APPENDIX G

Forensic Evaluation

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INTRODUCTION

The purpose of this document is to describe the forensic evaluation of several sediment samples collected during B120 assessment activities to assess whether hydrocarbon-related constituents in those samples were related to the B120 oil spill. The samples assessed in this appendix are those that exceeded ecological guidelines[1] discussed in Section 9 of the main document. In general, this evaluation consisted of reviewing the laboratory results and assessing the presence or absence of certain compounds as well as evaluating the relative concentration of specific constituents in these samples. This evaluation was conducted using standard forensic methods for characterizing hydrocarbons.

The primary constituents of concern associated with the B120 oil spill are polycyclic aromatic hydrocarbons (PAH), a small component of No. 6 fuel oil. These compounds are not unique to the fuel oil spilled in Buzzards Bay, but are ubiquitous[2] throughout most of the world, and can be derived from vegetation (biogenic), petroleum (petrogenic), or combustion of biogenic or petrogenic substances (pyrogenic). In general, biogenic and pyrogenic PAH can readily be distinguished from petrogenic PAH based on the general composition of the PAH. For example, petrogenic PAH contain both "parent" and "alkylated" PAH. Parent PAH consist simply of fused aromatic rings. Alkylated PAH consist of fused aromatic rings with "side-chains", which are straight or branched chains of hydrocarbons attached to various points on the ring structure. However, combustion removes these side-chains, and the resultant pyrogenic PAH consist primarily of parent PAH compounds (i.e., no hydrocarbon chains attached). Therefore, the PAH "signature" in pyrogenic material shows higher concentrations of parent PAH relative to alkylated PAH. The chemical differences among PAH from different petroleum sources (e.g., B120 source oil compared to other petroleum sources), or mixtures of PAH from multiple sources are more subtle and require closer evaluation as described in detail below.

The primary laboratory analyses used for this forensic evaluation were PAH and biomarker analyses. The results of PAH analysis provide the pattern, distribution, and relative concentrations of PAH compounds, which is known as a "fingerprint." This fingerprint represents the history of the PAH origin, processing, and other traces of how it was handled or transported. Forensic evaluation of PAH results has proven highly useful for identifying

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[1] *Ecological screening guidelines for sediments developed by Long et al. 1995.*

[2] *Besides the transport and handling of oils and other fossil fuels, PAH mixtures are found anywhere there is or has been fire, other incomplete combustion of organic matter, or in natural oil seeps, coal outcrops, and peat bogs, all of which derive from the conversion of plant and animal debris over geologic time. Examples of combustion sources include industrial furnaces and residential fireplaces or stoves, vehicle exhaust, volcanic activity, and forest fires throughout in the world (Simoneit 2002; API 2002). In addition, long-range atmospheric (aeolian) transport circulates combusted material into remote areas, including the artic and oceanic regions (Ohkouchi et al. 1999; Rogge et al. 1999; Simcik et al. 1997; Bjőrseth et al. 1979). Hence, a background signature of pyrogenic PAH can be found in both recently deposited and prehistoric sediments, such as those deposited in the Pleistocene glacial period (Barrick and Prahl 1987). The detection of PAH has more to do with the sensitivity of analytical techniques than whether PAH might be present in some form in environmental samples containing at least some organic material.*

environmental samples dominated by biogenic PAH, pyrogenic PAH, or petrogenic PAH that are from distinctly different sources.

To further evaluate some samples, hydrocarbon biomarker analysis was conducted to examine the potential for B120 oil in the environmental samples. The analysis of biomarkers aid in identifying the hydrocarbon source in weathered hydrocarbon samples, which may no longer have a fingerprint similar to the original source material. Biomarkers are a group of compounds that (in fossil fuels) are the remains of biochemicals altered over geological time during the formation of crude oil (e.g., Ourisson and Rohmer, 1992; Simoneit, 2005 and citations within).

The primary biomarkers evaluated as part of this effort were terpanes (primarily hopanes and oleanane) and steranes. Terpanes derive from the breakdown of organic material in higher order, terrestrial plants, like trees and shrubs. Hopanes are a subgroup of terpanes that are ubiquitous in fossil fuels because they derive from the breakdown of lipid material in bacterial cell walls (Ourisson and Rohmer 1992). Oleanane is a terpane biomarker for angiosperms, or flowering plants (ten Haven and Rulkötter 1988), and occurs in fossil fuels formed from Cretaceous source rocks or younger, in mixed terrestrial/marine environments (Moldowan et al., 1994, Murray et al., 1997). Steranes derive from the breakdown of sterol compounds in plant or animal material, such as cholesterol.

The particular distribution of hydrocarbon biomarkers found in a fossil fuel can indicate the type of rock material, geologic period, and environment (e.g. vascular plants, late Cretaceous, freshwater or marine, anoxic depositional environment) in which the fuel was originally formed. Several examples of specific biomarker applications, and the supporting literature, are summarized at http://www.oiltracers.com/biomarker.html.[3]

Fossil fuels contain dozens of biomarkers but the concentrations of only 18α-oleanane, C_{29}-hopane, and C_{30}-hopane[4] were considered for this evaluation of environmental samples from the Buzzards Bay area. There are a number of other hopanes but these two routinely quantified hopanes typically have the highest concentrations compared to other biomarkers and are therefore more useful. Sterane concentrations were not quantified in these samples, but the distribution of detected steranes was evaluated using ion chromatograms, as described below.

LABORATORY ANALYSES

The following analyses were conducted in order to evaluate whether the hydrocarbons present are indicative of B120 oil, whether the hydrocarbons are primarily non-B120 oil hydrocarbons, or whether there is a mixture of B120 and non-B120 hydrocarbons in the selected samples:

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[3] *Link last verified on July 24, 2006*

[4] *The chemical notation for these two hopanes is 17α(H),21β(H)-30-norhopane (i.e., C_{29}-hopane) and 17α(H),21β(H)-hopane (i.e., (C_{30}-hopane).*

- Quantitative results were assessed for 56 individual or groups of PAH and related compounds by gas chromatography (GC)/mass spectroscopy (MS), including sulfur- and nitrogen-containing aromatic hydrocarbons (e.g., dibenzothiophenes, carbazole).

- Quantitative results were reviewed for three characteristic biomarkers by GC/MS, as well as qualitative fingerprints of homologous biomarker series.[5]

- The total hydrocarbon fingerprint was obtained as the graphical output (chromatogram) from the chemical analysis of each sample by GC with flame ionization detection (FID). This qualitative fingerprint represents the relative contribution of all hydrocarbons that were extracted from the sample, only some of which are eventually identified and quantified. The fingerprint typically includes clearly resolved components as well as an unresolved complex mixture (UCM) of hydrocarbons. The shape or dominance of the UCM can be indicative of particular hydrocarbon sources or how physical and microbial processes have affected less stable components.

- In some cases, assessments were made of the qualitative fingerprint of the total petroleum hydrocarbons by GC/FID, which is dominated by aliphatic[6] hydrocarbons. Quantitative results for *n*-alkanes[7] and specific branched hydrocarbons, namely pristane and phytane were also reviewed in a few instances. The n-alkanes, pristane, and phytane are a subset of aliphatic hydrocarbons of both biogenic and fossil origin, and so are ubiquitous in the environment. Their specific origin can usually be distinguished by their composition. For example, the "odd-even" dominance of *n*-alkanes is one assessment, and refers to the degree to which concentrations of "odd-numbered" *n*-alkanes (i.e., those with an odd number of carbon atoms) are greater than adjacent "even-numbered" *n*-alkanes (i.e., with an even number of carbon atoms). In oils, these concentrations are similar (i.e., no odd-even preference). In contrast, terrestrial plant waxes typically show a strong odd-carbon preference, especially in the range of n-C_{23} to n-C_{33}.

The TPH and alkane assessments were used in some instances to assess the presence of non-B120 oils, the extent of weathering, and to identify the relative contribution of recent biogenic sources (particularly terrestrial plants). PAH and biomarker results were used to accomplish the primary objective of assessing the absence or potential contribution of B120 source oil and the presence of other PAH sources as follows:

- Identify distinguishing characteristics of the PAH mixture in the B120 source oil;

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[5] *The biomarker fingerprints are created as "ion chromatograms" using GC/MS, analogous to the total hydrocarbon chromatograms by GC/FID. These ion chromatograms can be used to not only distinguish fresh and combusted materials but also fresh oils of different types and geological formation. The specific ions used are m/z 191 for terpanes, m/z 217 for steranes, and m/z 218 for β,β-steranes. The term "m/z" refers to mass to charge ratio, which is the molecular weight of the most frequently detected ion when the compound is broken into fragments in the mass spectrometer.*

[6] *The carbon atoms in aliphatic hydrocarbons are linked only in chains that are either straight, branched, or in simple rings that do not have aromatic bonds like benzene. Examples of simple aliphatic hydrocarbons include octane, isooctane, and cyclohexane. Steranes and hopanes are aliphatic hydrocarbons with multiple non-aromatic rings.*

[7] n-*Alkanes only contain carbons bonded in straight (i.e., normal) chains.*

- Identify distinguishing characteristics of PAH mixtures from other source materials (i.e., non-B120 hydrocarbons); and
- Compare these characteristics to PAH detected in sediment samples in determining the presence or absence of B120 source oil.

PRIMARY CHEMICAL CHARACTERISTICS RELATED TO B120 SOURCE OIL

Table G-1 lists sediment samples that were selected for forensic evaluation (i.e., samples exceeding ecological benchmarks). Table G-2 summarizes the chemical characteristics that were forensically evaluated for the unaltered source oil, weathered B120 source oil, and sediment samples that were dominated by petrogenic or pyrogenic sources . Table G-3 provides a summary of quantitative indicators used to distinguish the presence or absence of B120 source oil in each specific sediment sample.

