THE NATURE AND SOURCES OF PAH IN SEDIMENTS IN THE VICINITY OF THE FORMER EXXONMOBIL TERMINAL

2014 INVESTIGATION

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EXECUTIVE SUMMARY

The Portland Harbor Superfund Site (SFS) boundaries extend from the Columbia Slough to the Broadway Bridge (River Miles 1.9 to 11.8). Sediment Management Areas and Comprehensive Benthic Risk areas (CBRA) within the SFS have been identified in the Portland Harbor Remedial Investigation/Feasibility Study (RI/FS). The Former ExxonMobil Terminal is located on the west shore of the Willamette River proximal to SMA 9D and two Comprehensive Benthic Risk Areas—CBRA 9D-2 and CBRA 9D-3—both located within SMA 9D (**Figure 1**). Since 1928, the Former ExxonMobil Terminal has provided the storage and distribution of fuel oils, gasoline and diesel fuels, which are potential sources of petroleum-derived (petrogenic) polycyclic aromatic hydrocarbons (PAH). Located upstream from the Former ExxonMobil Terminal are the McCormick & Baxter property and the Northwest Natural-Gasco (Gasco) property. These sites are documented sources of creosote and manufactured gas plant (MGP) tar wastes, respectively, to the river sediments. Creosote and MGP tar are potent sources of combustion-derived (pyrogenic) PAH.

In 2014, NewFields sampled sediments in order to determine the source(s) of the PAH impacting sediments in SMA 9D. Sediment samples were collected from upstream of the McCormick & Baxter Property to downstream of SMA 9D, offshore of the former Linnton Plywood Property (**Figures 15, 16a-d**). The study area was more extensive than the area encompassed by SMA 9D to provide information on (1) the potential migration of upstream sources of PAH into SMA 9D, (2) potential sources within the SMA 9D area, and (3) potential PAH impacts in the area immediately downstream of SMA 9D (Section 4.0).

Contamination was primarily evaluated by the presence and composition of total petroleum hydrocarbons (TPH) and polycyclic aromatic hydrocarbons (PAH). Several key distinctions between the chemical composition of creosote and MGP tars versus petroleum are used in forensic fingerprinting of potential sources of PAH contamination. Creosote and MGP tars are composed primarily of pyrogenic PAH, while petroleum is comprised primarily of petrogenic PAH. Pyrogenic and petrogenic PAH are readily differentiated by the relative amounts of parent PAH and alkylated isomers (alkylated PAH) (Section 2). Petroleum contains a significantly higher proportion of alkylated PAH than creosote or MGP tars. In addition, the concentration of PAH in petroleum products is lower than in creosote or MGP tars. For the purpose of this report, PAH are described in several manners; 1) Sum of EPA Priority Pollutant PAH (TPAH16), 2) Percentage of alkylated PAH isomers (%Alkyl PAH) (i.e., a measure of the relative degree of petroleum influence) and 3) Total Polycyclic Aromatic Hydrocarbons (TPAH: sum of parent and alkylated PAH concentrations). Differences in these three metrics are used to determine whether the sources of PAH contamination is petrogenic (petroleum-derived), pyrogenic (creosote or MGP-derived), or mixtures thereof. Total petroleum hydrocarbons (TPH) are an additional measurement used to distinguish commercial fossil fuels from one another as well as recognize the presence of naturally occurring organic matter in sediments.

Remedial Investigation data provided TPAH16 concentrations that exhibited a spread of PAH at any given river mile, indicated a dramatic spike between River Miles 6 and 7 where the McCormick & Baxter (River Mile 6.8 – 7.2) and Gasco (River Mile 6.1 – 6.4) properties are located. Elevated, but progressively lower concentrations of TPAH16 are found downstream from this area to SMA 9D, CBRAs 9D-2 and 9D-3 as well as sediments proximal to the Former ExxonMobil Terminal (**Figure 6**). The pattern and levels of TPAH16 contamination along the western bank of the river from the Gasco property to downstream areas indicated that TPAH16 contaminants migrated from the Gasco property to sediments near and in

SMA 9D and other downstream areas (Figure 7). This finding is further substantiated by the additional studies conducted by Newfields as described below.

In this study, NewFields found that the upstream sediments contained low concentration mixtures of diffuse anthropogenic PAH (e.g., a mix of petrogenic and pyrogenic PAH) (Section 6.1). TPH and TPAH concentrations ranged from 51 to 207 mg/Kg and 537 to 743 µg/Kg, respectively. The upstream sediments reflect concentrations within the range found in typical urban "background" sediments. The %Alkyl PAH in the upstream sediment samples ranged from 23% (highly pyrogenic) to 71% with an average of 48%. This variability in %Alkyl PAH indicates that the upstream sediments contain PAH that are heterogeneous, but primarily pyrogenic in nature. The gas chromatograms of these samples exhibit features characteristic of urban background hydrocarbon contamination.

Slightly downstream from where the upstream samples were collected is the McCormick & Baxter property. TPH and TPAH concentrations ranged from 97 to 268 mg/Kg and 341 to 4,505 µg/Kg, respectively (Section 6.2). These levels are slightly elevated compared to the upstream samples. The %Alkyl PAH level observed in one of the two sediment samples (S27-S) from this area was 59%, indicative of a mixture of pyrogenic and petrogenic PAH. For sample S26-S the %alkyl PAH was 26% consistent with a highly pyrogenic source. Thus, sediments in the vicinity of the McCormick & Baxter property were variable in PAH composition, reflecting upstream conditions mixed with PAH of pyrogenic origin. The wood treating product creosote used on the McCormick & Baxter property is the most likely source of the pyrogenic PAH contamination in these samples. The gas chromatograms of the two samples from this area are consistent with those from the upstream "background" samples with the exception of the presence of additional resolved peaks that are the pyrogenic, 4-ring parent PAH.

Downstream from the McCormick & Baxter property and on the western bank of the river, a dramatic elevation in PAH contamination was observed adjacent to the Gasco property (Section 6.3). Samples from the immediate vicinity of the Gasco property contained TPH and TPAH concentrations that greatly exceeded the hydrocarbon contaminant levels observed in any other areas investigated in this study. TPH concentrations in this area ranged from 62 to 35,300 mg/Kg with an average concentration of 8,120 mg/Kg in the three sampling stations proximal to the Gasco Property shoreline. TPAH concentrations ranged from 9,027 to 13,408,000 µg/Kg. The %Alkyl PAH values ranged from 10 to 31% indicative of PAH that are highly pyrogenic in nature. This conclusion is further support by the PAH histograms which show the well-recognized pattern of pyrogenic PAH (**Figure 22**). Thus, the Gasco samples have a chemical composition indicative of tar wastes released during former MGP operations at the site.

This characteristic pattern of pyrogenic PAH contamination is seen to spread from the vicinity of the Gasco Property to SMA 9D, indicative of the downstream transport and deposition of wastes and/or impacted sediments from the upstream Gasco Property area. The PAH levels in sediments downstream of the Gasco site were lower than the area adjacent to the Gasco property, but were still significantly elevated compared to the upstream "background" samples, but substantially lower than observed in the area proximal to the Gasco property. TPH and TPAH concentrations in SMA 9D ranged from 49 to 9,590 mg/Kg and 1,913 to 3,308,740 µg/Kg, respectively (Section 6.4). Some of the lowest TPAH concentrations occurred immediately offshore of the Former ExxonMobil Terminal. The gas chromatograms of the majority of samples from this area exhibit characteristics of dominantly MGP tars. However, the gas chromatograms of four samples from three different sample locations showed characteristics of a weathered, broad boiling range petroleum such as a heavy fuel oil intermingled with other pyrogenic and naturally occurring hydrocarbons (**Figure 27**).

The former Linnton Plywood property is located immediately downstream of SMA 9D. TPH and TPAH concentrations in this area ranged from 180 to 279 mg/Kg and 1,742 to 2,626 µg/Kg, respectively (Section 6.5.1). The TPH levels are similar to those observed among the upstream samples and thus, are consistent with urban background. The TPAH levels are slightly elevated compared to the upstream area and further analysis indicated that the PAH in these samples are highly pyrogenic.

Terminal 4, Slip 3 is located downstream of SMA 9D. TPH and TPAH concentrations in this area ranged from 136 to 292 mg/Kg and 2,371 to 14,374 µg/Kg, respectively. Similar to the Linnton property area, the TPH levels are consistent with urban background levels and the PAH were determined to be highly pyrogenic in nature.

In conclusion a clear gradient of pyrogenic PAH contamination downstream from the Gasco property to the Former ExxonMobil Terminal was established. With the exception of two localized sampling locations (one offshore of US Moorings [just downstream of Gasco] and the other just offshore of the Former ExxonMobil Terminal), there was no evidence of meaningful petroleum-derived PAH in the SMA 9D sediments downstream of the Gasco site. Pyrogenic PAH-rich MGP tars from the Gasco property are the overwhelming source of PAH to immediate downstream sediments of the site, including the entirety of SMA 9D, the two Comprehensive Benthic Risk Areas within SMA 9D, and offshore of the Former ExxonMobil Terminal.

1.0 INTRODUCTION

Polycyclic aromatic hydrocarbons (PAH) are chemicals of potential concern found in sediments of the Portland Harbor Superfund Site (SFS). Based on several rounds of Remedial Investigation data developed by the Lower Willamette Group and from available private party studies, it is evident that PAH in the Portland Harbor SFS are ubiquitous, and found both in the surface sediment layer (< 30 cm), as well as deeper horizons of the sediment column (Lower Willamette Group 2011). The widespread occurrence of PAH in urban sediments is common, and has long been known to result from non-point discharges of PAH from storm water runoff, and from certain kinds of industrial point sources that can release PAH to waterways (e.g., Youngblood and Blummer 1975; Laflammme and Hites 1978; Eagenhouse et al. 1982; Stout et al. 2004). Focused investigations are typically needed to identify the primary and other contributing sources of PAH to urban waterways.

The Portland Harbor Superfund Site area extends from the Columbia Slough to the Broadway Bridge along the Willamette River, defined as between Willamette River Mile (RM) 1.9 to RM 11.8. The river is divided into mile-long segments of the Willamette River that are measured upstream of the confluence of the Willamette and Columbia Rivers (RM 0). The River in this area is slow moving and tidally influenced during much of the year. The River has been periodically dredged to a depth of about 40 feet allowing for vessel traffic along the lower reach of the River. Numerous industries, including an oil gasification plant, ship repair facilities, bulk oil storage and transfer facilities, agricultural chemical manufacturing, rail car construction, wood treating facilities, and port facilities operated or continue to operate, along the shore of the river (NOAA at http://www.darrp.noaa.gov/northwest/portharbor/).

Sediment Management Areas (SMA) within the SFS were defined in the LWG's 2011 Draft Remedial Investigation (RI) report as "areas and volumes of sediments contributing to unacceptable risks segregated into discrete units for the purposes of the identification and evaluation of remedial technologies in the feasibility study" (Lower Willamette Group 2011). Further, discrete areas that exhibited the potential for unacceptable risk to the benthic invertebrate communities were identified as comprehensive benthic risk areas (CBRA). The CBRAs were identified based on a combination of bioassay results, concentrations of chemicals of potential concern (COPC), and bioaccumulation modeling. Areas where COPC concentrations were shown or predicted to exceed sediment quality values (SQVs), or where organisms were predicted to accumulate COPCs to concentrations above tissue toxicity reference values (TRVs) were identified as potential benthic risk areas.

The Former ExxonMobil Terminal is located on the west shore of the Willamette River between approximately River Miles 4.9 to 5.4. The Former ExxonMobil Terminal is proximal to Sediment Management Area 9D (SMA 9D) which was identified in the LWG 2011 Draft RI report and which spans the center of the river to the western shoreline of the Willamette River from approximately the Former ExxonMobil Terminal to the margins of the upstream U.S. Moorings Property between approximately RM 5.0 and 6.1. (**Figure 1**). Two comprehensive benthic risk areas identified in the LWG 2011 Draft RI report—CBRA 9D-2 and CBRA 9D-3—are located within SMA 9D. The Former ExxonMobil Terminal occupies an area of about 29 acres on the western bank of the Willamette River. The site is bounded on the north and south by other petroleum distribution facilities, on the west by St. Helens Road, and on the east by the Willamette River. The facility stored and distributed fuel oils, gasoline, and diesel fuels since about 1928. ExxonMobil was the sole owner of the facility until 2001, when the product storage and distribution portions were sold to Shore Terminals. ExxonMobil maintains ownership of a lubricant distribution facility that occupies 5 acres in the northwest portion of the site (Acton Mickelson Environmental, Inc. 2008).

Prior to the NewFields 2014 investigation, there was limited data of forensic chemistry quality to fully describe the characteristics of PAH in SMA 9D. Furthermore, there were only limited measurements of PAH along the immediate shoreline of the Former ExxonMobil Terminal. The ability to understand potential contribution of PAH from the Former ExxonMobil Terminal (as well as other nearby properties) was limited by this lack of data.

ExxonMobil hired NewFields to carry out a forensic chemistry investigation to better understand the nature of PAH in the vicinity of SMA 9D, and to determine the extent, if any, of potential contributions of PAH to the Willamette River from the Former ExxonMobil Terminal. The field work for this investigation was conducted in August, 2014. The study included collection of surface and deeper sediments upstream, within the footprint of, and just downstream of SMA 9D. These sediments were subjected to a forensic hydrocarbon chemical analysis to discern the type(s) of PAH present in the sediments. Complementing the conventional forensic analysis of the sediments was a solid phase micro-extraction (SPME) study of the dissolved phase pore water concentrations of PAH in SMA 9D. This aspect of the investigation, carried out by scientists from Texas Tech University (TTU), was performed in order to provide insight into the chemical makeup of dissolved phase pore water PAH that might pose potentially adverse effects to benthic organisms.

In advance of the forensic investigation, NewFields understood that the Northwest Natural-Gasco Property (Gasco Property) was a dominant source of PAH to the study area (see discussion below in Section 3). A manufactured gas plant (MGP) had been operated at the Gasco Property, where high concentration, PAH-rich MGP tar wastes were released to the river (Hahn and Associates 2007). The potential that PAH from the Gasco Property might have affected SMA 9D and the Benthic Risk Areas within the SMA was evaluated in this investigation.

2.0 PAH – A FORENSIC CHEMISTRY PERSPECTIVE

PAH compounds are ubiquitous in the environment (ATSDR 1995). They originate from a large number of sources which can be broadly classified as biogenic, petroleum-derived (petrogenic), or combustion-derived (pyrogenic).

- Biogenic sources are natural sources of PAH. PAH from these naturally occurring processes arise from the geologic processes that accompany the degradation of natural organic matter.
- Petroleum-derived (petrogenic) sources have both natural and anthropogenic origins. Natural sources of PAH include natural seeps and petroleum-containing rock outcroppings. Anthropogenic sources of PAH arise directly from crude oil or refined petroleum products. Often in environmental investigations, the PAH from these kinds of sources are observed in media contaminated with spilled oil or fuel. In urban environments, petroleum-derived PAH can arise from a wide array of materials including pavement asphalt, building materials, fuels, and oils.
- Combustion-derived (pyrogenic) sources are generally anthropogenic sources of PAH which include those derived from fires, combustion of petroleum products, combustion and conversion of coal, and metallurgical processing. Notably, urban air and urban soils are impacted by PAH that arise from tailpipe exhausts, controlled and uncontrolled combustion typical of urban areas, and tar-derived construction materials.

Petroleum and pyrogenic materials contain hundreds of PAH parent and alkylated isomers. The 16 EPA Priority Pollutant PAH (listed in bold in Table 1) are a small subset of a much larger number of parent and alkylated PAH assemblages. Forensic chemists measure groups of similar alkylated PAH, and report them as alkyl homologues with different levels of alkyl substitution, i.e., the sums of C1-, C2-, C3- and C4-substituted parent (substituted) PAH (Douglas et al. 2007). See Table 1 for a listing of the PAH and alkylated PAH measured in the 2014 NewFields investigation.

Because of their varied natural and anthropogenic sources, PAH are commonly found in sediments from urban, rural, and remote environments. PAH preferentially adsorb to sediments because of their affinity for particulate surfaces. PAH are common in sediments. They migrate to sediments via atmospheric deposition, point and non-point discharges, land runoff, and landside point-source releases of PAH-containing wastes. Because of their ubiquity, PAH are present at some *background* concentration in water, soil and sediments. Background concentrations of PAH in environmental media are dependent upon many variables, but are consistently higher in urbanized areas than in rural areas due to the higher degree of anthropogenic activities in urbanized areas (EPRI 2003) and have generally increased over the past 100 years due to increased urbanization (Yan et al. 2005).

Stout et al. (2004) compiled concentrations and distribution of PAH in “urban background” sediments (i.e. unaffected directly by point source discharges) from various waterways. The vast majority (96%) of the urban background-impacted sediments studied contained less than 20,000 µg/Kg Total EPA Priority Pollutant PAH (TPAH16). Sediments containing significantly higher concentrations of PAH were suggested by Stout et al. to indicate the presence of, or additional contributions from, one or more point sources.

2.1 Source Characteristics of PAH

While there are a multiplicity of sources of PAH found in the environment, the origins of PAH are generally classified either as petroleum-derived (petrogenic) or combustion-derived (pyrogenic) (Douglas et al. 2007). Petroleum-derived PAH are dominated by lower molecular weight 2- through 3-ring PAH and their C1 to C4 alkyl homologues that occur in “bell shaped” distributions that favor the alkyl homologues; pyrogenic PAH are dominated by 4- through 6-ring parent PAH, with significantly lesser amounts of alkyl homologues. The pyrogenic PAH occur in patterns dominated by the parent (unsubstituted) PAH, with systematically decreasing amounts of higher alkyl homologues, i.e. a “sloped” distribution of the parent PAH and its related alkylated homologues.

GC chromatograms and the PAH histograms for several common petroleum products (crude oil, heavy fuel oil (HFO), diesel fuel) are contrasted with that of a pyrogenic manufactured gas plant tar in **Figure 2.** Note that the petroleum products contain only modest concentrations of PAH—typically in the low tens of thousands of parts per million**.** The classic “bell shaped” distribution of alkylated PAH homologues are is clearly evident among the petroleum products. Note that crude oil is composed of the broadest range of 2- through 4-ring alkylated PAH homologues, and contains only traces of higher molecular weight 5- and 6-ring PAH like benzo(a)pyrene. By virtue of distillation, diesel fuel contains only 2- and 3-ring alkylated PAH. By contrast, the pyrogenic MGP tar is comprised of a broad range of 2- through 6-ring PAH, with each class of PAH dominated by the parent, alkyl unsubstituted, PAH compound.

Often, investigations of the nature and sources of PAH are limited to the use of so-called EPA Priority Pollutant PAH data. The 16 Priority Pollutant PAH are 2- through 6 ring parent (alkyl unsubstituted) PAH that are measured for regulatory purposes (See Table 1, listed in bold). There are no alkylated PAH measured in Priority Pollutant data sets, which limits the ability to recognize mixtures of petroleum- and combustion-derived PAH (Stout et al. 2015). Basic assessments of EPA Priority Pollutant data sets can offer some insight into the potential nature of PAH. For example, investigators have examined the low molecular weight PAH to high molecular weight PAH ratio, or examined cross-plots of well recognized PAH ratios that are potential indicators of petrogenic or pyrogencially dominated PAH assemblages (e.g., Zemo 2009). While such approaches are useful, they are inherently limited by the lack of alkylated PAH data. For example, when examining ratios of high molecular weight PAH such as fluoranthene to pyrene (FL0/PY0) or indeno(1,2,3-c,d)pyrene to benzo(g,h,i)perylene (IND/GHI) in a mixture of petroleum and pyrogenic PAH from coal tar, the data will in most cases indicate the presence of pyrogenic PAH and discount the presence of petroleum. This is because most petroleum contains little meaningful high molecular weight PAH, and as such, analyses of these types are biased to responding to the presence of the high molecular weight, pyrogenic PAH. Thus, in order to develop the most useful metrics to determine the presence and relative amounts of petrogenic and pyrogenic PAH in sediments, it is necessary to utilize data that are more robust than those based simply on EPA Priority Pollutant PAH.

Data sets that contain alkylated PAH data allow the sediment investigator to identify more accurately the contributions from both petrogenic and pyrogenic PAH. A convenient means to classify the type(s) of PAH in sediments (i.e., petrogenic-dominant or pyrogenic-dominant, or mixtures thereof) is to evaluate the proportion of alkylated PAH found in the samples. A simple but powerful metric--% Alkyl PAH—can be calculated from environmental data, and compared to literature reference materials in order to ascertain the PAH source characteristics found in sediments. The metric is defined as:

%Alkyl PAH = (∑C1, -C2-, C3-, and C4-alklyated homologues of 2-, 3- and 4-ring PAH)/(∑Parent+alkylated PAH)

This ratio simply compares the relative amount of the sum of alkyl-substituted PAH (abundant in petroleum hydrocarbons) to the sum of total PAH in samples. Review of data for various kinds of petroleum (e.g., crude oils, heavy fuel oils, distillate fuels), pyrogenic materials (e.g. MGP tars, creosote), and urban dust, and urban background sediment offer a framework to classify the %Alkyl PAH values for the “pure” source materials, and mixtures thereof.

Material[a]	**Typical %Alkyl PAH**[b]
Diesel Fuel (Fresh)	89%
Diesel Fuel (Weathered)	98%
Heavy Fuel Oil #6 (Fresh)	86%
Heavy Fuel Oil (Weathered)	96%
Coal Oil Tar (Fresh)	18%
Coal Oil Tar (Weathered)	25%
Urban Dust (NIST 1649a)	36%
Urban Background Sediment[c]	28%

[a] Data from NewFields petroleum and hydrocarbon products chemical analysis library. Data available upon request.

[b] Based on 53 parent and C_1-C_4 alkylated PAH.

[c] Data from Stout et al. 2004. Data available upon request.

For classification purposes, it is reasonable to identify that PAH of pure petroleum origin contain >85% alkylated PAH, PAH from pure MGP tars contain less than 25-30% %Alkyl PAH, and PAH from atmospheric particulates contain alkyl PAH <40%. Mixtures of purely petrogenic materials and purely pyrogenic materials have %Alkyl PAH values between these endmember values. Thus, the degree of "petrogenicity" or "pyrogenicity", and the relative contribution of petroleum versus pyrogenic mater, can be evaluated using these benchmarks.

2.2 Features of PAH in Urban Sediments

Stout et al. (2004) studied the PAH features of sediments from 9 waterways in the United States. They report that "urban background" sediment contain PAH that are dominantly pyrogenic mixtures of PAH, with an median %Alkyl PAH of 28% (**Figure 3a**) At the same time, the PAH data from Stout et al. (2004) do exhibit a range in the %Alkyl PAH content among the sample data (%Alkyl PAH from 14% to 65%). **Figure 3b** is a sediment sample from that dataset with a %Alkyl PAH value of 14%, representative of a highly pyrogenic material; the PAH compounds are dominated by combustion-derived 5- and 6-ring PAH, and lower molecular weight PAH that exhibit highly skewed pyrogenic alkyl homologue distributions. **Figure 3c** is a sediment sample from the dataset with a %Alkyl PAH value of 65%—a value that indicates a mixture of petrogenic and pyrogenic PAH. The presence of significant high molecular weight 5- and 6-ring PAH in the sample arise from combustion sources, and exemplify the contributions of pyrogenic PAH. The presence of petrogenic PAH compounds in the sample is evidenced by the classic "bell shaped" alkyl PAH pattern for naphthalene family, and the relatively elevated concentrations of C1- C2-, C3- and C4- alkyl homologues for other PAH groups that result in a less skewed alkyl PAH pattern than would otherwise be expected for a pyrogenic material. These observations derived from the Stout et al. 2004 dataset demonstrate that, in urban sediments, a range of PAH character exists, and likely is a result of varying inputs of petrogenic and pyrogenic materials to the sediments.

In summary, the %Alkyl PAH metric provides a means to identify the general nature and potential localized petrogenic or pyrogenic features of PAH within a sediment system. We use this metric as an important tool to identify the nature of PAH, and the contributions of pyrogenic and petrogenic PAH in sediments evaluated in this investigation.

3.0 EXISTING LWG DATA PROVIDES FRAMEWORK FOR THE 2014 FORENSIC INVESTIGATION

Sediment data, and other types of environmental characterization data, were collected in the Portland Harbor Study Area during the numerous investigations conducted by the Lower Willamette Group as part of the Remedial Investigation/Feasibility Study (RI/FS) in the Superfund Site. These data, along with data from historical and private party studies is compiled in the LWG's data portal maintained by the LWG. The LWG data portal contains datasets from the following studies:

- Portland Harbor Site Characterization Assessment (SCRA database);
- Portland Harbor Remedial Investigation (RI database);
- Portland Harbor Feasibility Study (FS database), including samples collected by GASCO, Arkema, and other studies conducted after the Remedial Investigation deadline;
- Portland Harbor Baseline Human Health Risk Assessment (BHHRA database); and
- Portland Harbor Baseline Ecological Risk Assessment (BERA database).

The collected LWG historical dataset reviewed by NewFields contains PAH data for 5,083 sediment samples, collected in the Study Area between River Mile 0.1 and 28.5. River Mile values decrease with increasing distance downstream, e.g. River Mile 28.5 is the most upstream location, and River Mile 0.1 is the most downstream location in the Portland Harbor Superfund Site area. In the analysis of LWG historical data set presented herein, all available PAH data are evaluated together, regardless of their date of sampling. It is recognized that changes in PAH concentration could, and likely did, occur in sediments over the sampling timeframe represented by the LWG historical dataset. However, simultaneously considering all of the data provides the most synoptic historical perspective of the occurrence of PAH in sediments of the Superfund Site.

Figure 4 presents a plan view of the occurrence of PAH in Portland Harbor sediment (all depths) between River Mile 14 (upstream) and River Mile 3 (downstream). Also shown in **Figure 4** are summary statistics for the concentrations of the sum of the EPA Priority Pollutant PAH (TPAH16) in the entire Superfund Site area. Inspection of **Figure 4** suggests that, while there are some near-shore areas of elevated PAH concentrations, TPAH16 concentrations upstream of approximately Mile 7 are generally low. There is an abrupt increase in TPAH16 concentration in the vicinity of the McCormick and Baxter Property (east shore of river) and the Gasco Property (west shore of river). A plot of TPAH16 versus river mile clearly illustrates this trend (**Figure 5**). The left panel of **Figure 5** uses a linear concentration scale to illustrate the dramatic spike in TPAH16 in sediments at approximately River Mile 6-7. The right panel of **Figure 5** is the Log_{10} transformed concentrations of TPAH16 in sediments. Noteworthy in these graphs is the fact that there is a significant spread in TPAH16 concentrations at any given river mile—an indication that PAH in the sediment are not homogenously distributed spatially and with depth in any given stretch of river. As a point of reference, Stout et al. (2004) report that the TPAH16 concentration in "urban background" sediments have an upper boundary of approximately 20,000 µg/kg. Using this metric, many of the sediments upstream of River Mile 7 (and most in the main channel of the river) fall in the "urban background" PAH concentration range.

As illustrated in **Figure 6**, the significant increase in TPAH16 in the River Mile 6 to 7 area is due to the presence of highly elevated PAH in the vicinity of the McCormick & Baxter Property (east side of river), and the Gasco Property (west side of river). The McCormick & Baxter Property (River Mile 6.8 – 7.2) is the site of former wood treating operations that utilized PAH-rich creosote as a treating agent (U.S. EPA, 1996). The Gasco Property (River Mile 6.1 – 6.4) is the site of a former manufactured gas plant (MGP) that released PAH-rich MGP tar to the sediments (Hahn and Associates, Inc. 2007). Creosote and MGP tar are pyrogenic materials that contain percent levels of PAH (e.g. tens to hundreds of thousands of parts per million), and when released to aquatic systems, they are recognized as potent sources of PAH to sediments (e.g., Emsbo-Mattingly et al. 2002). In contrast, petroleum products contain relatively low concentrations of PAH (hundreds of parts per million), and when released to aquatic systems, are much lower relative sources of PAH than pyrogenic creosote or MGP tar.

The sediment management area SMA 9D, as well as the CBRAs 9D-2 and 9D-3, are downstream of the Gasco Property and the McCormick & Baxter Property, approximately between River Miles 5.0 and 6.1 (**Figure 1**). The Former ExxonMobil Terminal is situated primarily downstream of these areas, between River Miles 4.9 and 5.4. These areas downstream of the Gasco Property have sediment with elevated TPAH16 (i.e., > 20,000 µg/kg—the typical upper bound of "urban background" PAH concentration).

A logical hypothesis for the occurrence of elevated concentrations of PAH in SMA 9D, sediments proximal to the Former ExxonMobil Terminal, and other sediments downstream of River Mile 6-7 is transport of creosote and MGP tar and/or contaminated sediment from offshore areas of the McCormick and Baxter Property and the Gasco Property, respectively. In particular, elevated PAH concentrations in SMA 9D and downstream sediments along the western margin of the river are likely to have been specifically affected by releases of PAH enriched materials and contaminated sediments from the Gasco Property that also is located on the western river shore. Basic spatial analysis of TPAH16 sediment data supports this hypothesis (**Figure 7**). Historically, the highest TPAH16 (>1,000,000 µg/kg) occur just offshore of the Gasco Property, just offshore of McCormick and Baxter Property, and within CBRA 9D-2. Elevated, but progressively lower concentrations of TPAH16 radiate downstream. In particular, the LWG historical data suggest that PAH-laden material and/or contaminated sediment migrate from the sediments just offshore of the Gasco Property, and contaminate downstream sediments in SMA 9D and other downstream areas. This analysis does not preclude some contribution of PAH from the McCormick and Baxter Property, but it is not unreasonable to conclude that given the proximity of the Gasco Property, it serves as the dominant source of PAH to nearby sediments on the west side of the river.

Trends in benzo(a)pyrene equivalents (BaPeq) from the LWG historical dataset

One measure of the potential toxicity of PAH can be expressed by the benzo(a)pyrene equivalent (BaPeq). The BaPeq is the weighted sum of the concentrations of seven carcinogenic, high molecular weight PAH compounds—namely, benzo(a)pyrene, benzo(a)anthracene, benzo(b)fluoranthene, benzo(k)fluoranthene, chrysene, dibenzo(a,h)anthracene and indeno(1,2,3-c,d)pyrene. Each of the individual PAH concentrations measured in a sample are multiplied by a toxicity potency factor that is a multiple relative to the toxicity potency of benzo(a)pyrene. When following EPA guidelines (EPA 1993), the potency factor for benzo(a)pyrene is set to 1.0. The remaining six PAH compounds have potency factors that range from 0.001 (chrysene) to 0.1 (benzo(a)anthracene, benzo(b)fluoranthene). It is important to note that the seven high molecular weight carcinogenic PAH used to compute BaPeq are predominantly of combustion (pyrogenic) origin—petroleum contains only *de minimis* amounts of these high molecular weight PAH compared to combustion-derived materials (Burgess et al. 2003). Thus, the occurrence and concentration trends observed for BaPeq in sediment samples reflect the varying inputs of combustion-derived PAH, e.g., pyrogenic materials like MGP tars and creosotes, tailpipe emission-derived PAH, and other PAH of combustion origin.

The LWG historical data provide a perspective on the trends of BaPeq in Portland Harbor sediments (**Figure 8**). The BaPeq spatial trends generally have the same features noted for TPAH16, e.g., relatively low values (median concentration of 40 µg/kg) upstream of approximately Mile 7. There is an abrupt increase in BaPeq concentration in the vicinity of the McCormick and Baxter Property (east shore of river), and the Gasco Property (west shore of river), with maximum values of 1,332,800 µg/kg just offshore of the Gasco site. A plot of BaPeq versus river mile clearly illustrates this trend (**Figure 9**). The left panel of **Figure 9** uses a linear concentration scale to illustrate the significant spike in BaPeq in sediments at approximately River Mile 6-7; the right panel of **Figure 9** is the Log_{10} transformed concentrations of BaPeq in sediments.

MGP tar is a potent source of high molecular weight PAH, and thus, of BaPeq. Based on the spatial distribution of BaPeq and its spatial correlation with TPAH16, It is reasonable to hypothesize that (analogous to the origins of PAH generally), elevated concentrations of BaPeq in SMA 9D, sediments proximal to the Former ExxonMobil Terminal, and other sediments downstream of River Mile 6-7 resulted from the transport of MGP tar and/or contaminated sediment from the Gasco Property.

Inferences of PAH source types from the LWG historical dataset

EPA Priority Pollutant PAH data alone are difficult to use to identify the type or types of PAH in sediment, e.g., petrogenic (PAH derived from oil), or pyrogenic (e.g., derived from pyrolysis [creosote, MGP tar, tar products], or simple combustion waste like tailpipe emissions waste). As described in

Section 2.1, the occurrence and relative distribution alkylated PAH compounds provides a critical key in assessing the nature (petrogenic, pyrogenic, or mixtures) of PAH in sediments.

As described above in Section 2.1, the %Alkylated PAH is significantly higher in petroleum than in pyrogenic materials such as MGP tar and other combustion waste. Literature data indicate that the Total PAH concentration of crude oil and varied petroleum products typically are made up of 85% or more C1-C4 alkylated PAH. Conversely, the Total PAH concentrations of pyrogenic MGP tars typically contain 25% or less C1-C4 alkylated PAH. "Urban background" PAH in sediment are generally recognized as a pyrogenically-dominated mixture of combustion and petroleum-derived PAH (Stout et al. 2004).

The LWG historical data set contains a subset of sediment samples that were analyzed for an abbreviated list of C1-C4 alkylated PAH compounds (740 samples from 543 widely dispersed locations). This data provides preliminary insight into the nature of PAH in the Superfund Site generally, and specifically in the vicinity of Former ExxonMobil Terminal. **Figure 10** is a graph of Total PAH versus %Alkyl PAH for the LWG historical dataset. Several observations can be drawn from this data:

- The highest concentration PAH samples are pyrogenic in nature (e.g. <25% Alkyl PAH); these samples contain no meaningful petroleum -derived PAH.
- Varying patterns of PAH character can be seen across the river system **(Figure 11)**.
  - There is a mixture of both pyrogenic-dominated (<50% alkylated PAH) and petrogenically dominated (>50%) sediments throughout the Superfund Site.
    - 72% are pyrogenically dominated
    - 28% are dominantly petrogenic in nature
  - With the exception of a few downstream samples, approximately 80% of samples classified as highly pyrogenic (<25% Alkyl PAH) occur in the vicinity, or immediately downstream, of the Gasco Property (**Figure 12**). The former manufactured gas plant that was situated on this site discharged pyrogenic-rich MGP tars to the river sediments.
  - There is a subset of sediment samples that are highly petrogenic in nature (>85% Alkyl PAH) that occur in discrete locations in the Superfund Site (**Figure 13**). Downstream of the Gasco Property, the only sediments found to contain highly petrogenic PAH were in deep sediments (>30 cm) immediately offshore of the Arco/BP Terminal (**Figure 14**). These deep, petroleum-impacted sediments were excavated in 2008 as part of a remedial action (U.S. EPA, 2009).
  - Outside of the samples at the BP-Arco Terminal, there were no sediments downstream of the Gasco Property that contained highly petrogenic or petrogenically dominated PAH—all other sediments in this area were pyrogenically dominated.

