

**Sources of PAH in Portland
Harbor/Willamette River Sediment –
West Side Sediment between River
Mile 3 and 9**

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Exxon Mobil Corporation
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¹ Additional parties who have sponsored this Report, but do not wish to be disclosed have been removed.

Summary

This report presents a brief summary of evidence indicating that polycyclic aromatic hydrocarbons (PAH) in sediments of the Portland Harbor segment of the Willamette River (PH) are not significantly derived from the petroleum storage facilities along the west bank of the Harbor owned or previously operated by Atlantic Richfield Company / BP West Coast Products LLC, Chevron Environmental Management Company, ConocoPhillips Company, Exxon Mobil Corporation, Kinder Morgan Liquids Terminals LLC, and Shell Oil Products US (collectively, the "Terminals"). The Terminals are located along the west bank between river mile 4.2 and 8.4 and consist of (from north to south): the Kinder-Morgan Linnton terminal, the BP Terminal 22T, the Exxon Mobil terminal, the Willbridge Cove terminals (Kinder Morgan, Chevron, and ConocoPhillips), and the Shell Equilon terminal (Fig. 1). The Terminals store and distribute petroleum products, principally gasoline and diesel fuel. They are not the only facilities in this stretch of river that handle or that have handled such products.

Multiple chemical indicators show that the vast majority of PAH in the Harbor sediments are derived from combustion-related sources, and are demonstrably different from the PAH assemblages in the petroleum products stored at the Terminals. The PAH assemblage in the Harbor sediments is similar to the PAH assemblage in Harbor area stormwater and to the PAH assemblages found in other urban areas. Further, PAH concentration transects along the west side of the river, together with chemical indicators, demonstrate a major input of PAH to the river sediments from the GASCO¹ site.

¹ NW Natural's GASCO facility formerly encompassed both the current GASCO property and much of what is now the Siltronic Corporation property.

Background on PAH Forensic Chemistry

Numerous studies show that the PAH in petroleum products (so-called “petrogenic” assemblages) can be chemically distinguished from the PAH from various combustion-related sources (so-called “pyrogenic” assemblages) (see, e.g., Boehm *et al.*, 1997; Boehm, 2006; Bence *et al.*, 1996). These pyrogenic sources include coal tar and creosote, which are derived from coal and oil gasification and wood-treating facilities, as well as combustion products such as ash, and soot from vehicles and industrial engines and burners. Such pyrogenic combustion products commonly occur in urban runoff (e.g., stormwater) and urban atmospheric dust.

Compound Name	Abbreviation
Naphthalene	N0
C1-Naphthalene	N1
C2-Naphthalene	N2
C3-Naphthalene	N3
C4-Naphthalene	N4
biphenyl	Bph
dibenzofuran	DbF
Acenaphthylene	AcI
Acenaphthene	Ace
Fluorene	F0
C1-Fluorene	F1
C2-Fluorene	F2
C3-Fluorene	F3
C4-fluorene	F4
Anthracene	AN
Phenanthrene	P0
C1-Phenanthrene/anthracene	P1
C2-Phenanthrene/anthracene	P2
C3-Phenanthrene/anthracene	P3
C4-Phenanthrene/anthracene	P4
Dibenzothiophene	D0
C1-Dibenzothiophene	D1
C2-Dibenzothiophene	D2
C3-Dibenzothiophene	D3
C4-dibenzothiophene	D4
Fluoranthene	FL
Pyrene	PY
C1-Fluoranthene/pyrene	FP1
C2-Fluoranthene/pyrene	FP2
C3-Fluoranthene/pyrene	FP3
Benzo(a)anthracene	BaA
Chrysene	C0
C1-Chrysene	C1
C2-Chrysene	C2
C3-Chrysene	C3
C4-Chrysene	C4
Benzo(b)fluoranthene	BbF
Benzo(k)fluoranthene	BkF
Benzo(e)pyrene	BeP
Benzo(a)pyrene	BaP
Perylene	Per
Dibenzo(a,h)anthracene	DA
Indeno(1,2,3-cd)pyrene	IP
Benzo(g,h,i)perylene	BgP
Bold = Priority Pollutant	

To understand the chemical characteristics that distinguish the PAH in petroleum products from other PAH contamination found in the river sediments of Portland Harbor, it is helpful to explain a few basic properties of PAH assemblages. PAH consist of molecular structures built from fused benzene rings (each with 6 carbon atoms). Of these PAH ring structures, 16 have been designated by EPA as Priority Pollutants (see Table 1 and Figure 2). The ring structures of the Priority Pollutants vary from 2-ring compounds (e.g., naphthalene) to 6-ring compounds (e.g., indeno[1, 2, 3 c,d]pyrene), and include 3-, 4-, and 5-ring compounds as well. Petroleum products consist predominantly of 2- and 3-ring PAH and contain very low or non-detectable concentrations of 4- to 6-ring PAH. Importantly, it is the carcinogenic 4- to 6-ring PAH that drive human health risk (EPA, 1993). Compared to pyrogenic materials such as coal tar and creosote, petroleum products contain 100 to 1000 times lower concentrations of total PAH. Thus, from the standpoint of absolute PAH concentration and low relative abundance of 4- to 6-ring PAH, petroleum products have a very low potential to drive human health risk. PAH in pyrogenic materials are much more likely to drive human health risk.

The 16 parent PAH compounds designated by EPA as Priority Pollutants have variants that are characterized by having carbon side chains attached to the basic parent compounds. These variations of the parent compounds are differentiated according to the number and length of the side chains, which are known as alkyl groups. Each family consisting of a parent PAH compound and the alkylated variation of the parent is known as a homologous series. For example, naphthalene with a one-carbon alkyl group attached is

called methyl naphthalene. Depending on where the alkyl group is attached to the parent structure, this variation might occur as the 1-methyl naphthalene or 2-methyl naphthalene isomer. Collectively, the naphthalene variations with one alkyl group are designated N1 ([N1-naphthalenes] = [1-methylnaphthalene] + [2-methylnaphthalene]). The parent PAH with no alkyl side chains is designated N0. Similarly, naphthalene variations with 2-carbon alkyl groups are designated N2, and so forth for variations with 3 and 4 alkyl groups (*i.e.*, N3 and N4). In an alkyl PAH analysis the individual alkylated compounds are not differentiated but are summed together and are assigned to one of the alkylated groups depending on the total number of carbon atoms in the alkyl group (*e.g.*, as N1, N2, N3, or N4; see Table 1 and Figure 2).

The relative abundance of the individual alkylated groups within a particular PAH family (*e.g.*, the naphthalenes, N0 through N4) is a powerful tool for differentiating petrogenic PAH assemblages, such as occur in petroleum, from pyrogenic assemblages, such as occur in coal tar and urban runoff. In petroleum, one of the alkylated PAH groups (*e.g.*, N2 or N3) within a family will be the most abundant (Fig. 3). In unweathered pyrogenic assemblages, the parent compound (*e.g.*, N0) will be the most abundant member of a PAH family (Fig. 3). These differences are highlighted in a comparison of a coal tar (pyrogenic) and a diesel fuel (petrogenic) (Fig. 4).