RATIOS OF "PARENT" PAH IN SOURCE OIL AND SEDIMENT SAMPLES

In the source oil collected from Tank 2 from the B120 barge on April 30, 2003, the ratio of fluoranthene to pyrene (FL:PY) concentrations is 0.14. The concentrations of these two individual PAH would decrease over time at approximately the same rate and would likely maintain a consistent ratio. Conversely, if this ratio is similar in the environmental samples to that found in the source oil, then B120 oil would be the suspected source of PAH in the sample pending evaluation of other characteristics. As presented in Table G-3, the FL:PY ratio for all other evaluated samples was greater than 0.7, indicating that B120 oil was not the source of PAH.

PRESENCE/ABSENCE OF ACENAPHTHYLENE

Acenaphthylene is a petrogenic PAH (Stout et al., 2004) that is useful in evaluating the presence of non-B120 petrogenic sources. Because acenaphthylene was not detected in the B120 source oil, detection of this compound in sediment samples indicates the presence of non-B120 hydrocarbons. As shown in the following sections and Table G-3, acenaphthylene was detected in all sediment samples, including those in which B120 oil was identified. This finding indicated an admixture of B120 oil and at least one additional PAH source in those samples.

DISTRIBUTION OF B120 SOURCE OIL BIOMARKERS

All samples discussed in this summary were analyzed for biomarker compounds, with the exception of three sediment samples (W2A02-MS01, W2A02-MS02, and W2A03-LIT-02).[8] Biomarkers were used in the following ways:

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[8] *These three samples were analyzed only for parent PAH, which was sufficient to determine that the PAH combustion sources dominated and accounted for any exceedances of sediment quality guidelines.*

- Ratios of selected PAH compounds to C_{29}-hopane or C_{30}-hopane were compared among sediment samples from different locations and the source oil. The PAH compounds used in these comparisons (i.e., fluoranthenes/pyrenes) are not easily volatilized and are more resistant to microbial degradation than 2- or 3-ringed PAH, such as naphthalenes or phenanthrenes. Large deviations in the PAH/hopane ratios compared with those in the source oil strongly support the conclusion that B120 oil was absent if there was little evidence of weathering (e.g., weathering limited to volatilization).

- Three "ion chromatograms" were used as qualitative fingerprints of the entire series of hopanes and steranes for comparing samples and the source oil. All hopanes break down during GC/MS analysis to form, among others, a characteristic fragment referred to as "ion 191." Analogously, steranes break down to form a characteristic fragment referred to as "ion 217," and certain steranes form a characteristic "ion 218." The combined three biomarker fingerprints are unique for each oil and can be compared even between weathered samples and the source oil because the biomarkers are highly resistant to degradation. Thus, the presence and composition of these compounds would indicate the presence of B120 oil, and the absence would confirm the B120 source oil was not present.

- The concentrations and distribution of compounds such as dibenzothiophene and associated alkylated compounds is another line of evidence to compare whether petroleum-derived PAH are due to B120 oil or an alternative source. Dibenzothiophenes are present in B120 oil in relatively low concentrations compared with some source materials like asphalt (Rogge et al. 1997). Some oils contain virtually no dibenzothiophenes, and when present, the specific composition is characteristic of not only the particular oil but of environmental weathering conditions as well.

CHEMICAL CHARACTERISTICS OF B120 SOURCE OIL

On April 30, 2003, several source oil samples were collected by the U.S. Coast Guard from Tank 2-P (the #2 port tank) and Tank #2 Starboard adjacent to the ruptured tank onboard the B120 barge and were sent to B&B Laboratories, Inc. (B&B) for analysis of PAH and aliphatic hydrocarbons. Figure G-1 presents an example of the distribution of these compounds in a representative sample of Tank 2-P oil.

UNALTERED SOURCE OIL

The B120 source oil is dominated by the following PAH compounds, which together comprise over 85 percent of the total PAH content:

- Naphthalenes (2-ringed PAH compounds) with carbon side-chains comprise approximately 32 percent of the total PAH content. Naphthalenes with two carbon side-chains (C2-naphthalenes) are the most abundant.

- Phenanthrenes (3-ringed PAH compounds) with carbon side-chains comprise 27 percent of the total PAH content. C2-Phenanthrenes are the most abundant of these PAH.

- Fluoranthenes/Pyrenes (4-ringed PAH compounds) with carbon side-chains comprise almost 15 percent of the total PAH content. Again, compounds with two carbon side-chains are the most abundant.

- Chrysenes (also 4-ringed PAH compounds) with carbon side-chains comprise almost 12 percent of the total PAH content. Chrysenes with either one or two carbon side-chains are similar in concentration.
- Five-ringed PAH, such as benzo[*a*]pyrene, benzo[*b*]fluoranthene, benzo[*k*]fluoranthene, as well as six-ringed PAH such as indeno[*1,2,3-c,d*]pyrene and benzo[*g,h,i*]perylene were detected at very low concentrations.

This PAH fingerprint of the B120 source oil is generally consistent with heavy fuels such as No. 6 fuel oil or Bunker C oil, and is valuable in assessing the potential behavior and persistence of the oil in the environment. The elevated 4-ring PAH concentrations distinguish No. 6 and Bunker C oils from many other petroleum sources (e.g., light- and mid-range distillates).

Biomarker analyses documented that the B120 source oil contained twice the amount of C_{30}-hopane as C_{29}-hopane, and did not contain oleanane. The sum of the C_{29}-hopane and C_{30}-hopane concentrations is equivalent to approximately 0.23 percent of the total PAH content.

WEATHERED SOURCE OIL

Once released into the environment, the PAH distribution of an oil changes in a generally predictable manner, depending on the extent of exposure to physical and microbial processes. For example, volatilization will rapidly decrease the concentration of 2-ringed naphthalenes relative to other PAH compounds, followed by the 3-ringed phenanthrenes/anthracenes. The 4-, 5-, and 6-ringed PAH compounds do not volatilize easily and so are preserved in the fingerprint of a weathered source oil sample.

Another important fate process is microbial degradation. The potential for microbial degradation varies within a PAH series [9] but the extent depends on many factors that control microbial growth and composition. Additional general and more specific chemical and physical characteristics can be used to distinguish oil sources and their degradation (e.g., Christensen et al., 2005; Wang and Fengas, 2003; Darling et al., 2002; Wang et al., 1998). In general, however, the cumulative effect of environmental degradation is:

- the loss of less alkylated PAH compounds due to weathering relative to more alkylated PAH compounds, which are more resistant to degradation;
- the loss of lower molecular weight ("lighter") compounds relative to higher molecular weight ("heavier") compounds; and
- the preservation of terpane (including hopane and oleanane) and sterane biomarkers relative to PAH compounds.

Because terpane and sterane biomarkers are highly resistant to degradation, their distribution can be used to compare weathered oils to source oils even when other characteristics of the oil have undergone substantial changes. This distribution of biomarkers is highly resistant to change following an oil spill, making the complete biomarker fingerprint a powerful confirmation or denial of the link between an environmental sample and the B120 source oil.

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[9] *Naphthalenes are an example of a PAH series, which includes the parent naphthalene, C1-naphthalene, C-2 naphthalene, C-3 naphthalene, and C4-naphthalene.*

Most of the samples discussed below had no observed oil in the samples during field collection (as had been reported for other sediment samples with elevated PAH concentrations due to B120 source oil). However, the laboratory results identified higher PAH concentrations relative to those in other samples, such that an influence from alternative sources was hypothesized. One other sample was reported by the public as possibly being petroleum-related (Harbor View W2A02-092905), although the appearance, texture, and odor were not consistent with B120 oil. Forensic evaluation of samples collected from specific locations is discussed below.

W2A-10 LONG ISLAND AND CAUSEWAY SOUTH

This segment is located in the town of Fairhaven, and includes a rugged peninsula that was heavily oiled soon after the spill. Although the peninsula shoreline is rocky, there is also some fringing salt marsh habitat. Cleanup efforts were limited along the shoreline near the southern tip of Long Island (also known as Hoppy's Landing) in order to avoid damage to marsh habitat that could result from intensive cleanup activities. A causeway linking West Island and Long Island stretches across the northern section of the segment, and a public boat ramp and boat storage area are located within approximately 650 feet of the southern point Long Island.

On July 14, 2004, a Police Department Regional Dive Unit was conducting training sessions near the public boat ramp at Hoppy's Landing. The Dive Unit reported oil in the shallow subtidal sediment between the floating dock and the causeway at the eastern shoreline of Long Island. The Dive Unit was training approximately 30 to 50 feet offshore in waters ranging in depth from 4 to 5 feet. Oiling conditions reported by the Dive Unit consisted of sheen surfacing when the bottom sediments were disturbed and oil droplets in the water. Additionally, the divers indicated they had oil spots on their wetsuits after the exercise.

W2A10-ST-S07 and (Duplicate) W2A10-ST-XXX – Samples Containing Evidence of B120 Oil

On July 22, 2004 ten sediment samples were collected from nine locations in the vicinity of the reported oil. No visible oil or sheen was observed, or odors detected observed during the survey or in samples with one exception. The exception was sample W2A10-ST-S07 that was collected approximately 25 feet from the north side of the floating dock, between the floating dock and the causeway. Upon retrieval of the sample from this location, a trace rainbow sheen, less than about a millimeter in size, was observed.

PAH concentrations in duplicate samples collected at location W2A10–ST-S07 were considerably greater than at all other locations, likely due to the observed sheen. PAH concentrations in all of the other samples collected at Long Island during this survey satisfied ecological benchmarks. PAH results in the duplicates (W2A10–ST-S07 and W2A10-ST-XXX) revealed that oil dominated the PAH distribution. Other hydrocarbons, including combustion-derived PAH and the biomarker 18α-oleanane were also detected in both samples (Table G-3). 18α-Oleanane is not a component of the B120 source oil but is found in other fossil fuels that could be combusted. Combustion-derived PAH detected in the vicinity of the floating dock are not surprising given that the area is used as a boat launch and several boats were moored in the immediate area. Potential contributions from un-combusted boat fuels are not likely to contribute to the PAH range observed in these samples because those fuels contain light hydrocarbons, not heavy diesel. However, exhaust from boat motors contains combustion PAH.