The LWG historical dataset provided an important insight into the occurrence and nature of PAH in the vicinity of the Former ExxonMobil Terminal. The LWG historical dataset was used to tailor a focused sampling plan for the current Investigation.

4.0 2014 FORENSIC INVESTIGATION STUDY AREA

The 2014 NewFields Forensic Investigation focused on characterizing the nature of PAH found in sediments in the SMA 9D area, between approximately RM 4.5 and 6.5. SMA 9D has its longitudinal axis generally along the western side of the river channel. Upstream reference samples were collected in the vicinity of RM 10.

Sediment samples for the investigation were collected from stations shown in **Figure 15.** Sample locations are shown in detail in **Figures 16a – 16d** and include:

- Upstream of the Gasco Property, in the vicinity of the navigation channel, and remote from potential shoreline point sources, i.e., representative of typical upstream sediments within the Harbor (**Figure 16a**).
- Just offshore of the Gasco Property, in the vicinity of PAH "hot spots" identified by previous investigations (**Figure 16b**).
- Downstream of the Gasco Property, within the footprint of SMA 9D, including samples from within the comprehensive benthic risk area CBRA 9D-3, and immediately proximal to CBRA 9D-2 (**Figure 16c**)
- Along the western side of the Willamette River channel, in the vicinity of Former ExxonMobil Terminal (**Figure 16c**).
- Downstream of SMA 9D, offshore of the Linnton Plywood Property (west shore of the river), and in Terminal 4, Slip 3 (east shore of the river) (**Figure 16d**).

Surface samples, described as 0 to 30 cm deep subsamples, were collected at all stations. At selected stations, where dredging might theoretically occur, sediment cores were collected. The cores yielded two horizons: a 0 to 30 cm surface subsample and a 61 to 91 cm subsample (2 to 3 feet). The two horizons provide a basis to evaluate any variations in sediment chemistry with depth.

Cross-river (eastern bank) samples were collected in two areas where the previous LWG RI investigation had identified the presence of elevated levels of PAH: offshore of the McCormick and Baxter Property (upstream of the Former ExxonMobil Terminal), and at Port of Portland Terminal 4, Slip 3 (downstream of the Former ExxonMobil Terminal).

4.1 Upstream of the Gasco Property

Upstream reference samples were comprised of three cores, collected from locations about 2 to 3 miles upstream of the Gasco Property (**Figure 16a**). These locations were purposefully located mid-channel, in an area relatively removed from nearby shoreline point sources. The purpose of these sample locations was to provide reasonable representations of reference sediments located upstream of the principal study area, i.e., RM 4.5 to RM 6.5.

4.2 McCormick and Baxter Property

Two surface samples were collected from locations on the eastern bank of the river proximal to the McCormick and Baxter Property (**Figure 16a**). This site is across river, and just upstream from the Gasco Property. These samples were collected to evaluate the PAH composition of sediments collected in proximity to a site that had released PAH-rich creosote wastes to the sediments. The LWG Remedial

Investigation demonstrated that offshore sediments adjacent to the McCormick and Baxter Property were significantly contaminated with PAH from the creosote wastes. These sediments were subsequently remediated, including placement of a cap in 2004 and 2005 on a nearshore area off of the McCormick and Baxter Property (Oregon DEQ at http://www.deq.state.or.us/lq/ECSI/ecsidetail.asp?seqnbr=74). The objective of collecting samples in this area in 2014 was to ascertain current PAH levels in sediment conditions just offshore of the remedial cap area.

4.3 Vicinity of the Gasco Property

Three cores (0-1' surface/2-3' subsurface) and two 0-1' surface samples were collected at locations just offshore the Gasco Property (**Figure 16b**). These cores were placed in areas where previous RI investigation data have shown concentration "hot spots" of PAH in sediments.

4.4 SMA 9D, Including CBRA 9D-2 and 9D-3 and Vicinity of the Former ExxonMobil Terminal

Forty-five sediment samples were collected from 27 stations within SMA 9D, including samples from within CBRA 9D-3, and immediately proximal to CBRA 9D-2 (**Figure 16c**). Highlights of this group of samples include:

- Just downstream of the Gasco Property three core samples (0-1' surface/2-3' subsurface) were collected at locations offshore of US Moorings. A series of four surface sediment samples was collected at locations along the navigational channel and the eastern margin of SMA 9D.

- Seven stations and 14 samples were collected offshore of the Former ExxonMobil Terminal. Five surface sediment samples were collected along the eastern margin of SMA 9D, about 700 feet offshore. Together, these surface samples are part of the network of sample locations across SMA 9D.

- CBRA 9D-2: It was not possible to collect meaningful samples directly from CRA-9D-2 because dredging had recently been carried out in that area. Instead, samples within approximately 10 meters from CBRA-9D-2. Two sediment cores were collected at locations proximal to CBRA 9D-2, also located just offshore the Former ExxonMobil Terminal. Subsamples from these cores were used as part of an *ex-situ* passive sampling, solid phase micro-extraction (SPME) evaluation to ascertain if dissolved phase pore water concentrations of PAH could be considered potentially harmful to benthic organisms.

- CBRA 9D-3: Four surface sediments were collected within CBRA 9D-3 and four cores were collected proximal to the CBRA. Subsamples from these cores were used as part of an *ex-situ* passive sampling, solid phase micro-extraction (SPME) evaluation to ascertain if dissolved phase pore water concentrations of PAH could be considered potentially harmful to benthic organisms.

- One sample of opportunity, a tar ball, was collected within CBRA-9D-3. This sample was characterized to ascertain if the tar ball represented material that was an important source of PAH to CBRA 9D-3, and the general SMA 9D area.

4.5 Additional Downstream Shoreline Properties

Six surface samples were collected offshore of the former Linnton Plywood Property, which is located just downstream of SMA 9D (**Figure 16d**). These samples were collected to evaluate the sediment condition downstream of SMA 9D.

Three surface samples were collected from locations within Terminal 4, Slip 3, which is located downstream of SMA 9D on the eastern shore of the river (**Figure 16d**). These samples were collected to evaluate the PAH composition of sediments collected at a downstream site where previous LWG RI investigation data had revealed unusually high concentrations of PAH. Nearshore areas in the Slip were remediated and capped in 2004 (Oregon DEQ at http://www.deq.state.or.us/lq/ECSI/ecsidetail.asp?seqnbr=272).

5.0 SAMPLE COLLECTION AND ANALYSES

The following sections provide a brief summary of the sample collection and laboratory analyses used in the NewFields 2014 Forensic Investigation. The detailed summary of the field and laboratory methods, including those used for supplemental sediment characterization of samples from the former Linnton Property, is presented in Appendix A. The field and laboratory work, including technical procedures, are described in more detail in the Field Sampling Plan (Appendix B) and the Laboratory QAPP (Appendix C).

5.1 Sample Collection

Field sampling operations were conducted from August 11th to August 22nd, 2014 by NewFields staff. Gravity Environmental provided the vessel and sediment sampling equipment. The field team collected seventy-four (74) samples for this study using several sampling techniques:

- A total of seventy (70) surface (0 to 1 foot) and subsurface (2 to 3 feet) sediment samples were collected within the study area using a power grab and a vibracore equipped with various configurations that were adapted to meet specific location and substrate conditions.
    - Thirteen surface and subsurface samples were collected proximal to CBRA 9D-2 and 9D-3 to determine pore water measurements for sediment assessment.
- One tar ball was collected within CBRA 9D-3.

After collection, the samples were stored in a secure location on ice and shipped to NewFields' alliance laboratory, Alpha Analytical Laboratory (Alpha; Mansfield, Massachusetts) for chemical fingerprinting analysis and to Texas Tech University for SPME analysis. The samples arrived intact and in good condition between August 13th and August 27th, 2014. Upon receipt of samples, the samples were logged into Alpha's laboratory information management system (LIMS) and given unique laboratory identifications. The samples were stored in a limited access refrigerator at 4°C until processed by the laboratory staff for chemical fingerprinting analysis.

The sample locations are shown in **Figure 15**. An inventory of the samples collected and the analyses performed in this investigation is provided Table 2. The table below summarizes the total number of field samples collected and the analyses performed on each matrix.

Matrix	Forensic Chemical Analyses				Ancillary Measurements		Pore Water Concentration
	TPH and n-alkanes	Parent and Alkyl PAH	High MW PAH	Petroleum Biomarkers	Grain-Size	TOC	Parent PAH
Sediment	70	70	70	70	70	70	NA
Tar Ball	1	1	1	1	1	1	NA
SPME	NA	13	NA	NA	NA	NA	13

5.2 Laboratory Analyses

The samples were analyzed using methods designed specifically for the forensic analysis of petroleum described in detail by Douglas et.al. (2007). These are the same methods conducted by the same laboratory used by the Federal Government and British Petroleum (BP) in the *Deepwater Horizon* oil blowout and fire investigation (NOAA, 2011).

Samples were analyzed using complimentary methods that allow for qualitative identification of the type(s) of hydrocarbons comprising the samples by gas chromatography, and the quantitative measurement of an extended list of alkylated PAH and petroleum biomarker compounds by gas chromatography/ mass spectrometry. Together, the resulting data can be used to reconcile PAH patterns and concentrations with likely sources. The analytical methods of analysis are presented below.

5.2.1 *Polycyclic Aromatic Hydrocarbons*

A modified EPA Method 8270C gas chromatography/mass spectrometry (GC/MS-SIM) method was used to determine the concentrations of semi-volatile compounds or compound groups, including a broad range of 2- to 6- ring PAH, selected alkylated PAH homologues, sulfur-containing aromatics (dibenzothiophenes) and other compounds useful for the identification of hydrocarbons sources in the environment. Distribution patterns of PAH compounds provide a useful tool for petroleum product identification and differentiation. These tools are particularly valuable for identifying petroleum (petrogenic material) in the presence of combusted or partially combusted matter (pyrogenic material). Table 1 lists the PAH target analytes measured in the study, and provide compound abbreviations used in graphical presentation of the data. The TPAH16 are shown in bold.

5.2.2 *TPH and Gas Chromatographic "Fingerprints"*

A modified EPA Method 8015B gas chromatography method was used to determine the total petroleum hydrocarbon (TPH) concentration (C_8-C_{44}), as well as concentrations of *n*-alkanes (C_9-C_{40}) and selected (C_{15}-C_{20}) acyclic isoprenoids (e.g., pristane and phytane) in the samples. A high resolution gas chromatogram produced by this method provides a detailed "fingerprint" of the hydrocarbons that compose the study samples. This analysis allowed for the characterization of the general boiling range(s) and type(s) of petroleum or other hydrocarbons present in the sample, as well as the degree(s) of weathering.

5.2.3 *Petroleum Biomarkers*

Using the same modified EPA Method 8270C as described above, petroleum biomarker compounds (triaromatic steroids, steranes and triterpanes) were determined. Petroleum biomarkers provide specific information pertinent to the characteristic and origins of petroleum. The distribution of biomarker compounds in petroleum is a function of geological source, refinery practices, and mixing.

5.2.4 *Pore Water Measurements for Sediment Assessment*

Ex-situ passive sampling and analysis was performed using solid phase micro extraction (SPME) and polydimethylsiloxane (PDMS) fibers. The PDMS extracts were analyzed for 14 parent PAH (Table 3) by Texas Tech University and a duplicate extract was analyzed for parent and alkylated PAH (Table 1) by Alpha Analytical. Freely dissolved concentrations of PAH in sediments were then determined based on the estimated fiber-water partition coefficients presented in Ghosh et al. (2014) and the SPME extract concentrations determined from both laboratories. A detailed description of SPME fiber preparation, extraction, analysis, and pore water measurements is provided in TTU's Report, *Ex-Situ Pore Water Measurements for Sediment Assessment* (Appendix E).

Additionally, three water samples were collected from just above the sediment surface in CBRA 9D-3. The intended purpose of these water samples was to compare dissolved phase river water concentrations of PAH to nearby sediment pore water measured using SPME fibers. The water samples were analyzed for parent and alkyl PAH as described above.

5.3 Results of Analysis

The complete Alpha Environmental Testing Reports (ETRs) including all sample preparation data, instrument calibrations, QC data and chromatograms is maintained on file by NewFields. A data summary containing pertinent gas chromatograms and tabulated results of all chemical analyses and quality control results is presented in Appendix E.

All analyses were conducted following established laboratory data quality objectives (DQOs) as described by Douglas et al. (2007). Appropriate laboratory quality control (QC) samples were processed along with the samples, which included a laboratory method blank (B), a laboratory control samples (LCS/LCSD), a sample duplicate (D), matrix spikes (MS), sediment reference material (SRM), and a reference oil. Resulting data underwent several levels of review. NewFields performed an independent review of the data generated by Alpha in order to ensure that DQOs were satisfied, and that the results were traceable to the raw data. NewFields also reviewed the data for compliance with the laboratory's documented procedures and established laboratory quality objectives. The data were found to be accurate and traceable, and met laboratory established method DQOs.

6.0 RESULTS OF THE 2014 FORENSIC INVESTIGATION

The results of NewFields 2014 Forensic Investigation are presented in this section of the report. Data for individual sample analyses are summarized in Table 4. Summary statistics for key hydrocarbon and PAH parameters by study area are presented in Table 5. In this section of the report, we refer to Total PAH—the sum of the parent and alkylated PAH listed in Table 1. This value is larger than the Total PAH16, which is a subset of Total PAH. A description of the general hydrocarbon features and an elucidation of the PAH characteristics of sediment samples are presented, from the most upstream (e.g., references samples collected in the River Mile 10 area) to downstream. Evidence for contributions of petroleum PAH in the vicinity of the Former ExxonMobil Terminal is discussed. The PAH characteristics in the CBRAs 9D-2 and 9D-3 are presented, and the results of the TTU SPME evaluation in these two areas are integrated into the analysis.

6.1 Upstream Reference Samples

Extractable hydrocarbons, reported as Total Petroleum Hydrocarbons (TPH), were measured in the six upstream reference samples collected near the middle of the channel in the vicinity of River Mile 10. The concentrations were low, and ranged from 51 mg/Kg (S30-Z) to 207 mg/Kg (S28-Z). The TPH concentrations measured in these samples are well within the range of typical "background" sediment, which have been reported to be 8 to 2,350 mg/Kg (Stout et al. 2004). The six upstream reference samples have similar chromatographic features. **Figure 17** is a gas chromatogram of the subsurface sediment collected at location S29, representing the sub-set of upstream reference samples. The chromatogram is characterized by a broad asymmetrical unresolved complex mixture (UCM) spanning the C_{15} to C_{40} carbon range with a number of resolved peaks superimposed over the UCM baseline. The various resolved peaks include odd carbon number-dominated normal alkanes (n-C_{25}, n-C_{27}, n-C_{29}, and n-C_{31}) emblematic of plant waxes derived from leaf debris in the sediments and natural organic matter (NOM). These characteristic features are consistent with urban background.

Total PAH concentrations measured in the six upstream reference samples ranged from 537 µg/Kg (S30-Z) to 743 µg/Kg (S28-Z). These concentrations are within the range of typical urban background sediment. The % alkyl PAH in the upstream reference samples ranged from 23% (S-30Z—highly pyrogenic) to 71% (S29-S), with an average of 48%. The variation in %Alkyl PAH is an indication that the upstream Reference samples that, while primarily pyrogenic in character, contain PAH that are heterogeneous in character. This observation is consistent with the %Alkyl PAH observed in the LWG historical dataset.

The distribution of PAH compounds for the most pyrogenic upstream sample (S30-Z) and the most petrogenically influenced samples (S29-S) is shown in **Figure 18a and Figure 18b**, respectively. In both cases, the dominant PAH compounds are the naturally occurring PAH (retene and perylene). Inspection of the PAH distributions in sample S30-Z (**Figure 18a**) shows that the PAH homologous series are dominantly pyrogenic in nature, with little evidence for the presence of petroleum-derived PAH. The PAH distributions in sample S29-S (**Figure 18b**) shows that that the PAH homologous series contain both petrogenic and pyrogenic features. Evidence of the presence of petrogenic PAH patterns in the sample include the inverse skewed alkyl homologue pattern for the phenanthrene/anthracenes (PA) (emblematic of a weathered petroleum PAH assemblage) , and elevated relative amounts of C1- to C4 alkyl homologues for the dibenzothiophene (DBT), naphthobenzothiophene (NBT), and chrysene (C) alkyl PAH series. The well recognized pattern of pyrogenic PAH is present i.e., skewed homologue patterns, with C_0->>C_1->C_2->C_3-substituted homologues for the fluoranthene/pyrene (FP) alkyl PAH series. High molecular weight 5- and 6-ring pyrogenic PAH also are present in the sample.

In summary, the Total PAH concentrations in the six upstream reference samples are low (<750 µg/Kg). The PAH patterns in the upstream samples are generally pyrogenic in character, with an average %Alkyl PAH value of 48%. However, there is some heterogeneity in the PAH makeup among the upstream samples, with evidence for varying amounts of petrogenic PAH present in some of the samples, including one with a %Alkyl PAH index as high as 71% (S29-S).

6.2 McCormick and Baxter

Two surface samples were collected in the vicinity of the McCormick and Baxter Property—one upstream of the Property (S27), and one proximal to the remediation area where sediments were capped in 2005 (S26).

Historically, wood treating activities had occurred at the McCormick and Baxter Property. Treating chemicals used at the site included coal tar-based creosote and diesel oil mixtures, pentachlorophenol (PCP) and diesel mixtures, and a variety of water- and ammonia-based solutions containing arsenic, chromium, copper, and zinc (US EPA, 1996). Soils at the site were contaminated with wood treating chemicals, including heavy metals, PAH, and PCP up to 80 feet below ground surface. Groundwater was also contaminated with similar contaminants. The contaminants have migrated to the Willamette River. Sediments near the site are contaminated with PAH to depths of up to 35 feet below the sediment surface (PTI, 1992).

Completed cleanup activities include soil excavation and disposal, upland soil capping, installation of a subsurface barrier wall, NAPL recovery and construction of a multi-layer sediment cap in the Willamette River. While the site has been monitored for years to ensure cleanup has been effective, there is still some evidence of contamination. Sheens have been often observed in the shoreline at low water levels (ODEQ, 2008).

Findings

Concentrations of TPH measured in the two surface sediment samples collected in the vicinity of McCormick and Baxter were 97 mg/Kg (S27-S) and 268 mg/Kg (S26-S). The TPH concentrations measured in these samples are well within the range of typical urban background sediment (8-2,350 mg/Kg: Stout et al. 2004), and reasonably similar to that measured in the upstream reference samples (range 51 mg/Kg to 207 mg/Kg). The gas chromatograms of S27-S and S26-S are presented in **Figures 19a and Figure 20a**, respectively. The gas chromatographic characteristics for both S27-S and S26-S were similar to the upstream reference samples. The gas chromatographic fingerprints for S27-S and S26-S have the well documented characteristics of background sediments described above, namely a broad unresolved complex mixture (UCM) of higher molecular weight, C_{15}-C_{40+} range, superimposed by a series of discrete peaks recognized as C_{25+} plant waxes and natural organic matter (NOM). Resolved peaks of pyrogenic, 4- ring parent PAH are observed in the gas chromatographic trace of the samples.

Total PAH concentrations measured in the two samples collected in the vicinity of McCormick and Baxter were 341 µg/Kg (S27-S) and 4,505 µg/Kg (S26-S). The PAH histograms for S27-S and S26-S are shown in **Figures 19b and Figure 20b**, respectively. The distribution of the PAH compounds found in sample S27-S was similar to the upstream reference samples. The %Alkyl PAH for S27-S is 59%, indicative of a mixture of pyrogenic and petrogenic PAH. The dominant PAH compounds are the naturally occurring PAH (retene and perylene). Low levels of 5- and 6-ring PAH, and a skewed homologous series of fluoranthene/pyrenes are sentinels for pyrogenic PAH contributions. The presence of low levels of petroleum-derived PAH are noted by a weathered assemblage of alkylated phenanthrene/anthracenes, and for the chrysene series, somewhat elevated relative amounts of C1- to C4 alkyl homologues than typically observed for purely pyrogenic PAH assemblages.

Inspection of the PAH histogram for S26-S, collected in the vicinity of the sediment cap, shows the distinct signature of a pyrogenic-sourced PAH assemblage. The %Alkyl PAH value for the sample is 26%—an indication of a highly pyrogenic PAH material. The PAH assemblage is characterized by a broad range of 2- to 6-ring PAH, dominated by phenanthrene (P0). The alkyl PAH for all the homologues are highly skewed, consistent with pyrogenic-sourced PAH. Significant relative amounts of pyrogenic 5- and 6-ring PAH are noted in the sample. It is likely that the PAH found in this sample is related to the PAH-rich wood treating product creosote, which was used historically at the McCormick and Baxter Property.

6.3 Gasco Property Vicinity

Eight sediment samples from 5 sampling stations (Table 4) were collected just offshore of the Gasco Property where previous LWG RI data had identified PAH concentration “hot spots” in the sediments. Three of the stations were located immediately proximal to the shoreline of the site, while two samples were collected offshore of the Gasco Property, but closer to the river channel (**Figure 13**).

Remedial investigations performed at the Gasco Property between 1994 and 2006 identified the presence of high levels of manufactured gas plant (MGP) related contamination. As discussed previously, MGP tar wastes are highly enriched in pyrogenic PAH. MGP- related tars and dense non-aqueous phase liquids (DNAPL) are present across a large portion of the site up to a maximum depth of 67 feet below ground surface (Hahn, 2007). The tar impacted area extends from the upland portion of the site and into the river. Based on riverbank inspections, which have been conducted at the site on a regular basis, a zone of tar balls has been observed along the riverbank.

In 2005, 15,000 cubic yards of visible tar and tar-laden sediment was removed from the riverbed at the highly contaminated Gasco Property. The area was then capped with clean sediment. The tar-like substance had been on the river bottom for several decades, creating a contaminated hot spot, and a long-term source of PAH in the middle of the river to downstream locations. In addition, while the tar body was being removed, a silt curtain was used in an attempt to prevent contamination of the river. However, during removal activities, water quality samples showed very high levels of PAH characteristic of tar (i.e., benzo(a)anthracene and benzo(a)pyrene) (Parametrix 2006), suggesting evidence of mobilization and downstream transport of PAH-contaminated source material sediment.

Findings

Concentrations of TPH measured in the eight samples collected in the vicinity of the Gasco Property ranged from 62 mg/Kg (S21-S, collected in the river channel) to 35,300 mg/Kg (S25-S, collected at the location where a sheen was observed during NewFields’ sampling activities in 2014 (Appendix C, Cruise Report)). The elevated TPH concentrations for the six samples collected from the three stations proximal to the Gasco Property shoreline (average 8,120 mg/Kg) are significantly higher than the upstream reference TPH range, and are consistent with the presence of highly contaminated sediments.

The high resolution gas chromatograms for the surface and subsurface sediments collected in the vicinity of the Gasco Property are presented in **Figure 21**. The fingerprints for all of the sediment samples, with the exception of S21-S, are consistent with the features of MGP tar-related waste (Douglas et al. 2007), namely a chromatogram dominated by individual peaks recognized as parent PAH compounds, with little meaningful UCM. These chromatograms are distinctly different than typical urban sediments (Stout et al. 2004), and specifically, the upstream reference samples. There is no chromatographic evidence for the presence of petroleum in these samples.

The gas chromatographic fingerprint for sample S21-S is consistent with typical urban background, namely a broad unresolved complex mixture of higher molecular weight, C_{15}-C_{40+} range, superimposed by a series of discrete peaks recognized as C_{25+} plant waxes and NOM.

The Total PAH concentrations measured in the eight samples collected in the vicinity of the Gasco Property were very high, and ranged from 9,027 µg/Kg (S21-S, collected in the river channel) to 13,408,400 µg/Kg (S25-S)—a concentration that is the equivalent to more than 1% PAH by weight. Among surface/subsurface sample pairs, the Total PAH concentrations were generally higher in the subsurface sediments (Table 4).

The PAH histograms for the eight surface and subsurface sediment samples collected in the vicinity of the Gasco Property are presented in **Figure 22**. Inspection of the PAH histograms clearly show that all of the major PAH homologous series are, in fact, pyrogenic. There is no evidence for petrogenic PAH patterns in the sample, i.e., "bell-shaped" alkyl homologue distributions, "reverse skewed" series for weathered petroleum, or other perturbations in alkyl homologue distributions that would indicate the presence of petroleum). Rather, all the major PAH homologue series in the samples show the well-recognized pattern of pyrogenic PAH, i.e., highly skewed homologue patterns for the naphthalene, phenanthrene, and fluoranthene/pyrene series. Additionally, significant relative amounts of pyrogenic 5- and 6- ring PAH are present in the samples.

The %Alkyl PAH values for all of the Gasco Property samples were very low (10 to 31)—an indicator that the PAH were highly pyrogenic in nature. Based on the PAH histograms and the low %Alkyl PAH values, there is no evidence for meaningful petroleum PAH in any of the Gasco-related samples.

The high concentrations of TPH, the classic gas chromatographic fingerprints of MGP tar, and the strongly pyrogenic PAH histograms observed for samples found in the vicinity of the Gasco Property are all fully consistent with the presence of MGP tar waste in the Gasco samples. The highly pyrogenic PAH found in these samples almost certainly arose from the release of the tar wastes to the river from the former MGP operations at the site. The very high concentrations of PAH proximal to the Gasco Property make this site the most reasonable, primary source of pyrogenic PAH to the downstream SMA 9D area.

6.4 SMA 9D

SMA 9D spans the Willamette River from approximately RM 5.0 to RM 6.1. This SMA is immediately downstream of the Gasco Property. Two CBRAs have been identified within the footprint of SMA 9D. They are identified as CBRA 9D-2 and CBRA 9D-3.

Forty-two samples were collected from 27 stations within SMA 9D (Table 4; **Figure 23**). Of those, four samples were collected from two stations proximal to CBRA 9D-2, and eight samples were collected from 6 stations in and proximal to CBRA 9D-3.

Findings

The TPH concentrations in sediments collected within SMA 9D ranged from 49 mg/Kg to 9,590 mg/Kg (Table 4; **Figure 24**). TPH concentrations tended to decrease downstream of the Gasco Property. Samples within SMA 9D with TPH concentrations less than the Upriver Reference samples (maximum TPH = 207 mg/kg) generally have gas chromatographic characteristics typical of urban sediments (Stout et al. 2004). These samples included S02-S, S04-S, S05-Z, S06-Z, S11-S, S12-S, S12-Z, S13-S, and S13-Z. The chromatographic features of these samples are characterized by a broad asymmetrical UCM spanning the C_{15} to C_{40} carbon range with a number of resolved peaks superimposed over the UCM baseline. The various resolved peaks include odd carbon number-dominated normal alkanes (n-C_{25}, n-C_{27}, n-C_{29}, and n-C_{31}) emblematic of plant waxes derived from leaf debris in the sediments and natural organic matter (NOM). In some cases, the chromatograms include the resolved peaks that are qualitatively recognized as high molecular weight 4- to 6-ring pyrogenic parent PAH.

The majority of samples within SMA 9D contained TPH concentrations significantly greater than the upstream reference samples. With the exception of 4 samples, the gas chromatograms for samples within SMA 9D with TPH concentrations significantly higher than the upstream reference samples exhibited characteristics of dominantly MGP tar (analogous to the MGP tar impacted Gasco Property samples), or mixtures of MGP tar residuals and background hydrocarbons (**Figure 25**). The features of these gas chromatograms are dominated by individual peaks recognized as parent PAH compounds, with little meaningful unresolved complex mixture (UCM: chromatographic “hump”). The similarity in hydrocarbon makeup between the majority of the downstream sediments in SMA 9D and those from the just-upstream Gasco Property indicate that Gasco Property-derived MGP tar contamination is the dominant source of hydrocarbons (and PAH) to the downstream sediment in SMA 9D.

Tarball sample confirms presence of MGP waste in SMA 9D: Reports by the field sampling staff indicated that sampling within SMA 9D, and particularly CBRA 9D-3, was challenging due to the tar balls impeding the coring process. One tar ball sample of opportunity was collected from within CBRA 9D-3 at location T05. The TPH concentration of that sample was 686,000 mg/Kg. The gas chromatogram of this tar ball (**Figure 26a**) is completely consistent with relatively fresh MGP tar—i.e., the classic gas chromatogram of MGP tar, including high concentrations of parent (alkyl unsubstituted) 2-, 3-, 4-, 5- and 6 ring PAH, and virtually no meaningful unresolved complex mixture (UCM) (Mattingly 2001; Douglas et al. 2007). In other words, the TPH component of the sample was comprised of virtually pure MGP-derived PAH compounds.

Four samples from three different stations—S19-S and S19-Z (offshore of US Moorings) and T03-Z and S03-Z (offshore the Former ExxonMobil Terminal)—exhibited chromatographic evidence for the presence of weathered, broad boiling range petroleum such as a heavy fuel oil, mixed with other pyrogenic and naturally occurring hydrocarbons (**Figure 27**). The chromatographic features of these samples include a broad bimodal UCM spanning the carbon range C_{10} to C_{40} that is reminiscent of residuals of weathered heavy fuel oil. The resolved peaks superimposed upon the UCM include a mixture of recalcitrant petroleum-derived isoprenoid hydrocarbons, high molecular weight 4- and 5-ring pyrogenic PAH, and natural organic plant wax matter.

All of the sediment samples in SMA 9D contain Total PAH concentrations significantly higher (1,913 µg/Kg – 3,308,740 µg/Kg) than the upstream reference Samples (537 - 743 µg/Kg)—see Table 4. The spatial distribution of Total PAH concentrations in SMA 9D is shown in **Figure 28**. Total PAH concentrations tend to decrease downstream of the Gasco Property, however there are some downstream locations that deviate from that trend and exhibit arguably higher concentrations of PAH (inset to **Figure 28**). These locations include:

- S-18S: a surface sediment just offshore of USA Moorings at RM 6.03.
  Total PAH = 2,925,176 µg/Kg
- T-05-S T-06S, and T-10S: three surface sediment samples from the CRBA 9D-3 (RM 5.65, RM 5.69 and 5.76, respectively). These samples contained Total PAH concentrations of 3,308,740 µg/Kg, 532,757 µg/Kg, and 407,692 µg/Kg, respectively.
- S10-Z and S10-S: the 2-3 foot and 0-1 foot intervals of sediment at location S10, just offshore of the easternmost point of the Former ExxonMobil Terminal at RM 5.47. Concentrations of Total PAH of 468,081 µg/Kg and 102,437 µg/Kg, respectively.
- S7-S: a mid-channel surface sediment at RM 5.36 containing Total PAH of 341,071 µg/Kg.
- S9-S: a mid-channel surface sediment at RM 5.51, containing Total PAH of 81,104 µg/Kg.

While all of the sediment samples in SMA 9D contain elevated levels of Total PAH, this group of samples appear to be particularly enriched, and likely represent areas of deposition of contaminated sediment or wastes from the upstream Gasco Property area. Conversely, some of the lowest Total PAH concentration samples were found immediately offshore of the Former ExxonMobil Terminal. This observation indicates that there is likely a preferred depositional pathway downstream of the Gasco Property that favors a mid-channel vector.

The PAH histograms for the samples collected in SMA 9D are strikingly similar to those for the samples collected in the vicinity of the Gasco Property, viz., pyrogenic-dominated assemblages characterized by high concentrations of parent PAH and significantly lesser amounts of alkylated homologues, as well as significant amounts of high molecular weight 5- and 6-ring PAH compounds of pyrogenic origin (**Figure 29**). The %Alkyl PAH for all the samples in SMA 9D (with the exception of samples S19-S, S19-Z, T-03, and S03-Z) had values less than 30. While there is a trace of petrogenic PAH noted in some of the samples (e.g., very low levels of alkylated phenanthrenes in S16-S, S14-S, S09-S, and S04-S-D), these contributions are in the ~5% range. Values in the <30 range are an indicator of the presence of highly pyrogenic PAH, that contain very little, if any, petroleum-derived PAH. It is interesting to note that all five of these samples that contain traces of petroleum are found along the mid-channel margin of SMA 9D, far from the shoreline. Traces of petroleum PAH mixed with these otherwise pyrogenic-dominated assemblages could arise from a number of logical sources. Most probable are contributions from the significant amounts of petroleum feedstock used at the former MGP at the Gasco Property (Hahn and Associates, Inc. 2007) that would co-mingle and migrate with the tar contaminated wastes found off of the Gasco property. Low level contributions of fuel-derived PAH from vessels plying the mid-channel are additional candidate sources for the small contribution of petroleum PAH in the samples. Finally ubiquitous urban background inputs, which contain remnants of petroleum-derived PAH, could contribute to the trace levels of petrogenic PAH found in the five SMA 9D sediments. Regardless, the downstream Former ExxonMobil Terminal is not a potential source of PAH in the upstream reaches of SMA 9D.

A plot of % Alkyl PAH versus Total PAH for the SMA 9D and upstream Gasco-related samples reveals a regular trend wherein the %Alkyl PAH values increase systematically with decreasing Total PAH concentrations (**Figure 30**). The highest Total PAH-containing samples contain virtually pure Gasco-derived MGP tar, which have %Alkyl PAH values of ~25 or lower. As the percent of MGP tar-derived PAH decreases in the lower Total PAH concentration sediments in SMA 9D, the percentage of "background" PAH in the samples increases. The upstream reference samples suggest background PAH contain an average %Alkyl PAH value of 51. As such, the %Alkyl PAH in the lower Total PAH concentration SMA 9D samples have somewhat higher %Alkyl PAH values than the higher Total PAH, purely pyrogenic MGP tar-containing samples.

The tarball sample of opportunity collected in CBRA 9D-3 at location T05 contained very high levels of PAH consistent with MGP waste. Total PAH for the tar ball was measured as 249,091,500 µg/Kg—equivalent to 25% Total PAH by weight. Further, the PAH histogram for the tar ball sample is completely consistent with a MGP tar waste (Douglas et al. 2007). **Figure 26b** illustrates the PAH distribution for the tar ball sample. The PAH features include abundant amounts of parent (alkyl unsubstituted) 2-, 3-, 4-, 5- and 6 ring PAH, with significantly lesser amounts of alkylated homologues. Significant amounts of high molecular weight 5- and 6-ring PAH compounds of pyrogenic origin make up the balance of the PAH distribution. The fact that the relative PAH concentrations are in order of phenanthrene > fluoranthene/pyrene > naphthalene is consistent with a MGP tar that can be classified as moderately weathered (Emsbo-Mattingly et al., 2002). The percent Alkylated PAH value for the tar ball sample was 20, which is consistent with a highly pyrogenic MGP tar material. This tar ball, and the others observed within SMA 9D, are clear evidence that MGP tar waste that emanated from the Gasco Property is almost certainly the major source of PAH in SMA 9D sediments.