With knowledge of the distinguishing characteristics of PAH assemblages in petrogenic material, such as that handled at the Terminals, an objective evaluation of the sources of the PAH in the sediments of Portland Harbor can be made.

Portland Harbor River Sediments

Two types of data are currently available on the PAH concentrations in Harbor sediments: data sets that include only the 16 EPA Priority PAH (the “parent” PAH), and data sets that include the more extended list of parent and alkylated PAH (>40 analytes). The primary source of data I have utilized is the *Portland Harbor Draft Remedial Investigation Report* (the “RI”) authored by the Lower Willamette Group (LWG, 2011). Most of these data are also available through the National Oceanic and Atmospheric Administration (NOAA) online watershed sediment data base. There are more than 2,400 analyses of parent PAH in Harbor surface sediment, and more than 400 analyses of alkylated PAH in Harbor surface sediment. The RI also contains data on PAH in stormwater and PAH on particulate matter in stormwater (*i.e.*, outfall sediment). Data from City of Portland outfall studies were also included in my review (City of Portland, 2010; downloaded from the Oregon DEQ FTP site).

Data on PAH in petroleum free product released at Terminal upland sites were obtained primarily from reports filed with the Oregon DEQ. These included both data on the parent PAH and alkyl PAH data. In 2011, additional alkyl PAH data were made available by the Terminals on representative samples of stored petroleum, soil, and free product from monitoring wells.

For the evaluation of the source of PAH in river sediment and the possible contribution by the Terminals, a down-river transect of PAH concentrations is very useful. Looking at the total concentration of parent

PAH in river sediments along the western shore, several important relationships are evident (Fig. 5). There are elevated concentrations of parent PAH in river sediments upstream of the farthest upstream Terminal. The median concentration of parent PAH in the river sediment from river mile 10 to river mile 9 is 789 ug/kg. There is a pronounced upward spike in parent PAH concentrations around river mile 6.5 adjacent to and downstream of the GASCO site. Notably, the median parent PAH concentration in river sediment from river mile 7 to 6 rises to over 20,000 ug/kg. A manufactured gas plant (MGP) operated at this site for over 40 years. In its early years wastes, including coal tar (a pyrogenic material), were discharged directly to the river (DEQ web site: <http://www.deq.state.or.us/lq/ECSI/ecsidetail.asp?segnbr=84>). This MGP plant used petroleum as a feedstock for part of its history and therefore is also a potential source of light (2- and 3-ring) petrogenic PAH, as well as a confirmed source of light and heavy pyrogenic PAH. Tar and other byproducts of both coal and petroleum gasification are pyrogenic in nature (Boehm, 2006). As is shown below, the PAH in sediments adjacent to and downstream of the GASCO site have the diagnostic pyrogenic signature (based on both parent and alkyl PAH data) associated with coal tar and creosote.

The relative proportions of 2- to 3-ring ("light") PAH and 4-, 5- and 6-ring ("heavy") PAH in a sediment sample are also relevant to identifying the source of the PAH. The PAH assemblage in urban runoff has a high percentage of the 4- through 6-ring heavy PAH, as do some wastes from manufactured gas plants. On the other hand, petroleum contains very low or even non-detectable concentrations of the 4- to 6-ring heavy PAH (*e.g.*, Stout *et al.*, 2001). PAH in fresh diesel fuel typically is less than 10% heavy PAH. PAH in free product samples from Terminals are less than 30% heavy PAH (*i.e.*, more than 70% 2- and 3-ring light PAH), with most samples consisting of less than 15% heavy PAH. Harbor surface sediment is highly skewed towards the heavy PAH (Fig. 6), averaging over 80% 4- to 6-ring PAH in sediments along the west side. Thus, based simply on this distribution, it is implausible that Terminal petroleum products could have contributed in a significant way to the PAH mass in the river sediment. In addition, detailed chemical comparisons of the complete PAH distribution (including alkylated forms) provide strong evidence that the Terminals are negligible contributors to PAH in the river sediment, and particularly to those driving risk, *i.e.*, the heavy PAH that also are the carcinogenic PAH.

As discussed above and illustrated in Figures 3 and 4, the shape of the concentration profile of a homologous series of alkylated PAH allows the determination of whether a PAH assemblage is derived from a petrogenic source (*e.g.*, petroleum) or a pyrogenic source (*e.g.*, coal tar or urban runoff). Differences between sources can be illustrated by comparing the alkyl PAH fingerprint of free product from a Terminal with a sample of river sediment just downstream of the GASCO site (Fig. 7). There is a dramatic difference in signature, including the shape of the individual homologous series, and the abundance of the heavy 4- to 6-ring PAH. The river sediment downstream of the GASCO site is enriched in 4-, 5-, and 6-ring PAH, while Terminal free product is enriched in 2- and 3-ring light PAH. Likewise, within each homologous series, the parent compound is most abundant in the river sediment adjacent to and downstream of the GASCO site, indicating a pyrogenic source. In the Terminal samples, one of the alkylated members of each homologous series is most abundant, as is typical of petrogenic materials.

All alkylated PAH data for Harbor sediment samples were examined to determine whether they had petrogenic or pyrogenic signatures. Each alkyl PAH homologous series (*e.g.*, naphthalenes, fluorenes, phenanthrenes, pyrenes, and chrysenes) was classified as pyrogenic if the parent compound had the highest concentration within a PAH family (see Fig. 3). The chrysene family (4-ring PAH) is discussed next as an example of this exercise because chrysene is one of the carcinogenic PAH.

Alkyl PAH data exist for 210 samples of Harbor surface sediment in the stretch of river where the Terminals are located (~RM 3 to ~RM9). Data were insufficient to classify the chrysenes in 11 of these samples. In 176 (88%) of the remaining 199 samples, the chrysenes have a clearly pyrogenic signature based on the alkyl PAH distribution (*i.e.*, the parent compound [CO] is most abundant). Of these 176 pyrogenic samples, 114 have a benzo(a)pyrene equivalent² (B(a)P eq) value in excess of the preliminary remediation goal (PRG) under consideration by EPA for the beach fisher sediment direct contact scenario³ (B(a)P eq. = 162 ug/kg) (Fig. 8). This PRG is used here for highly conservative illustration purposes only; the in-water sediment benzo(a)pyrene equivalent value under consideration is 423 ug/kg⁴. Of the 23 samples that do not have a clearly pyrogenic signature, only 4 have a benzo(a)pyrene equivalent value in excess of 162 ug/kg. Two of these 4 samples were collected off shore of BP Terminal 22T and were within the approximately 50,000 square foot area that has since been excavated and replaced with clean fill. The other two sediment samples have benzo(a)pyrene equivalent values that are below the lowest Remedial Action Level (RAL) currently under consideration for use in alternatives analysis in the ongoing feasibility study, which is 600 ug/kg⁵. Note that in this data set virtually all the exceedances of the PRG for benzo(a)pyrene equivalent are downstream of the GASCO site. These findings demonstrate that (1) chrysene, and by their compositional association, other heavy PAH, have a pyrogenic source and are not derived from the Terminals, and (2) the exceedances of the PRG for benzo(a)pyrene equivalent are almost exclusively associated with pyrogenic sources.