The combustion component in these samples is evident based on the concentrations of parent PAH concentrations relative to those in the B120 source oil. The combustion component accounts for low concentrations of compounds such as acenaphthylene, which is absent in the B120 source oil (see the following section). In addition, the duplicate samples had an increased proportion of 5-, and 6-ring PAH compounds relative to other PAH compounds, as well as an increased FL:PY ratio.

The phenanthrenes/anthracenes, fluoranthenes/pyrenes, and chrysenes in the two samples were reasonably consistent with the fingerprint of the B120 source oil. The FL:PY ratio in samples W2A10–ST-S07 and W2A10-ST-XXX was also consistent with the FL:PY ratio in B120 source oil. However, these diagnostics alone were insufficient to confirm the presence of B120 source oil because nearly all of the naphthalenes and a substantial amount of the fluorenes were no longer present, indicating a weathered oil.

The biomarker results indicated that these samples contained the B120 source oil but the detection of 18α-oleanane indicated a mixture with one or more substances, including the combusted material. That material could be a combusted fuel containing 18α-oleanane. The potential for a contribution from another fuel containing 18α-oleanane exists but it would have been a minor component compared with the B120 oil and combustion products.

In summary, the PAH assemblage in sediment samples W2A10-ST-S07 and W2A10-ST-XXX likely derived from weathered B120 source oil, with an additional, secondary influence from pyrogenic and potential alternative petrogenic sources.

W2A-02 HARBOR VIEW

The Harbor View segment is located east of the entrance to New Bedford Harbor, and is adjacent to the Pope's Beach (W2A-03) segment. Two marsh inlets (Boys Creek and Girls Creek) are located near the boundary between the two segments. A Superfund site, Atlas Tack, is located at the upstream end of Boys Creek. Under contract to the U.S. Environmental Protection Agency (U.S. EPA), Weston Solutions, Inc. collected sediment samples from Boys Creek during the Remedial Investigation at Atlas Tack, and reported concentrations of semi-volatile organic compounds (SVOCs), including PAH, of a minimum of 800 µg/kg total SVOC (0.8 mg/kg) in each sediment sample (U.S. EPA, 1995). The following is a discussion of intertidal sediment samples collected from this segment during the Phase II characterization.

W2A02-MS01 and W2A02-MS02 – Samples Containing Other Oils

The PAH fingerprint of samples W2A02-MS-01 and –MS-02 is compared in Figure G-2a and Figure G-2b, respectively, with that of the same parent PAH compounds in the B120 source oil. Alkylated PAH compounds were not measured in the analyses of W2A02-MS samples but quantitative PAH indicators are summarized in Table G-3 for Sample W2A02-MS-02. There are important differences between the sample fingerprints and that of the spilled oil. The figure shows that phenanthrene was detected in the B120 oil and both of these samples, at a relatively similar concentration to chrysene in the two sediment samples. That distribution is similar to that in several combustion products. Low concentrations of 2-ringed PAH and other 3-ringed PAH other than phenanthrene is consistent with some pyrogenic sources, although a contribution by a weathered petrogenic source cannot be discounted.

Acenaphthylene is also present in W2A02-MS02 samples at a concentration greater than that of the other 3-ringed PAH compounds but is absent in the B120 source oil. It is unlikely that a source contributes solely acenaphthylene and no other 2- or 3-ringed PAH. In addition, there are other fuel oils that contribute acenaphthylene in a pattern similar to the observed fingerprint.[10] This fingerprint difference with the spilled oil is further evidence that another source or sources other than the B120 oil account for the PAH assemblage in these samples. However, the presence of acenaphthylene is not characteristic of the B120 source oil.

The hydrocarbon pattern of the 4-, 5-, and 6-ring PAH (fluoranthene through benzo[*g,h,i*]perylene) in Figure G-2 is particularly characteristic of PAH from combustion sources. In combustion sources, fluoranthene is typically present in similar or greater concentrations than pyrene, and both are present in higher concentrations than chrysene and benz[*a*]anthracene. The relatively high concentration of the 4-, 5- and 6-ringed PAH compounds compared to these 2-, and 3-ringed PAH compounds is consistent with a dominant combustion source.

Therefore, a combustion source accounts for the 4-, 5-, and 6-ring PAH fingerprint despite similarities of some of the "parent" PAH pattern with that of B120 oil. Known environmental process cannot alter the relative proportion of fluoranthene and pyrene, or the relative proportion of 4-ringed PAH to 6-ringed PAH in the B120 oil to yield the observed fingerprint of the samples. There is virtually no evidence of B120 source oil in the higher molecular weight PAH range in these two samples.

In summary, the PAH assemblage in sediment samples W2A02-MS01 and -MS02 are derived from a dominant pyrogenic source but are also influenced by an alternative petrogenic (i.e., non-B120 oil) source.

W2A02-P2-M01 through M03 – Samples Containing Other Oils

As seen in Figure G-3 and Table G-3, there is no correspondence between the major hydrocarbon components of these samples and the B120 source oil sample. In particular, the 4-, 5-, and 6-ring PAH distribution of the samples is dominated by PAH compounds characteristic of a combustion source. In addition, acenaphthylene, a 3-ring compound characteristic of many petrogenic sources, is absent in B120 oil but found in all of these sediment samples. An alternative petrogenic source other than B120 oil is possible because small amounts of acenaphthylene are present in conjunction with naphthalenes and a dissimilar alkylated PAH distribution than that of B120 oil. Combustion sources also can contribute small quantities of 2-and 3-ring PAH (Kado et al., 1996; National Park Service, 1997; Conde et al., 2005). Overall, PAH compounds in these samples are dominated by a combustion source with a small contribution by a petrogenic source that is not B120 oil.

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[10] *Pyrogenic sources can also contribute small quantities of acenaphthylene and other parent 3-ring compounds, but a petrogenic sources is more likely in this case because of the overall distribution.*

Sample W2A02-P2-M-02 contained the highest total PAH concentration of these three samples. Figure G-4 displays the fingerprint of B120 oil normalized[11] to the concentrations of C-4 phenanthrenes/anthracenes in sample W2A02-P2-M-02. This alkylated PAH group is persistent relative to less alkylated phenanthrene/anthracene groups and has relatively low volatility compared with 2-ring and other 3-ring PAH compounds. Therefore, if B120 oil had been present in this sample, the 2- and 3-ring PAH compounds would be unlikely to be found at a concentration higher than the observed C-4 phenanthrene/anthracene concentration. This "normalization" in Figure G-4 shows that not only does the B120 source oil have a dissimilar distribution than the sample, but that its potential contribution could only be minor. A combination of combustion and an alternative petrogenic source than B120 oil account for the entire hydrocarbon distribution in these samples.

Figures G-5, G-6, and G-7 compare the ion chromatograms for the three characteristic hydrocarbon biomarkers (m/z 191, 217, 218) in sample W2A02-P2-M-03 and the B120 source oil. In all cases, the biomarker distribution for the sample differs from that for the B120 oil, even discounting the left-hand portion of the distribution, which can be subject to interferences. The difference is consistent with the finding of acenaphthylene in all samples, other variations in the 2- and 3-ring PAH distributions, and the dominance of combustion PAH. The detailed forensic analysis corroborates the conclusion that there is no evidence that B120 oil contributes in any way to the total PAH concentration. The distinctly different distribution of biomarkers and alkylated PAH confirms that B120 oil is not the source of PAH.

In summary, the PAH assemblage in sediment samples W2A02-P2-M01, - M02, and -M03 are derived from a dominant pyrogenic source, but are also influenced by an alternative petrogenic (i.e., non-B120 oil) source.

W2A02-092905-01 and W2A02-092905-02 – Samples Containing Other Materials

A "black sediment" sample was collected from the Harbor View area on September 29, 2005. One sample was analyzed solely for parent PAH (W2A02-09205-01). Based on those results, additional PAH analyses were conducted on a split sample W2A02-092905-02. Figure G-8 compares the PAH results with those of the B120 oil and a sediment sample from W3A05 that contained almost no petrogenic material. A clear difference between B120 oil and the sediment samples is the low concentration of "parent" PAH relative to alkylated PAH in the B120 oil, which tend to maximize in concentration as C2-alkylated forms. Samples dominated by combustion PAH tend to have relatively high concentrations of "parent" PAH and then declining concentrations with increasing alkylation; a pattern most clearly seen with W3A05-P2-LIT-02 in Figure G-8. The W2A02 samples contained some petrogenic and substantial pyrogenic characteristics, but few that resembled B120 oil (Table G-3).

As shown in Figure G-9, the W2A02 sample was dominated by terrestrial plant material, indicated by elevated concentrations of odd-numbered *n*-alkanes in the range *n*-C_{15} to *n*-C_{31}, rather than the approximately equal concentration of even- and odd-numbered n-alkanes

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[11] *PAH concentrations in the B120 oil were normalized for comparison with each sample by dividing by the ratio of the C4-phenanthrenes/anthracenes concentrations in the B120 oil and each sample. This method enables samples of widely varying concentrations in different matrices (oil and sediment) to be placed into perspective. In this case, the normalization allows an evaluation of the maximum potential contributioin of B120 oil to the total PAH content in sediment sample W2A02-P2-M-02.*

characteristic of petroleum sources (e.g., Figure G-1). These alkane analyses indicated that petrogenic hydrocarbons could be present at no more than trace quantities, especially considering that two petroleum indicators, n-C_{18} and phytane, are undetected in this sample (Figure G-9). The relatively high percentage of parent PAH compounds in the Harbor View sample distinguishes it as primarily composed of combustion-derived material, although it does contain petrogenic material unrelated to B120 source oil (Figure G-8). The PAH pattern in this Harbor View sample and the B120 oil differ substantially, as follows:

- The Harbor View sample contains relatively high concentrations of parent 4-ringed PAH (e.g., pyrene, benzo[a]pyrene, chrysene) compared with alkylated PAH compounds. The PAH fingerprint is generally consistent with primarily a substantial contribution from a combustion source (e.g., soot from burned fossil fuels such as oil and coal, or biomass fuels such as wood).