Samples containing evidence for petrogenic PAH: Four samples fall off the trend line shown in **Figure 30**—S19-S and S19-Z (offshore of US Moorings) and S03-Z and T03-Z (offshore of the Former ExxonMobil Terminal). These samples have anomalously higher %Alkyl PAH values than other samples in SMA 9D with similar Total PAH content. This suggests the presence of additional petroleum-derived PAH input in these four samples. Only these four anomalous samples that were identified by gas chromatography to contain some petroleum residues with the characteristics of weathered Heavy Fuel Oil.

The PAH histograms for these four samples show the impressions of petrogenic PAH, mixed with other pyrogenic PAH compounds (**Figure 31**). These petrogenic influences are expressed by "bell shaped" (fresh) or "inverse sloped" (weathered) alkylated petroleum PAH profiles for certain PAH homologues, or unusually higher proportions of C1-, C2-, C3- and C4-alkylated homologues in otherwise pyrogenically dominated homologue groups. Of course, these petroleum PAH are mixed with substantial amounts of pyrogenic PAH, as evidenced by the presence of "skewed" alkyl PAH groups, and by the presence of other higher molecular weight 5- and 6-ring combustion-derived PAH. It is calculated that these four samples contain approximately 10-20% additional petroleum PAH than otherwise was observed in other sediments in SMA 9D. These four samples represent the only examples of sediments in SMA 9D that contain an appreciable contribution of petroleum-derived PAH.

6.5 Downstream Study Areas (Former Linnton PlywoodProperty and Terminal 4, Slip 3)

Sediment samples were collected downstream of SMA 9D, in two areas:

- Five surface sediment samples from immediately off the former Linnton Property along the west shore of the river between RM 4.5 and RM 4.8.

- Three surface sediment samples within Terminal 4, Slip 3 area on the east shore of the river, at approximately RM 4.6.

A summary of the results from chemical measurements for the Linnton Property and Terminal 4, Slip 3 samples is presented in Table 4.

6.5.1 Former Linnton Plywood Property

The TPH concentrations measured in the surface samples collected downstream from the SMA 9D area offshore of the former Linnton Plywood Property were consistently low, and ranged from 180 mg/kg to 279 mg/Kg. The TPH concentrations measured in these samples are consistent with those levels observed in urban background sediment (Stout et al. 2004), and reasonably similar to that measured in the upstream reference samples (range 51 mg/Kg to 207 mg/Kg).

The gas chromatographic characteristics for all six of the sediment samples from offshore of the Linnton Property were very similar to one another, and characteristic of typical urban sediments (**Figure 32**). The gas chromatographic fingerprints exhibit a broad unresolved complex mixture (UCM) of higher molecular weight, C_{15}-C_{40+} range hydrocarbons, superimposed by a series of peaks including the C_{25+} plant waxes and other peaks typical of NOM. Resolved peaks of pyrogenic, 4- ring parent PAH are observed in the gas chromatographic trace of the samples.

The Total PAH concentrations measured in the five samples collected off of the Linnton Property ranged from 1,748 µg/kg to 2,626 µg/kg (Table 4). These concentrations are uniform, but all about a factor of two higher than upstream reference samples (537 – 743 µg/kg). These concentrations are similar to the lowest Total PAH concentrations measured in SMA 9D.

Inspection of the PAH histograms for the Linnton samples (**Figure 33**) reveals significant relative amounts of the naturally occurring PAH retene and perylene, followed by PAH homologues that are consistent with dominantly pyrogenic assemblages, i.e., relatively high concentrations of parent PAH and significantly lesser amounts of alkylated homologues, as well as significant amounts of high molecular weight 5- and 6-ring PAH compounds of pyrogenic origin. The %Alkyl PAH values for the six Linnton samples range from 32 to 38, which is consistent with highly pyrogenic derived PAH . There is no meaningful evidence of the presence of petroleum or petroleum-derived PAH in the Linnton Property sediment samples. The fact that the concentrations of Total PAH in the Linnton Property samples are approximately a factor of two greater than found in upstream reference samples, and the PAH assemblages in the samples are highly pyrogenic in nature, suggests the presence of the same, but more diluted, pyrogenic PAH that contaminate the upstream SMA 9D samples, namely MGP derived pyrogenic PAH. The historic operations at the site did not use any creosote-based products for plywood production (Oregon DEQ at http://www.deq.state.or.us/lq/ECSI/ecsidetail.asp?seqnbr=2373). Thus, the site is not a likely candidate for pyrogenic PAH found in nearby, offshore sediments.

6.5.2 Terminal 4, Slip 3

The TPH concentrations measured in the three surface sediment collected across the river and downstream of the SMA 9D in Terminal 4, Slip 3 area was low (136 mg/kg, 241 mg/kg and 292 mg/kg). The TPH concentrations measured in these samples are well within the range of typical urban background sediment (Stout et al. 2004), and similar to that measured in the upstream reference samples (range 51 mg/Kg to 207 mg/Kg).

The major gas chromatographic characteristics for the three surface sediment samples from Terminal 4, Slip 3 were generally consistent in feature with typical urban background sediments (**Figure 34**). The gas chromatographic fingerprints exhibit a broad unresolved complex mixture (UCM) of higher molecular weight, C_{15}-C_{40+} range hydrocarbons, superimposed by a series peaks including the C_{25+} plant waxes and other peaks typical of NOM. Prominent resolved peaks qualitatively identified as the pyrogenic, 4- ring parent PAH fluoranthene and pyrene are observed in the gas chromatographic trace of the samples. The TPH and gas chromatographic fingerprints alone do not indicate the presence of sediments significantly contaminated with hydrocarbons.

The Total PAH concentrations measured in the three samples collected off of the Terminal 4, Slip 3 was 2,371 µg/kg, 7,534 µg/kg and 14,374 µg/kg (Table 4). These concentrations are significantly higher than upstream reference samples (537 – 743 µg/kg), and indicative of PAH contamination in the Terminal 4, Slip 3 area.

Inspection of the PAH histograms for the Terminal 4, Slip 3 sediments (**Figure 35**) show PAH assemblages that are dominantly pyrogenic assemblages, i.e., relatively high concentrations of parent PAH and significantly lesser amounts of alkylated homologues, as well as significant amounts of high molecular weight 5- and 6-ring PAH compounds of pyrogenic origin. The %Alkyl PAH values for the three Terminal 4, Slip 3 samples were 19, 20 and 21, which is indicative of PAH of a highly pyrogenic origin. There is no evidence for the presence of petroleum or petroleum-derived PAH among the three Terminal 4, Slip 3 samples.

6.6 Trends in Benzo(a)pyrene Equivalents (BaPeq)

The calculated concentrations for BaPeq for the sediment samples collected in this investigation are summarized in Table 4. A spatial depiction of the BaPeq in the study area is shown in **Figure 36**. The general spatial trend in sediment BaPeq follows that the same pattern observed in the historic LWG dataset (Section 3.0), viz., low concentration upstream of the Gasco Property, followed by an abrupt increase in BaPeq in the vicinity of, an immediately downstream of the Gasco site. The concentrations of BaPeq in the upstream reference samples were low (15-47 µg/kg). The highest BaPeq were noted just offshore of the Gasco Property (367,890 µg/kg in surface sample S25-S). BaPeq in SMA 9D ranged from 146 µg/kg to 181,156 µg/kg, and averaged 10,581 µg/kg. The BaPeq within and just upstream of CBRA 9D-3 were particularly high, with surface sediments exhibiting the highest values (T05-S: 181,156 µg/kg, T06-S: 31,291 µg/kg; T07-S: 10,343 µg/kg; T10-S: 30,407 µg/kg.

It is interesting to note that the highest BaPeq in SMA 9D tend toward the middle of the river channel (including in CBRA 9D-3); lower concentrations of BaPeq tend to occur in SMA 9D along the west bank of the SMA, and just offshore of the Former ExxonMobil Terminal. This pattern is analogous to trends observed for Total PAH in study area sediments.

The fact that (a) the seven high molecular weight PAH that comprise BaPeq are documented to arise from primarily pyrogenic PAH sources and (b) the nature of the PAH found at and just downstream of the Gasco property in SMA 9D are overwhelmingly pryogenic in nature support a conclusion that fugitive MGP tar and tar-contaminated sediments emanating from sediments offshore of the Gasco Property are the source of elevated BaPeq in SMA 9D. There is no evidence of contribution of petroleum to the BaPeq.

6.7 SPME Investigation of Pore Water Accommodated PAH in Sediment Adjacent to CBRA 9D-2 and in CBRA 9D-3

In CBRA 9D-2 and CBRA 9D-3, PAH have been identified as chemicals of concern that may pose potential risk to aquatic organisms in sediments (Integral Consulting, Inc., 2012). Bulk sediment concentrations are often employed to screen sediments for the presence of chemicals of concern, but this measure indicates little about the bioavailability of these chemicals, and does not directly indicate mobility, exposure and risk. Measurement of PAH in the interstitial pore water of sediments provides a much more direct indicator of bioavailability and mobility. In addition, limiting the pore water measurements to the freely dissolved concentration (C_{free}) provides the best indicator of organism exposure and risk (Mayer et al. 2014).

Scientists from Texas Tech University evaluated the freely dissolved concentrations (C_{pw}) of polycyclic aromatic hydrocarbons (PAH) in sediments from the vicinities of CBRA 9D-2 and CBRA 9D-3. The full TTU technical report is provided in **Appendix E**. A summary of the findings from the TTU investigation are presented below.

Background

Dissolved phase concentrations of PAH were evaluated in selected sediment samples using *ex-situ* passive sampling, solid phase polydimethylsiloxane (PDMS) solid phase microextraction (SPME) techniques (PDMS-SPME). This approach involves bringing sediments collected from the field back to the laboratory so that equilibrations with passive samplers (i.e. PDMS and SPME coated fibers) can be performed. PDMS-SPME extracts were analyzed for EPA Priority Pollutant PAH, i.e. PAH16, by TTU using high pressure liquid chromatography (HPLC) methods; a duplicate extract was provided to NewFields for analysis of parent and alkylated PAH using the GC/MS techniques described in Section 5.2.4. Extract concentrations were converted to corresponding PAH freely dissolved pore water concentrations (C_{pw}) using the following equation:

$$C_{pw} = \frac{C_{PDMS}}{K_{PDMS}\ f_{ss}}$$

where C_{PDMS} is the equilibrium concentrations measured in PDMS (µg/L), K_{PDMS} is the PDMS-water partitioning coefficient and f_{ss} is the fraction steady-state achieved. The measured extract concentrations were converted to equilibrium concentrations measured in PDMS (C_{PDMS}) and further converted to corresponding PAH aqueous concentrations (C_{pw}) using regression relationships between PDMS-water partitioning coefficients (K_{PDMS}) with hydrophobicity ($\mathrm{Log}K_{\mathrm{PDMS}}=0.725\times\mathrm{Log}K_{\mathrm{OW}} + 0.479$) as measured by the SMILES octanol-water partition coefficient (K_{ow}) (Ghosh et al., 2013).

Estimated freely dissolved PAH concentrations were used to estimate the potential for effects on benthos using narcosis secondary chronic values (SCV) for each PAH and collectively by assuming an additive toxic unit (TU) approach (Burgess et al., 2013).

Thirteen sediment samples from eight locations were analyzed for dissolved phase PAH concentrations **(Figure 37).** Samples from two stations were taken just outside CBRA 9D-2 (T03-S, T03-Z, T04-S, T04-Z, T04-Z-D); samples from three stations were taken from within CBRA 9D-3 (T05-S, T06-S, T07-S); samples from three locations were taken just outside of CBRA 9D-3 (T08-S, T08-Z, T09-S, T09-Z and T10-S). The abbreviation “S” denotes surface (0-1 ft), “Z” denotes subsurface (2-3 ft) and “D” denotes field duplicate.

Findings

Table 3 in **Appendix E** presents the pore water concentrations of PAH calculated for the samples in this investigation. The pore water concentrations for fluorene, acenaphthene, phenantherene, anthracene, flouranthene, and pyrene in samples labelled T05-S and T06-S exceeded the sediment pore water guidelines (Narcosis SCV, Burgess et al. (2013). These samples were both taken from within CBRA 9D-3. TTU scientists noted that samples T05-S and T06-S contained an oily phase, as well as black coarse sediment particles. Despite the apparent presence of an oily phase, the variability between replicates was not significantly different between these samples and the rest of the samples. This suggests that any oily phase did not interfere with the SPME analysis and resulting dissolved PAH concentration results.

In samples T07-S, T09-Z and T10-S the C_{pw} of acenaphthene, phenanthrene, and fluoranthene were slightly below the sediment pore water guidelines for individual compounds (see **Tables 3** and **4** in **Appendix E**). Sample T07-S was taken from within CBRA 9D-3. Samples T09-Z and T10-S were taken just outside of CBRA 9D-3. In samples T08-S, T08-Z and T09-S the estimated pore water concentrations were far below sediment pore water criteria. Samples T08-S/Z and T09-S were taken just outside of CBRA 9D 3.

In the case of alkylated PAH mainly C1-, C2-, C3-Naphthalenes, C1-Phenanthrenes/Anthracenes, 1-Methylnaphthalene and 2,6-Dimethylnaphthalene exceeded SCVs in samples T05-S and T06-S **(**for details see **Table 5** in Appendix E). These two samples were taken from within CBRA 9D-3. Other alkylated PAH were below threshold values in samples T07-S, T09-Z and T10-S as well as all other samples (**Table 5,** Appendix E).

Toxicity Units (TU): The PAH pore water concentrations as determined by SPME for samples T05-S, T06-S, T07-S, T09-Z and T10-S were used to calculate toxic units (TUs) using narcosis chronic toxicity values using the following equation:

$$TU = \frac{C_{pw}}{SCV}$$

where if TU_i <1, adverse effects are unlikely to occur and if TU_i >1, adverse effects may occur (Burgess et al. 2013).

The sum of TU values (ΣTU) for all measured compounds was also calculated for each location. Due to the similar mode of action for PAH, the ΣTU is a better indicator of whether a particular location poses potential risks to benthic organisms. The ΣTU values for parent PAH based on HPLC and GC/MS measurements (all data pooled) are reported in **Table 6 of Appendix E**.

Although, the individual PAH pore water concentrations in samples T07-S and T10-S were slightly below the SCVs, the ΣTUs exceeded unity (**Table 6, Appendix E**). The TU values for parent PAH (i.e., fluorene, acenaphthene, phenantherene, anthracene, flouranthene, and pyrene) in samples T05-S and T06-S were >1, as were ΣTU values (**Table 6**). Sample T09-Z exhibited ΣTU ~1 (slightly below 1 by TT and slightly >1 by Alpha Analytical). The TU values for parent plus alkylated PAH (**$\mathrm{PAH}_{\Sigma 34}$,** Alpha Analytical) was less than a factor of 2 higher than for the TU measured **$\mathrm{PAH}_{\Sigma 14}$** due to the contribution of alkylated PAH (see **Table 5**) and the same locations were identified as ΣTU>1.

In summary, SPME measurements of PAH pore water concentrations in sediments and calculation of TU values indicate potential adverse effects to sediment benthic organisms only in sample locations T05-S, T06-S, T07-S, T09-Z and T10-S. Sample locations T05-S, T06-S, T07-S are within CBRA 9D-3, whereas locations T09-Z and T10-S are located immediately adjacent to CBRA 9D-3. None of the samples taken proximal to CBRA 9D-2 exhibited TU values indicative of potential adverse effects to benthic organisms, including the one sample (T03-Z) identified to contain some contribution (10-20%) of petroleum PAH.

Bulk sediment chemistry in the vicinity of CBRA 9D-3

Texas Tech University's SPME-PDMS investigation suggested that pore water concentrations of PAH in and around CBRA 9D-3 might have the potential to cause adverse effects to benthic organisms. The nature of PAH in CBRA 9D-3 were described generally in Section 6.4. In that section, we explain that PAH found in SMA 9D were highly pyrogenic in nature, and reminiscent of PAH-enriched MGP tar waste found in sediments immediately offshore of the Gasco Property. A tar ball found in SMA 9D was actually obtained from the CBRA 9D-3 area, and the composition of that high PAH-containing material (249,091,500 µg/Kg) was confirmed to be a moderately weathered MGP tar waste.

In this section, we focus specifically on the hydrocarbon and PAH chemistry of the samples taken from and nearby CBRA 9D-3. This analysis supports the understanding of the sources of PAH that are responsible for the elevated PAH in CBRA 9D-3, and which give rise to dissolved phase PAH pore water concentrations that that may cause potential adverse effects to sediment benthic organisms.

Findings

The TPH concentrations measured in the CBRA 9D-3 samples were generally highest in those collected within the CBRA (T05, T06, T07) and the station just upstream of the CBRA (T10)—see Table 4. The TPH among these samples ranged from 309 mg/kg (T07-S) to 9,590 mg/kg (T05-S) (Table 4). The GC/FID fingerprints for these highly impacted samples are presented in the left panel of **Figure 38**. The fingerprints of the remaining samples collected from stations outside and cross-current of CBRA 9D-3 are shown in the right panel of **Figure 38**. These samples, collected at surface and depth from stations T08 and T09, have generally lower TPH (range: 333-684 mg/kg) than the more highly impacted samples listed above.

The gas chromatograms for the highly impacted sample (CBRA 9D-3 samples T05-S, T06-S, T07-S, and the just-upstream T10-S) are emblematic of MGP tar-related waste, e.g., high concentrations of parent (alkyl unsubstituted) 2-, 3-, 4- 5- and 6 ring PAH, and virtually no meaningful unresolved complex mixture (UCM)—the classic gas chromatogram for MGP tar.

The fingerprints for the samples collected outside and cross-current of CBRA 9D-3 (T08 and T09 series) have lower TPH values, ranging from 333-684 mg/kg. The gas chromatographic fingerprints of these samples are more typical of urban sediments, viz., the gas chromatographic fingerprints exhibit a broad unresolved complex mixture (UCM) of higher molecular weight, C_{15}-C_{40+} range hydrocarbons, superimposed by a series peaks including the C_{25+} plant waxes and other chromatographic peaks typical of natural organic material (NOM). Resolved peaks of pyrogenic, 4- ring parent PAH are readily observed in the gas chromatographic trace of sample T09-Z.

The Total PAH concentrations measured in the most impacted samples (within CBRA 9D-3: T05-S, T06-S and T07-S, and just upstream-T10-S) were high and ranged from 105,896 µg/kg to 3,308,740 µg/kg. The PAH histograms for these samples are illustrated on the left panel of **Figure 39**. The PAH histograms are very similar to the Gasco Property related sediment samples and the tar ball sample found in CBRA 9D-3: abundant amounts of parent (alkyl unsubstituted) 2-, 3-, 4-, 5- and 6 ring PAH, with significantly lesser amounts of alkylated homologues (c.f. **Figure 22 and 26**). Significant amounts of high molecular weight 5- and 6-ring PAH compounds of pyrogenic origin make up the balance of the PAH distribution. Three of the four samples (T05-S, T06-S and T10-S) have relative PAH concentrations of approximately phenanthrene > fluoranthene/pyrene > naphthalene. This feature is consistent with moderately weathered MGP tar (Emsbo-Mattingly et al. 2002). The percent Alkylated PAH value for these four samples is 22 or less, which is consistent with a highly pyrogenic MGP tar.

The Total PAH concentrations for the samples collected outside and cross-current of CBRA 9D-3 (T08 and T09 series) are lower than the highly impacted samples, and ranged from 5,016 µg/kg to 53,469 µg/kg. The PAH histograms are very similar to the highly impacted samples found in CBRA 9D-3: abundant amounts of parent (alkyl unsubstituted) 2-, 3-, 4-, 5- and 6 ring PAH, with significantly lesser amounts of alkylated homologues. Significant amounts of, high molecular weight 5- and 6-ring PAH compounds of pyrogenic origin make up the balance of the PAH distribution. These lower Total PAH concentration samples also showed the impressions of the naturally occurring biogenic PAH retene and perylene. These PAH are observed simply because the pyrogenic PAH occur in the same concentration range as the biogenic compounds.

The four lower PAH concentration samples had %Alkyl PAH values of 26-30. While the %Alkyl PAH are just slightly higher than in the more highly impacted samples, these values are consistent with highly pyrogenic PAH material. The four samples are somewhat more weathered than the higher concentration samples found in CBRA 9D-3; this is evidenced by the generally lower levels of more labile phenanthrene compared to fluoranthene/pyrene (Emsbo-Mattingly et al. 2002). Regardless of absolute sample concentration, it is reasonable to conclude that the PAH found in the four samples collected outside and cross-current of CBRA 9D-3 (T08 and T09 series) are simply diluted versions of the higher concentration PAH found in and just upstream of CBRA 9D-3, namely highly pyrogenic MGP tar material. There is no evidence for the presence of petroleum PAH in the lower concentration T08 and T09 samples.

PAH Profiles for Dissolved Phase PAH in Pore Water

The Texas Tech University SPME-PDMS study identified certain sediments in and proximal to CBRA 9D-3 containing dissolved phase PAH pore water concentrations in sediments with corresponding TU values that are sufficiently high to pose potential adverse effects to sediment benthic organisms. These sample locations included T05-S, T06-S, T07-S, T09-Z and T10-S. The bulk sediment chemistry of these samples (discussed above) clearly show that the PAH in the sediment are of pyrogenic origin, and consistent in composition with PAH-containing MGP tar waste.

The SPME extracts collected during the Texas Tech University SPME-PDMS study were analyzed for alkylated PAH concentrations. **Figure 40** compares the PAH histograms calculated for the pore waters, compared to the PAH measured in the bulk sediment for samples T03-Z, T05-S, T06-S, T07-S, T09-Z and T10-S. In each case, it is evident that:

- The PAH found in the SPME extract (i.e, pore water) contained abundant 2-, 3- and 4-ring PAH; those PAH are highly pyrogenic in nature, i.e., abundant amounts of parent (alkyl unsubstituted) PAH, with significantly lesser amounts of alkylated homologues.
- The calculated pore water PAH histograms are relatively enriched in 2- and 3-ring PAH, and contain much lower relative amounts of higher molecular weight 4-, 5- and 6-ring PAH, compared to the bulk sediment. This is a result of the much higher solubility of the lower

molecular weight 2- and 3-ring PAH than the higher molecular weight PAH, which leads to a dissolved phase preferentially enriched in the more soluble compounds (Lee et al. 1992).

- There is no evidence for petroleum-derived PAH in the calculated dissolved phase.

The calculated dissolved phase PAH found in CBRA 9D-3 are of pyrogenic origin, and can be reconciled as the water accommodated fraction of the PAH observed in the bulk sediments. The PAH in the bulk sediments have been determined to have characteristics of moderately weathered MGP tar residuals. It is reasonable to conclude that the MGP tar residues in SMA 9D that have their origins in the former Gasco Property are the source of the dissolved phase PAH in the sediments.

7.0 CONCLUSIONS

The Former ExxonMobil Terminal is located at 9420 N.W. St. Helens Road, in Portland, along the Willamette River, between River Miles 4.9 to 5.4 in the Portland Harbor Superfund Site. The Former ExxonMobil Terminal is at the downstream end of Sediment Management Area 9D (SMA 9D). Within the SMA are two comprehensive benthic risk areas (CBRA 9D-2 and CBRA 9D-3) that have been designated to pose the potential for unacceptable risk to benthic invertebrate communities. PAH compounds have been identified as chemicals of potential concern in the SMA and CBRAs.

NewFields conducted an investigation into the nature and origins of PAH compounds in sediments in the vicinity of the Former ExxonMobil Terminal and in particular, in the area identified in the LWG 2011 Draft RI as SMA 9D. The goal of the investigation was to ascertain the principal type(s) of PAH in the area around the Former ExxonMobil Terminal, within SMA 9D and the CBRAs, and to ascertain if there was evidence for meaningful amounts of petroleum-derived PAH in the sediments of this study area.

NewFields analyzed sediments for a number of hydrocarbon chemistry parameters, including an extended list of parent (unsubstituted) and C1- to C4 alkylated PAH. This extended analyte list afforded the ability to better identify the source characteristics of PAH compared to data derived solely from regulatory-based analyses of the 16 EPA Priority Pollutant PAH. NewFields also considered existing Portland Harbor Superfund Site RI data in its inquiry. Key findings from this investigation include:

- PAH concentrations in the main stem of the Willamette River are generally low upriver of the Gasco Property, which is located at approximately River Mile (RM) 6.1 – 6.4. Three upstream reference samples collected in the RM 10 area had an average Total PAH of 630 µg/kg.
- The composition of PAH in sediments upriver of the Gasco Property is variable, and contains mixtures of petroleum- and combustion-derived PAH. Portland Harbor Superfund Site RI data show that the concentrations of PAH in the main stem of the river upriver of the Gasco Property are generally consistent with documented “urban background” levels in sediments.
- Portland Harbor Superfund Site RI data show a significant increase in sediment PAH concentration at and downstream of the RM 6 area, which coincides with the location of the Gasco Property, the site of a former manufactured gas plant. Records indicate that this MGP released pyrogenic PAH-rich tar wastes to the river. The Gasco Property is immediately upstream of SMA 9D.
- Data from this investigation document that very high concentrations of pyrogenic PAH exist in the sediments proximal and downstream of the Gasco Property. Total PAH ranged from 9,027 µg/kg to 13,408,400 µg/kg. Gas chromatography fingerprints and PAH histograms demonstrate these PAH are consistent in chemical character with PAH-rich MGP tar wastes.

- Forty-five sediment samples were collected by NewFields in SMA 9D. All but four contained PAH of high concentration, and of highly pyrogenic character. While the Total PAH concentrations in SMA 9D are somewhat lower than measured in sediments just offshore the Gasco Property (Total PAH from 1,913 µg/kg to 3,308,740 µg/kg), the characteristics of the PAH in the sediments are consistent with those offshore the Gasco Property, i.e., the PAH in the sediments of SMA 9D arise overwhelmingly from pyrogenic PAH-rich MGP waste. There is no evidence for petroleum-derived PAH in the sediments of SMA 9D.
- A tar ball was discovered and collected by NewFields from CBRA 9D-3. The tar ball contained very high levels of PAH (249,091,500 µg/kg). The PAH chemistry of the tar ball was completely consistent with the features of a moderately weathered pyrogenic MGP tar. The finding of this tar ball in CBRA 9D-3 is clear evidence for downstream transport of highly contaminated MGP waste from the Gasco Property into SMA 9D.
- Four samples collected in SMA 9D—a surface (0-1') and subsurface (2-3') sample from one station offshore US Moorings, and a surface (0-1') and subsurface (2-3') sample from one station offshore of the Former ExxonMobil Terminal contained PAH that were a mixture of petroleum and pyrogenic origin. Analysis suggests these samples contained 10-20% additional petroleum PAH in comparison to other sediments in SMA 9D. In both cases, other surrounding sediments did not contain evidence for petroleum PAH; thus the findings of these petroleum-derived PAH appear highly localized.
- Texas Tech University determined the dissolved phase pore water PAH chemistry of sediments from thirteen sediment samples collected and around CBRA 9D-2 and CBRA 9D-3. Only sediments from in and around the most upstream CBRA 9D-3 exhibited dissolved phase PAH concentrations that could potentially cause adverse biological effects to benthic organisms. These sediment samples contained high concentrations of PAH. The PAH chemistry of those samples were highly pyrogenic in nature, and consistent in character with PAH-rich MGP tar waste found offshore of the Gasco Property. There was no evidence for petroleum PAH in these sediments.
- The data in this report support the conclusion that the PAH impacts in SMA 9D are related to pyrogenic PAH derived from MGP wastes from to the Gasco site that have been released to the river, and not impacts from petroleum related sources, including the Former ExxonMobil Terminal.

8.0 REFERENCES

Acton Mickelson Environmental, Inc. 2008. 2007 Annual Ground Water Monitoring and Remediation Report. February 8, 2008.

Agency for Toxic Substances and Disease Registry. 1995. Toxicological Profile For Polycyclic Aromatic Hydrocarbons. Agency for Toxic Substances and Disease Registry Division of Toxicology/Toxicology Information Branch 1600 Clifton Road NE, E-29 Atlanta, Georgia 30333

Burgess, R.M., Abrens, M.J., and Hickey, C.W. (2003). Geochemistry of PAH in aquatic environments: source, persistence, and distribution. In: Douben, P. (ed): PAH: An ecotoxicological perspective. John Wiley & Sons, Ltd. West Suxxex, England.

Douglas, G.D., Emsbo-Mattingly, S.D., Stout, S.A., Uhler, A.D., and McCarthy, K.J. (2007) Chemical fingerprinting of hydrocarbons and polychlorinated biphenyls. In: Introduction to Environmental Forensics, 2nd Ed., B. Murphy and R. Morrison, Eds., Academic Press, New York, pp. 317-459.

Eganhouse, R.P., D.L. Blumfield, and I.R. Kaplan. 1982. “Petroleum hydrocarbons in stormwater runoff and municipal wastes: input to coastal waters and fate in marine sediments”. Thalassia Jugoslavica. 18(1-4):411-431.

Environmental Geochemistry Consulting. (2010). Forensic Evaluation of U.S. Moorings, Portland OR. Prepared for US Army Corps of Engineers, Seattle District. Contract No. W912W-08-P-0047.

Environmental Protection Agency. (1993). Provisional guidance for quantitative risk assessment of polycyclic aromatic hydrocarbons. EPA/600/R-93/089. Office of Research and Development, Washington, DC.

Electric Power Research Institute. (2003). Polycyclic aromatic hydrocarbons in surface soils in Illinois: Background PAH. EPRI No. 1011376, Palo Alto, CA.

Emsbo-Mattingly, S.D., Uhler, A.D., Stout, S.A., McCarthy, K.J., Douglas, G., Brown, J.S., Boehm, P.D. (2002) Polycyclic aromatic hydrocarbon (PAH) chemistry of MGP tar and source identification in sediment. In Sediments Guidance Compendium (A. Coleman, Ed). Electric Power Research Institute, Technical Report 1005216, pp. 1-41.

Ghosh,U., Driscoll,S.K., Burgess, R.M., Jonker, M.T., Reible, D., Gobas, F., Choi, Y., Apitz, S.E., Maruya, K.A., Gala, W.R., Mortimer, M., Beegan, C. (2014). Passive sampling methods for contaminated sediments: Practical guidance for selection, calibration, and implementation. Integrated Environmental Assessment and Management. April 2014; 10(2): 210-223.

Hahn and Associates, Inc. 2007. Remedial Investigation Report NW Natural – Gasco Facility 7900 NW St. Helens Road Portland, Oregon. April 30, 2007.

Integral Consulting, Inc. (2014). Portland Harbor RI/FS Remedial Investigation Report, Draft Final, August 29, 2011.

Integral Consulting, Inc. (2012). Portland Harbor RI/FS Draft Feasibility Study, March 30, 2012.

Krone, C.A., Brown, D.W., Burrows, D.G., Bogar, R.G., Chan, S.-L., Varanasi, U. (1989). A method for analysis of butyltin species and measurement of butyltins in sediment and English Sole livers from Puget Sound. Marine Environmental Research 27 (1989), 1-18.

Laflamme, R.E. and R.A. Hites. 1978. “The global distribution of polycyclic aromatic hydrocarbons in recent sediments”. Geochim. Cosmochim. Acta. 42:289-303.

Lee, L.S., Rao, S.C., and Okuda, I. (1992). Equilibrium partitioning of polycyclic aromatic hydrocarbons from coal tar into water. Environ. Sci. Tehcnol. 26: 2110-2115.

Lundegard, P.D. (2011). Sources of PAH in Portland Harbor/Willamette River Sediment – West side Sediment between River Mile 3 and 9. Prepared for ARCO/BP West Coast Products LLC, Chevron Environmental Management Company, ConocoPhillips Company, Kinder Morgan Liquids Terminal LLC, and Shell Oil Products US.

Parametrix. (2006). GASCO Early removal Action Construction Oversight Report. Prepared for US Environmental Protection Agency. November 16, 2006.

PTI Environmental Services. (1992). McCormick and Baxter Creosoting company Remedial Investigation Report. Prepared for Oregon Department of Environmental Quality, Portland, OR.

Stout, S.A., Uhler, A.D., and Emsbo-Mattingly, S.D. (2004) Comparative evaluation of background anthropogenic hydrocarbons in surficial sediments from nine urban waterways. Environ. Sci. Technol., 38(11): 2987-2994.

Stout, S.A., Emsbo-Mattingly, S.D., Douglas, G.S., Uhler, A.D., and McCarthy, K.J. (2015). Beyond 16 priority pollutant PAH: A review of PACs used in environmental forensic chemistry. Polycyclic Aromatic Compounds 0: 1-31.

Uhler, A.D., Stout, S.A., and Douglas, G.S. (2006) Chemical heterogeneity in modern marine residual fuel oils In: Oil Spill Environmental Forensics: Fingerprinting and Source Identification, Z. Wang and S.A. Stout, Eds., Elsevier Publishing Co., Boston, MA, pp. 327-348.

U.S. EPA. 1996. Record of Decision. McCormick and Baxter Creosoting Company, Portland Plant. Portland Oregon.

U.S. EPA. 2009. Portland Harbor Superfund Site Update For Lower Columbia Basin PCB Workshop – July 2009.

Yan, B, T Abrajano, R F Bopp, D A Chaky, L A Benedict, S N Chillrud. (2005). Molecular Tracers of Saturated and Polycyclic Aromatic Hydrocarbon Inputs into Central Park Lake, New York City. Environmental Science and Technology 39[18], 7012-7019. 2005.

Youngblood, W.W. and M. Blummer. (1975). Polycyclic aromatic hydrocarbons in the environment: homologous series in soils and recent marine sediments. Geochm. Cosmochim. Acta 39: 1303-1314. Zemo, D. (2009). Use of parent polycyclic aromatic hydrocarbons (PAH) proportions to attribute PAH sources in sediments: A case study from the Pacific Northwest. Environ. Foren. 10: 229-239.