Although alkyl PAH data are not currently available to me for stormwater outfalls, data on the Priority Pollutant (parent) PAH are available and can be used for comparison to the river sediment. Cross plots of the ratios of PAH demonstrate a strong similarity between the PAH assemblage in the river sediment with the PAH in stormwater and outfall sediment (Fig. 9).

The close match between stormwater outfall PAH and the PAH in the river sediment is further demonstrated by comparison of relative abundance profiles of the 16 Priority Pollutant PAH taken together (Fig. 10). In contrast, the relative abundance profiles of NAPL samples from the Terminals are nothing like the profile of the river sediment (Fig. 11). In addition, the Priority Pollutant chemical signature (*i.e.*, relative proportions of light and heavy PAH) for PAH in petroleum at the Terminals is very different from the signature of PAH in the river sediment. This finding is consistent with forensic studies of PAH in sediments of other urban waterways in North America (*e.g.*, Stout *et al.*, 2001). These

² The benzo(a)pyrene equivalent is a calculated parameter that represents the equivalent concentration of seven carcinogenic compounds (4- to 6-ring PAH). The concentration of each compound is weighted by its relative toxicity where the toxicity of benzo(a)pyrene is assigned a concentration weighting of 1.0.

³ LWG, September 15, 2011, Status of Draft Feasibility Study for PCI Group page 2 and 3.

⁴ LWG, September 15, 2011, Status of Draft Feasibility Study for PCI Group page 3.

⁵ EPA Letter, August 11, 2011, addressed to Mr. Bob Wyatt of the Lower Willamette Group; table of RAL values.

chemical comparisons using the Priority Pollutant PAH are consistent with the conclusion that urban runoff is very likely a major contributor to PAH in the river sediments.

Conclusions

Together, the multiple lines of evidence summarized here demonstrate that PAH derived from petroleum products stored at the Terminals contribute in a negligible way to the PAH assemblages in the Portland Harbor river sediment. PAH in the river sediments average more than 80% 4- to 6-ring heavy PAH, consistent with a combustion source. Conversely, PAH in free product at the Terminals are less than 30% 4- to 6-ring heavy PAH (mostly less than 15%). Down-river transects of PAH concentrations in Harbor sediment show a pronounced upward spike adjacent to and downriver of the GASCO site, indicating large inputs of PAH from this site. In Harbor sediment samples with a benzo(a)pyrene equivalent in excess of the PRG, PAH have a strongly pyrogenic character based on evaluation of parent and alkyl PAH. Chemical fingerprinting strongly implicates both urban stormwater and the GASCO site as the predominant contributors to PAH in Harbor sediment along the west side of the River between river miles 3 and 9 where the petroleum Terminals exist.

Citations

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http://response.restoration.noaa.gov/topic_subtopic_entry.php?RECORD_KEY%28entry_subtopic_topic%29=entry_id,subtopic_id,topic_id&entry_id%28entry_subtopic_topic%29=376&subtopic_id%28entry_subtopic_topic%29=5&topic_id%28entry_subtopic_topic%29=2
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FIGURES

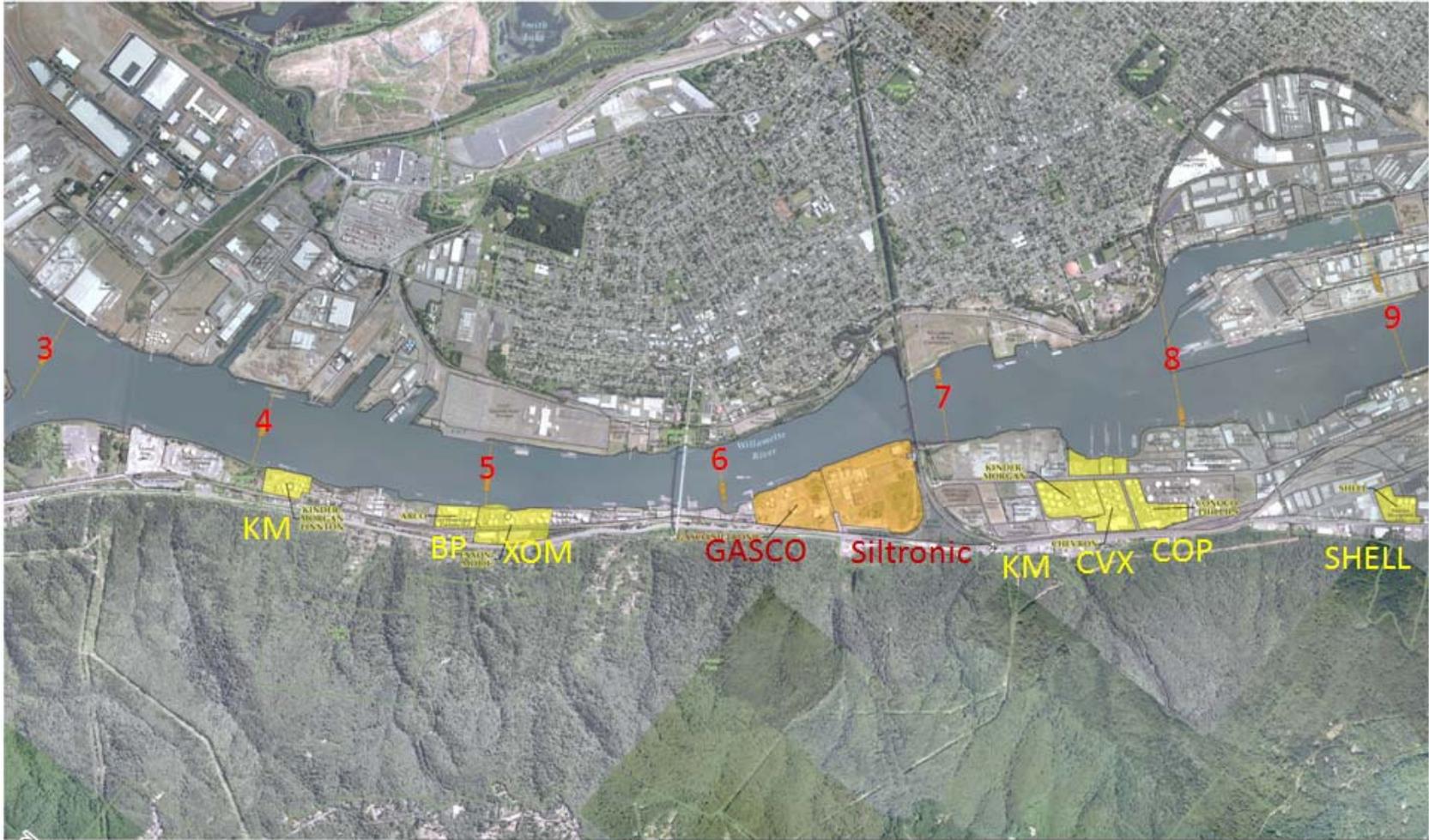


Figure 1 – Map of the Willamette River from river mile 3 to river mile 9 showing locations of the Terminals and the former GASCO site. KM = Kinder Morgan, BP = British Petroleum, XOM = Exxon Mobil, CVX = Chevron, COP = ConocoPhillips