- Relatively high concentrations of 5-ringed and 6-ringed PAH compounds (benzo[*b*]fluoranthene and higher) compared with alkylated PAH compounds, which is also typical of hydrocarbons with a combustion-type signature rather than the B120 oil.

- Dominant C1-fluorenes and C1-phenanthrene/anthracenes compared to dominant C2-fluoranthenes and C2-phenanthrenes/anthracenes for those two PAH groups, which is a change that cannot be accounted for by weathering processes.

- Increased ratio of the summed concentration of fluoranthene and pyrene (F&P) to that of C_{30}-hopane compared with this ratio in the B120 source oil (F&P:C_{30}-hopane ratios of 28 and 8.9, respectively). The F&P:C_{30}-hopane ratio in the Harbor View sample is three times higher than the F&P:C_{30}-hopane ratio in the source oil, but this ratio should decline with weathering because fluoranthene and pyrene are less stable than C_{30}-hopane. The results are consistent with the Harbor View sample having a different source that contained less C_{30}-hopane than the B120 source oil.

Therefore, chemical analyses indicate that the Harbor View "black sediment" has heavier PAH compounds than the B120 source oil, with a signature consistent with a combustion source, and lighter PAH from a source with a different composition than B120 oil. The source(s) may be dominated by biomass (e.g., wood/plants) rather than fossil fuels, possibly wood ash from a beach fire. Although the Harbor View material likely contains more than one source material, the PAH signature cannot be accounted for by weathering of B120 oil based on known processes, confirming that the Harbor View sample cannot be composed of the B120 oil.

In summary, the PAH assemblage in W2A02-092905-01 and -02 are most likely derived from burned fuels unrelated to the B120 oil and other pyrogenic sources.

W2A-03 POPE'S BEACH

This shoreline segment is located adjacent to the Harbor View segment and the Atlas Tack Superfund site, and is composed of mixed sand and gravel beach, and salt marsh.

W2A03-LIT-02 – Sample Containing Other Oils

The "parent" PAH distribution of this sample is shown in Figure G-3; other characteristics are summarized in Table G-3. It was clearly dominated by combustion-derived PAH because: 1) the FL:PY ratio was greater than 1.0 (source oil FL:PY ratio is 0.14); 2) there was a consistent decline in concentrations from "parent" PAH to increasingly alkylated forms; and 3) relatively high concentrations of both 4-, 5-, and 6-ring PAH were present compared with concentrations of 2-ring PAH. The difference in the phenanthrene:anthracene ratio is not consistent with known environmental weathering processes. The low levels of 2-ring PAH compounds, including the presence of acenaphthylene, are consistent with a minor contribution from a petrogenic source, or petrogenic source unrelated to B120 oil.

In summary, the PAH assemblage in sediment sample W2A03-LIT-02 is dominated by a pyrogenic source with potential contribution from a petrogenic source other than the B120 source oil.

W2A03-P2-M-03 – Sample Containing Other Oils

Sample W2A03-P2-M-03 contains similar characteristics of the W2A03-LIT-02 sample (Figure G-3; Table G-3) but more information was available because this sample was submitted for additional forensics tests, including analysis of alkylated PAH. Like W2A03-LIT-02, this sample contains similar proportions of fluoranthene and pyrene, although the FL:PY ratio is slightly <1. The sample is distinguished by a substantially higher proportion of certain 5- and 6-ring PAH than those from other sampling locations.

In summary, the PAH assemblage in sediment sample W2A03-P2-M-03 is dominated by a pyrogenic source with a potential contribution from a petrogenic source other than the B120 source oil.

W3A05 – ROUND HILL

This segment is located in Dartmouth, and consists primarily of a small public beach with parking access.

W3A05-P2-LIT-02 – Sample Containing Virtually No Oils

Table G-3 shows that there is no indicators suggesting a correspondence between the major PAH components of the sample and the B120 oil sample. The fact that 18α-oleanane is not detected in this sample, which is the only shared characteristic with B120, is inconsequential because oils containing 18α-oleanane are not common. The 4-, 5-, and 6-ring PAH distribution of the sample is dominated by PAH compounds characteristic of a combustion source, including similar proportions of fluoranthene and pyrene (Figure G-3). In addition, acenaphthylene, a 3-ring compound characteristic of many petrogenic sources and also contributed in small amounts by combustion sources, is absent in B120 oil but found in this sediment sample (Figures G-3 and G-8).

As previously discussed, Figure G-8 illustrates how the signature of this sample is almost entirely consistent with pyrogenic, and not petrogenic sources. The relatively high concentrations of "parent" 3- and 4-ringed PAH and then declining concentrations with increasing alkylation is consistent for the series of fluorenes, phenanthrene/anthracenes, fluoranthenes/pyrenes, and benz[*a*]anthracenes/ chrysenes.

There is a small potential for naphthalenes from a petrogenic source, although some pyrogenic sources contain naphthalenes. If some of the naphthalenes observed in Figure G-8 for sample

W3A05-P2-LIT-02 derive from a petrogenic source, they must be trivial given the pyrogenic character of the other PAH series, and the fact that C_{30}- and C_{29}-hopane are undetected. Not only are these two compounds undetected but the entire biomarker ion chromatograms for terpanes and steranes are nearly devoid of compounds, suggesting that any contribution from a petrogenic source is trivial in this particular sample. Contributions almost exclusively from combustion sources account for the near absence of biomarkers, the presence of only small amounts of acenaphthylene and other low molecular weight PAH, and the dissimilar alkylated PAH distribution to that in the B120 source oil.

In summary, the PAH assemblage in sediment sample W3A05-P2-LIT-02 is almost exclusively derived from pyrogenic sources.

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Table G-1. Summary of sediment samples selected for forensic evaluation

Sampling Location	"Parent" PAH Analysis	Forensic PAH Analysis	TPH Chromatogram	Biomarker Analysis	Quantitative Alkane analysis
W2W-10 Long Island and Causeway South (collected July 2004)					
W2A10-ST-S09	•	•	•	•	
W2A10-ST-XXX	•	•	•	•	
W2A-02 Harbor View					
W2A02-MS01 and MS02	•				
W2A02-P2-M01	•	•	•	•	
W2A02-P2-M02	•	•	•	•	
W2A02-P2- M03	•	•	•	•	
W2A02-092905-02		•	•	•	•
W2W-03 Pope's Beach					
W2A03-LIT-02	•				
W2A03-P2-M-03	•	•	•	•	
W3A-05 Round Hill					
W3A05-P2-LIT-02	•	•	•	•	
B-120 Source Oil		•	•	•	•

Table G-2. Summary of PAH indicators by source type

PAH Indicator	**B120 Source Oil**	B120 Weathered Oil	Other Petrogenic Sources	Pyrogenic Source (including tars/creosote)
% Parent Naphthalene	3.6% - 2.8%	0% - 12%	Low	Low potential due to losses during pyrolysis but source-dependent
% Parent Benzothiophene[1]	2.5% - 4%	0% - 14%	Low	
% Parent Fluorene[1]	7.7% – 8.1%	0% - 12%	Low	
% Parent Phenanthrene + Anthracene[1]	7.2% – 7.6%	0% - 12%	Low	High (>50%)
% Parent Dibenzothiophene[1]	8.0% – 8.5%	0% - 12%	None to moderate	None to moderate
% Parent Fluoranthene + Pyrene[1]	8.7% - 9.2%	0% - 25%	Low	High (>60%)
% Parent Chrysene[1]	9.1% - 9.6%	0% - 25%	Low	High (>50%)
% Parent 4-, 5-, and 6-Ring PAH [2]	14% - 14.7%	10% - 40%	Low	High (>75%)
% C_{30}-hopane of total PAH	0.13% - 0.16%	0.1% -1.5%	<2%	No hopane to low
Fluoranthene / Pyrene Ratio [3]	0.14 – 0.16	0.1 - 0.8	<0.8	0.8 to 1.4
(Fl + Py) / C_{30}-hopane Ratio [4]	8.6 – 9.8	2 – 10	Unknown – 10	No hopane to high
C_{30}-hopane / C_{29} hopane Ratio[5]	1.9 – 2.1	1 - 2.4	No hopane to uncertain	No hopane to uncertain
Acenaphthylene Present? [6]	No	No	Low potential	None to low potential
18α-Oleanane Present? [7]	No	Yes	Yes – source specific	Possible – source specific

[1] Percentages of parent PAH compounds relative to measured PAH parent plus alkylated PAH concentrations for different PAH series (excluding naphthobenzothiophenes, which not consistently reported in all analysis of these sediments)

[2] Fluoranthene, pyrene, benz[a]anthracene, chrysene, benzofluoranthenes, benzo[e]pyrene, benzo[a]pyrene, indeno(1,2,3-c,d)pyrene, dibenzo(a,h)anthracene, and benzo(g,h,i)perylene.

[3] Pyrene dominates in petrogenic sources; fluoranthene and pyrene are approximately equal ind pyrogenic sources

[4] Expected to decrease over time, as fluoranthene and pyrene weather, while hopane does not appreciably weather.

[5] Somewhat variable but source-specific and not expected to be subject to weathering

[6] PAH compound associated with most oils and a low potential with combustion products

[7] Biomarker specific to fossil fuels derived from angiosperms (flowering plants) and is therefore from oil that is Cretaceous age or younger.