Tables

Table 1. Polycyclic Aromatic and Related Heterocyclic Target Analytes.[a]

Abbr.	Compound	Abbr.	Compound
D0	cis/trans-Decalin	**FL0**	**Fluoranthene**
D1	C1-Decalins	**PY0**	**Pyrene**
D2	C2-Decalins	FP1	C1-Fluoranthenes/Pyrenes
D3	C3-Decalins	FP2	C2-Fluoranthenes/Pyrenes
D4	C4-Decalins	FP3	C3-Fluoranthenes/Pyrenes
BT0	Benzothiophene	FP4	C4-Fluoranthenes/Pyrenes
BT1	C1-Benzo(b)thiophenes	NBT0	Naphthobenzothiophenes
BT2	C2-Benzo(b)thiophenes	NBT1	C1-Naphthobenzothiophenes
BT3	C3-Benzo(b)thiophenes	NBT2	C2-Naphthobenzothiophenes
BT4	C4-Benzo(b)thiophenes	NBT3	C3-Naphthobenzothiophenes
N0	**Naphthalene**	NBT4	C4-Naphthobenzothiophenes
N1	C1-Naphthalenes	**BA0**	**Benz[a]anthracene**
N2	C2-Naphthalenes	**C0**	**Chrysene**/Triphenylene
N3	C3-Naphthalenes	BC1	C1-Chrysenes
N4	C4-Naphthalenes	BC2	C2-Chrysenes
B	Biphenyl	BC3	C3-Chrysenes
DF	Dibenzofuran	BC4	C4-Chrysenes
AY	**Acenaphthylene**	**BBF**	**Benzo[b]fluoranthene**
AE	**Acenaphthene**	**BJKF**	**Benzo**[j]**+[k]fluoranthene**
F0	**Fluorene**	BAF	Benzo[a]fluoranthene
F1	C1-Fluorenes	**BEP**	Benzo[e]pyrene
F2	C2-Fluorenes	**BAP**	**Benzo[a]pyrene**
F3	C3-Fluorenes	PER	Perylene
A0	**Anthracene**	**IND**	**Indeno[1,2,3-cd]pyrene**
P0	**Phenanthrene**	**DA**	**Dibenz[a,h]anthracene**
PA1	C1-Phenanthrenes/Anthracenes	**GHI**	**Benzo[g,h,i]perylene**
PA2	C2-Phenanthrenes/Anthracenes	CAR	Carbazole
PA3	C3-Phenanthrenes/Anthracenes		
PA4	C4-Phenanthrenes/Anthracenes	2MN	2-Methylnaphthalene
RET	Retene	1MN	1-Methylnaphthalene
DBT0	Dibenzothiophene	26DMN	2,6-Dimethylnaphthalene
DBT1	C1-Dibenzothiophenes	167TMN	1,6,7-Trimethylnaphthalene
DBT2	C2-Dibenzothiophenes	4MDT	4-Methyldibenzothiophene
DBT3	C3-Dibenzothiophenes	2MDT	2/3-Methyldibenzothiophene
DBT4	C4-Dibenzothiophenes	1MDT	1-Methyldibenzothiophene
BF	Benzo(b)fluorene	3MP	3-Methylphenanthrene
		2MP	2/4-Methylphenanthrene
		2MA	2-Methylanthracene
		9MP	9-Methylphenanthrene
		1MP	1-Methylphenanthrene

[a] US EPA Priority Pollutant PAH compounds listed in bold.

Table 2. Samples and Analyses.

Station ID	Study Area	Sample ID	Depth Interval	Forensic Chemical Analyses				Ancillary Measurements		Characterization	SPME Pore Water	
				TPH and n-alkanes	Parent and Alkyl PAH	High MW PAH	Petroleum Biomarkers	Grain-Size	TOC	COPC	Parent PAH	Parent and Alkyl PAH
S-02	SMA9D	PH14-S02-S	0 - 1 ft	X	X	X	X	X	X	--	--	--
S-03		PH14-S03-S	0 - 1 ft	X	X	X	X	X	X	--	--	--
		PH14-S03-Z	2 - 3 ft	X	X	X	X	X	X	--	--	--
S-04		PH14-S04-S	0 - 1 ft	X	X	X	X	X	X	--	--	--
S-05		PH14-S05-S	0 - 1 ft	X	X	X	X	X	X	--	--	--
		PH14-S05-Z	2 - 3 ft	X	X	X	X	X	X	--	--	--
S-06		PH14-S06-S	0 - 1 ft	X	X	X	X	X	X	--	--	--
		PH14-S06-Z	2 - 3 ft	X	X	X	X	X	X	--	--	--
S-07		PH14-S07-S	0 - 1 ft	X	X	X	X	X	X	--	--	--
S-08		PH14-S08-S	0 - 1 ft	X	X	X	X	X	X	--	--	--
		PH14-S08-Z	2 - 3 ft	X	X	X	X	X	X	--	--	--
S-09		PH14-S09-S	0 - 1 ft	X	X	X	X	X	X	--	--	--
S-10		PH14-S10-S	0 - 1 ft	X	X	X	X	X	X	--	--	--
		PH14-S10-Z	2 - 3 ft	X	X	X	X	X	X	--	--	--
S-11		PH14-S11-S	0 - 1 ft	X	X	X	X	X	X	--	--	--
S-12		PH14-S12-S	0 - 1 ft	X	X	X	X	X	X	--	--	--
		PH14-S12-Z	2 - 3 ft	X	X	X	X	X	X	--	--	--
S-13		PH14-S13-S	0 - 1 ft	X	X	X	X	X	X	--	--	--
		PH14-S13-Z	2 - 3 ft	X	X	X	X	X	X	--	--	--
S-14		PH14-S14-S	0 - 1 ft	X	X	X	X	X	X	--	--	--
S-15		PH14-S15-S	0 - 1 ft	X	X	X	X	X	X	--	--	--
		PH14-S15-Z	2 - 3 ft	X	X	X	X	X	X	--	--	--
S-16		PH14-S16-S	0 - 1 ft	X	X	X	X	X	X	--	--	--
S-17		PH14-S17-S	0 - 1 ft	X	X	X	X	X	X	--	--	--
		PH14-S17-Z	2 - 3 ft	X	X	X	X	X	X	--	--	--
S-18		PH14-S18-S	0 - 1 ft	X	X	X	X	X	X	--	--	--
S-19		PH14-S19-S	0 - 1 ft	X	X	X	X	X	X	--	--	--
		PH14-S19-Z	2 - 3 ft	X	X	X	X	X	X	--	--	--
S-20		PH14-S20-S	0 - 1 ft	X	X	X	X	X	X	--	--	--
		PH14-S20-Z	5 - 6 ft	X	X	X	X	X	X	--	--	--
S-21	Gasco vicinity	PH14-S21-S	0 - 1 ft	X	X	X	X	X	X	--	--	--
S-22		PH14-S22-S	0 - 1 ft	X	X	X	X	X	X	--	--	--
		PH14-S22-Z	2 - 3 ft	X	X	X	X	X	X	--	--	--
S-23		PH14-S23-S	0 - 1 ft	X	X	X	X	X	X	--	--	--

Station ID	Study Area	Sample ID	Depth Interval	Forensic Chemical Analyses				Ancillary Measurements		Characterization	SPME Pore Water	
				TPH and n-alkanes	Parent and Alkyl PAH	High MW PAH	Petroleum Biomarkers	Grain-Size	TOC	COPC	Parent PAH	Parent and Alkyl PAH
S-24		PH14-S24-S	0 - 1 ft	X	X	X	X	X	X	--	--	--
		PH14-S24-Z	2 - 3 ft	X	X	X	X	X	X	--	--	--
S-25		PH14-S25-S	0 - 1 ft	X	X	X	X	X	X	--	--	--
		PH14-S25-Z	2 - 3 ft	X	X	X	X	X	X	--	--	--
S-26	McCormick and Baxter	PH14-S26-S	0 - 1 ft	X	X	X	X	X	X	--	--	--
S-27		PH14-S27-S	0 - 1 ft	X	X	X	X	X	X	--	--	--
S-28	Upriver Reference	PH14-S28-S	0 - 1 ft	X	X	X	X	X	X	--	--	--
		PH14-S28-Z	2 - 3 ft	X	X	X	X	X	X	--	--	--
S-29		PH14-S29-S	0 - 1 ft	X	X	X	X	X	X	--	--	--
		PH14-S29-Z	2 - 3 ft	X	X	X	X	X	X	--	--	--
S-30		PH14-S30-S	0 - 1 ft	X	X	X	X	X	X	--	--	--
		PH14-S30-Z	2 - 3 ft	X	X	X	X	X	X	--	--	--
S-31	Term. 4, Slip 3	PH14-S31-S	0 - 1 ft	X	X	X	X	X	X	--	--	--
S-32		PH14-S32-S	0 - 1 ft	X	X	X	X	X	X	--	--	--
S-33		PH14-S33-S	0 - 1 ft	X	X	X	X	X	X	--	--	--
S-34	Linnton Property	PH14-S34-S	0 - 1 ft	X	X	X	X	X	X	X	--	--
S-35		PH14-S35-S	0 - 1 ft	X	X	X	X	X	X	X	--	--
S-36		PH14-S36-S	0 - 1 ft	X	X	X	X	X	X	X	--	--
S-37		PH14-S37-S	0 - 1 ft	X	X	X	X	X	X	X	--	--
S-38		PH14-S38-S	0 - 1 ft	X	X	X	X	X	X	X	--	--
T-03	CBRA 9D-2	PH14-T03-S	0 - 1 ft	X	X	X	X	X	X	--	X	X
		PH14-T03-Z	2 - 3 ft	X	X	X	X	X	X	--	X	X
T-04		PH14-T04-S	0 - 1 ft	X	X	X	X	X	X	--	X	X
		PH14-T04-Z	2 - 3 ft	X	X	X	X	X	X	--	X	X
T-05	CBRA 9D-3	PH14-T05-S	0 - 1 ft	X	X	X	X	X	X	--	X	X
		PH14-T05-TB	0 - 1 ft	X	X	X	X	X	X	--	--	--
		PH14-T05-W	River Bottom	--	--	--	--	--	--	--	--	--
T-06		PH14-T06-S	0 - 1 ft	X	X	X	X	X	X	--	X	X
T-07		PH14-T07-S	0 - 1 ft	X	X	X	X	X	X	--	X	X
T-08		PH14-T08-S	0 - 1 ft	X	X	X	X	X	X	--	X	X
		PH14-T08-Z	2 - 3 ft	X	X	X	X	X	X	--	X	X
T-09		PH14-T09-S	0 - 1 ft	X	X	X	X	X	X	--	X	X
		PH14-T09-Z	2 - 3 ft	X	X	X	X	X	X	--	X	X
		PH14-T09-W	River Bottom	--	--	--	--	--	--	--	--	--
T-10		PH14-T10-S	0 - 1 ft	X	X	X	X	X	X	--	X	X

Table 3. PAH Compounds Measured by Texas Tech University.

Abbr.	Compound
NAP	Naphthalene
FL	Fluorene
ACE	Acenaphthene
PHE	Phenanthrene
ANT	Anthracene
FLU	Fluoranthene
PYR	Pyrene
CHR	Chrysene
BaA	Benz[a]anthracene
BbF	Benzo[b]fluoranthene
BkF	Benzo[k]fluoranthene
BaP	Benzo[a]pyrene
DBA	Dibenz[a,h]anthracene
BghiP + InP	Benzo[ghi]perylene+Indeno[1,2,3-cd]pyrene

Table 4. Summary Statistics for Key Hydrocarbon and PAH Parameters Measured in the Sediment and Tar Ball Samples.

Station ID	Study Area	Matrix	Depth	RM	TPH (mg/Kg)	Total PAH16 (µg/Kg)	Total PAH (µg/Kg)	% Alkyl PAH	% TPAH	% 2-and3-ring Alkyl PAH	% 4-ring Alkyl PAH	BaP EQ (µg/Kg)[1]
S30-S	Upriver	Sediment	0 - 1 ft	10.09	136	233	537	52	0	56	45	23
S30-Z	Upriver	Sediment	2 - 3 ft	10.09	51	525	743	23	1	26	15	47
S29-S	Upriver	Sediment	0 - 1 ft	9.09	125	140	539	71	0	88	43	15
S29-Z	Upriver	Sediment	2 - 3 ft	9.09	203	353	724	46	0	58	37	36
S28-S	Upriver	Sediment	0 - 1 ft	8.55	199	318	659	47	0	61	31	27
S28-Z	Upriver	Sediment	2 - 3 ft	8.55	207	170	579	67	0	82	49	18
S27-S	Baxter	Sediment	0 - 1 ft	7.04	97	123	341	59	0	74	45	13
S26-S	Baxter	Sediment	0 - 1 ft	6.7	268	3,038	4,505	26	2	25	19	245
S25-S	Gasco	Sediment	0 - 1 ft	6.44	35,300	9,734,900	13,408,400	23	38	14	8	367,890
S25-Z	Gasco	Sediment	2 - 3 ft	6.44	3,180	735,350	1,021,441	23	32	18	7	33,893
S24-S	Gasco	Sediment	0 - 1 ft	6.35	552	127,939	160,620	12	29	14	5	13,678
S24-Z	Gasco	Sediment	2 - 3 ft	6.35	5,000	1,707,270	2,061,185	10	41	8	3	147,619
S23-S	Gasco	Sediment	0 - 1 ft	6.27	4,630	1,524,160	1,966,939	16	42	11	5	93,122
S22-S	Gasco	Sediment	0 - 1 ft	6.17	1,370	116,479	187,101	31	14	31	18	11,054
S22-Z	Gasco	Sediment	2 - 3 ft	6.17	3,320	716,750	1,027,350	25	31	22	6	39,650
S21-S	Gasco	Sediment	0 - 1 ft	6.14	62	7,010	9,027	14	15	29	6	874
S20-S	SMA 9D	Sediment	0 - 1 ft	6.07	350	12,818	18,650	26	5	18	20	807
S20-Z	SMA 9D	Sediment	2 - 3 ft	6.07	1,130	61,783	83,210	19	7	19	10	5,181
S18-S	SMA 9D	Sediment	0 - 1 ft	6.03	6,220	2,434,700	2,925,176	10	47	4	3	95,007
S19-S	SMA 9D	Sediment	0 - 1 ft	5.97	1,160	38,241	78,466	46	7	45	23	3,114
S19-Z	SMA 9D	Sediment	2 - 3 ft	5.97	1,430	68,838	172,118	55	12	46	30	4,655
S17-S	SMA 9D	Sediment	0 - 1 ft	5.91	422	11,086	17,304	28	4	38	21	1,508
S17-Z	SMA 9D	Sediment	2 - 3 ft	5.91	640	12,088	19,207	30	3	43	23	1,687
S17-Z-D	SMA 9D	Sediment	2 - 3 ft	5.91	672	13,113	20,705	29	3	42	23	1,788
S16-S	SMA 9D	Sediment	0 - 1 ft	5.87	389	54,283	87,070	31	22	50	14	6,706
S15-S	SMA 9D	Sediment	0 - 1 ft	5.76	605	17,767	26,928	27	4	36	16	1,931
S15-Z	SMA 9D	Sediment	2 - 3 ft	5.76	298	11,823	21,231	39	7	64	16	1,354
S14-S	SMA 9D	Sediment	0 - 1 ft	5.74	256	42,986	60,554	21	24	52	11	6,669
S13-S	SMA 9D	Sediment	0 - 1 ft	5.64	90	1,175	1,913	31	2	42	29	146
S13-Z	SMA 9D	Sediment	2 - 3 ft	5.64	131	2,681	4,798	37	4	58	24	351
S11-S	SMA 9D	Sediment	0 - 1 ft	5.61	49	3,186	4,367	18	9	63	12	565

Station ID	Study Area	Matrix	Depth	RM	TPH (mg/Kg)	Total PAH16 (µg/Kg)	Total PAH (µg/Kg)	% Alkyl PAH	% TPAH	% 2-and3-ring Alkyl PAH	% 4-ring Alkyl PAH	BaP EQ (µg/Kg)[1]
S12-S	SMA 9D	Sediment	0 - 1 ft	5.56	117	3,437	5,242	27	4	26	21	346
S12-Z	SMA 9D	Sediment	2 - 3 ft	5.56	114	3,971	6,173	30	5	32	16	361
S09-S	SMA 9D	Sediment	0 - 1 ft	5.51	330	58,755	81,104	19	25	69	11	10,032
S10-S	SMA 9D	Sediment	0 - 1 ft	5.47	878	72,462	102,437	22	12	26	9	6,433
S10-Z	SMA 9D	Sediment	2 - 3 ft	5.47	2,220	363,571	468,081	15	21	19	5	35,382
S08-S	SMA 9D	Sediment	0 - 1 ft	5.40	261	2,607	4,461	35	2	45	30	342
S08-Z	SMA 9D	Sediment	2 - 3 ft	5.40	389	6,593	10,064	27	3	38	20	870
S07-S	SMA 9D	Sediment	0 - 1 ft	5.36	1,010	231,394	341,071	26	34	30	10	21,801
S06-S	SMA 9D	Sediment	0 - 1 ft	5.33	341	3,581	5,837	31	2	47	25	501
S06-Z	SMA 9D	Sediment	2 - 3 ft	5.33	59	1,455	2,222	28	4	46	15	159
S05-S	SMA 9D	Sediment	0 - 1 ft	5.28	270	3,655	5,725	29	2	39	23	490
S05-Z	SMA 9D	Sediment	2 - 3 ft	5.28	83	5,812	7,907	22	10	18	8	278
S04-S	SMA 9D	Sediment	0 - 1 ft	5.23	59	6,273	9,282	24	16	65	16	1,042
S04-S-D	SMA 9D	Sediment	0 - 1 ft	5.23	199	25,577	38,375	25	19	72	16	4,534
S03-S	SMA 9D	Sediment	0 - 1 ft	5.21	250	4,814	7,500	28	3	44	21	642
S03-Z	SMA 9D	Sediment	2 - 3 ft	5.21	405	2,463	5,580	51	1	65	40	292
S02-S	SMA 9D	Sediment	0 - 1 ft	5.19	111	7,049	10,006	23	9	28	11	678
T10-S	CBRA 9D-3	Sediment	0 - 1 ft	5.76	1,020	327,002	407,692	13	40	16	5	30,407
T07-S	CBRA 9D-3	Sediment	0 - 1 ft	5.72	309	82,541	105,896	15	34	26	6	10,343
T09-S	CBRA 9D-3	Sediment	0 - 1 ft	5.72	410	3,231	5,016	28	1	37	20	396
T09-Z	CBRA 9D-3	Sediment	2 - 3 ft	5.72	684	33,912	53,469	30	8	35	18	3,932
T06-S	CBRA 9D-3	Sediment	0 - 1 ft	5.69	1,540	393,563	532,757	20	35	20	7	31,291
T08-S	CBRA 9D-3	Sediment	0 - 1 ft	5.69	344	5,715	8,557	26	2	38	17	742
T08-Z	CBRA 9D-3	Sediment	2 - 3 ft	5.69	333	5,382	8,159	27	2	36	19	708
T05-TB	CBRA 9D-3	Tar Ball	0 - 1 ft	5.65	686,000	183,033,100	249,091,500	20	36	20	7	NA
T05-S	CBRA 9D-3	Sediment	0 - 1 ft	5.65	9,590	2,385,360	3,308,740	22	35	21	7	181,156
T03-S	CBRA 9D-2	Sediment	0 - 1 ft	5.20	260	1,802	3,110	35	1	43	31	240
T03-Z	CBRA 9D-2	Sediment	2 - 3 ft	5.20	338	2,166	5,249	53	2	67	46	276
T04-S	CBRA 9D-2	Sediment	0 - 1 ft	5.19	242	1,643	2,928	37	1	55	29	204
T04-Z	CBRA 9D-2	Sediment	2 - 3 ft	5.19	287	2,897	4,597	30	2	41	24	380
T04-Z-D	CBRA 9D-2	Sediment	2 - 3 ft	5.19	255	2,947	4,663	29	2	45	23	426
S34-S	Linnton	Sediment	0 - 1 ft	4.78	180	1,605	2,626	32	1	47	22	182
S35-S	Linnton	Sediment	0 - 1 ft	4.68	217	1,067	1,850	36	1	49	28	103

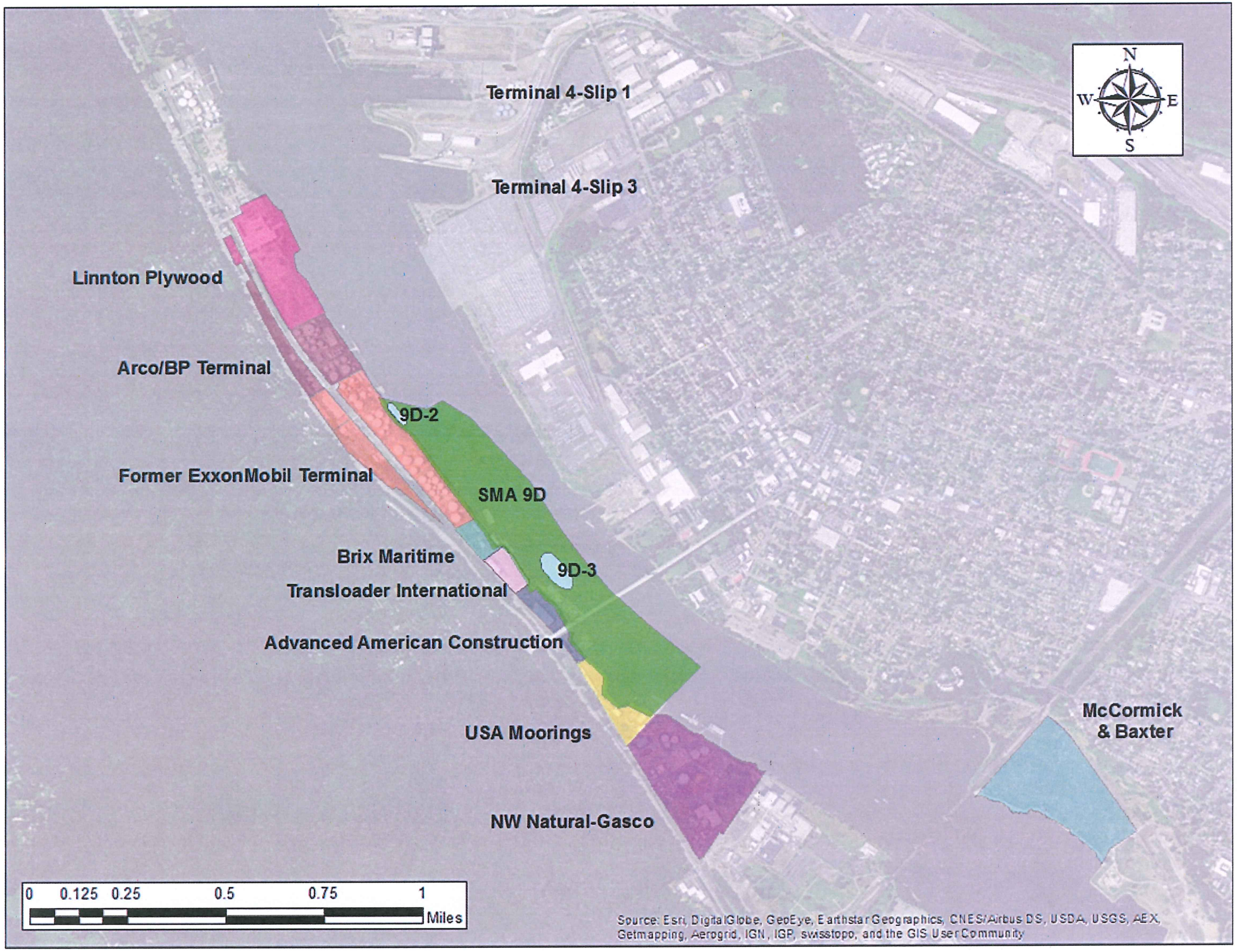
Station ID	Study Area	Matrix	Depth	RM	TPH (mg/Kg)	Total PAH16 (µg/Kg)	Total PAH (µg/Kg)	% Alkyl PAH	% TPAH	% 2-and3-ring Alkyl PAH	% 4-ring Alkyl PAH	BaP EQ (µg/Kg)[1]
S35-D	Linnton	Sediment	0 - 1 ft	4.68	264	1,441	2,393	33	1	44	26	162
S36-S	Linnton	Sediment	0 - 1 ft	4.64	271	981	1,742	37	1	46	29	65
S37-S	Linnton	Sediment	0 - 1 ft	4.54	279	1,093	1,878	35	1	42	27	93
S38-S	Linnton	Sediment	0 - 1 ft	4.51	223	970	1,748	38	1	58	26	78
S33-S	Terminal 4	Sediment	0 - 1 ft	4.62	136	1,678	2,371	21	2	37	14	241
S32-S	Terminal 4	Sediment	0 - 1 ft	4.57	241	5,358	7,534	20	3	32	15	820
S31-S	Terminal 4	Sediment	0 - 1 ft	4.57	292	10,483	14,374	19	5	29	11	1,132

[1] PEFs for cPAH were assigned PEFs from EPA 1993 Guidance Document.

Table 5. Summary Statistics for Key Hydrocarbon and PAH Parameters by Study Area.

	Depth Interval	n	TPH (mg/Kg)				TPAH (µg/Kg)				%Alkyl PAH			
			Min	Max	Avg	Median	Min	Max	Avg	Median	Min	Max	Avg	Median
Upriver Reference														
	All	6	51	207	154	168	537	743	630	619	23	71	51	49
	0-1'	3	125	199	153	136	537	659	579	539	47	71	56	52
	2-3'	3	51	207	154	203	579	743	682	724	23	67	45	46
McCormick and Baxter														
	All	2	97	268	182	182	341	4,505	2,423	2,423	26	59	42	42
	0-1'	2	97	268	182	182	341	44,505	2,423	2,423	26	59	42	42
Gasco														
	All	8	62	35,300	6,677	3,250	9,027	13,408,400	2,480,258	1,024,396	10	31	19	19
	0-1'	5	62	35,300	8,383	1,370	9,027	13,408,400	3,146,417	187,101	12	31	19	16
	2-3'	3	3,180	5,000	3,833	3,320	1,021,441	2,061,185	1,369,992	1,027,350	10	25	19	23
SMA 9D														
	All	45	49	9,590	812	338	1,913	3,308,740	202,302	10,064	10	55	28	28
	0-1'	28	49	9,590	967	336	1,913	3,308,740	293,077	17,977	10	46	26	26
	2-3'	17	59	2,220	557	338	2,222	468,081	52,790	8,159	15	55	32	30
Linnton														
	All	6	180	279	239	244	1,742	2,626	2,039	1,864	32	38	35	36
	0-1'	6	180	279	239	244	1,742	2,626	2,039	1,864	32	38	35	36
Terminal 4, Slip 3														
	All	3	136	292	223	241	2,371	14,374	8,093	7,534	19	21	20	20
	0-1'	3	136	292	223	241	2,371	14,374	8,093	7,534	19	21	20	20

Figures



Source: Esri, DigitalGlobe, GeoEye, Earthstar Geographics, CNES/Airbus DS, USDA, USGS, AEX, Getmapping, Aerogrid, IGN, IGP, swisstopo, and the GIS User Community

Figure 1. The focus of NewFields 2014 Forensic Investigation: Sediment Management Area 9D (SMA 9D), including two Comprehensive Risk Areas (CBRAs) 9D-2 and 9D-3.

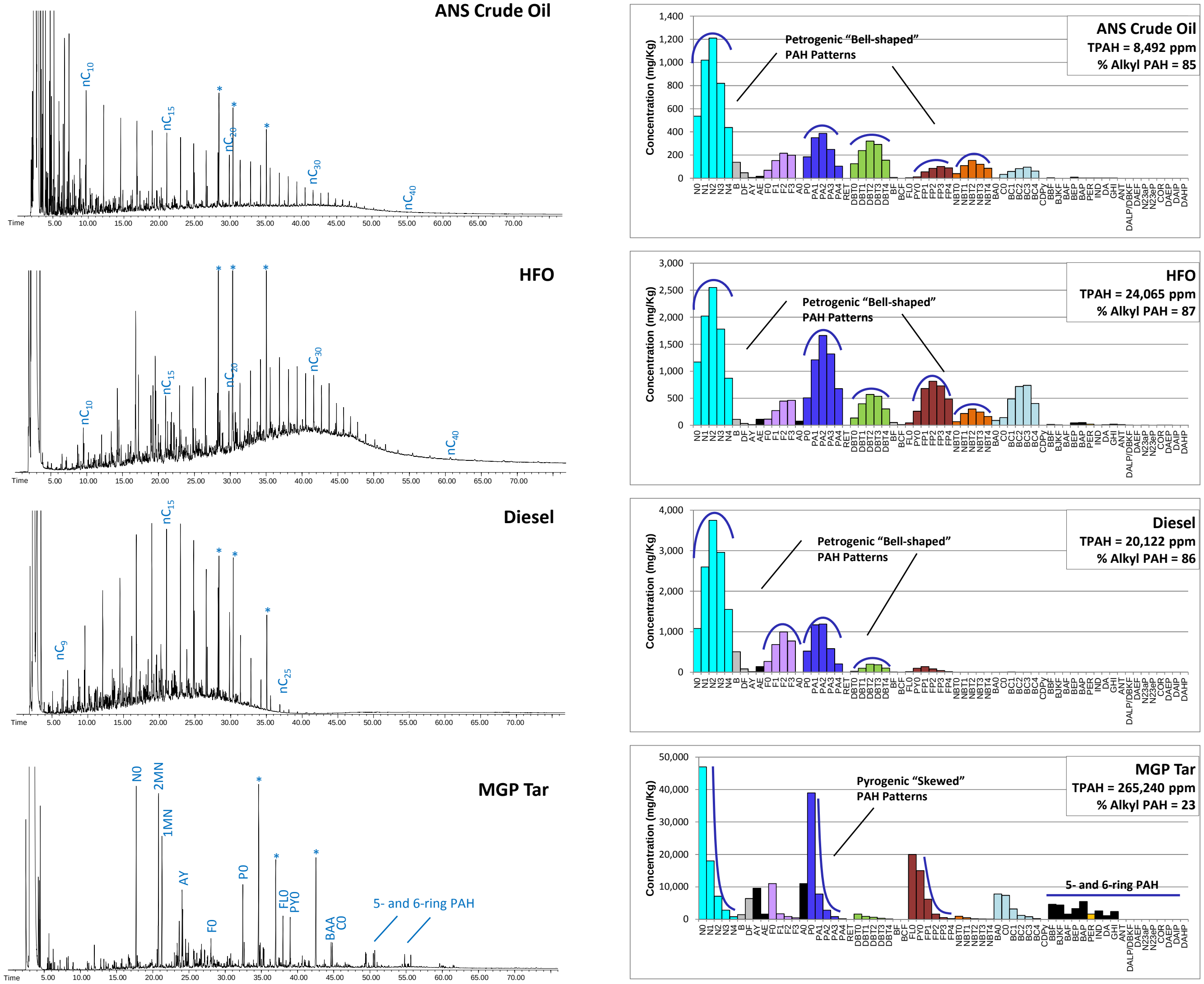


Figure 2. Gas chromatograms and the PAH histograms for common petroleum products (crude oil, HFO, diesel fuel) and a representative pyrogenic MGP tar.

'*': laboratory-added internal standards.