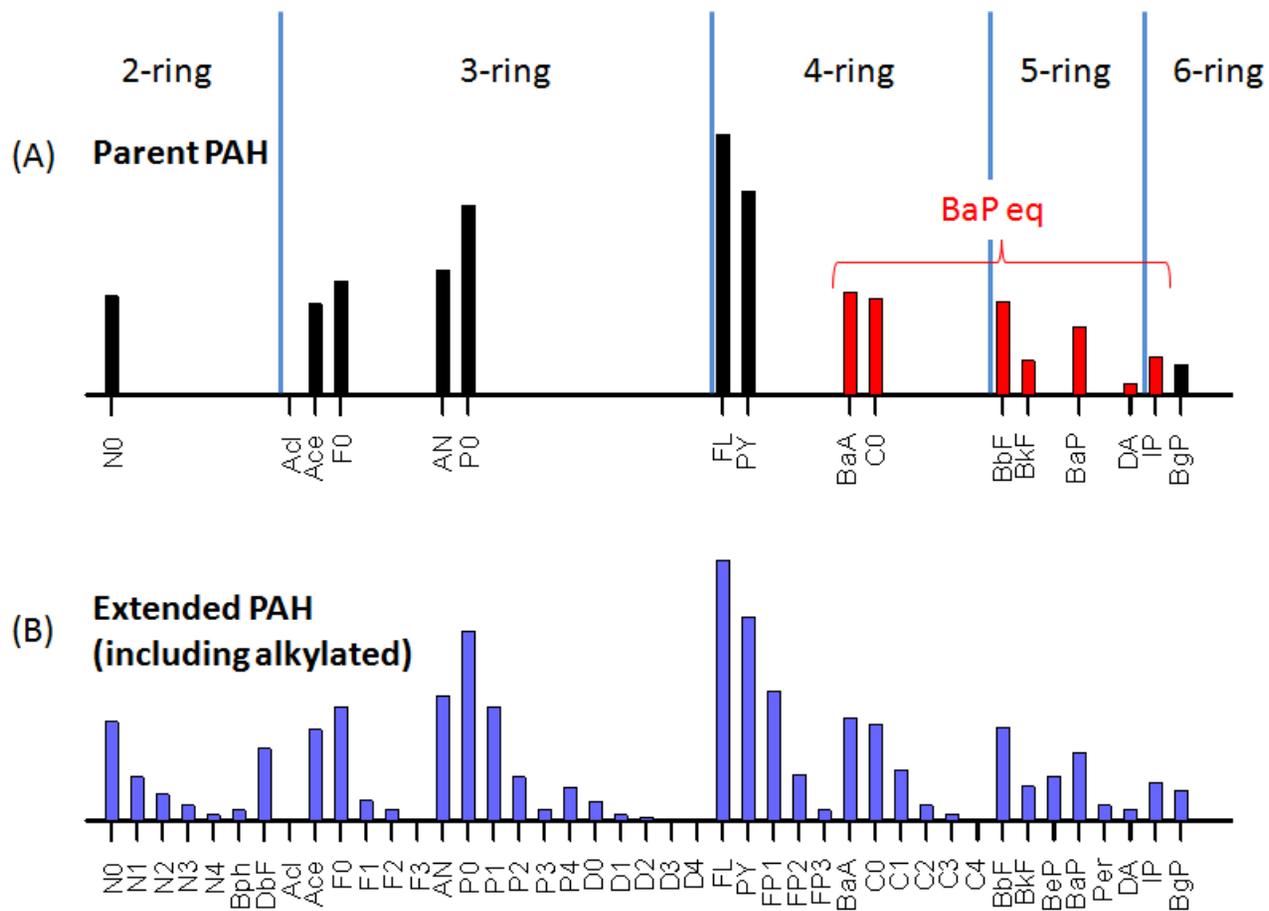


Figure 2 – Bar chart showing relative concentrations of PAH in a pyrogenic coal tar. (A) Only the 16 Priority Pollutant (parent) PAH. Red bars represent carcinogenic compounds that contribute to the calculation of the benzo(a)pyrene equivalent; (B) 16 parent PAH plus the additional PAH that are included in a typical analysis of alkylated PAH. See Table 1 for explanation of abbreviations.

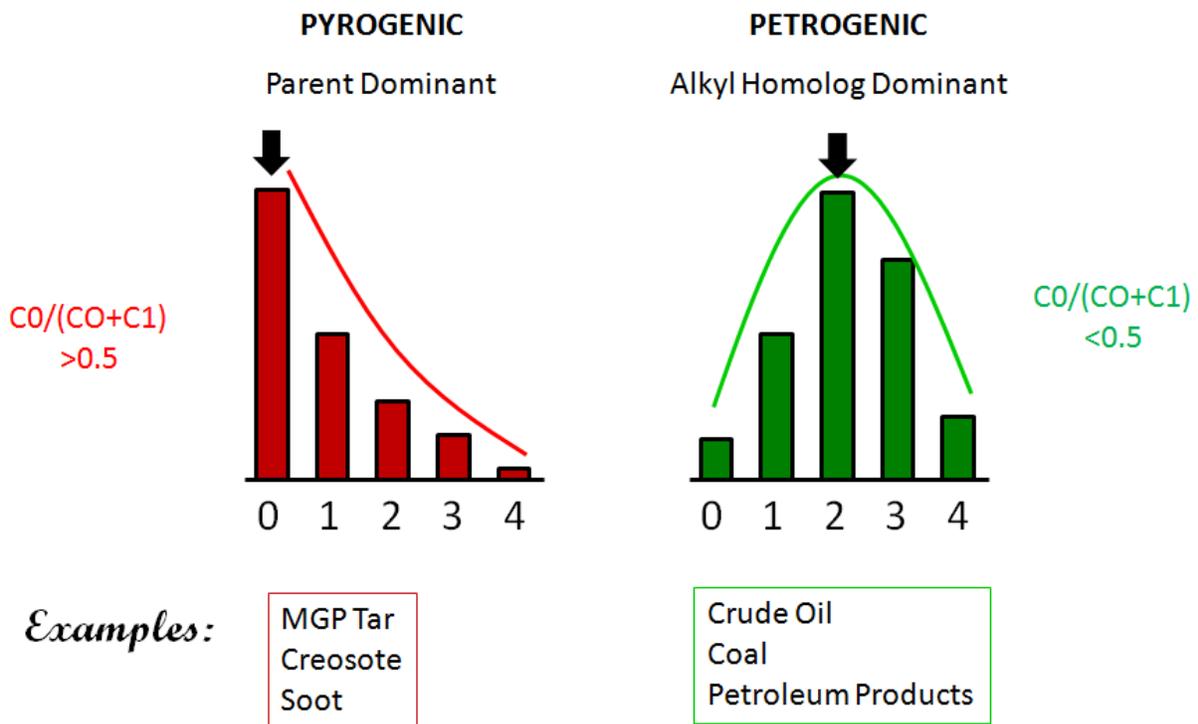


Figure 3 – Comparison of the relative abundance of the individual alkylated groups within a PAH family for pyrogenic (left) and petrogenic (right) materials. In PAH assemblages derived from pyrogenic sources the parent (C0) is the most abundant member of a PAH family. Whereas in PAH assemblages derived from petrogenic sources one of the alkylated members is most abundant (typically either C2 or C3).

