	1.5
Phenanthrene	15	1.6	11	15	22
Anthracene	1.7	0.79	1.2	1.5	2.3
Fluorene	9.5	3.1	7.7	8.7	10
Acenaphthene	15	5.3	11	28	13
Fluoranthene	3.1	1.5	2.3	3.7	5.8
Chrysene	0.16	0.12	0.13	0.13	0.23
Pyrene	2.4	1.1	1.5	3	3.6
Acenaphthylene	0.65	0.063	0.32	0.21	0.14
Benz(a)anthracene	0.24	0.16	0.19	0.28	0.31
Benzo(a)pyrene	0.033[b]	0.021	0.018	0.052	0.029
Dibenzofuran	9.7	3.4	8.2	11	10
96 hr Leaching Period					
Naphthalene	0.025	0.016	0.025	0.021	0.023
2-Methylnaphthalene	19	0.004	6	9.7	0.62
Phenanthrene	15	0.021	12	18	22
Anthracene	1.6	0.125[b]	1.2	1.8	2.4
Fluorene	12	0.14	9.6	13	12
Acenaphthene	19	8.3	15	36	16
Fluoranthene	2.6	0.96	1.6	3.8	5.7
Chrysene	0.17	0.065	0.13	0.19	0.4
Pyrene	2.2	0.52	1.2	3.1	3.9
Acenaphthylene	0.62	0.1	0.38	0.27	0.16
Benz(a)anthracene	0.26	0.072	0.18	0.33	0.54
Benzo(a)pyrene	0.03	0.014	0.019	0.057	0.058
Dibenzofuran	13	2.8	11	17	12

336 hr Leaching Period					
Naphthalene	0.012[a]	0.0062	0.012[a]	0.0325[a]	0.0055[a]
2-Methylnaphthalene	0.73	0.0017[a]	0.47	1.2	0.0017[a]
Phenanthrene	33	0.23[a]	33	71	2.2[a]
Anthracene	5.2	0.24[a]	3.4	8.7	1.1[a]
Fluorene	33	0.0017[a]	31	59	0.12
Acenaphthene	38	0.025[a]	36	110	24
Fluoranthene	4.4	1.4	4.2	11	5.8
Chrysene	0.24	0.059	0.26	0.35	0.23
Pyrene	2.6	0.0088	2.6	6.9	1.1
Acenaphthylene	1.1	0.0055[a]	0.89	1.8	0.68
Benz(a)anthracene	0.31	0.04	0.31	0.55	0.3
Benzo(a)pyrene	0.052	0.012	0.055	0.08	0.036
Dibenzofuran	31	0.0017[a]	31	73	0.66

[a] Analyte undetected at reported minimum detection limit, ½ MDLs used for undetected values.

Table B2. Creosote Chemicals Measured in Leach Water 7°C

	Pile Sample Concentration (ng/mL)				
Analyte	P1	P2	P3	P4	P5
24 hr Leaching Period					
Naphthalene	380	0.019	0.024	300	0.063
2-Methylnaphthalene	54	0.23	6.8	36	12
Phenanthrene	30	16	18	39	49
Anthracene	3.4	2.8	1.9	4	6.2
Fluorene	22	9.2	13	23	23
Acenaphthene	33	12	18	57	29
Fluoranthene	3.9	4.7	3.4	7.7	13
Chrysene	0.17	0.38	0.25	0.38	0.84
Pyrene	3.3	3.6	2.8	6.5	8.3
Acenaphthylene	0.85	0.13	0.4	0.26	0.27
Benz(a)anthracene	0.25	0.45	0.33	0.56	1.1
Benzo(a)pyrene	0.033	0.11	0.064	0.15	0.22
Dibenzofuran	22	8.1	13	28	22
48 hr Leaching Period					
Naphthalene	89	0.0094	0.012	120	0.014
2-Methylnaphthalene	28	0.029	5	18	1.5
Phenanthrene	15	1.6	11	15	22
Anthracene	1.7	0.79	1.2	1.5	2.3
Fluorene	9.5	3.1	7.7	8.7	10
Acenaphthene	15	5.3	11	28	13
Fluoranthene	3.1	1.5	2.3	3.7	5.8
Chrysene	0.16	0.12	0.13	0.13	0.23
Pyrene	2.4	1.1	1.5	3	3.6
Acenaphthylene	0.65	0.063	0.32	0.21	0.14
Benz(a)anthracene	0.24	0.16	0.19	0.28	0.31
Benzo(a)pyrene	0.033[a]	0.021	0.018	0.052	0.029
Dibenzofuran	9.7	3.4	8.2	11	10
96 hr Leaching Period					
Naphthalene	0.025	0.016	0.025	0.021	0.023
2-Methylnaphthalene	19	0.0036	6	9.7	0.62
Phenanthrene	15	0.021	12	18	22
Anthracene	1.6	0.125[a]	1.2	1.8	2.4
Fluorene	12	0.14	9.6	13	12
Acenaphthene	19	8.3	15	36	16
Fluoranthene	2.6	0.96	1.6	3.8	5.7
Chrysene	0.17	0.065	0.13	0.19	0.4
Pyrene	2.2	0.52	1.2	3.1	3.9
Acenaphthylene	0.62	0.1	0.38	0.27	0.16
Benz(a)anthracene	0.26	0.072	0.18	0.33	0.54
Benzo(a)pyrene	0.03	0.014	0.019	0.057	0.058
Dibenzofuran	13	2.8	11	17	12

	336 hr Leaching Period				
Naphthalene	0.012[a]	0.0062	0.012[a]	0.0325[a]	0.0055[a]
2-Methylnaphthalene	0.73	0.0017[a]	0.47	1.2	0.0017[b]
Phenanthrene	33	0.23[a]	33	71	2.2[b]
Anthracene	5.2	0.24[a]	3.4	8.7	1.1[b]
Fluorene	33	0.0017[a]	31	59	0.12
Acenaphthene	38	0.025[a]	36	110	24
Fluoranthene	4.4	1.4	4.2	11	5.8
Chrysene	0.24	0.059	0.26	0.35	0.23
Pyrene	2.6	0.0088	2.6	6.9	1.1
Acenaphthylene	1.1	0.0055[a]	0.89	1.8	0.68
Benz(a)anthracene	0.31	0.04	0.31	0.55	0.3
Benzo(a)pyrene	0.052	0.012	0.055	0.08	0.036
Dibenzofuran	31	0.0017[a]	31	73	0.66

[a] Analyte undetected at reported minimum detection limit, ½ MDLs used for undetected values.