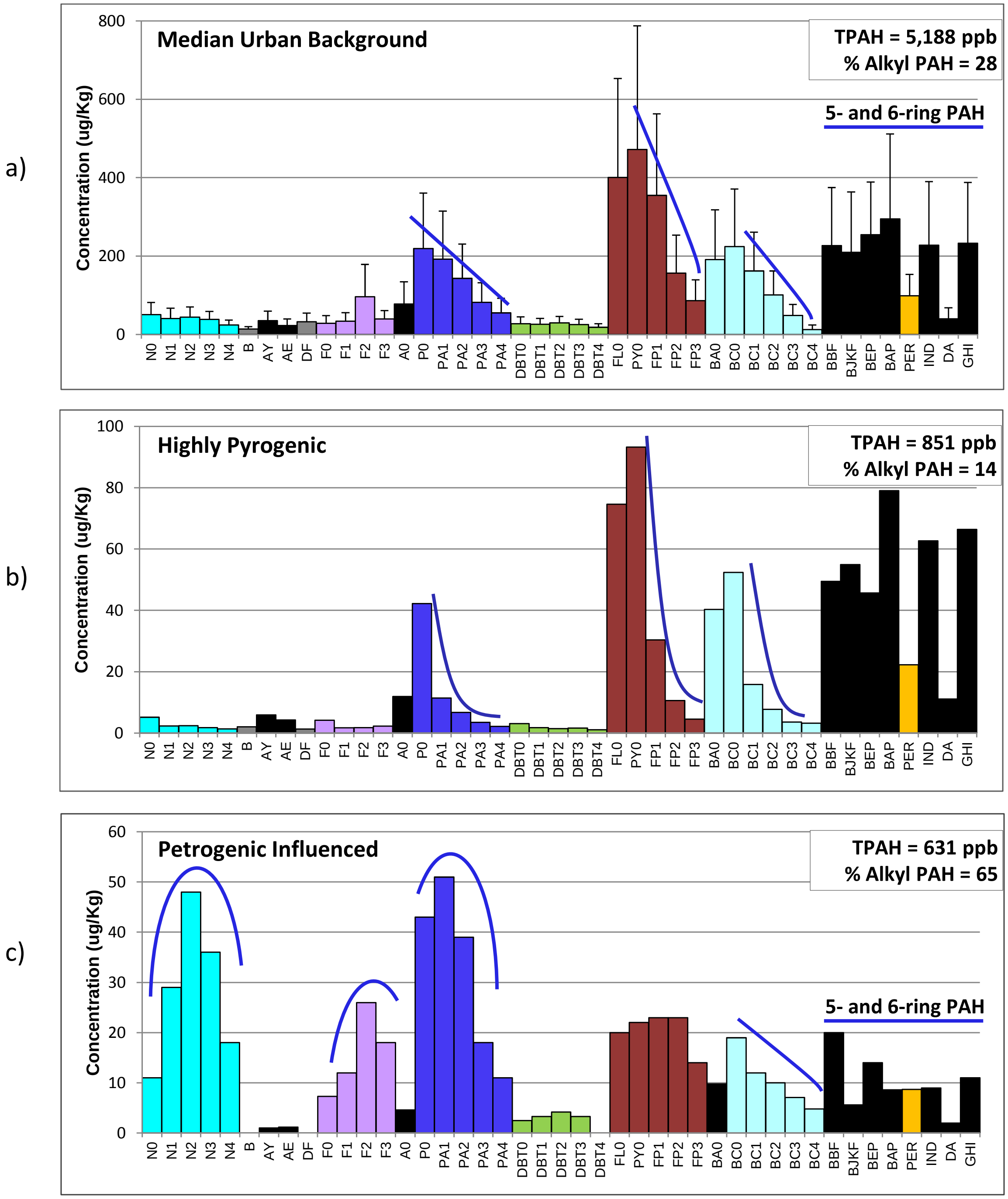
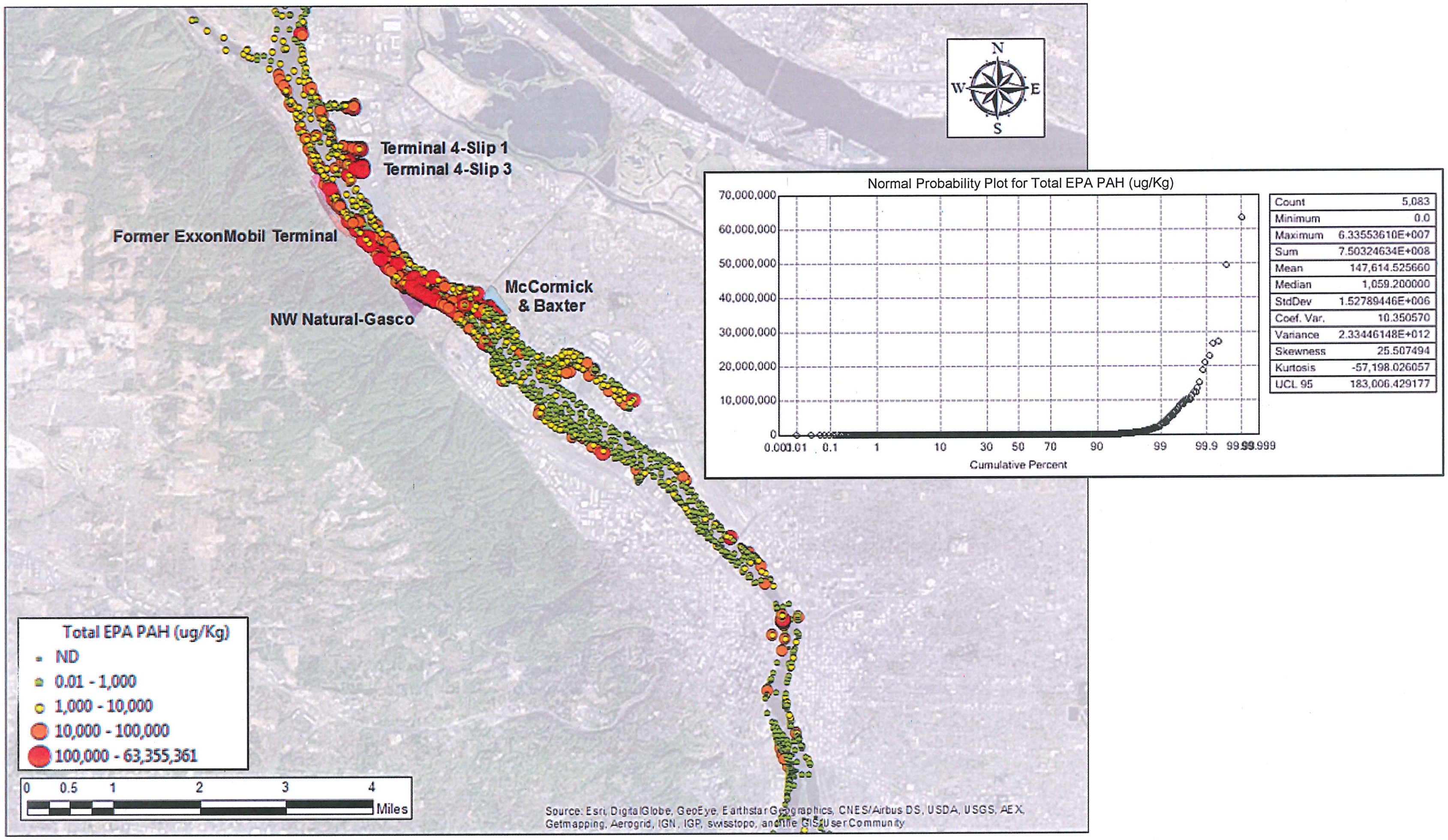


Figure 3. PAH features of U.S. "urban background" sediments reported by Stout et al. 2004.

Figure 3a: Median PAH histogram for 280 sediments from nine urban waterways, showing that sediments are a dominantly pyrogenic mixtures of PAH. Median %Alkyl PAH of 28%.

Figure 3b: PAH histogram from the most pyrogenic sediment: %Alkyl PAH = 14.

Figure 3c: PAH histogram from the most petrogenic sediment: %Alkyl PAH = 65.

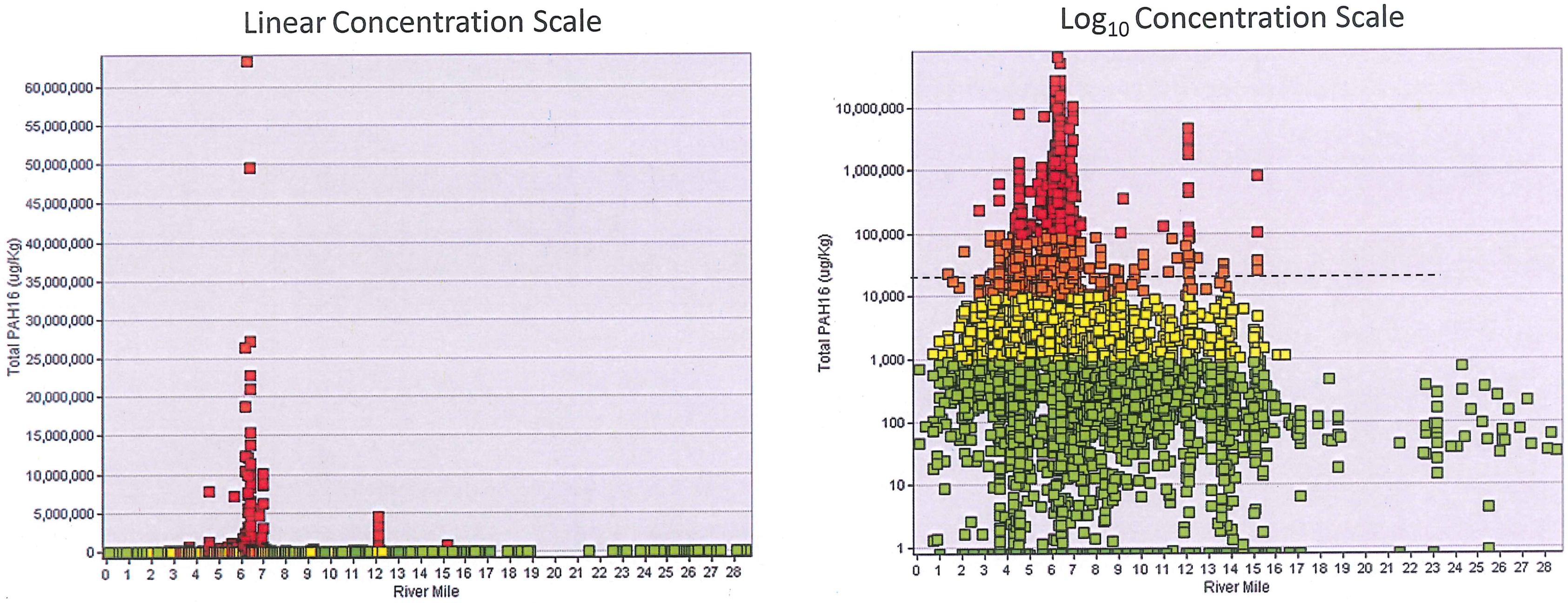


Count	5,083
Minimum	0.0
Maximum	6.33553610E+007
Sum	7.50324634E+008
Mean	147,614.525660
Median	1,059.200000
StdDev	1.52789446E+006
Coef. Var.	10.350570
Variance	2.33446148E+012
Skewness	25.507494
Kurtosis	-57,198.026057
UCL 95	183,006.429177

Source: Esri, DigitalGlobe, GeoEye, Earthstar Geographics, CNES/Airbus DS, USDA, USGS, AEX, Getmapping, Aerogrid, IGN, IGP, swisstopo, and the GIS User Community

Figure 4. Concentration distribution of Total EPA Priority Pollutant PAH in the Portland Harbor Superfund Site area. Inset: Concentration frequency chart and summary statistics.

Source: Lower Willamette Group Historical Dataset.


Linear Concentration Scale

Log$_{10}$ Concentration Scale

Figure 5. Concentration of Total PAH16 vs River Mile in the Portland Harbor Superfund Site area. Left panel: linear concentration scale; Right panel: Log$_{10}$ concentration scale. Dashed line: upper limit of “urban background” sediments proposed by Stout et al. (2004).

Note: The color scale shown in this figure represents the same concentration scale shown in Figure 4.

Source: Lower Willamette Group Historical Dataset.

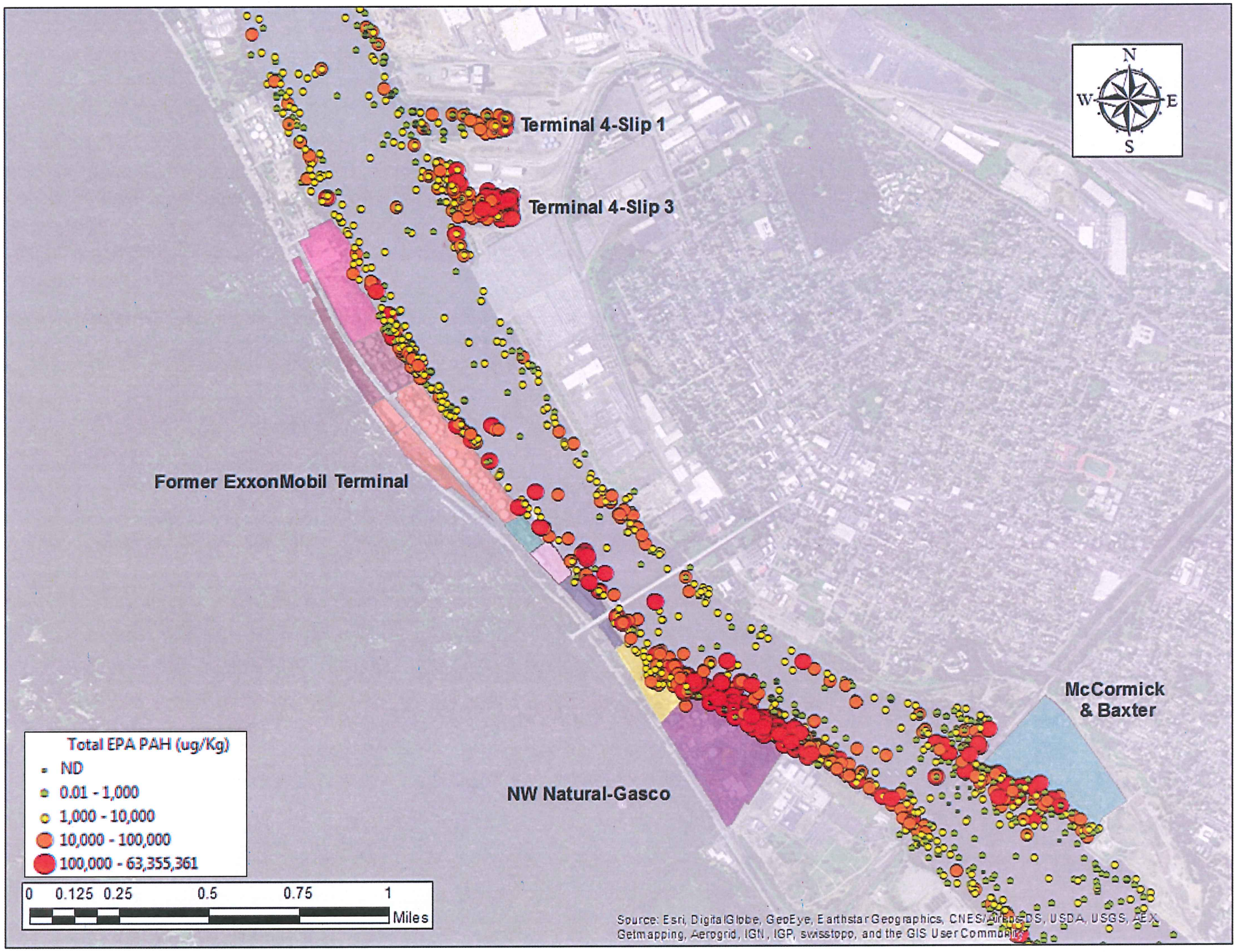
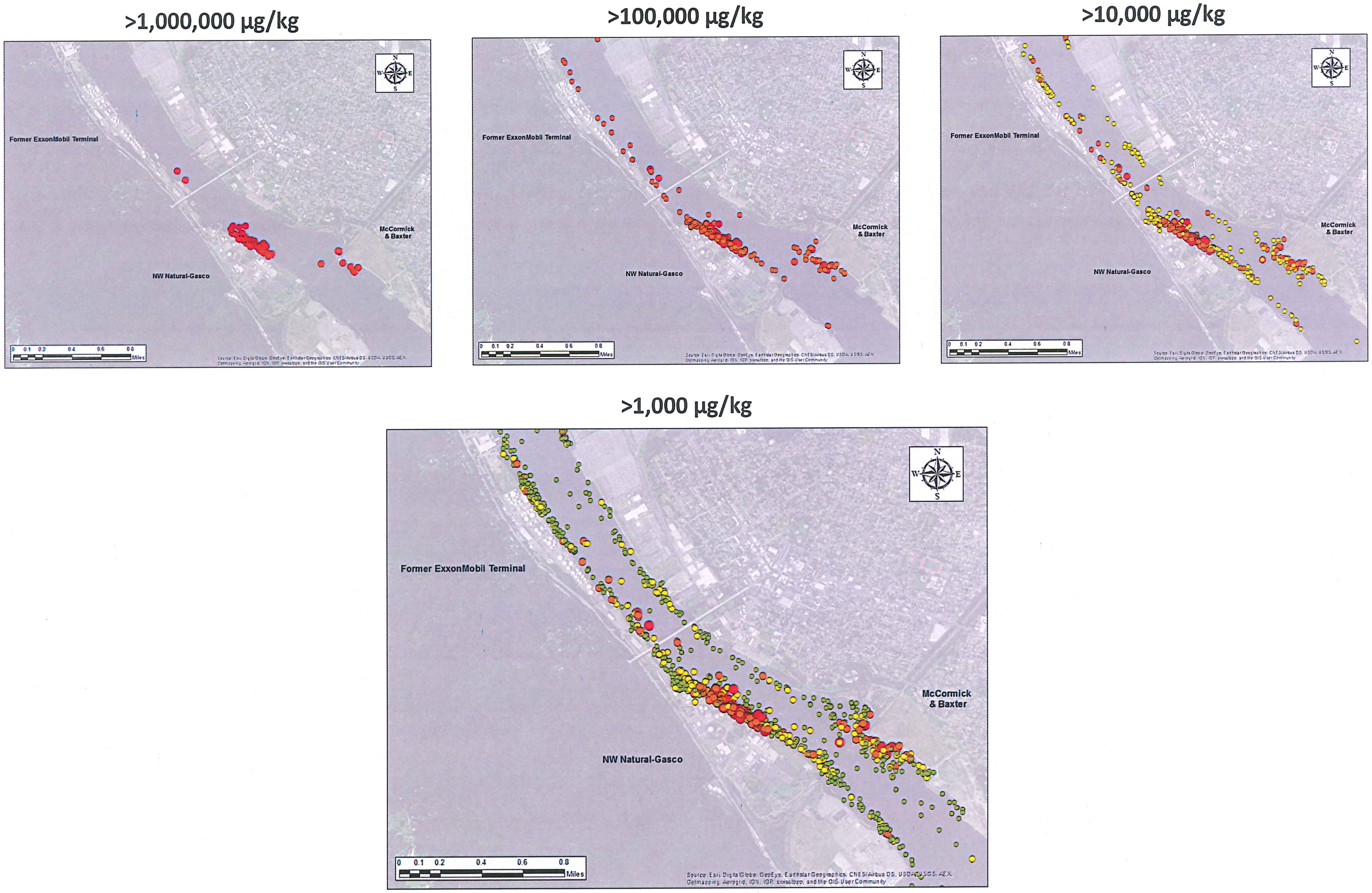


Figure 6. Concentration distribution of historic Total PAH16 in the vicinity of the Former ExxonMobil Terminal. Highest Total PAH16 concentrations noted at the Gasco Property and McCormick and Baxter Property.

Source: Lower Willamette Group Historical Dataset.


>1,000,000 µg/kg

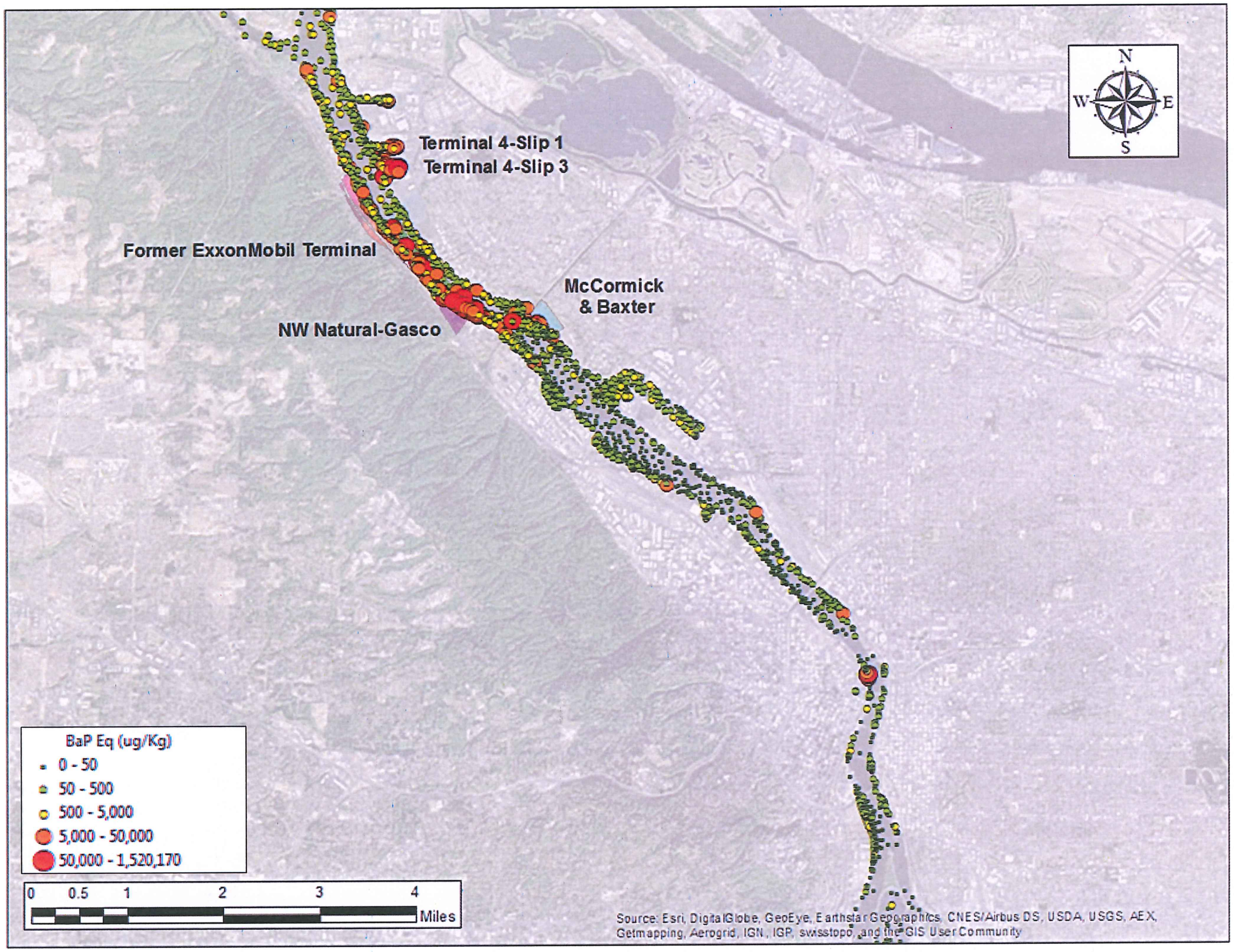
>100,000 µg/kg

>10,000 µg/kg

>1,000 µg/kg

Figure 7. Progressive concentration distribution maps for historic Total PAH16 in the vicinity of the Former ExxonMobil Terminal. Highest Total PAH16 concentrations at the Gasco Property and the McCormick and Baxter Property. Along the west bank of the river, progressively lower concentrations of PAH radiate downstream from the Gasco property into SMA 9D, and other downstream sediments.

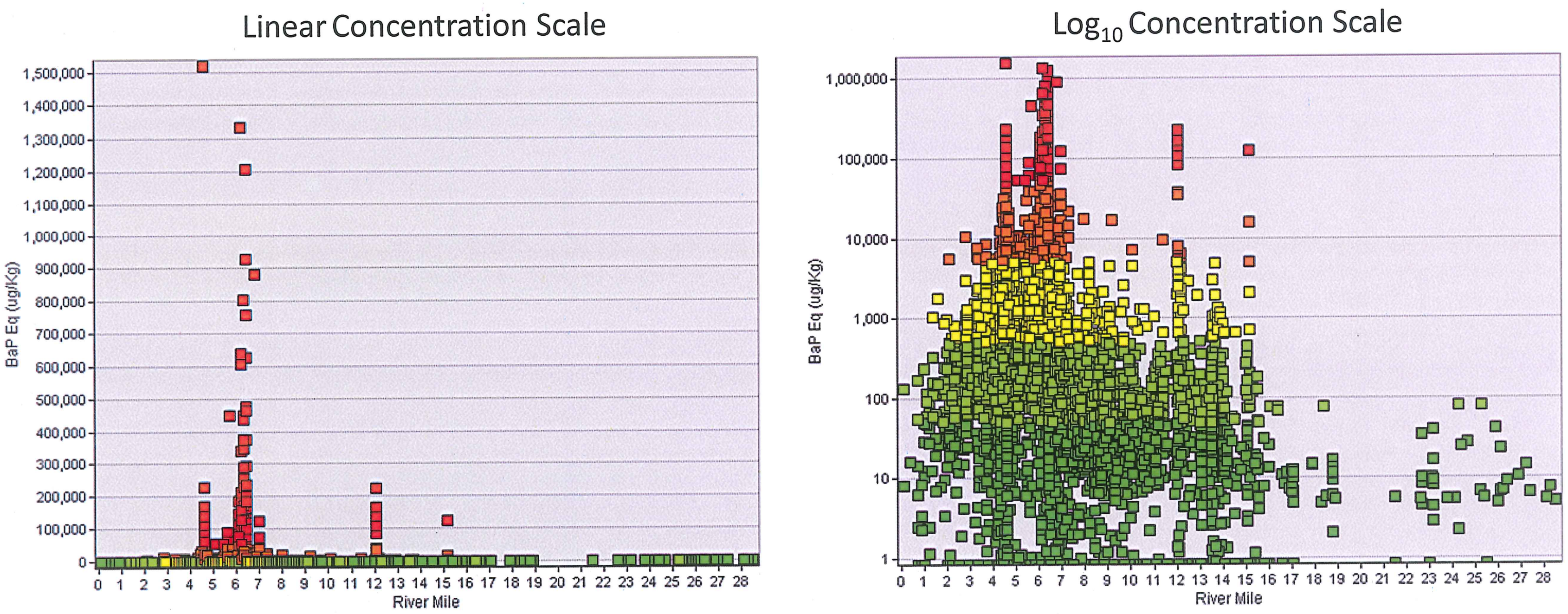
Source: Lower Willamette Group Historical Dataset.



Source: Esri, DigitalGlobe, GeoEye, Earthstar Geographics, CNES/Airbus DS, USDA, USGS, AEX, Getmapping, Aerogrid, IGN, IGP, swisstopo, and the GIS User Community

Figure 8. Distribution of BaPeq for historic Portland Harbor sediments.

Data Source: Lower Willamette Group Historical Dataset.


Linear Concentration Scale

Log$_{10}$ Concentration Scale

Figure 9. Concentration of BaPeq vs River Mile in the Portland Harbor Superfund Site area.
Left panel: linear concentration scale; Right panel: Log$_{10}$ concentration scale.

Note: The color scale shown in this figure represents the same concentration scale shown in Figure 8.

Source: Lower Willamette Group Historical Dataset.

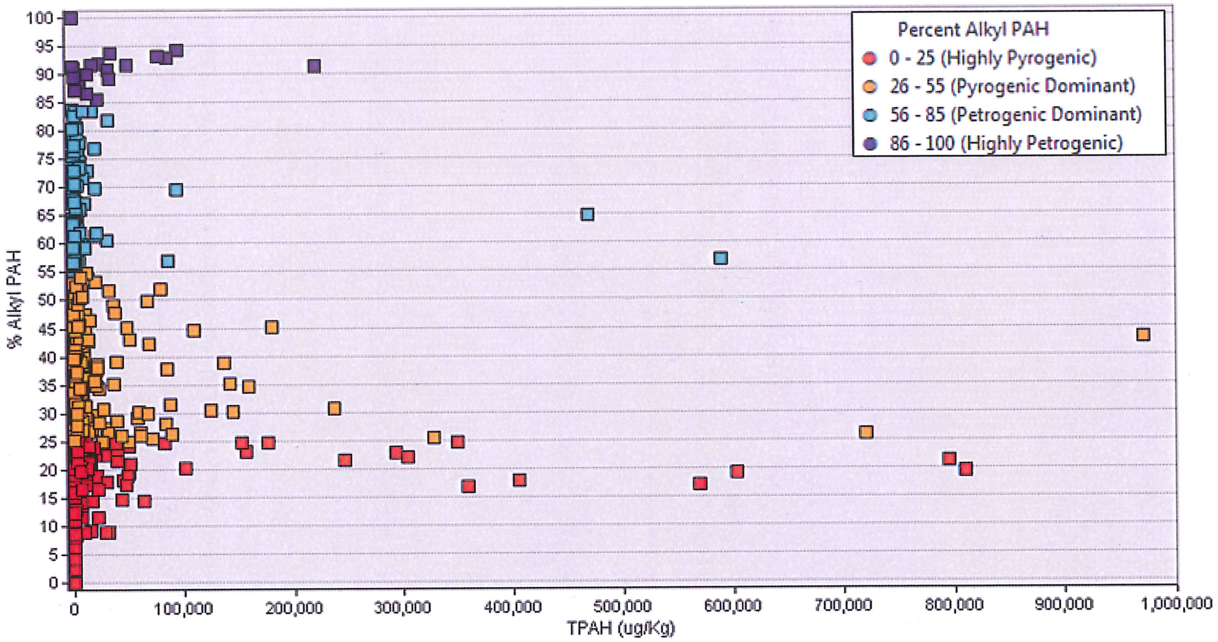
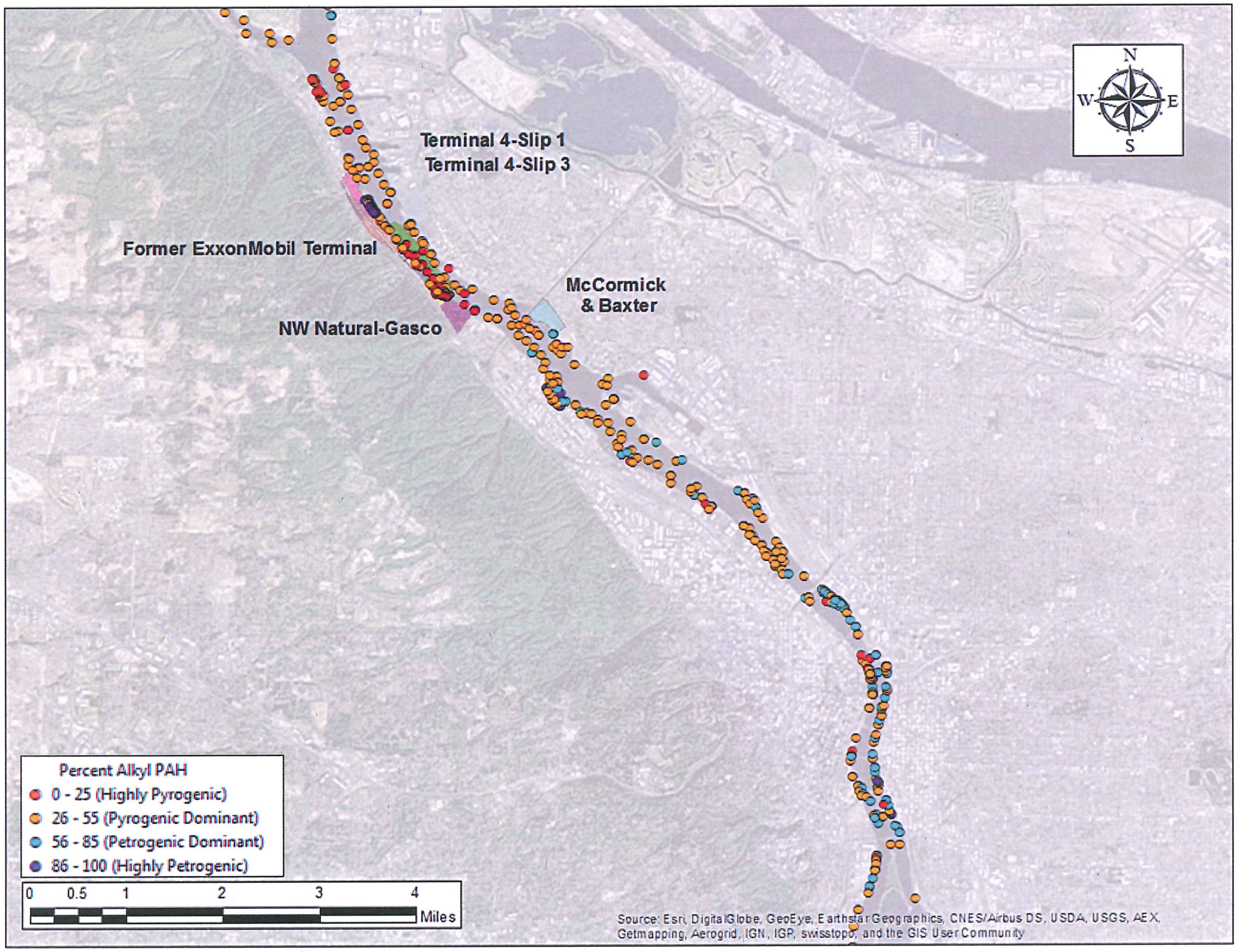


Figure 10. Total PAH vs % Alkyl PAH computed for Portland Harbor Sediments.

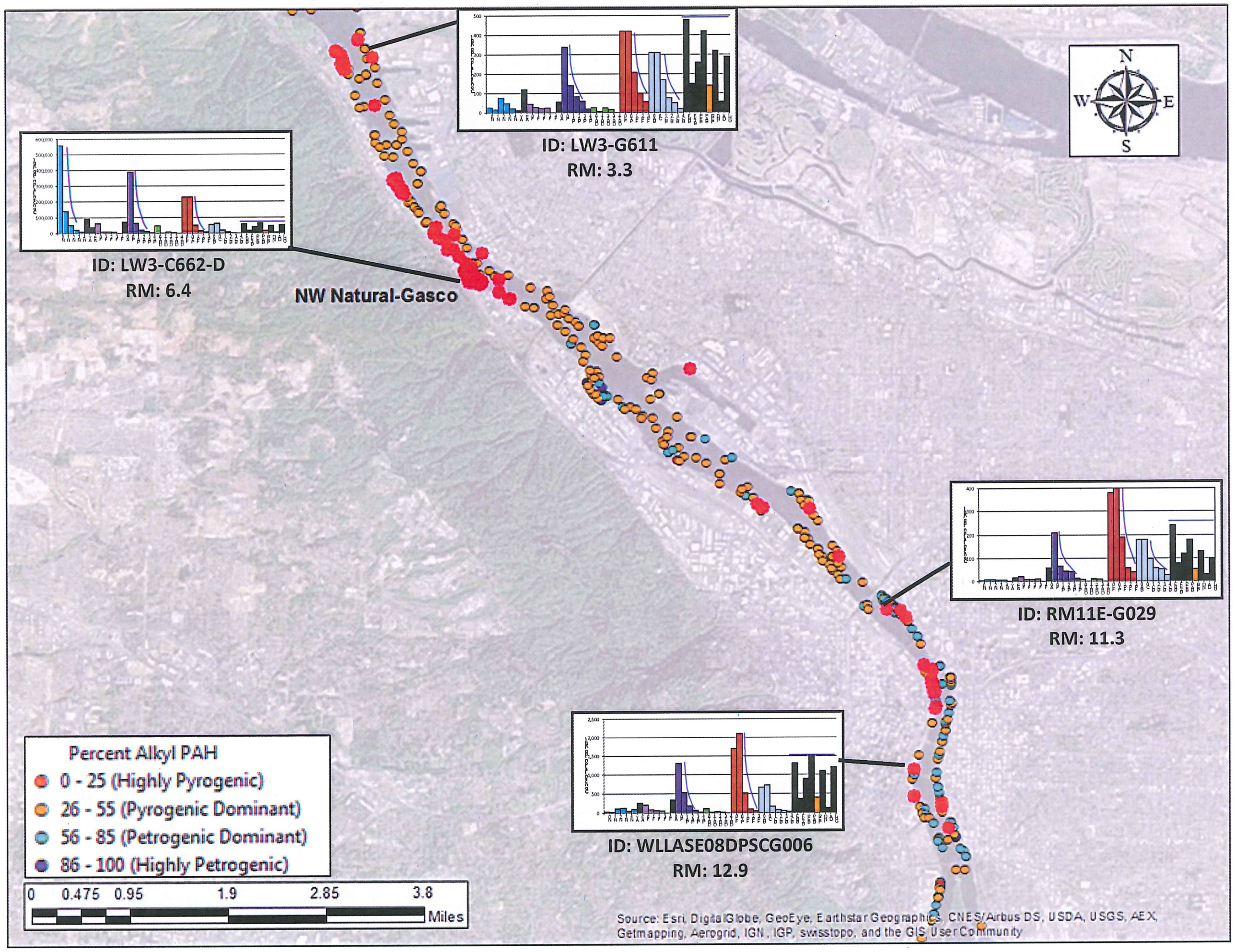
Source: Lower Willamette Group Historical Dataset.



Source: Esri, DigitalGlobe, GeoEye, Earthstar Geographics, CNES/Airbus DS, USDA, USGS, AEX, Getmapping, Aerogrid, IGN, IGP, swisstopo, and the GIS User Community

Figure 11. Distribution of % Alkyl PAH—reflecting variations in the degree of petrogenic and pyrogenic character of PAH—for historic Portland Harbor sediments.