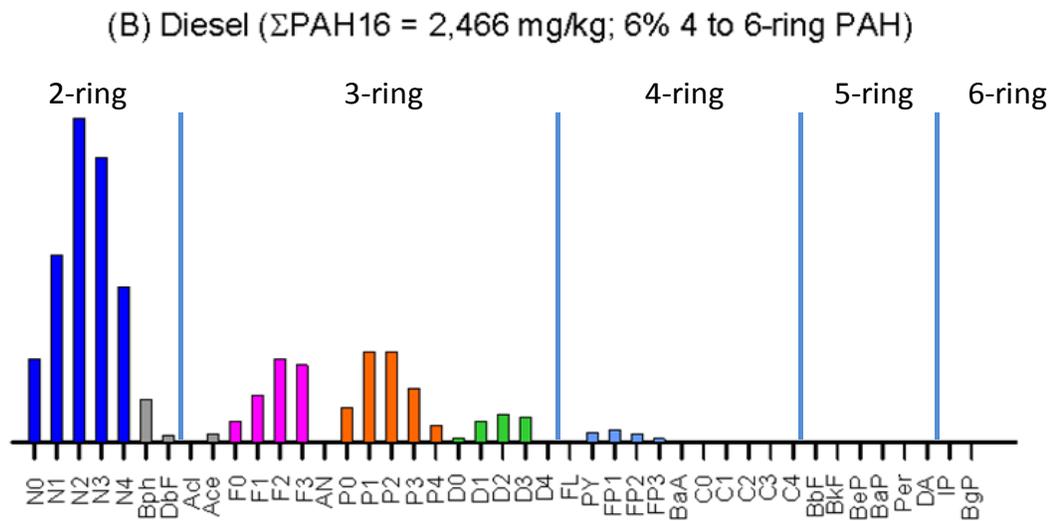
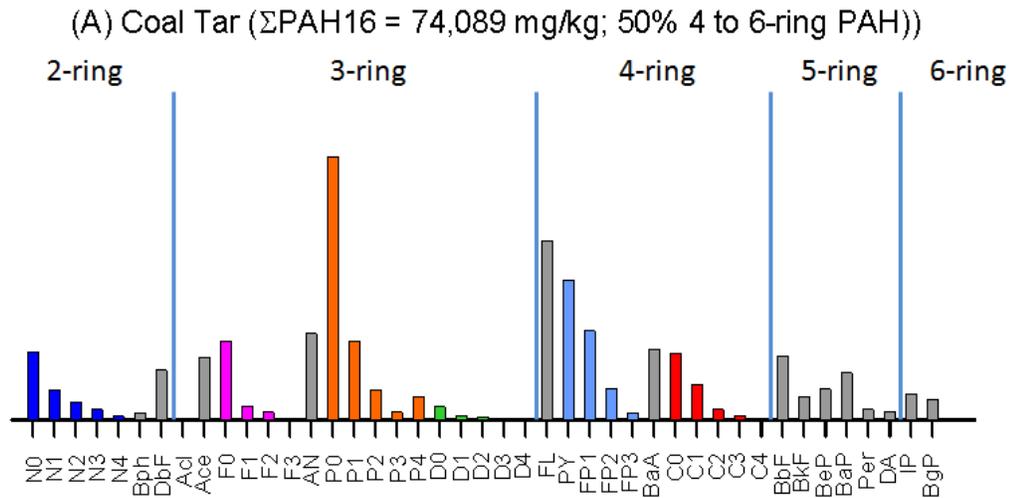


Figure 4 – Relative abundance of parent and alkyl PAH in a coal tar (A) and a #2 diesel fuel (B). Individual homologous series are colored coded for reference. Note difference in the total amount of PAH, the relative abundance of 4- to 6-ring PAH and in the shape of the individual homologous series (each series is color coded). In the pyrogenic coal tar the parent compound within a homologous series is most abundant. In the diesel fuel one of the alkylated members is most abundant within a homologous series.

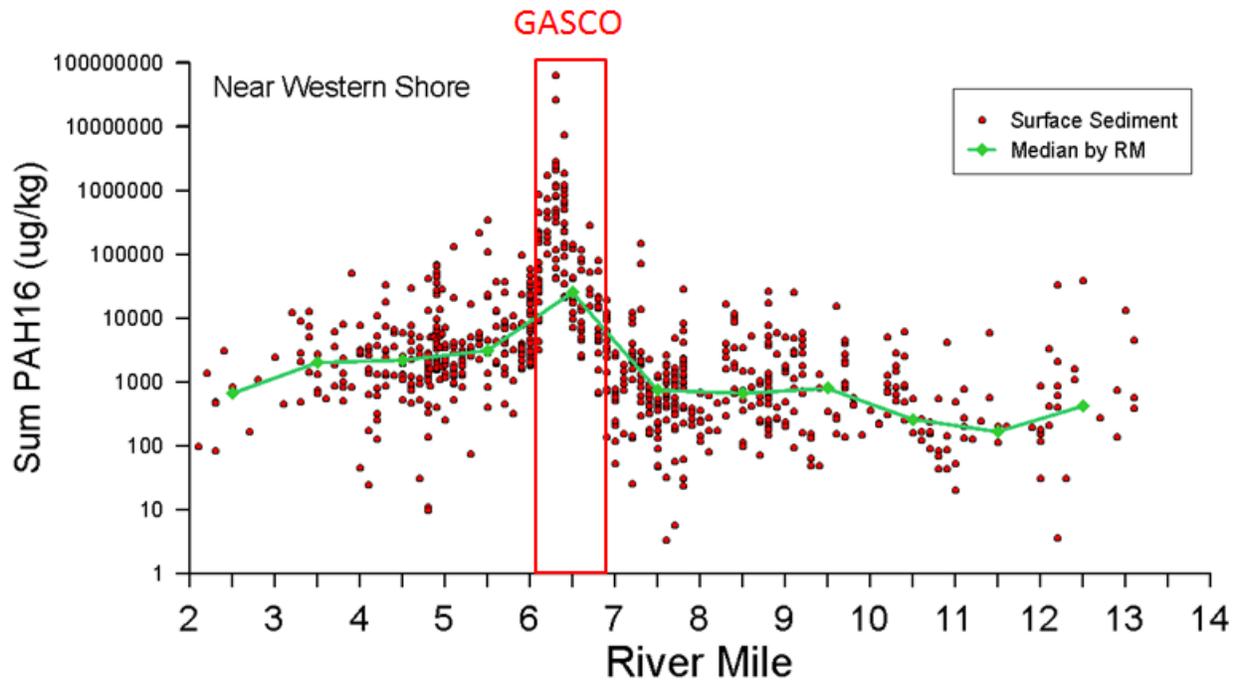


Figure 5 – Transect of the sum of the 16 parent PAH in surface sediment along the west side of the Willamette River. Note pronounced upward spike in concentrations in front of the GASCO site (Y-axis is a logarithmic scale). Median concentrations remain elevated for several miles downstream of the GASCO site. Note also that PAH concentrations are elevated upstream of the most upstream Terminal (River Mile 8.5 and greater).