Table G-3. Summary of PAH indicators used to support or reject evidence of B-120 PAH contributions

PAH Indicator	W2A10-ST-		W2A02-					W2A03-		W3A05-P2-	**B-120**
	S07	XXX	MS02	P2-M01	P2-M02	P2-M03	092905-02	LIT-02	P2-M-03	LIT-02	**Source oil**
% Parent Naphthalene	9	11	N/A	4	20	21	5	N/A	18	17	**4**
% Parent Benzothiophene[1]	11	14	N/A	2	11	12	3	N/A	ND	ND	**3**
% Parent Fluorene[1]	5	6	N/A	14	32	25	13	N/A	12	63	**8**
% Parent Phenanthrene & Anthracene[1]	4	6	N/A	41	54	55	40	N/A	46	70	**7**
% Parent Dibenzothiophene[1]	3	4	N/A	16	31	21	15	N/A	21	41	**8**
% Parent Fluoranthene & Pyrene[1]	17	23	N/A	61	74	72	65	N/A	66	76	**9**
% Parent Chrysene[1]	13	13	N/A	39	53	47	48	N/A	52	65	**9**
% Parent 4-, 5-, and 6-Ring PAH [2]	30	36	84 [3]	69	81	82	75	76 [3]	79	84	**15**
% C_{30}-hopane of total PAH	1.1	1.2	N/A	0.6	0.3	0.3	1.85	N/A	1.1	No hopane	**0.15**
Fluoranthene / Pyrene Ratio	0.74	0.79	1.42	0.86	1.03	0.84	0.94	1.35	1.00	1.28	**0.14**
(Fl + Py) / C_{30}-hopane Ratio	10.5	7.5	N/A	35	87	72	28.6	N/A	19	No hopane	**8.9**
C_{30}-hopane / C_{29} hopane Ratio	1.14	1.21	N/A	0.86	1.03	0.84	1.4	N/A	1.02	No hopane	2.0
18α-Oleanane Present?	Yes	Yes	N/A	No	Yes	Yes	Yes	N/A	No	No	No
Acenaphthylene Present?	Yes	Yes	N/A	Yes	Yes	Yes	Yes	N/A	Yes	Yes	No
Substantial biomarker ion match?	Yes	Yes	N/A	No	No	No	No	N/A	No	No	–

Shaded cells indicate values that provided evidence against a B-120 source contribution, or for a mixture of sources. Only samples WA210-ST-S07 and –XXX were considered to contain primarily B-120 source oil as a component based on consideration of all PAH indicators as well as review of ion chromatograms. Samples W2A10-ST-S07 and W2A10-ST-XXX contained B-120 (based on quantitative and qualitative indicators) as well as another fossil fuel (based on the 18α-oleanane content). All samples contained combustion-derived PAH compounds as a minor or dominant component.

ND = Not detected N/A = Not applicable (analysis not conducted).

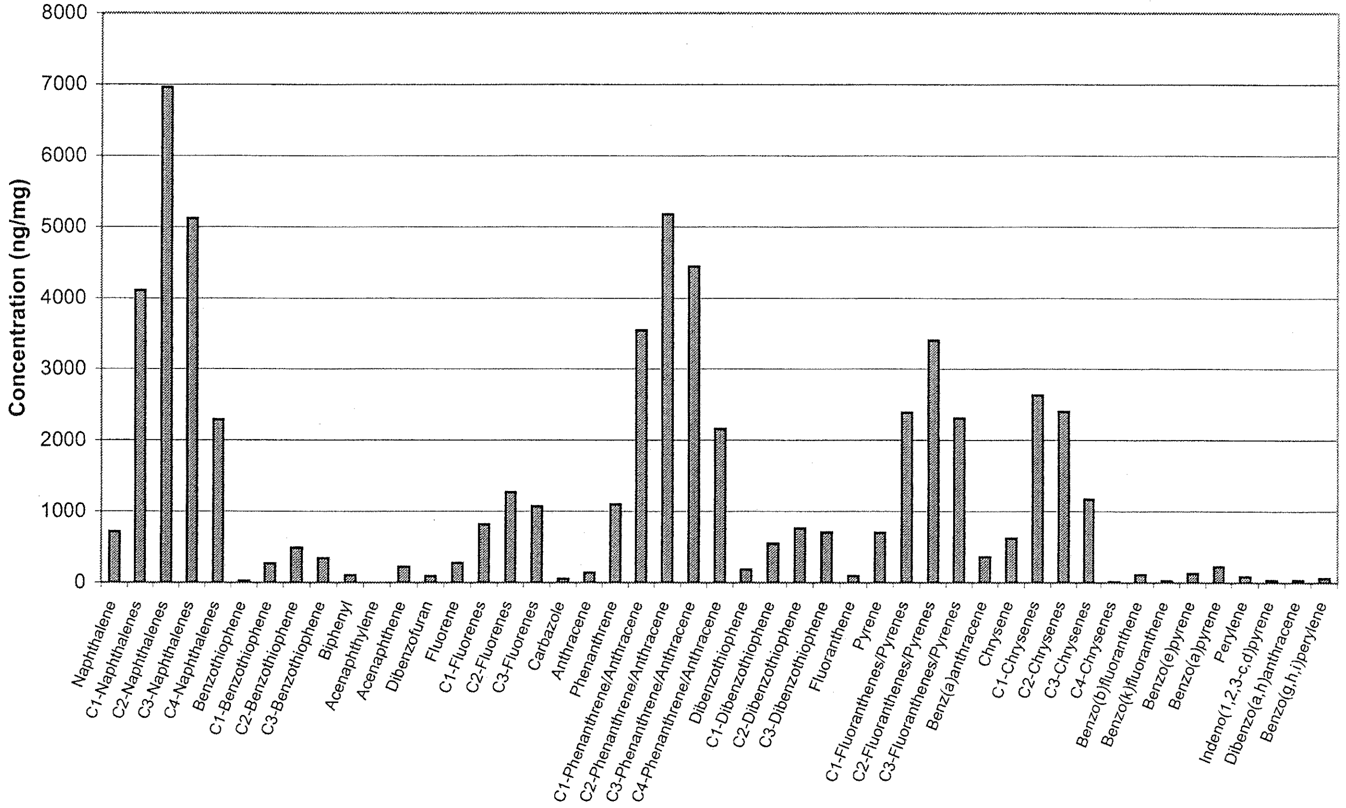
[1] Percentages of parent PAH compounds relative to measured PAH parent plus alkylated PAH concentrations for different PAH series (excluding naphthobenzothiophenes, which not consistently reported in all analysis of these sediments)

[2] Fluoranthene, pyrene, benz[a]anthracene, chrysene, benzofluoranthenes, benzo[e]pyrene, benzo[a]pyrene, indeno(1,2,3-c,d)pyrene, dibenzo(a,h)anthracene, and benzo(g,h,i)perylene.

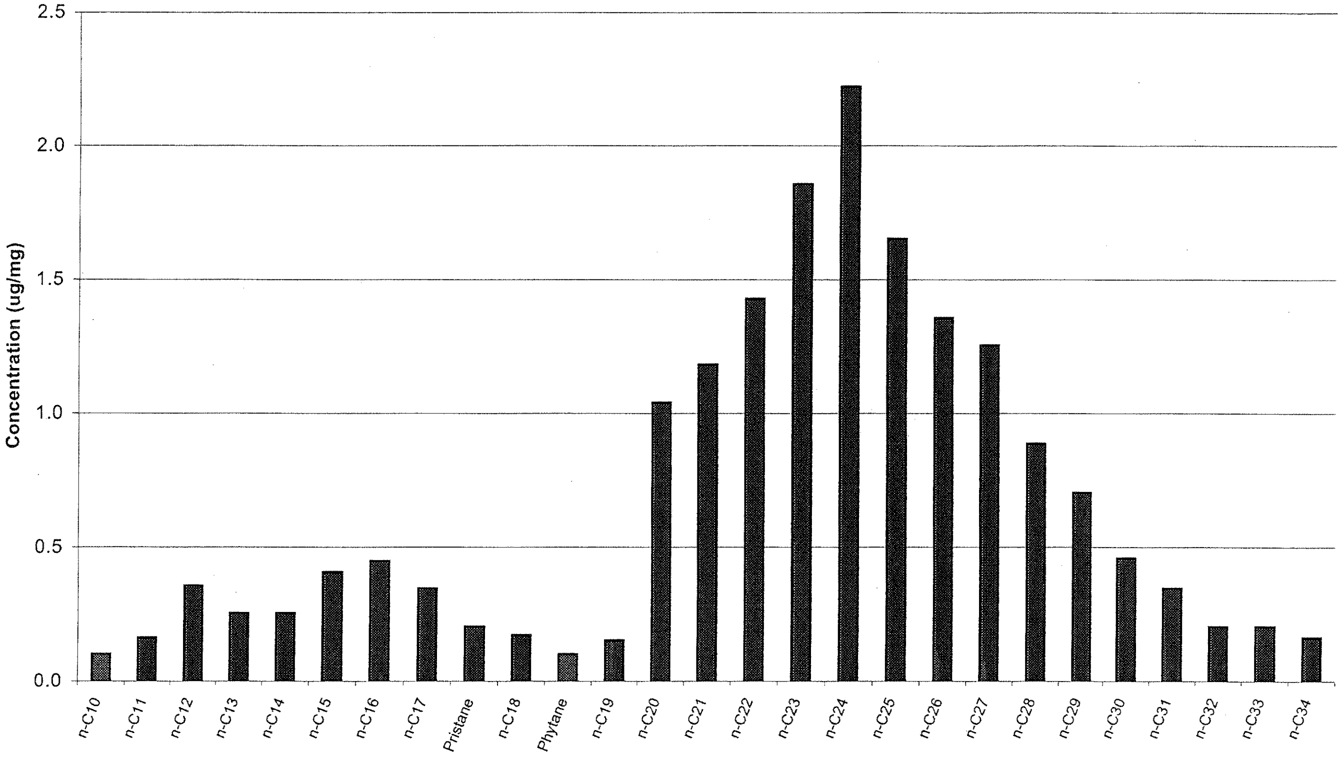
[3] Percent 4-, 5-, and 6-ringed PAH in samples W2A02-MS01 and W2A03-P2-LIT-02 determined solely on the basis of the 16 detected "priority pollutant" parent PAH plus 2-methylnaphthalene. A complete forensic analysis was not conducted on these samples. However, the analysis is still useful because the high content of 4-, 5-, and 6-ringed PAH compounds in these samples (76%-84%) compared with that of 2- and 3-ringed parent PAH content is strongly suggestive of a dominant combustion origin, even without alkylated PAH results other than 2-methylnaphthalene.