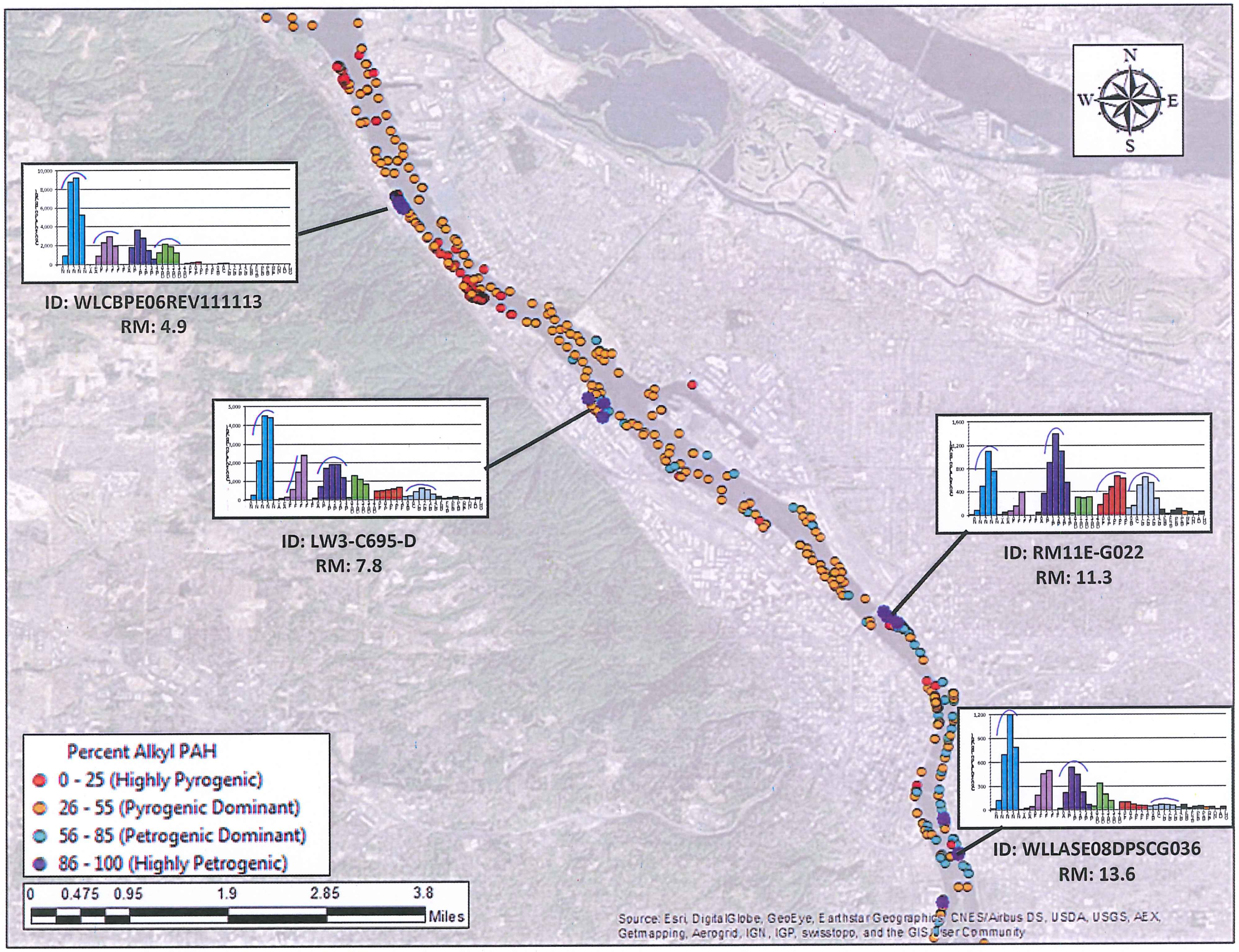
Data Source: Lower Willamette Group Historical Dataset.



Source: Esri, DigitalGlobe, GeoEye, Earthstar Geographics, CNES/Airbus DS, USDA, USGS, AEX, Getmapping, Aerogrid, IGN, IGP, swisstopo, and the GIS User Community

Figure 12. Distribution of % Alkyl PAH for historic Portland Harbor sediments. Locations of samples containing highly pyrogenic (%Alkyl PAH <25%) are depicted in red. Vast majority of sediments found proximal to, and downstream of, the Gasco Property (~80%) were highly pyrogenic in nature. Compositional histograms (with sample ID and River Mile (RM) location) illustrate examples of highly pryogenic PAH assemblages.

Data Source: Lower Willamette Group Historical Dataset.



Source: Esri, DigitalGlobe, GeoEye, Earthstar Geographics, CNES/Airbus DS, USDA, USGS, AEX, Getmapping, Aerogrid, IGN, IGP, swisstopo, and the GIS User Community

Figure 13. Distribution of % Alkyl PAH for historic Portland Harbor sediments. Locations of samples containing highly petrogenic PAH (%Alkyl PAH >85%) are depicted in blue. Compositional histograms (with sample ID and River Mile (RM) location) illustrate examples of highly petrogenic PAH assemblages.

Data Source: Lower Willamette Group Historical Dataset.

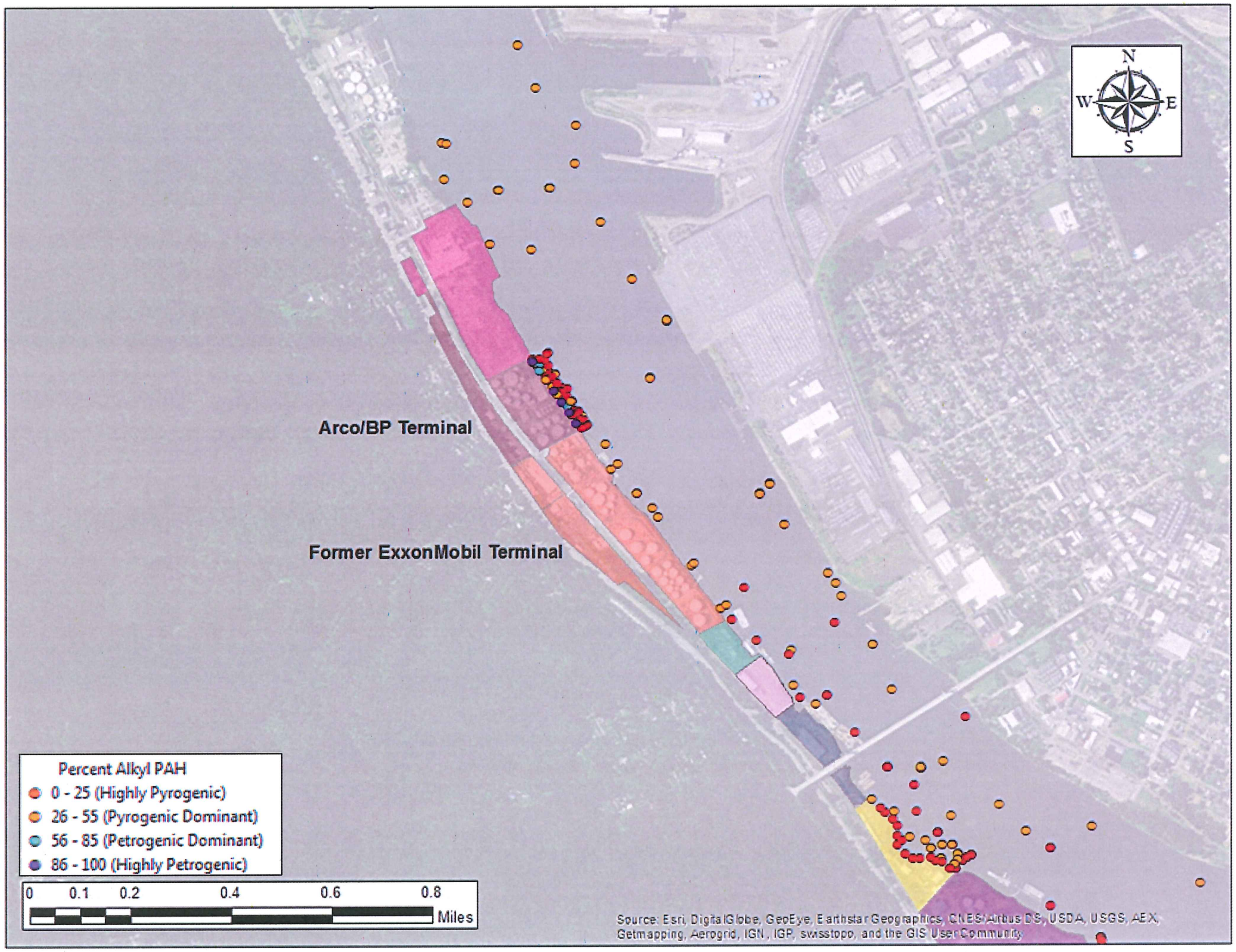
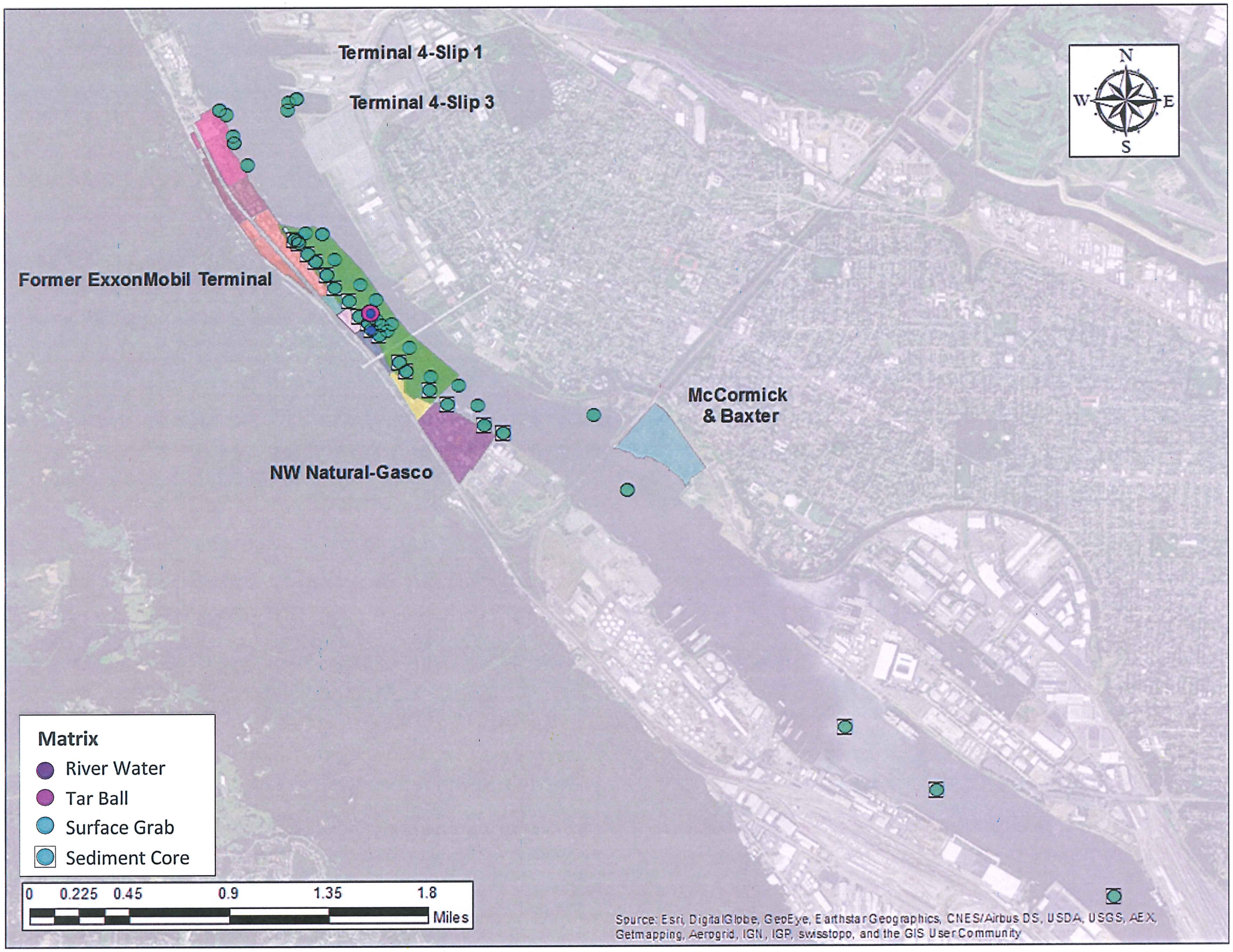


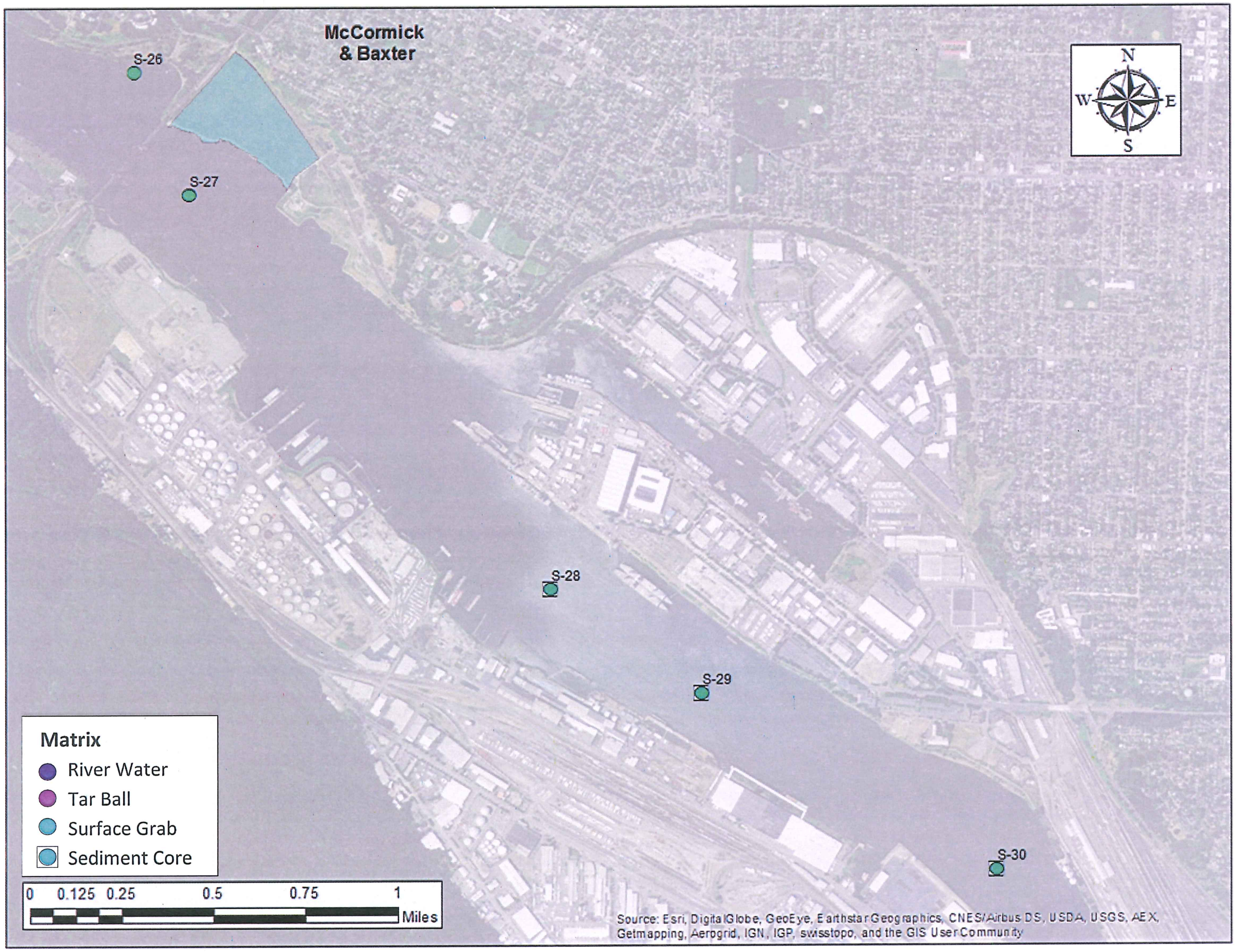
Figure 14. Distribution of % Alkyl PAH for historic Portland Harbor sediments downstream of RM 7. Locations of samples containing highly petrogenic (%Alkyl PAH >85%) are depicted in blue, and occur in at depth (>30 cm) at the Arco/BP Terminal. The affected sediments were removed from the riverbed during remedial action in 2008.

Data Source: Lower Willamette Group Historical Dataset.



Source: Esri, DigitalGlobe, GeoEye, Earthstar Geographics, CNES/Airbus DS, USDA, USGS, AEX, Getmapping, Aerogrid, IGN, IGP, swisstopo, and the GIS User Community

Figure 15. Sample Locations – NewFields 2014 Forensic Investigation.

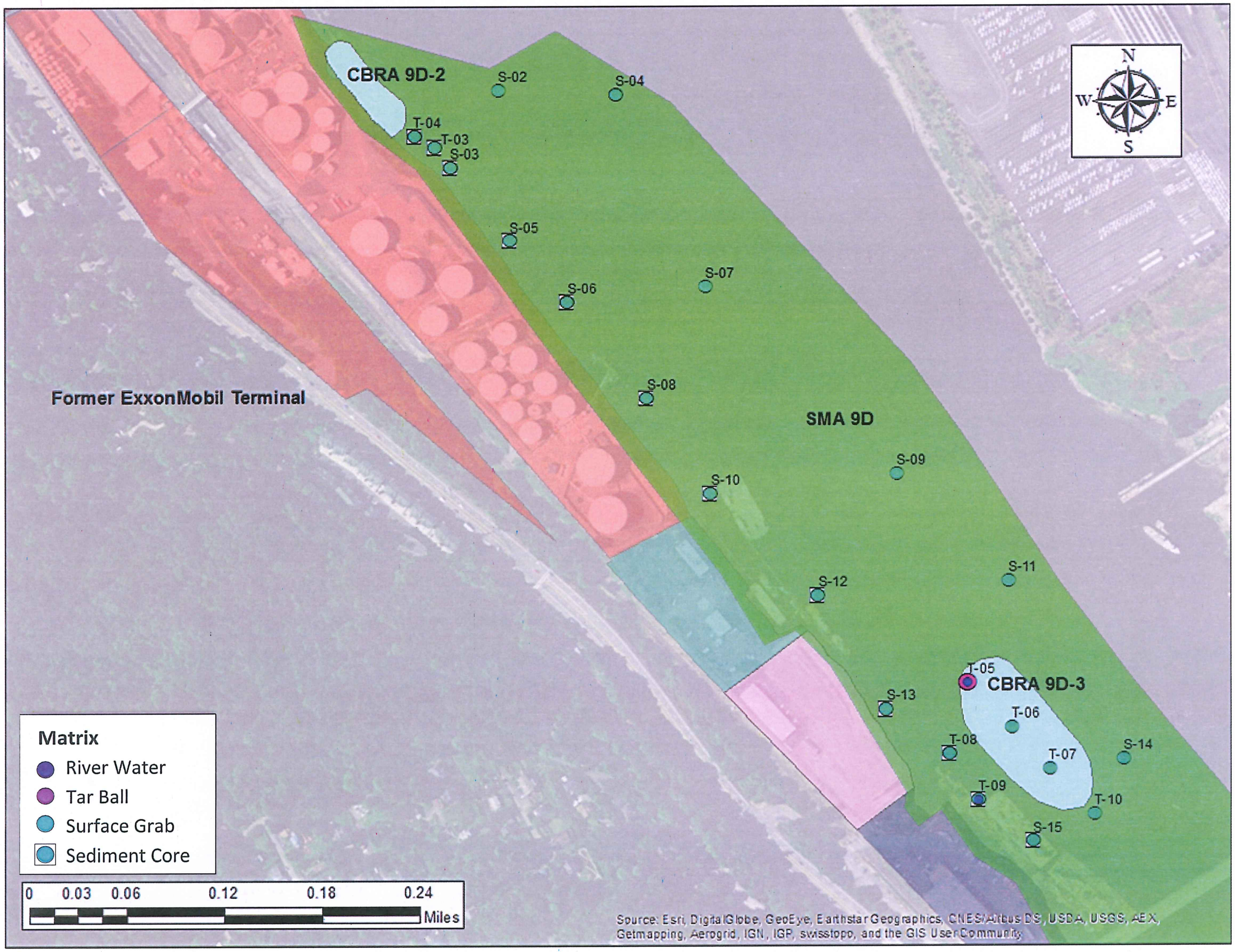


Source: Esri, DigitalGlobe, GeoEye, Earthstar Geographics, CNES/Airbus DS, USDA, USGS, AEX, Getmapping, Aerogrid, IGN, IGP, swisstopo, and the GIS User Community

Figure 16a. Sample locations upstream of the Gasco Property proximal to the McCormick and Baxter Property and in the vicinity of the navigational channel.

Source: Esri, DigitalGlobe, GeoEye, Earthstar Geographics, CNES/Airbus DS, USDA, USGS, AEX, Getmapping, Aerogrid, IGN, IGP, swisstopo, and the GIS User Community

Figure 16b. Sample locations in the vicinity, and just downstream of the Gasco Property.



Source: Esri, DigitalGlobe, GeoEye, Earthstar Geographics, CNES/Airbus DS, USDA, USGS, AEX, Getmapping, Aerogrid, IGN, IGP, swisstopo, and the GIS User Community

Figure 16c. Sampling locations within SMA 9D, including CBRA 9D-2 and 9D-3 and Vicinity of the Former ExxonMobil Terminal.

Figure 16d. Sample locations downstream of SMA 9D, offshore of the Linnton Property and in Terminal 4 Slip 3.

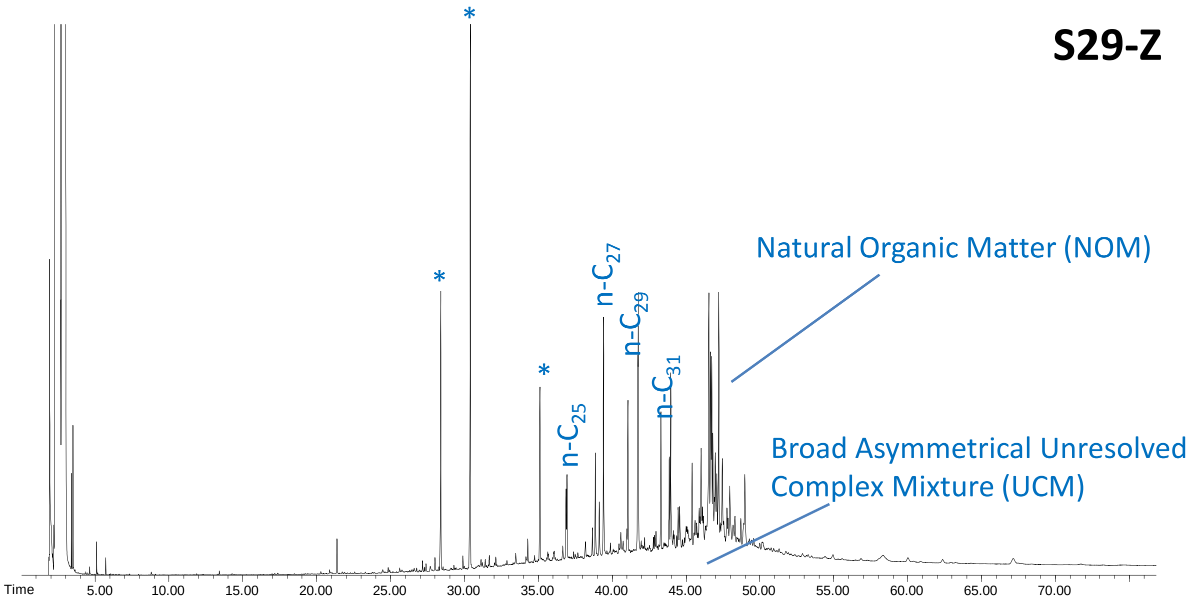


Figure 17. Gas chromatogram of the subsurface sediment collected at S29, representing the sub-set of upstream reference samples. Features of this gas chromatogram are typical of urban sediments remote from strong point sources of pyrogenic or petrogenic hydrocarbon contamination.

'*': laboratory-added internal standards

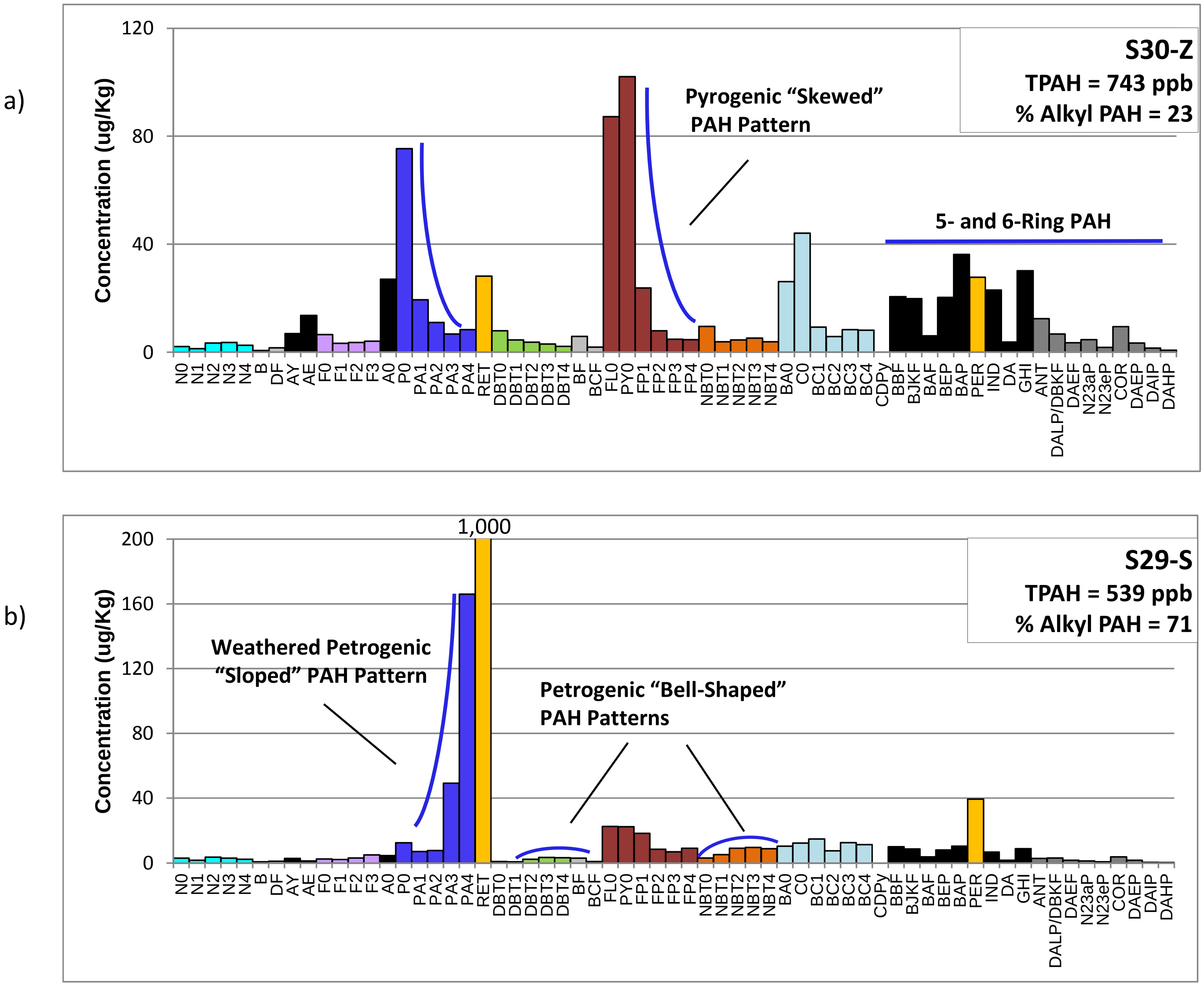


Figure 18. PAH histograms for the upstream reference samples.

Figure 18a: The distribution of PAH compounds for the most pyrogenic upstream sample (S30-Z).
Figure 18b: The distribution of PAH compounds for the most petrogenically influenced upstream sample (S29-S).

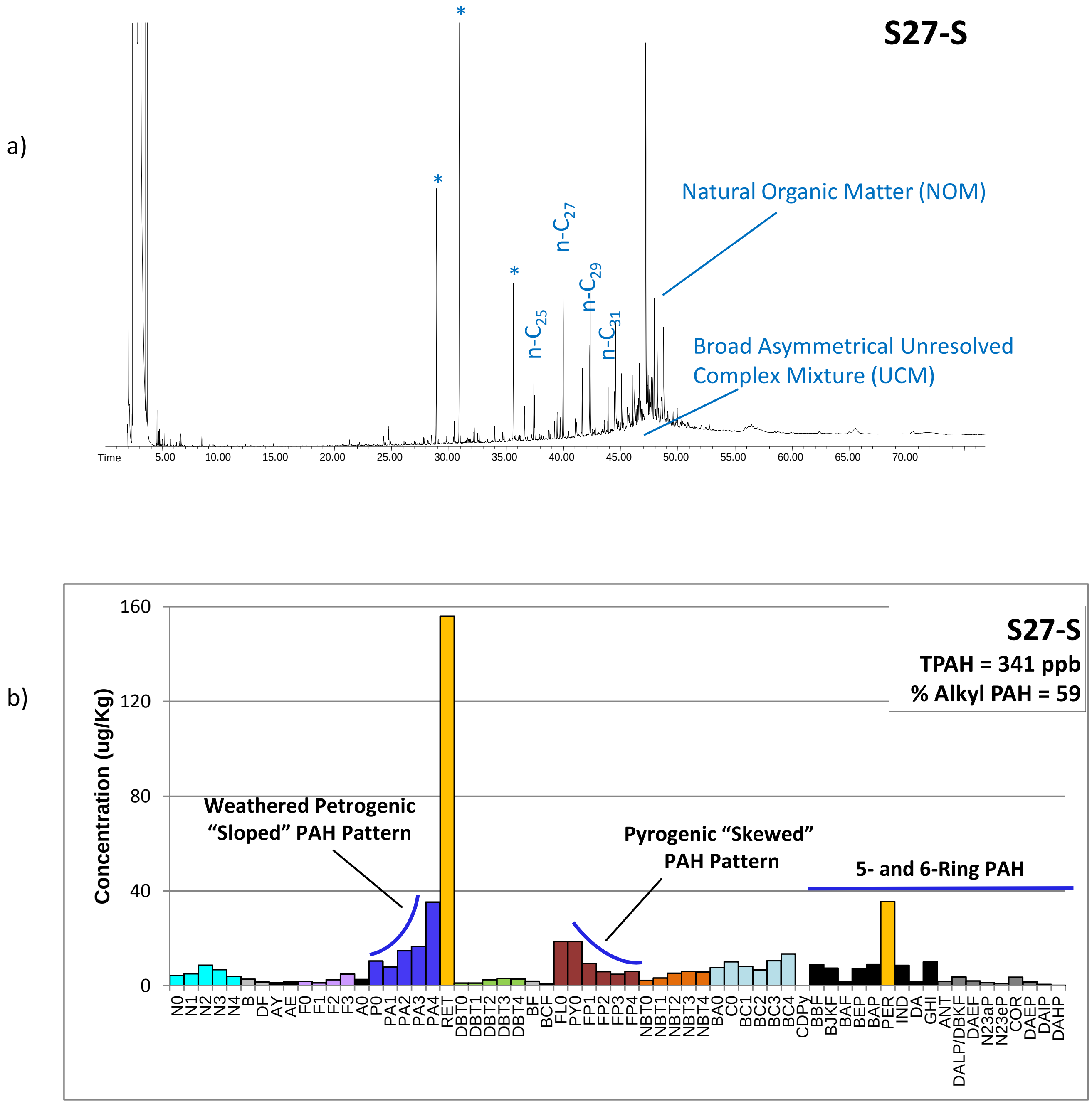


Figure 19. Compositional analysis of surface sample collected from McCormick and Baxter Property sampling station S27.

Figure 19a: Gas chromatogram.
Figure 19b: PAH histogram.

'*': laboratory-added internal standards

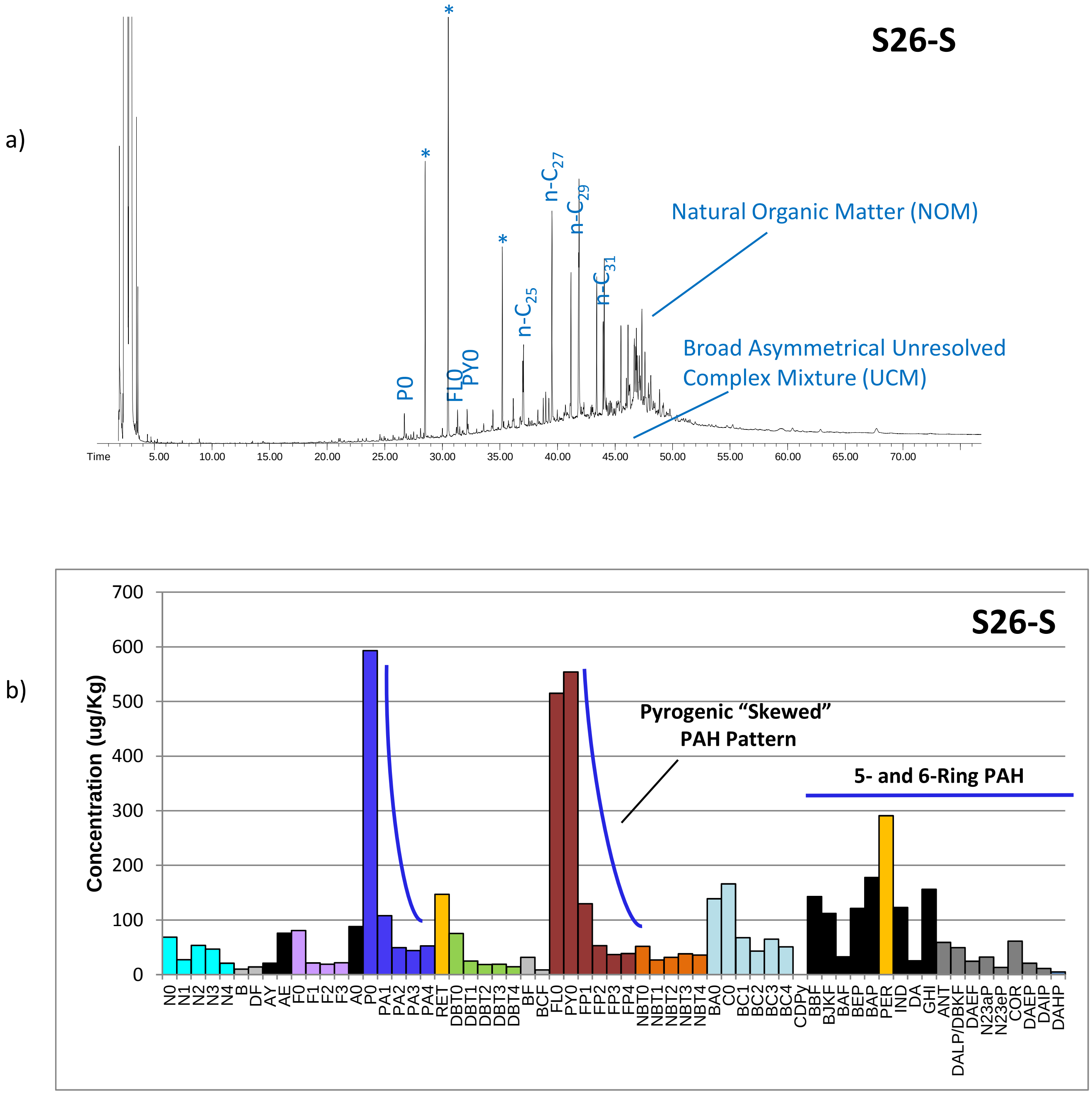


Figure 20. Compositional analysis of surface sample collected from McCormick and Baxter Property sampling station S26.