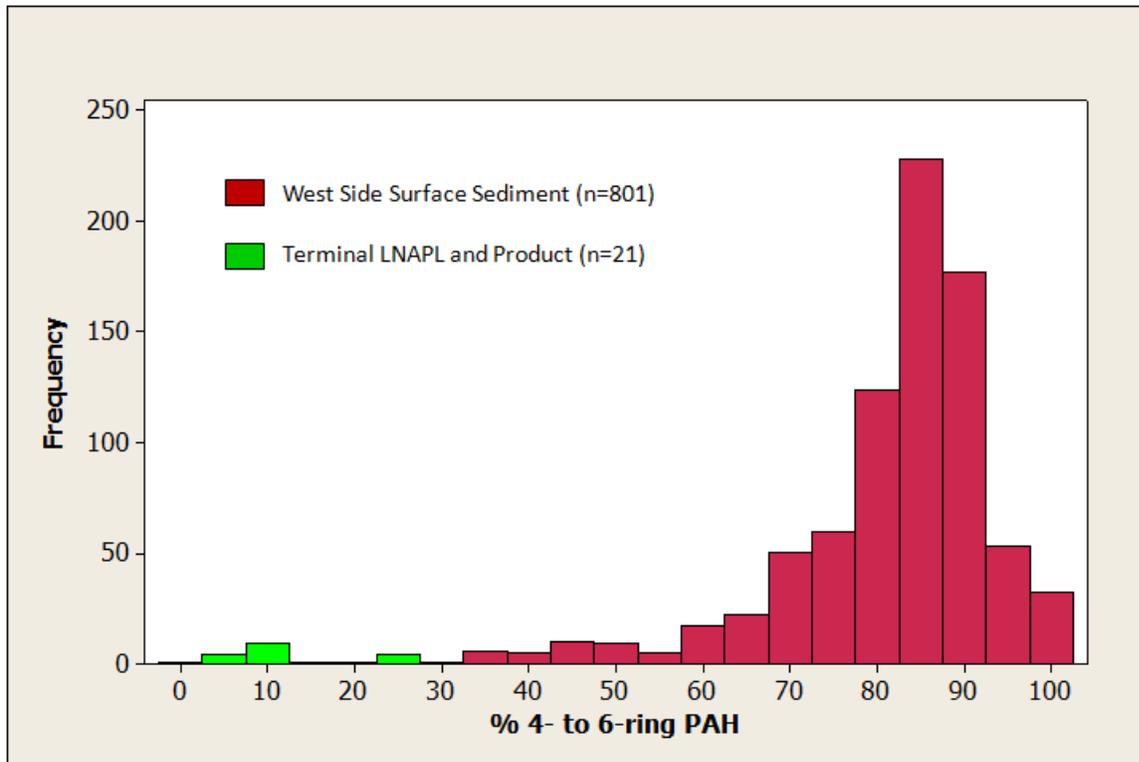


Figure 6 – Histogram showing the weight percent of the sample PAH that is comprised of heavy, 4- to 6-ring PAH in west side surface sediment (red) and Terminal LNAPL and product samples (green). Values are based on the 16 parent PAH.

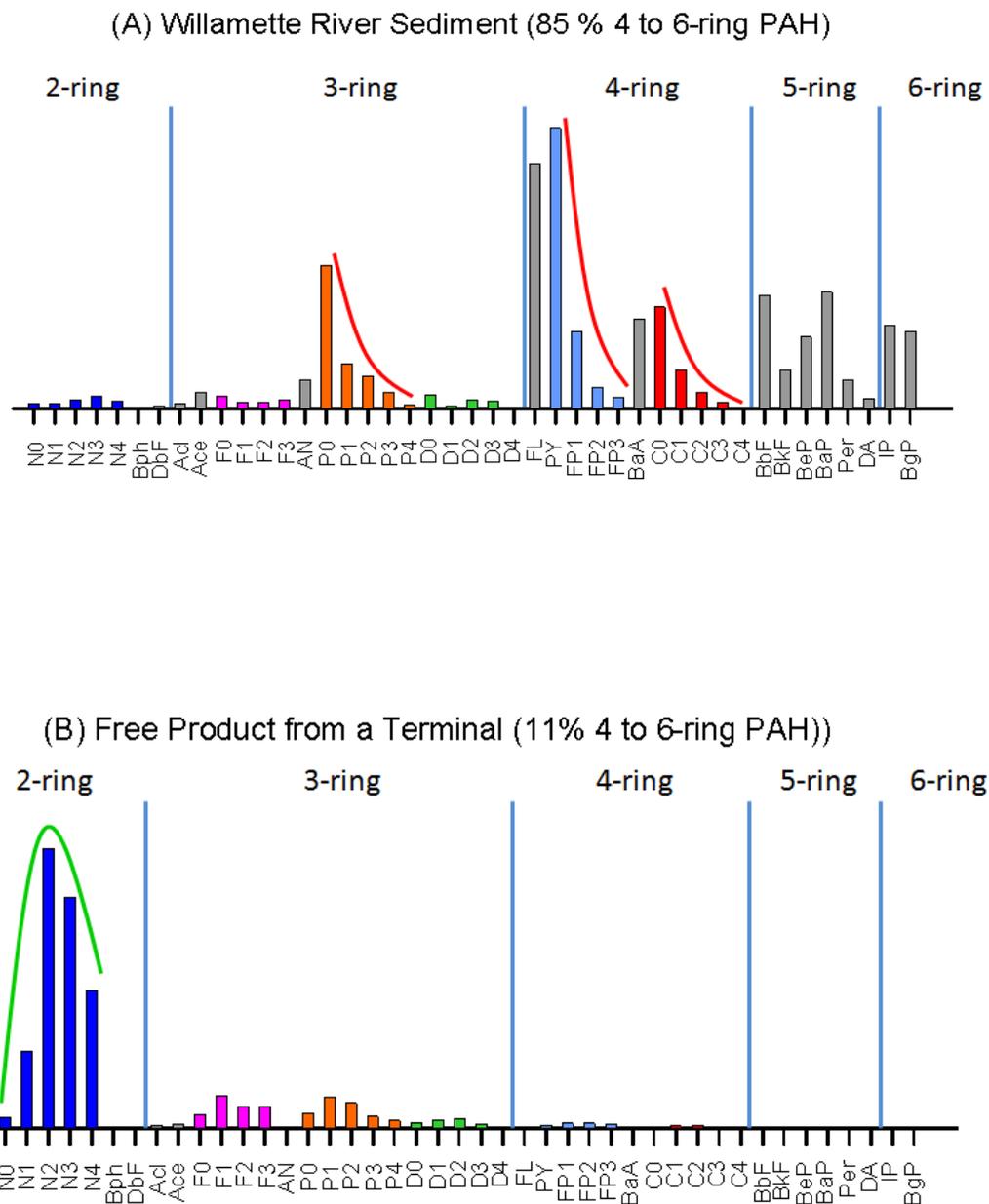


Figure 7 – Alkyl PAH bar charts for (A) a Willamette River surface sediment sample just downstream of the GASCO site, and (B) a representative sample of free product from one of the Terminals. Note the dramatic difference in signature, including the shape of the individual homologous series, and the relative abundance of the light 2- and 3-ring PAH and heavy 4- to 6-ring PAH. The river sediment is enriched in 4-, 5-, and 6-ring PAH, while Terminal free product is enriched in 2- and 3-ring PAH. Likewise, the parent compound is most abundant in the river sediment within each homologous series, indicating a pyrogenic source.