Figure G-1. Representative Hydrocarbon Distribution in B120 Oil [a]

PAH and Related Compounds



n-Alkanes



[a] PAH and alkane analyses considered representative of those for the eight B120 source oil samples collected and tested.

Figure G-2a. Comparison of W2A02-MS01 with B120 Source Oil

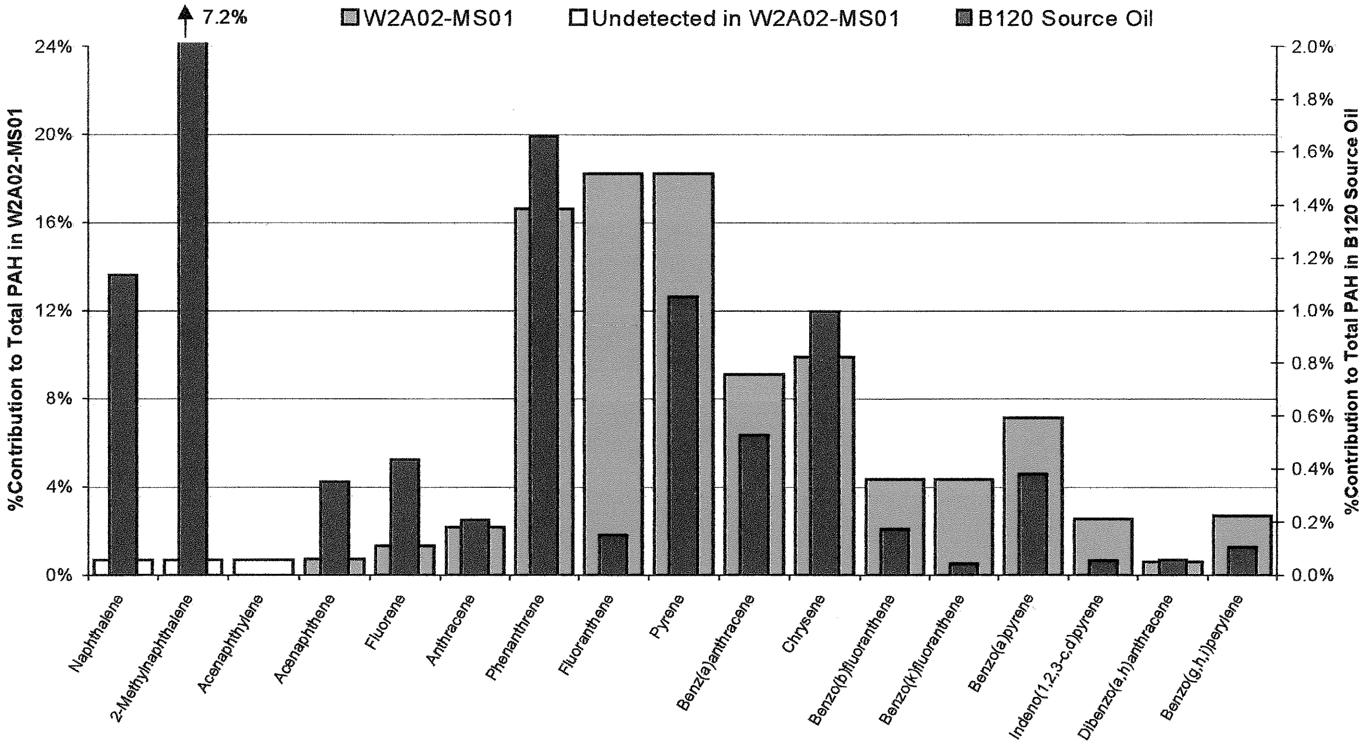


Figure G-2b. Comparison of W2A02 -MS02 with B120 Source Oil

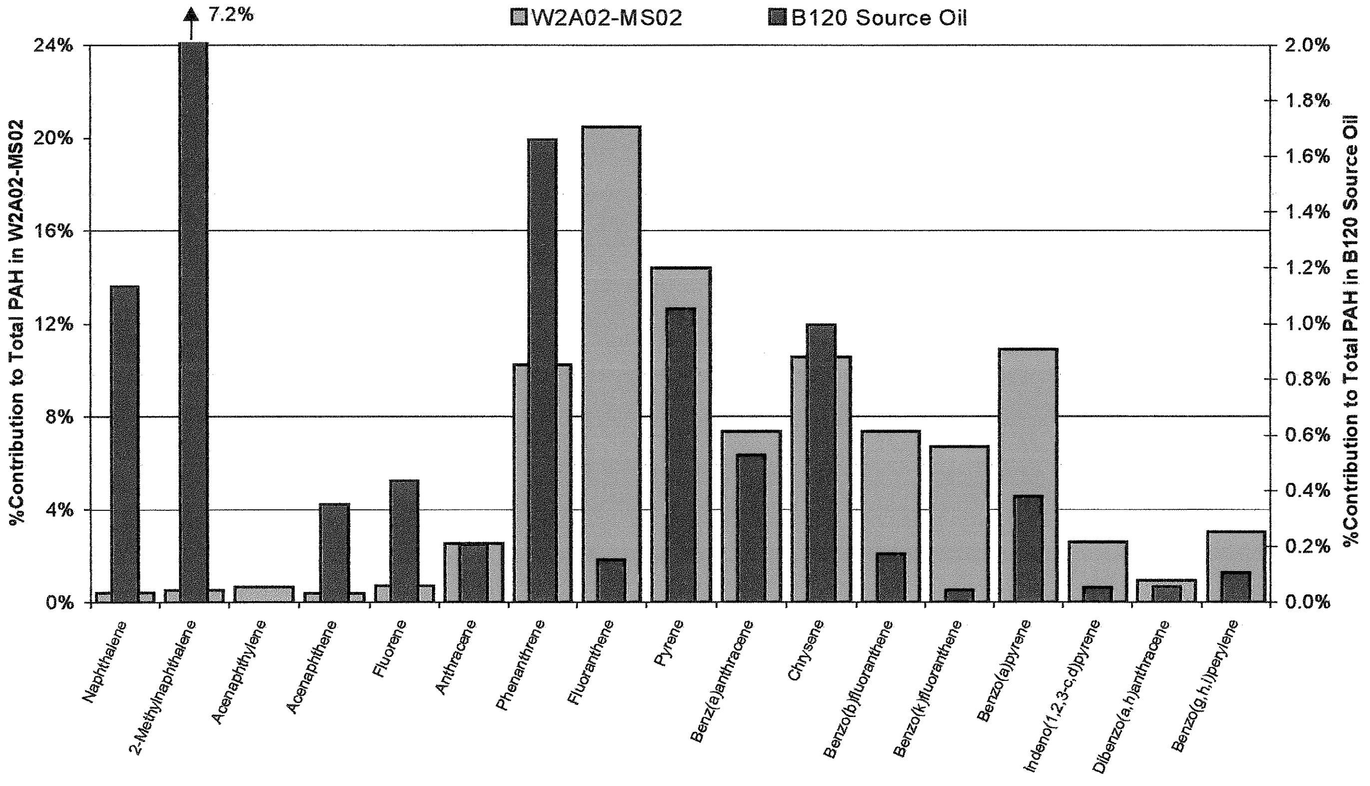
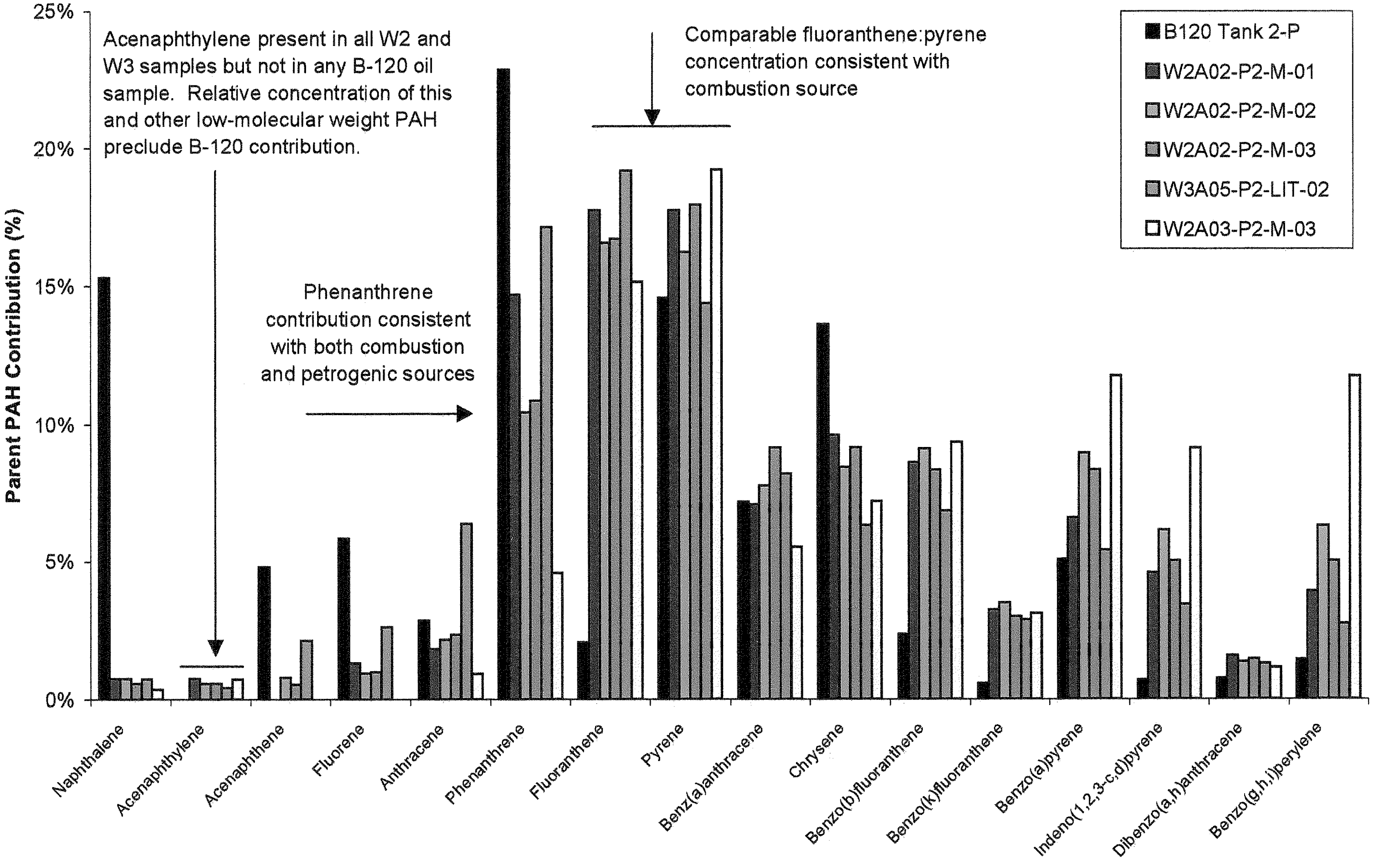