Figure 20a: GC/FID Chromatogram.
Figure 20b: PAH Histogram.

'*': laboratory-added internal standards

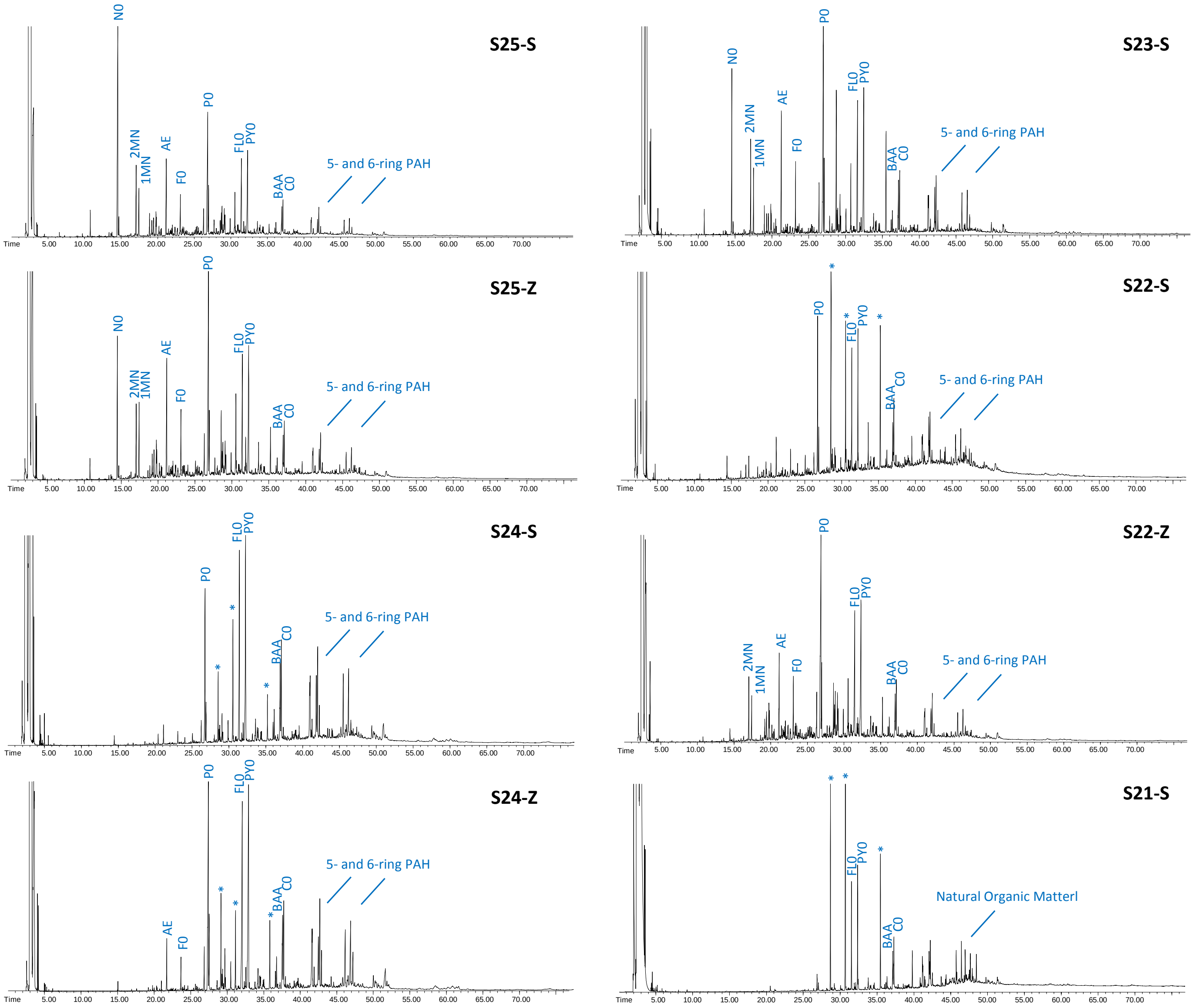


Figure 21. Gas chromatograms of the surface and subsurface sediment samples collected in the vicinity of the Gasco Property.

'*': laboratory-added internal standards

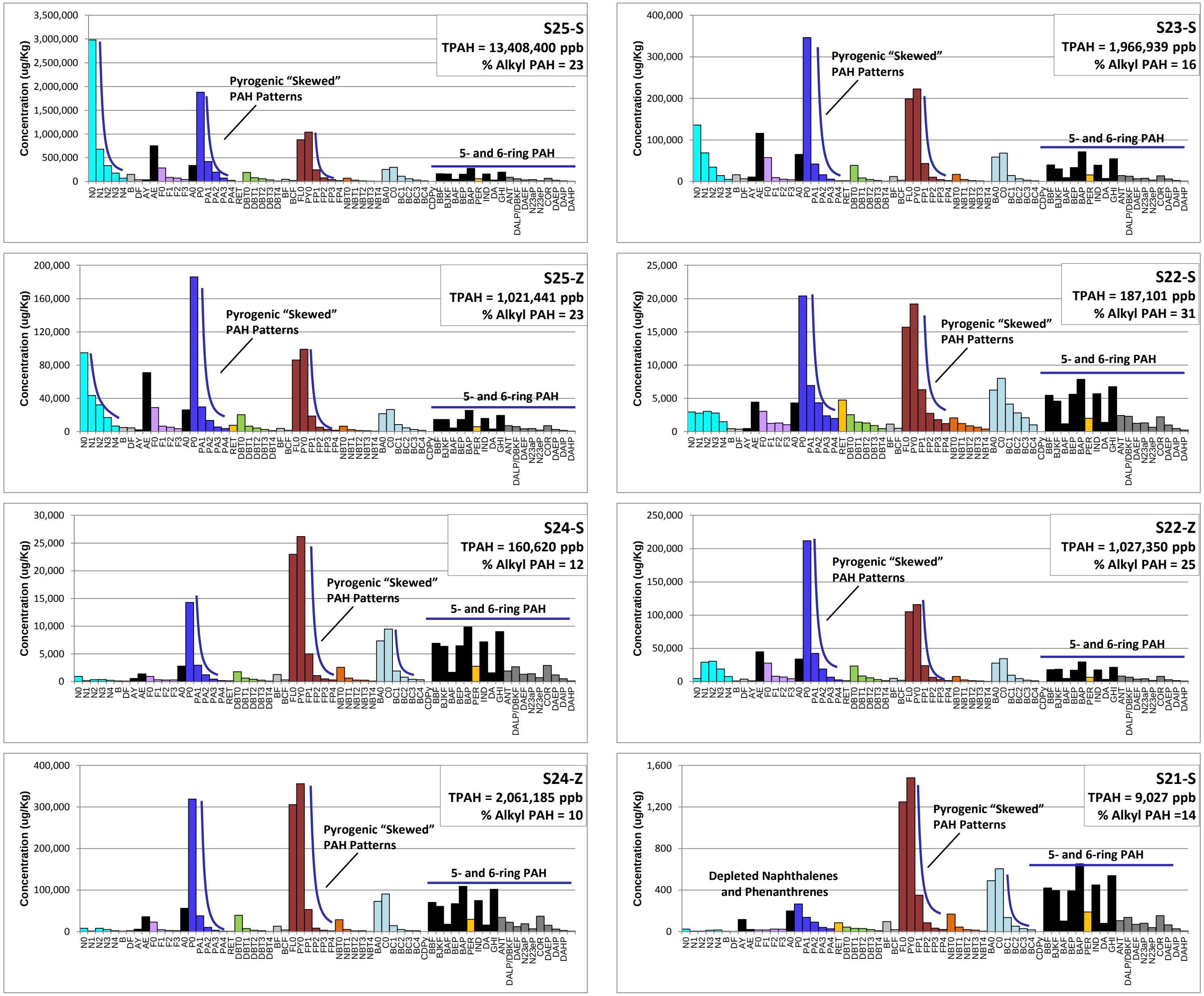


Figure 22. PAH histograms of the surface and subsurface sediment samples collected in the vicinity of the Gasco Property. All PAH histograms and % Alkyl PAH values are consistent with PAH of highly pyrogenic origin.

Source: Esri, DigitalGlobe, GeoEye, Earthstar Geographics, CNES/Airbus DS, USDA, USGS, AEX, Getmapping, Aerogrid, IGN, IGP, swisstopo, and the GIS User Community

Figure 23. SMA 9D sample locations, including CBRAs 9D-2 and 9D-3.

Source: Esri, DigitalGlobe, GeoEye, Earthstar Geographics, CNES/Airbus DS, USDA, USGS, AEX, Getmapping, Aerogrid, IGN, IGP, swisstopo, and the GIS User Community

Figure 24. TPH concentration distributions within SMA 9D.

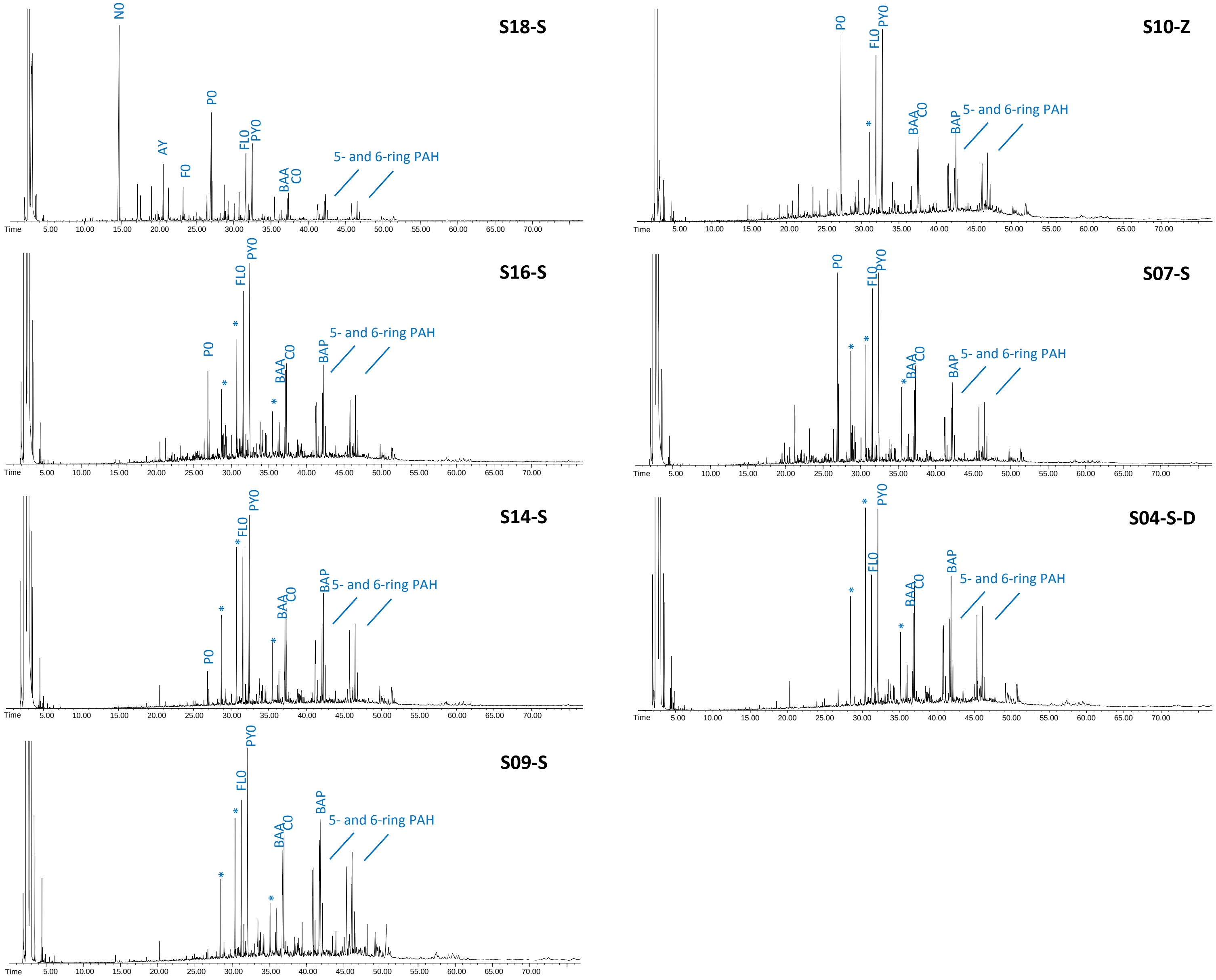


Figure 25. Gas chromatograms of the surface sediment samples collected within SMA 9D.
'*': laboratory-added internal standards.

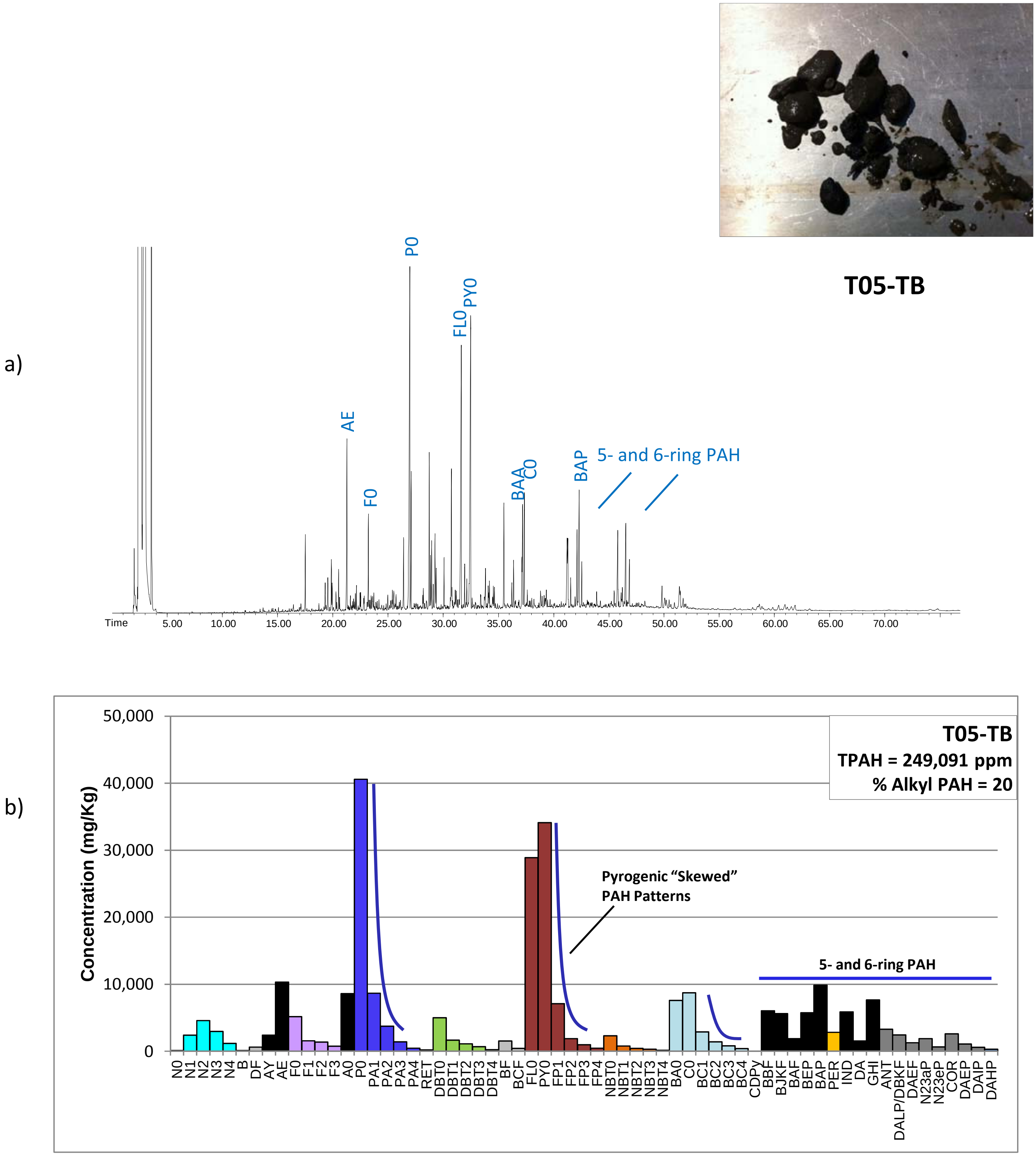


Figure 26. Gas chromatogram (a) and PAH histogram (b) for the tar ball sample of opportunity T-05, collected in CBRA 9D-3. Photograph of tar ball sample shown in upper right.

'*': laboratory-added internal standards

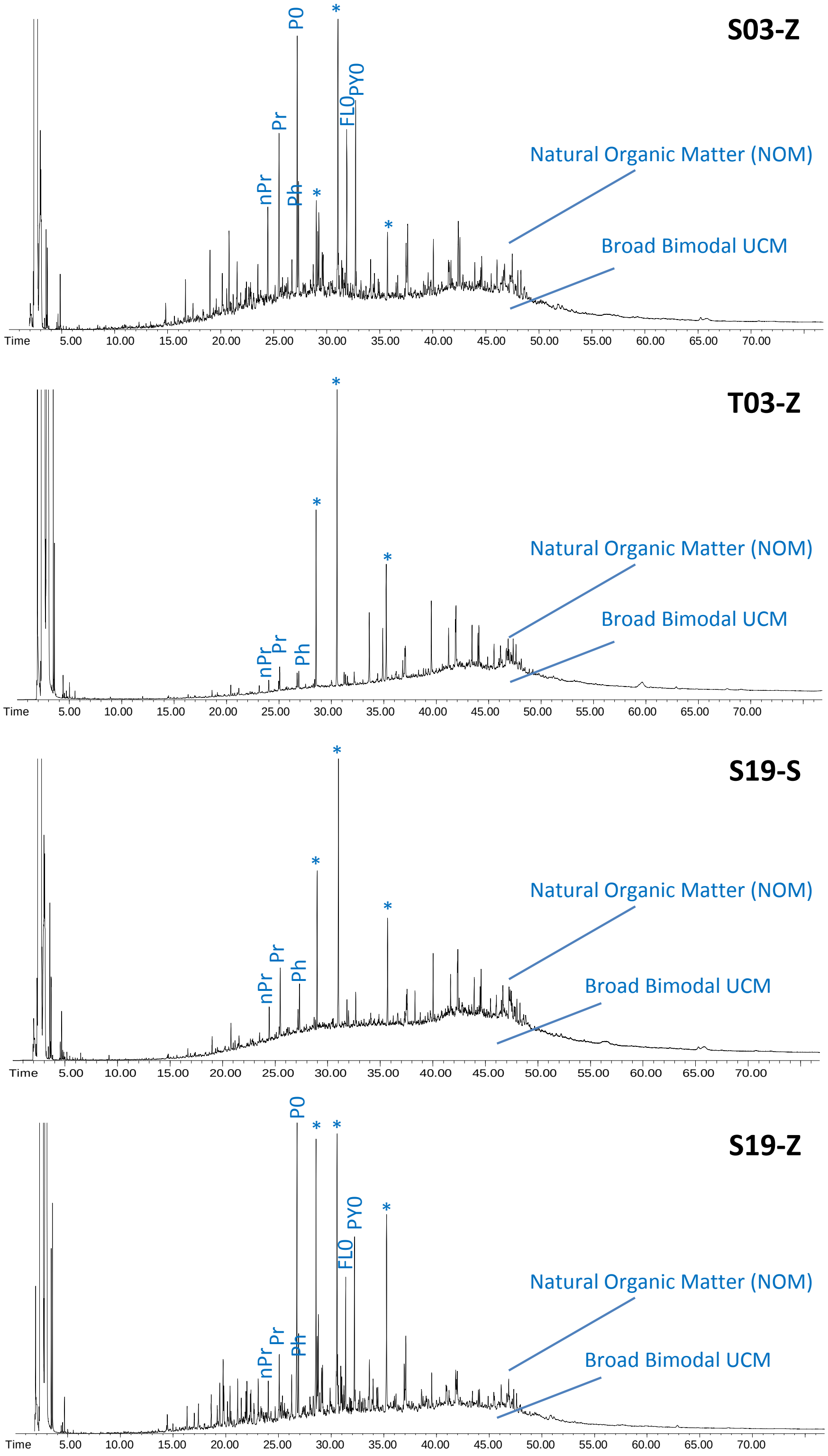
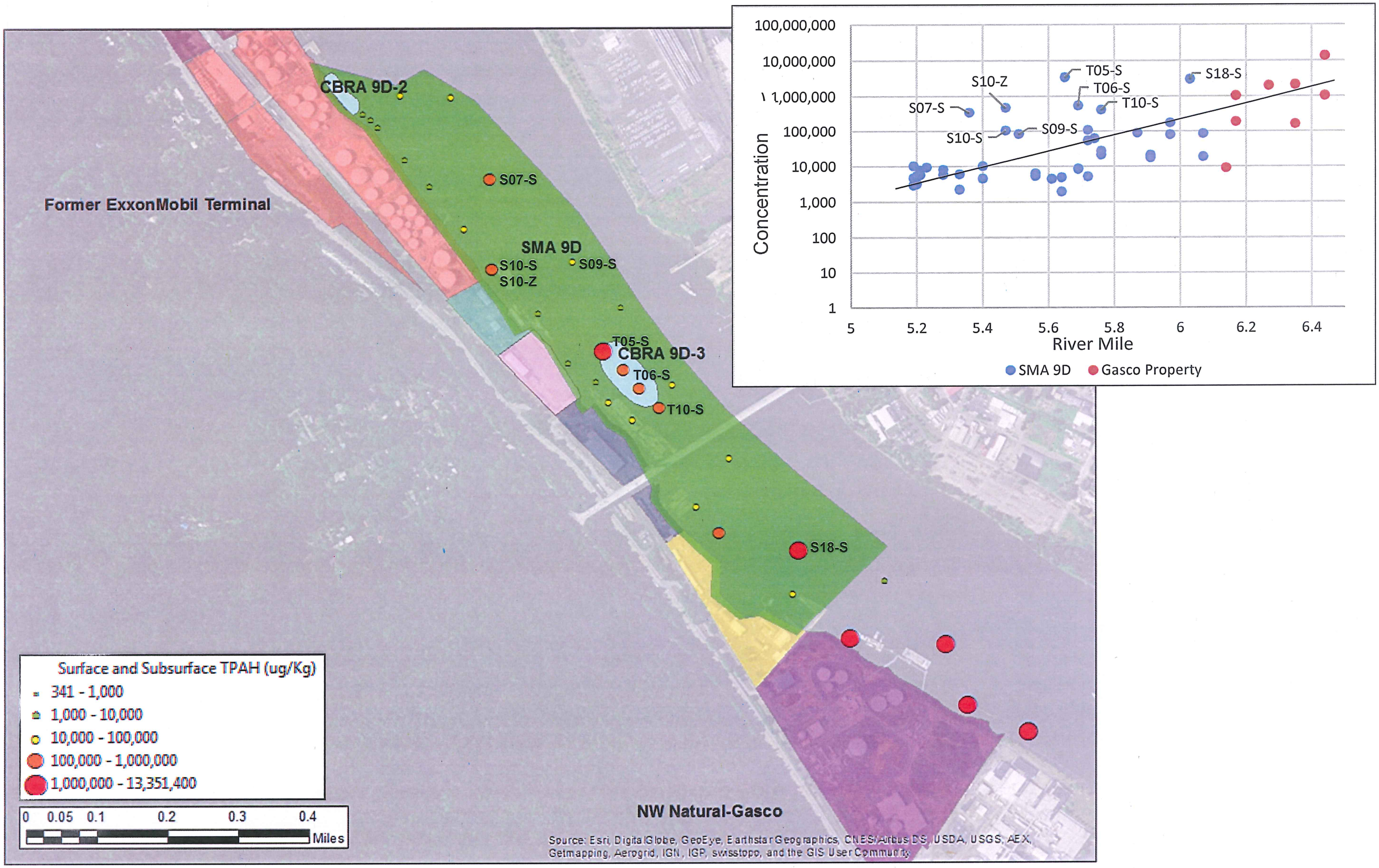


Figure 27. Gas chromatograms of the four samples from the NewFields 2014 investigation that exhibited evidence for the presence of weathered, broad boiling range petroleum.

'*': laboratory-added internal standards.



Source: Esri, DigitalGlobe, GeoEye, Earthstar Geographics, CNES/Airbus DS, USDA, USGS, AEX, Getmapping, Aerogrid, IGN, IGP, swisstopo, and the GIS User Community

Figure 28. Total PAH concentrations within SMA 9D. Inset: Total PAH concentrations tend to decrease downstream of the Gasco Property; some downstream locations that deviate from that trend, and show anomalously higher concentrations of Total PAH.

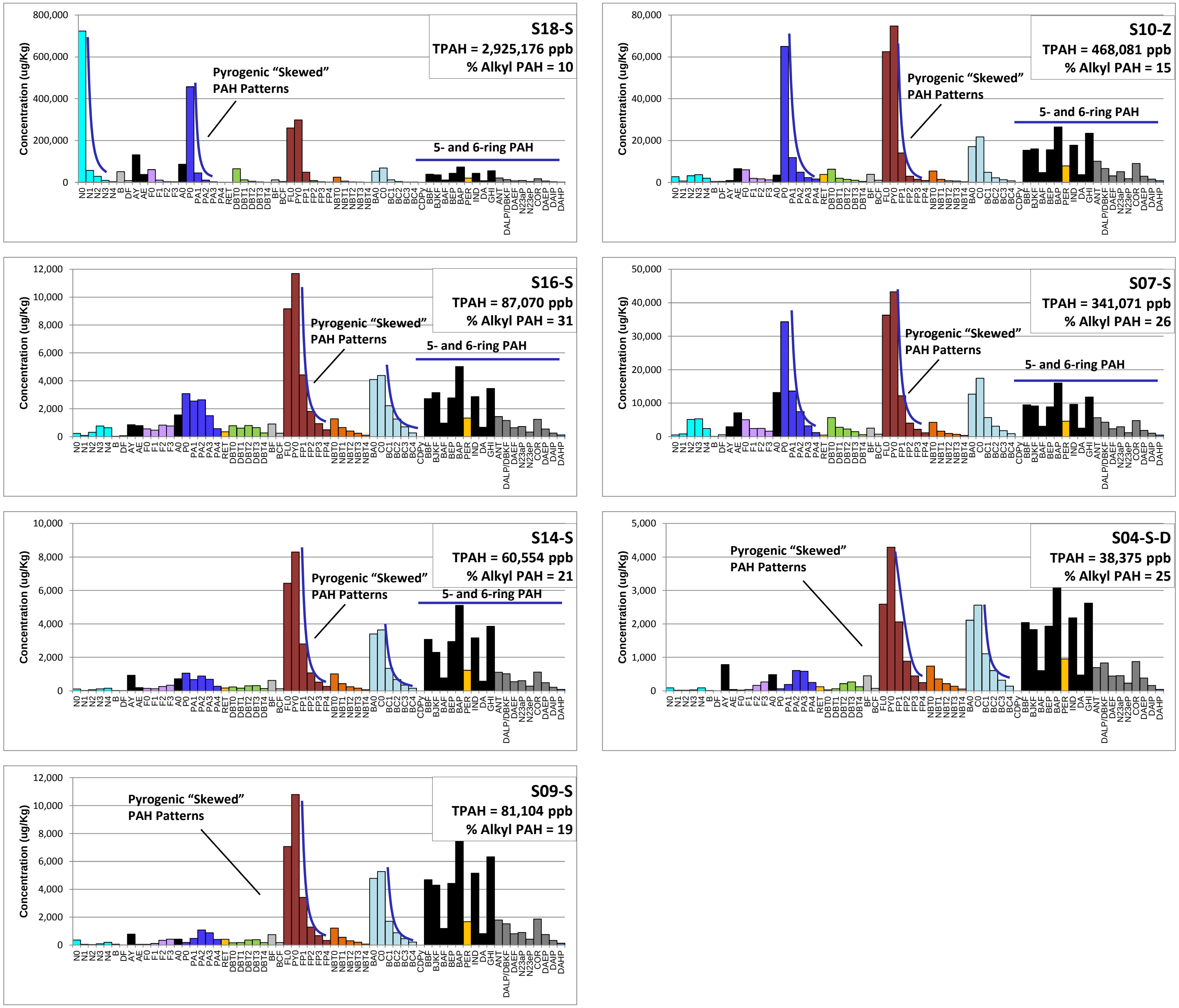


Figure 29. The PAH histograms of surface sediment samples collected in SMA 9D.

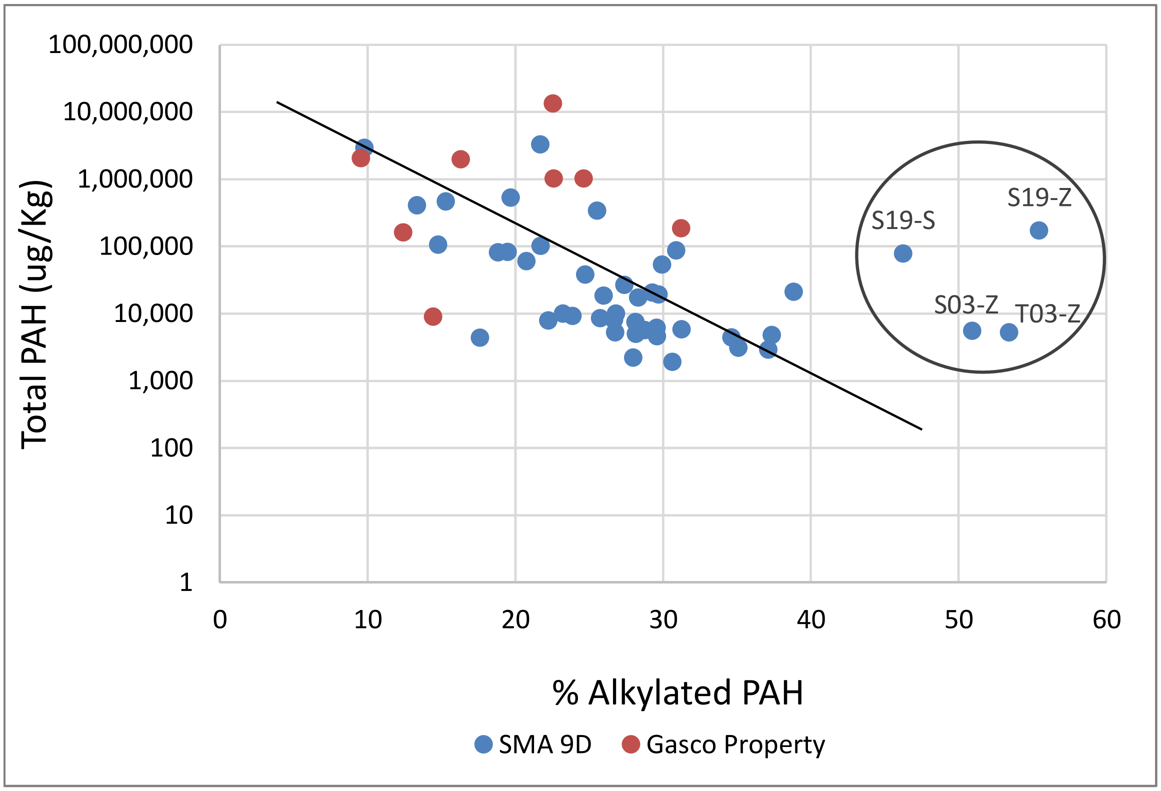


Figure 30. A plot of % Alkyl PAH versus Total PAH for the SMA 9D and upstream Gasco Property samples. The circled samples contain anomalously high % Alkyl PAH.