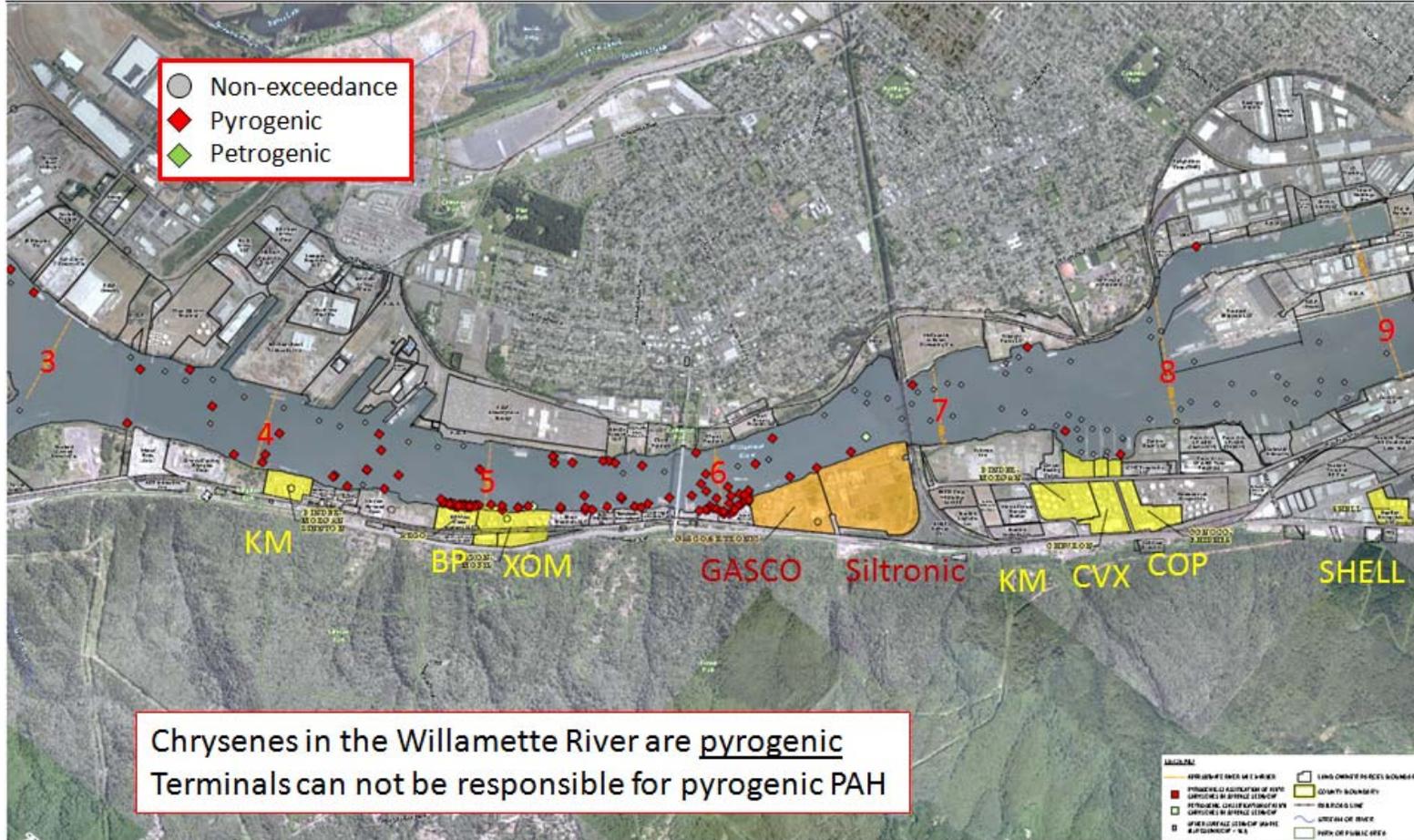


Figure 8 – Map showing whether chrysenes have a pyrogenic or petrogenic signature at surface sediment locations where the current PRG for the benzo(a)pyrene equivalent (162 ug/kg) is exceeded. Note that there are few exceedances upstream of the GASCO site, and that downstream of the GASCO site chrysenes are predominantly pyrogenic in origin. Pyrogenic PAH cannot be derived from petroleum releases at the Terminals.

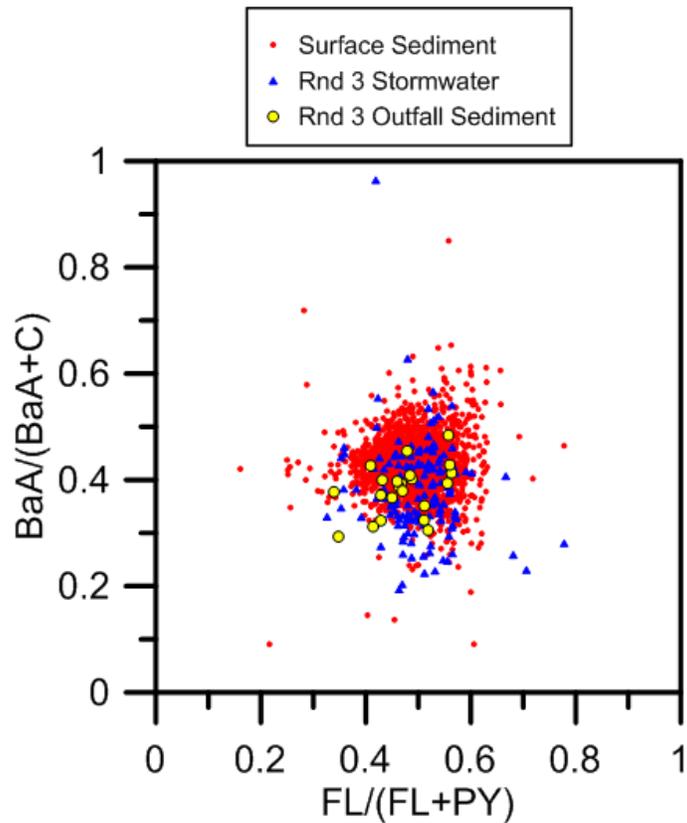


Figure 9 – Comparison of PAH ratios for Portland Harbor river surface sediment (red circles), Round 3 stormwater (blue triangles), and Round 3 outfall sediment (yellow squares). These data demonstrate that stormwater and outfall sediment strongly resemble the Harbor river sediment. Compounds shown on this plot are abundant in Harbor sediment (e.g., Figure 7), but are only present in very low, or non-detectable, concentrations in free product from the Terminals. [BaA = Benzo(a)anthracene, C = Chrysene, FL = Fluoranthene, and PY = Pyrene]