Figure G-3. PAH Fingerprint Comparison of W2A and W3A Sediment Samples and B120 Source Oil



Acenaphthylene present in all W2 and W3 samples but not in any B-120 oil sample. Relative concentration of this and other low-molecular weight PAH preclude B-120 contribution.

Phenanthrene contribution consistent with both combustion and petrogenic sources

Comparable fluoranthene:pyrene concentration consistent with combustion source

Figure G-4. B120 Source Oil Normalized to C4-Phenanthrene Component of W2A02-P2-M-02

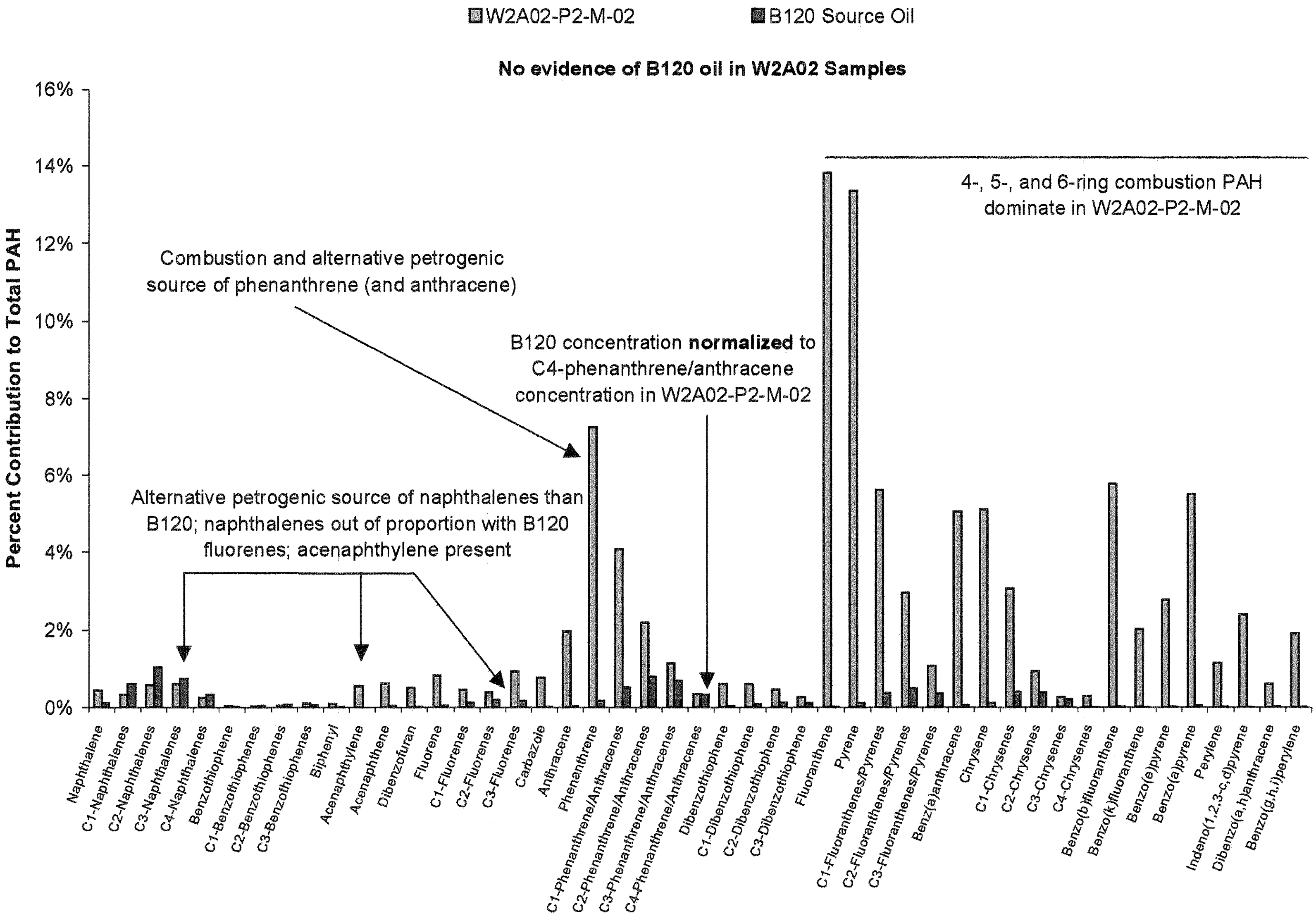
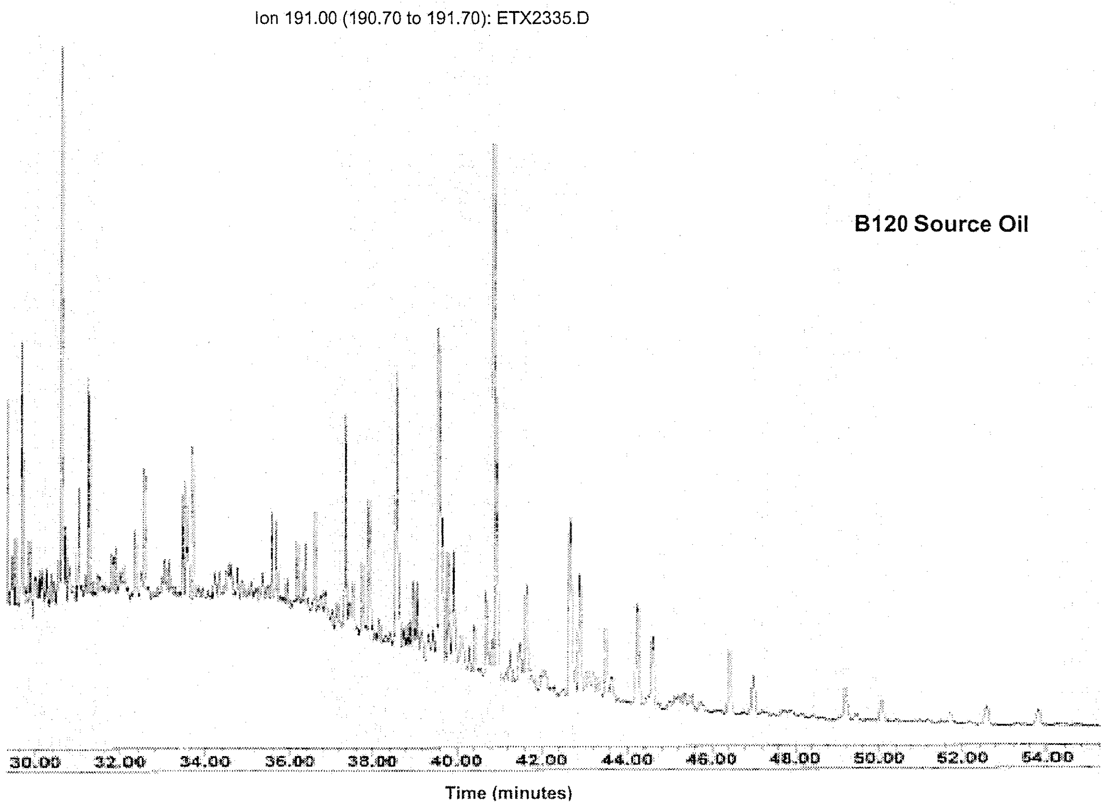


Figure G-5. Comparison of Ion 191 Chromatograms: W2A03-P2-M-03 and B120 Source Oil