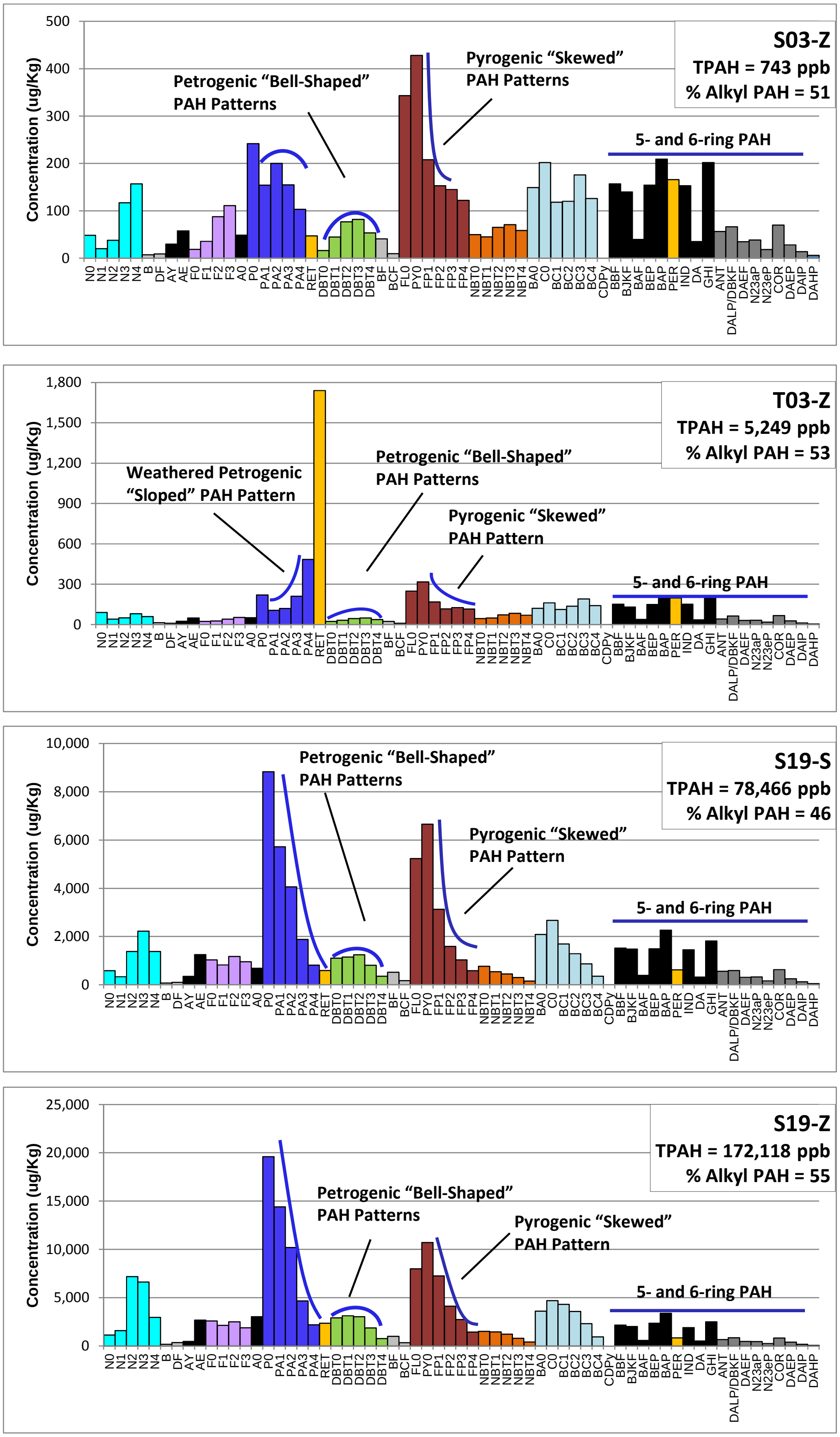


Figure 31. PAH histograms for the four samples that contained measurable contributions of petrogenic PAH, mixed with other pyrogenic PAH compounds.

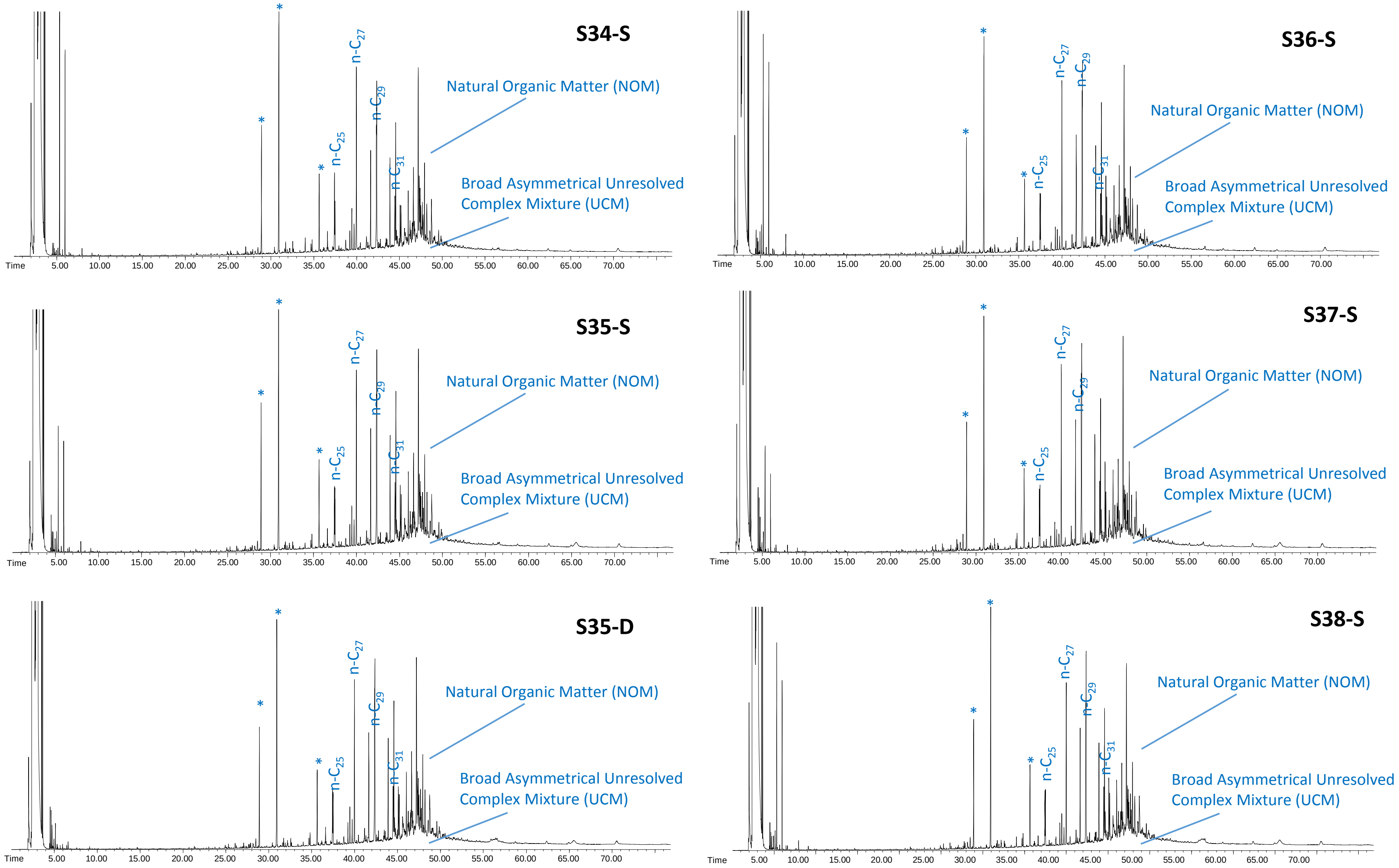


Figure 32. Gas chromatograms of the surface sediment samples collected within Linnton Property.

'*': laboratory-added internal standards

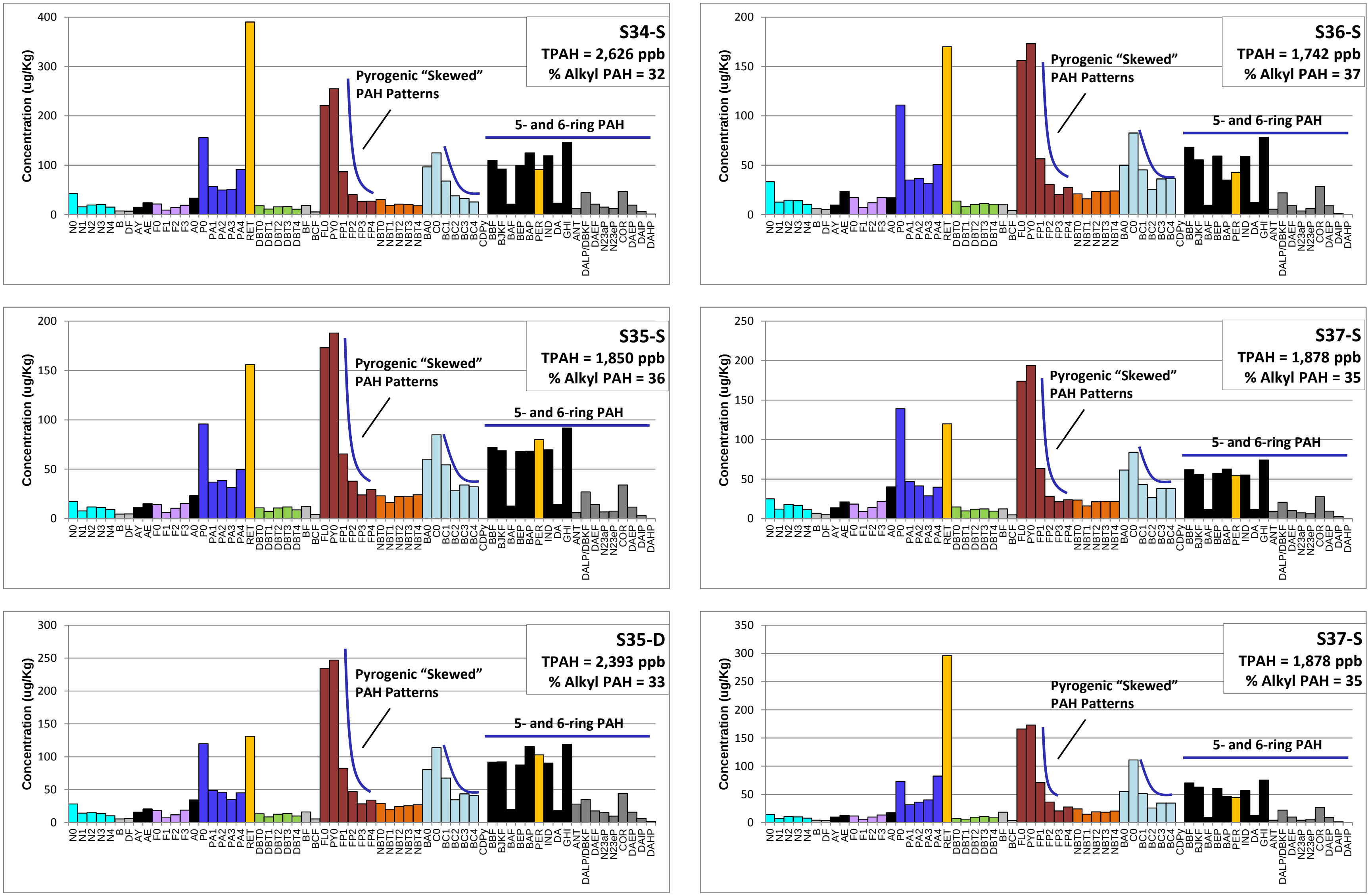


Figure 33. PAH histograms of the surface sediment samples collected within Linnton Property.

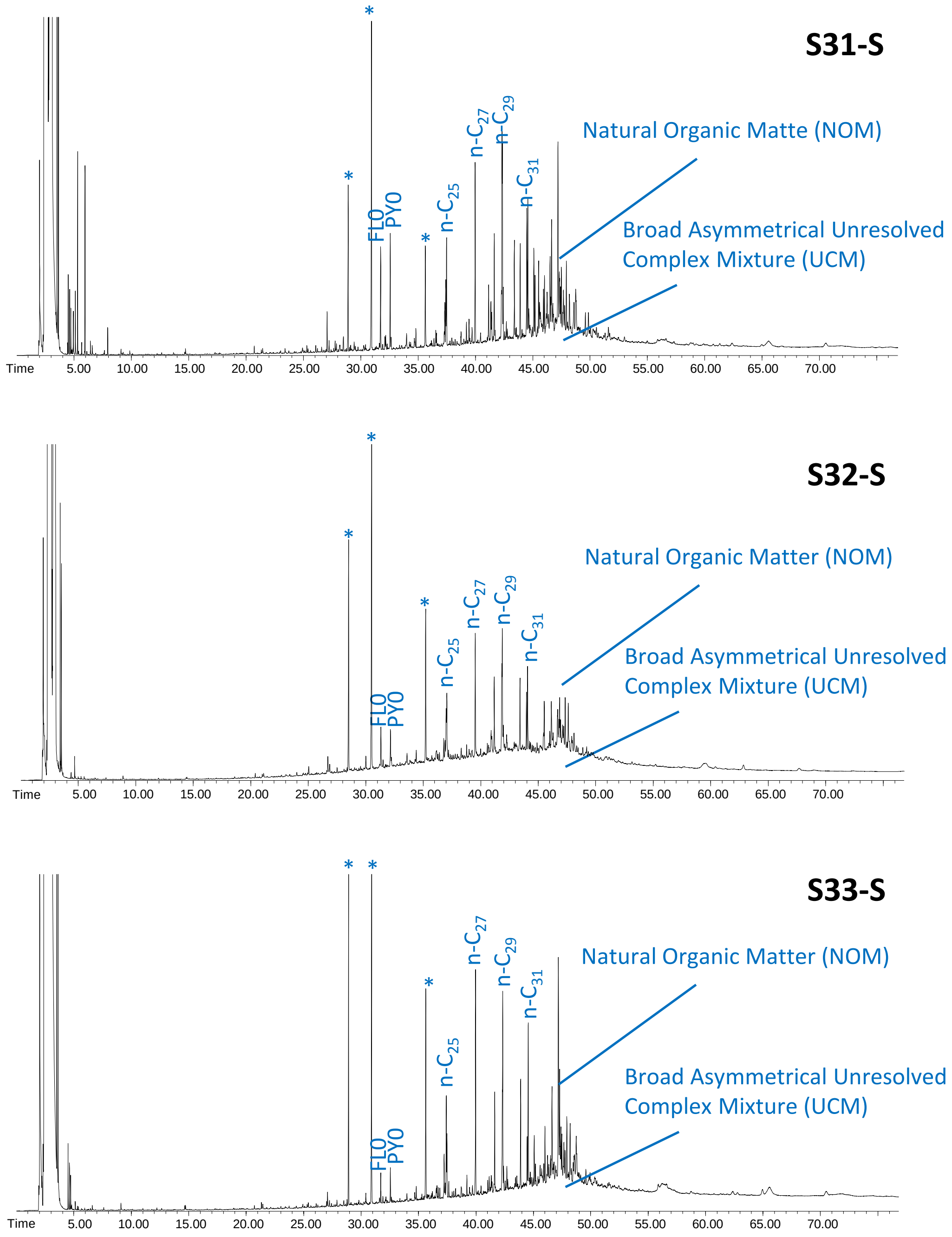
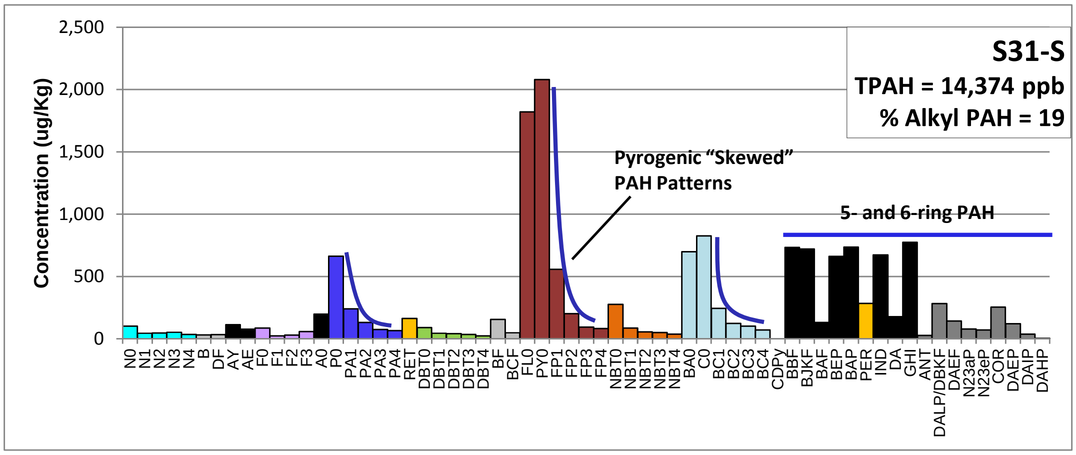
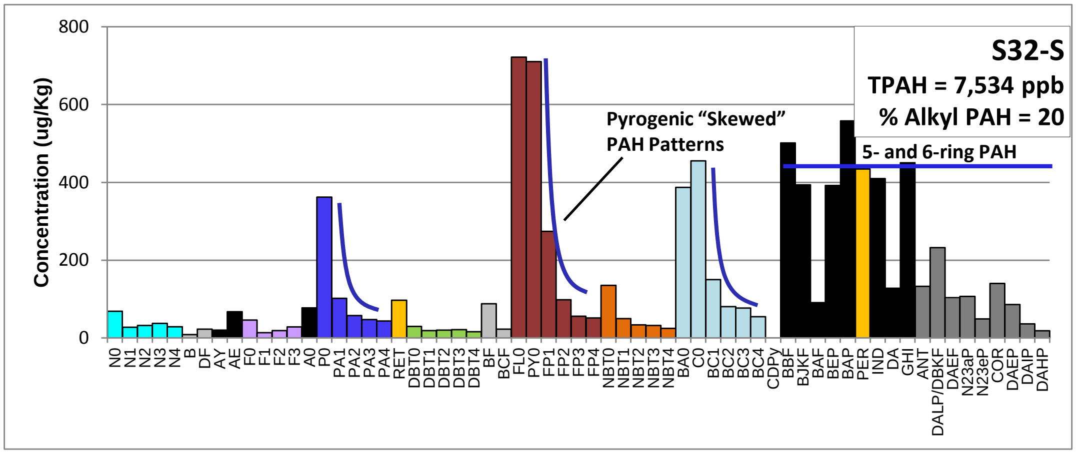


Figure 34. Gas chromatograms for the three surface sediment samples from Pier 4, Terminal 3.

‘*’: laboratory-added internal standards





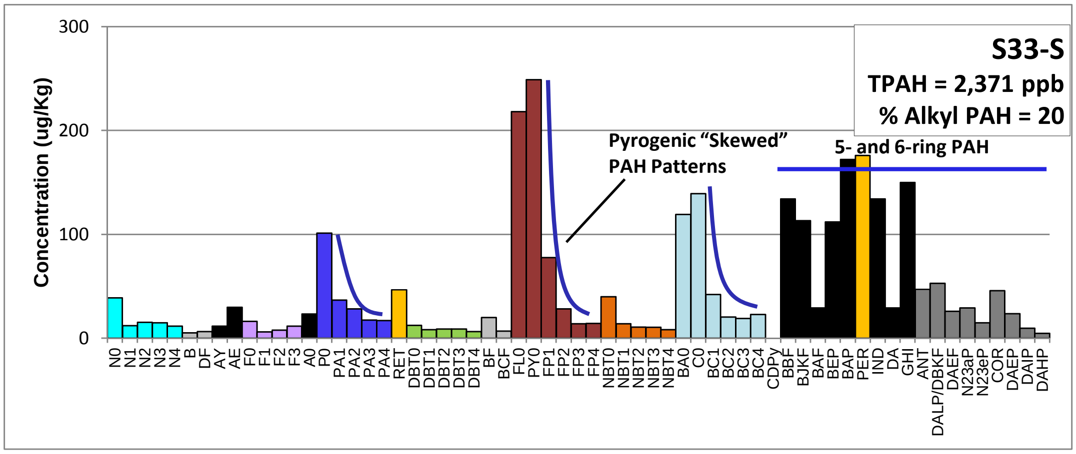
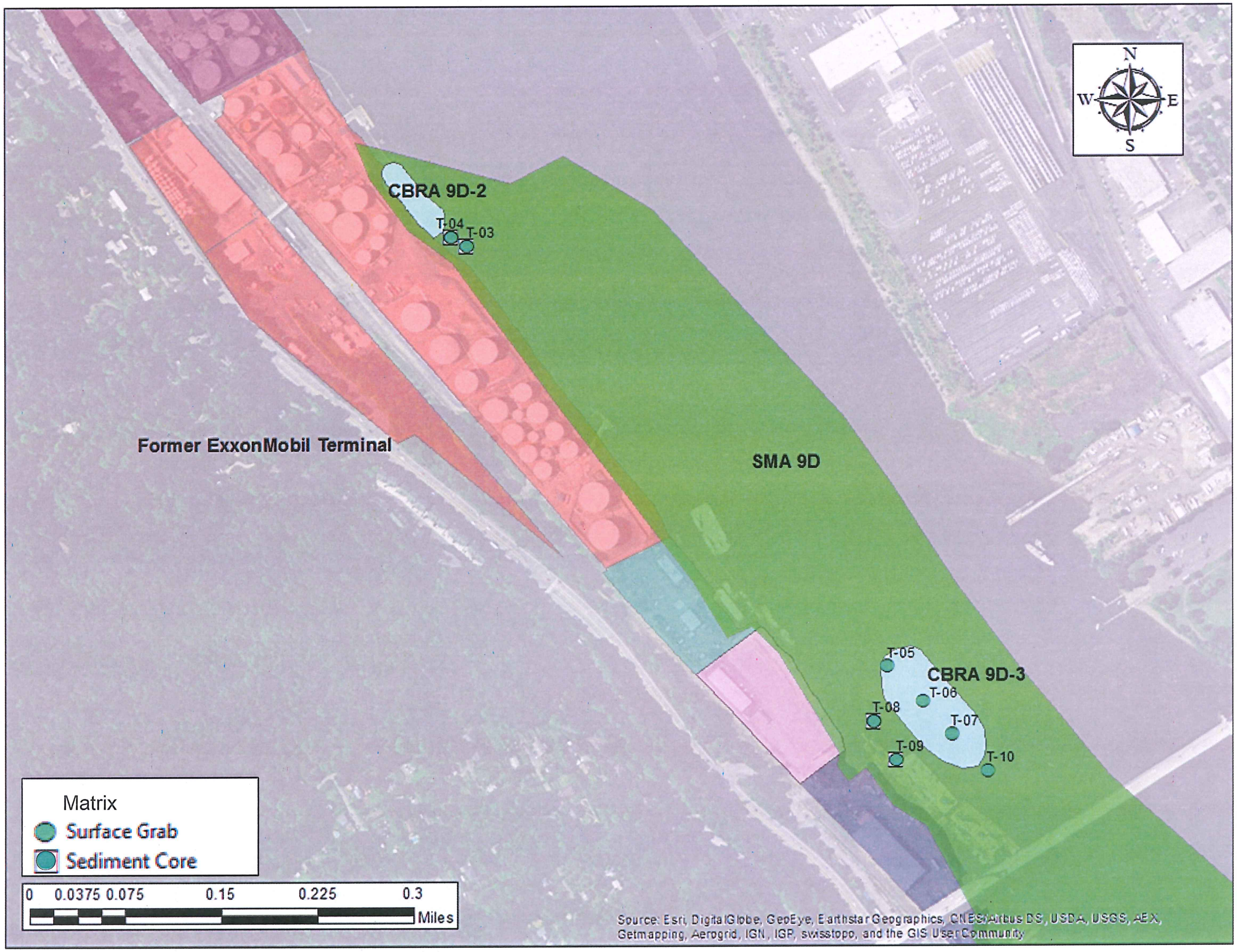


Figure 35. PAH histograms for the three surface sediment samples from Terminal 4, Slip 3.

Source: Esri, DigitalGlobe, GeoEye, Earthstar Geographics, CNES/Airbus DS, USDA, USGS, AEX, Getmapping, Aerogrid, IGN, IGP, swisstopo, and the GIS User Community

Figure 36. Spatial distribution of BaPeq within the Study Area.



Source: Esri, DigitalGlobe, GeoEye, Earthstar Geographics, CNES/Airbus DS, USDA, USGS, AEX, Getmapping, Aerogrid, IGN, IGP, swisstopo, and the GIS User Community

Figure 37. Sample locations for the samples collected for PDMS-SPME analysis.

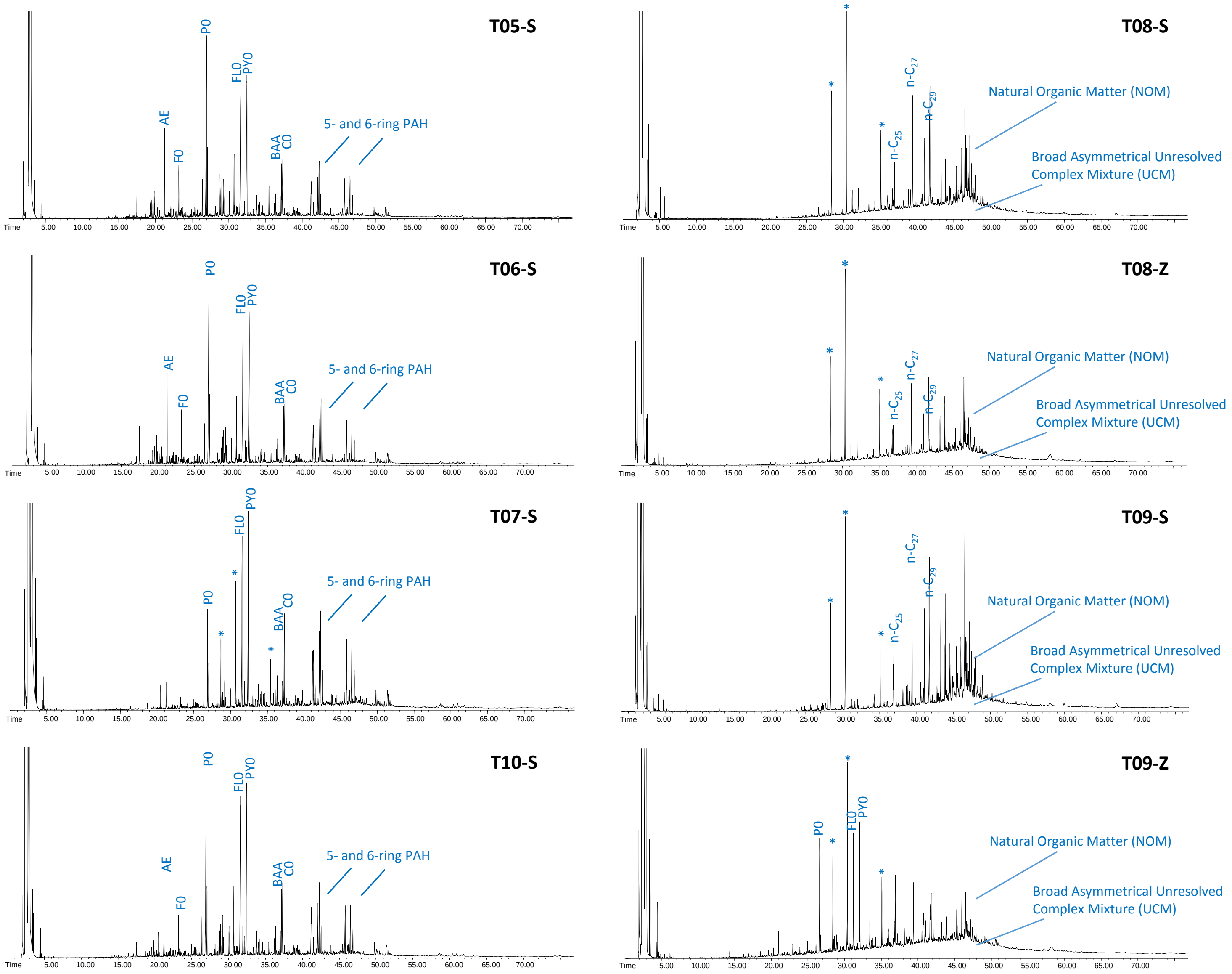


Figure 38. Gas chromatograms of the surface sediment samples collected within and just upstream of CBRA 9D-3 (left panel) and samples collected immediately adjacent and cross-current to CBRA 9D-3 (right panel).

'*': laboratory-added internal standards

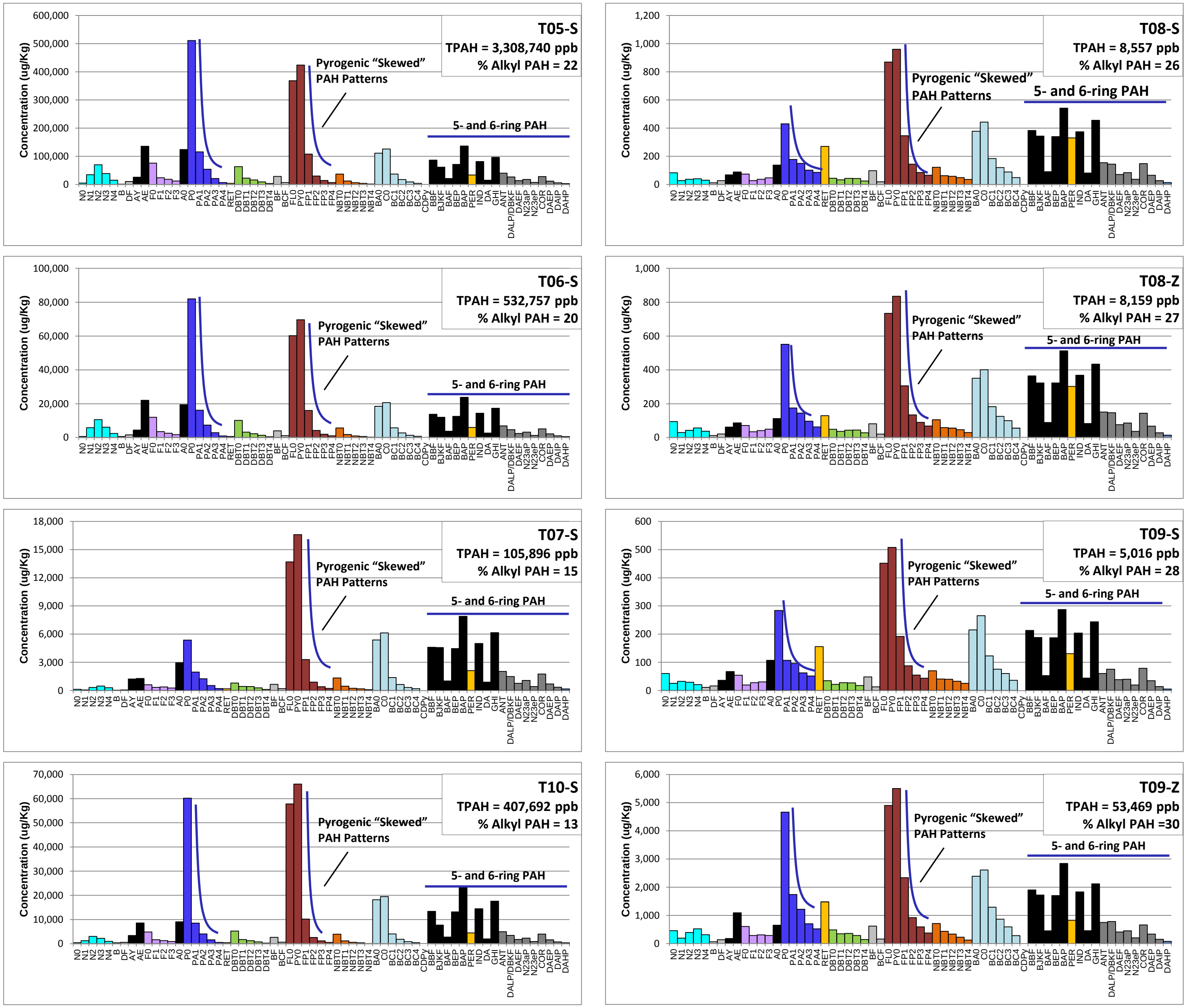


Figure 39. PAH histograms of the surface sediment samples collected within and just upstream of CBRA 9D-3 (left panel) and surface and subsurface samples collected adjacent and cross-current to CBRA 9D-3 (right panel).

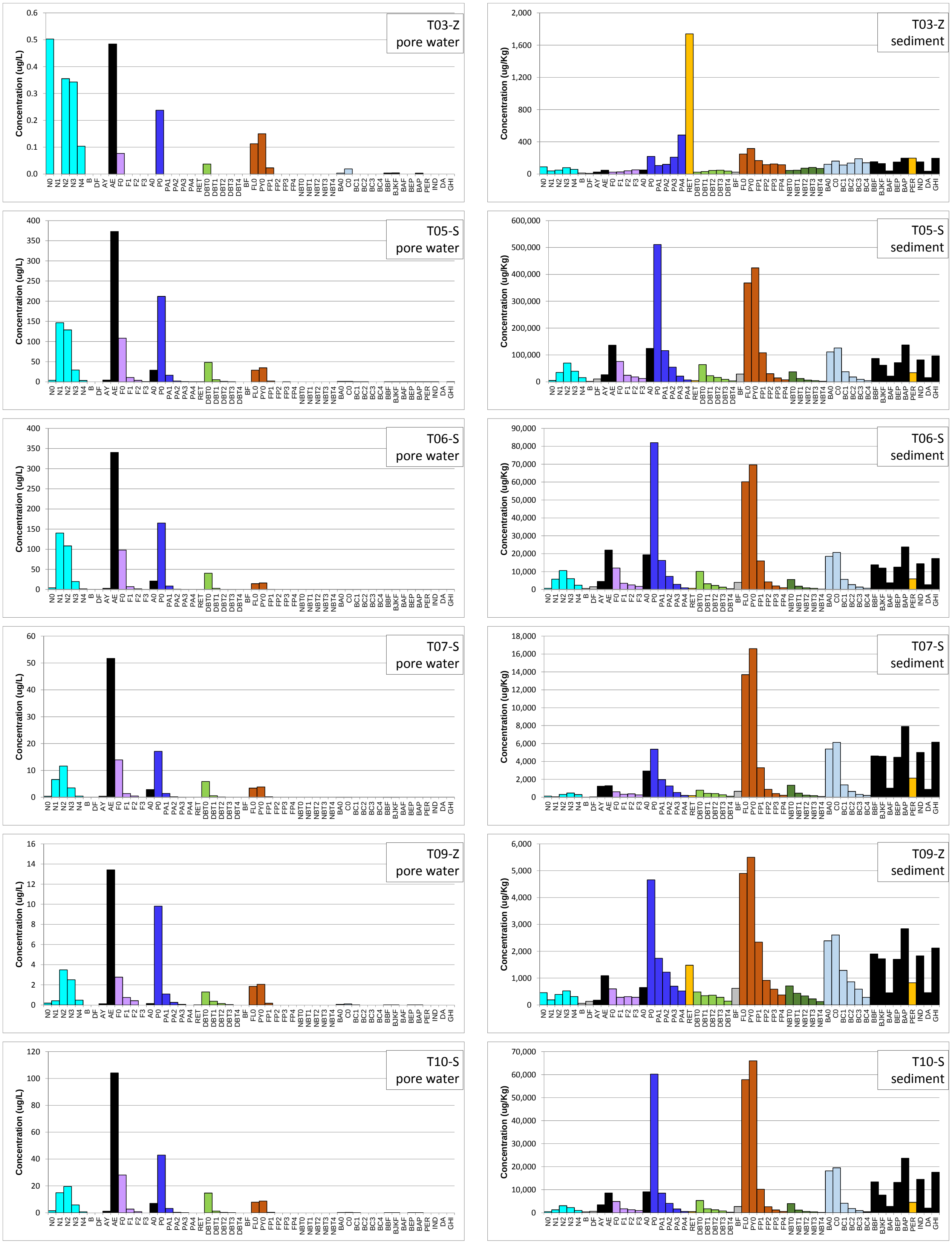


Figure 40. PAH histograms comparing calculated pore water concentrations (left panel) and the PAH measured in the bulk sediment (right panel) for samples T03-Z, T05-S, T06-S, T07-S, T09-Z and T10-S.