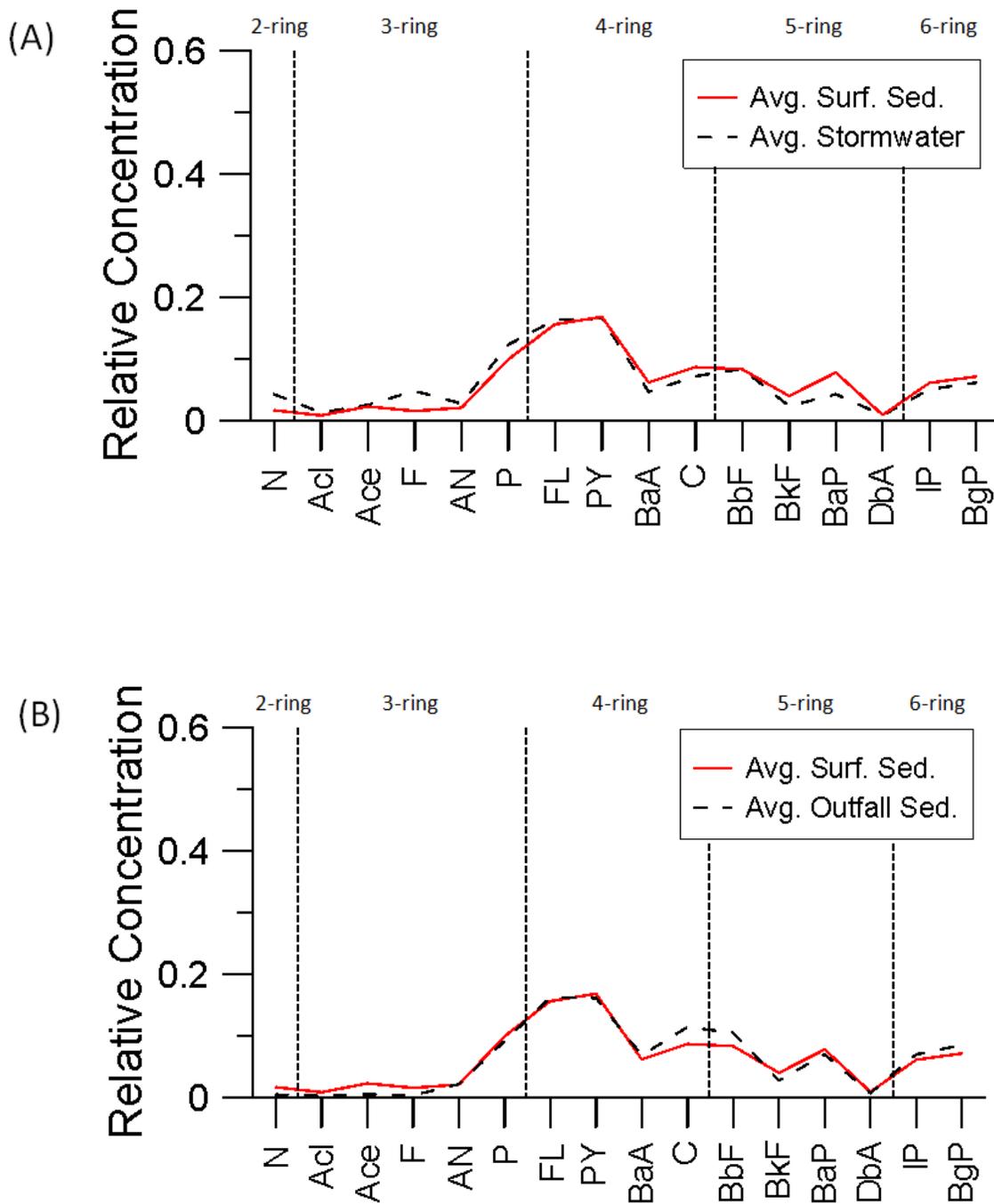


Figure 10 – Profiles comparing relative abundance of 16 parent PAH in Harbor river surface sediment with (A) Round 3 stormwater and (B) Round 3 outfall sediment. Note that the river sediment samples strongly resemble the stormwater and outfall sediment samples. See Table 1 for compound abbreviations.

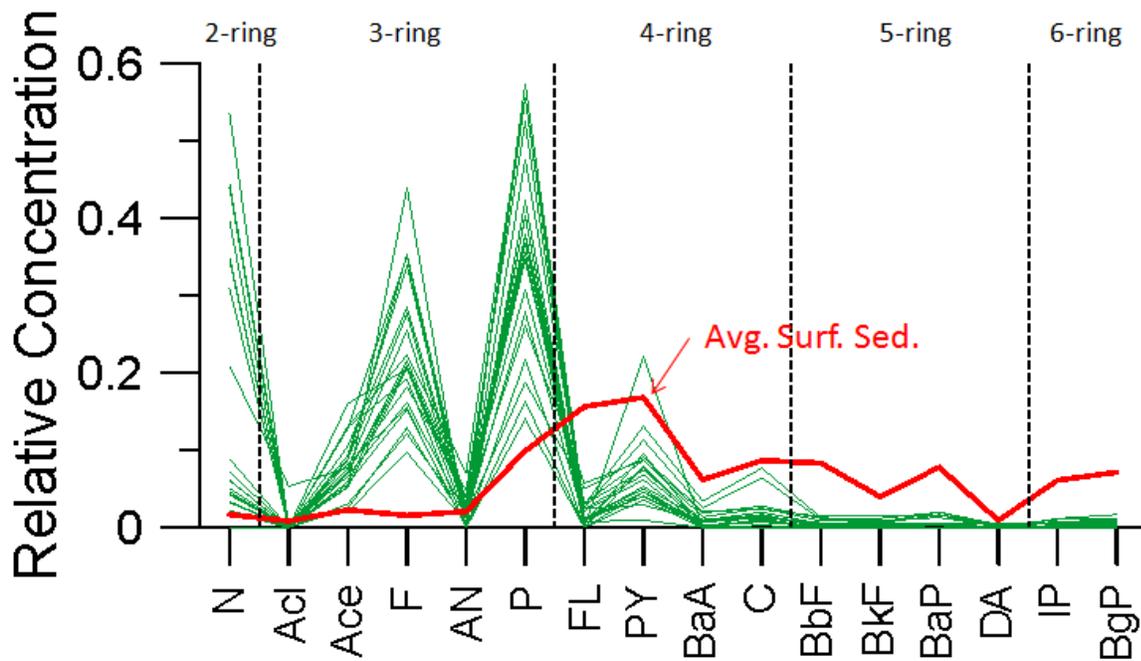


Figure 11 – Profiles comparing the relative abundance of 16 parent PAH in Harbor river surface sediment (heavy red line) with petroleum free product samples from the Terminals (green lines). The chemical signatures of the petroleum free product samples differ considerably from that of the river sediment.