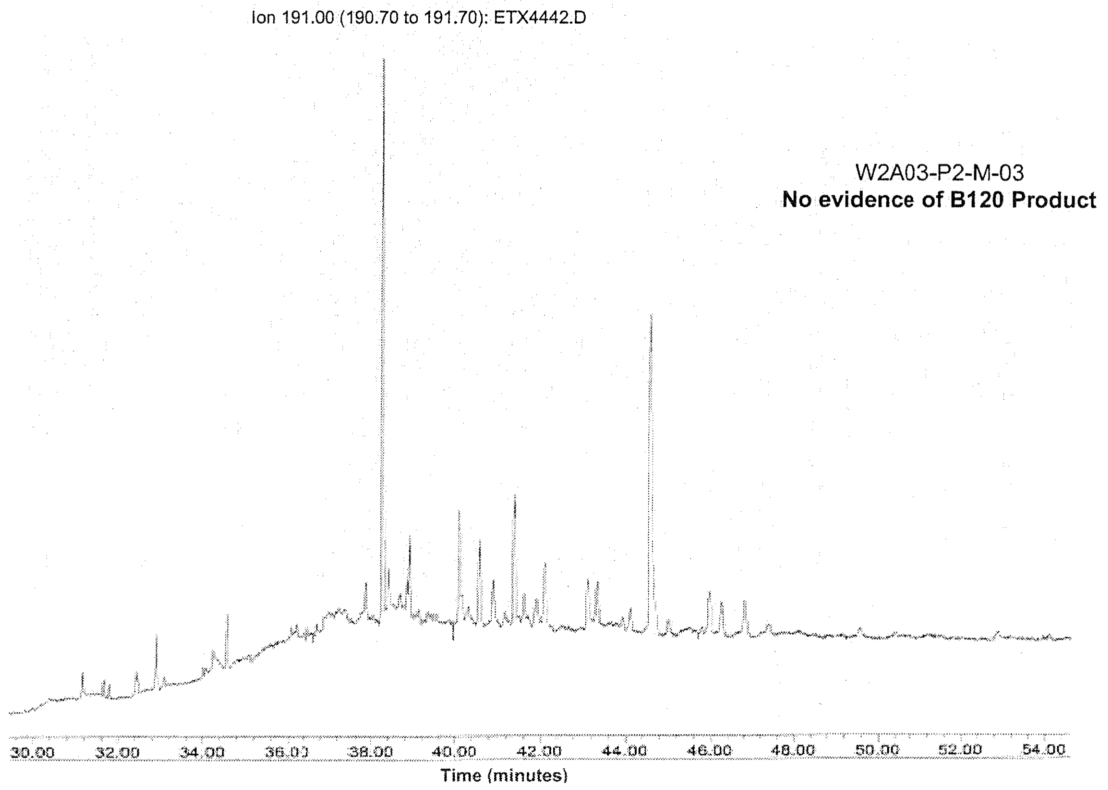


Figure G-6. Comparison of Ion 217 Chromatograms: W2A03-P2-M-03 and B120 Source Oil

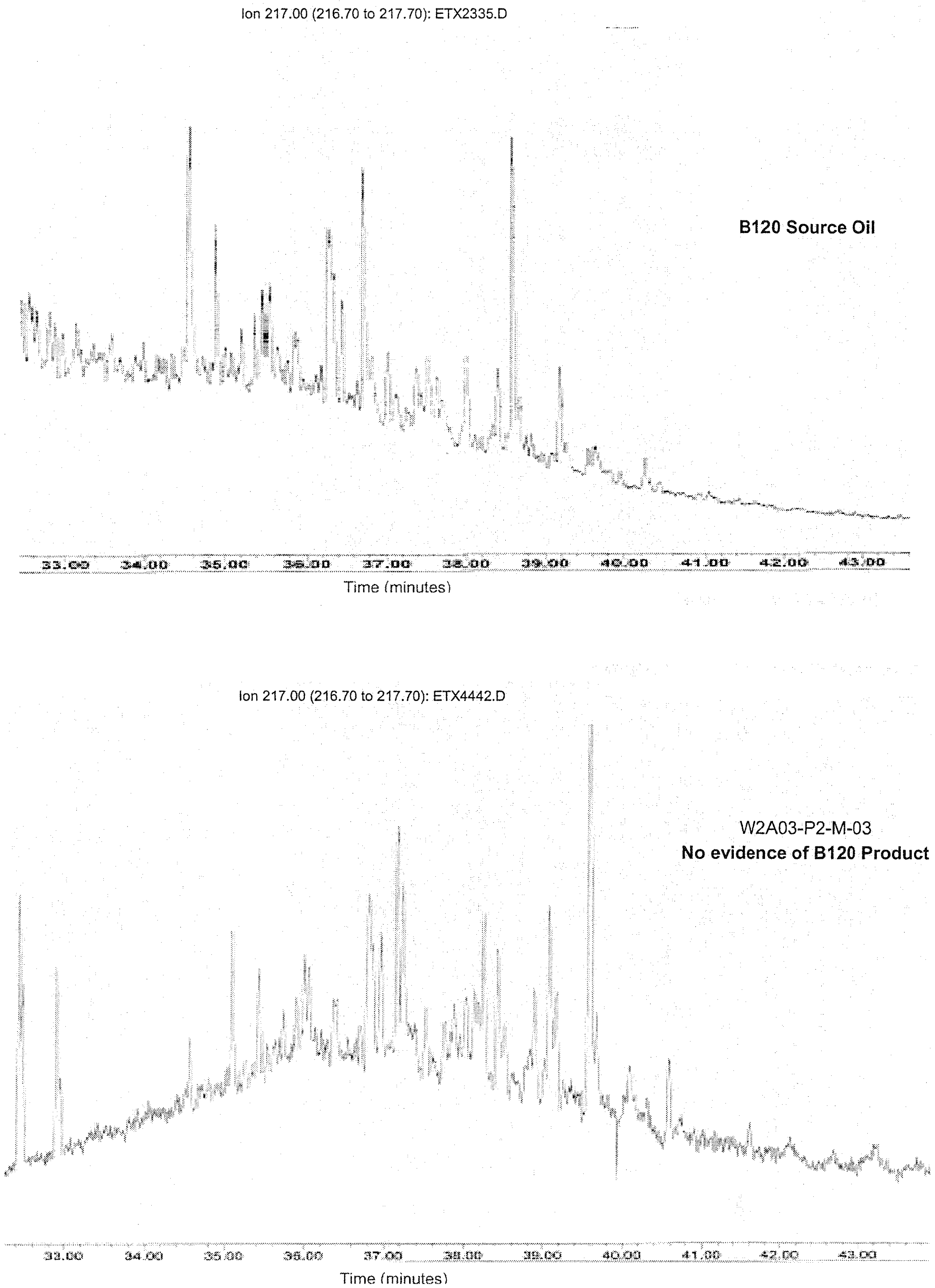
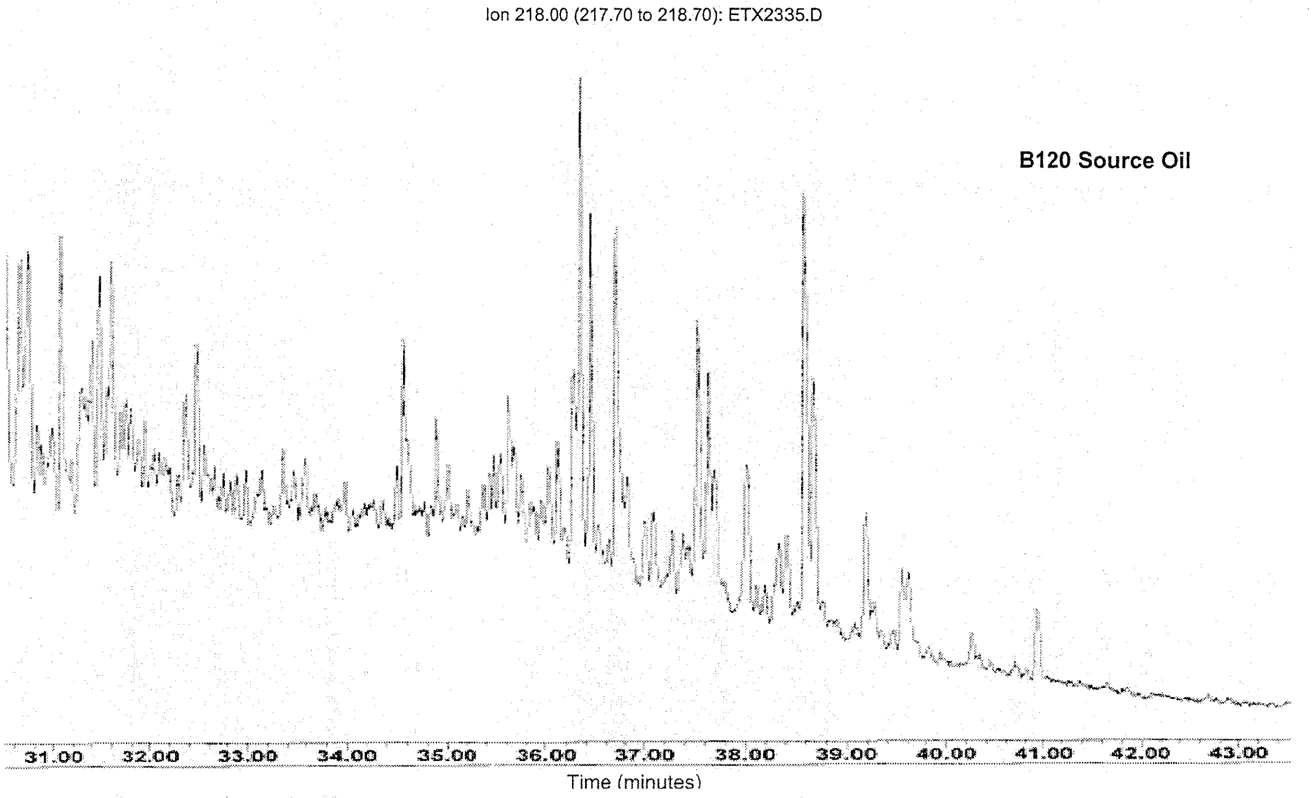


Figure G-7. Comparison of Ion 218 Chromatograms: W2A03-P2-M-03 and B120 Source Oil



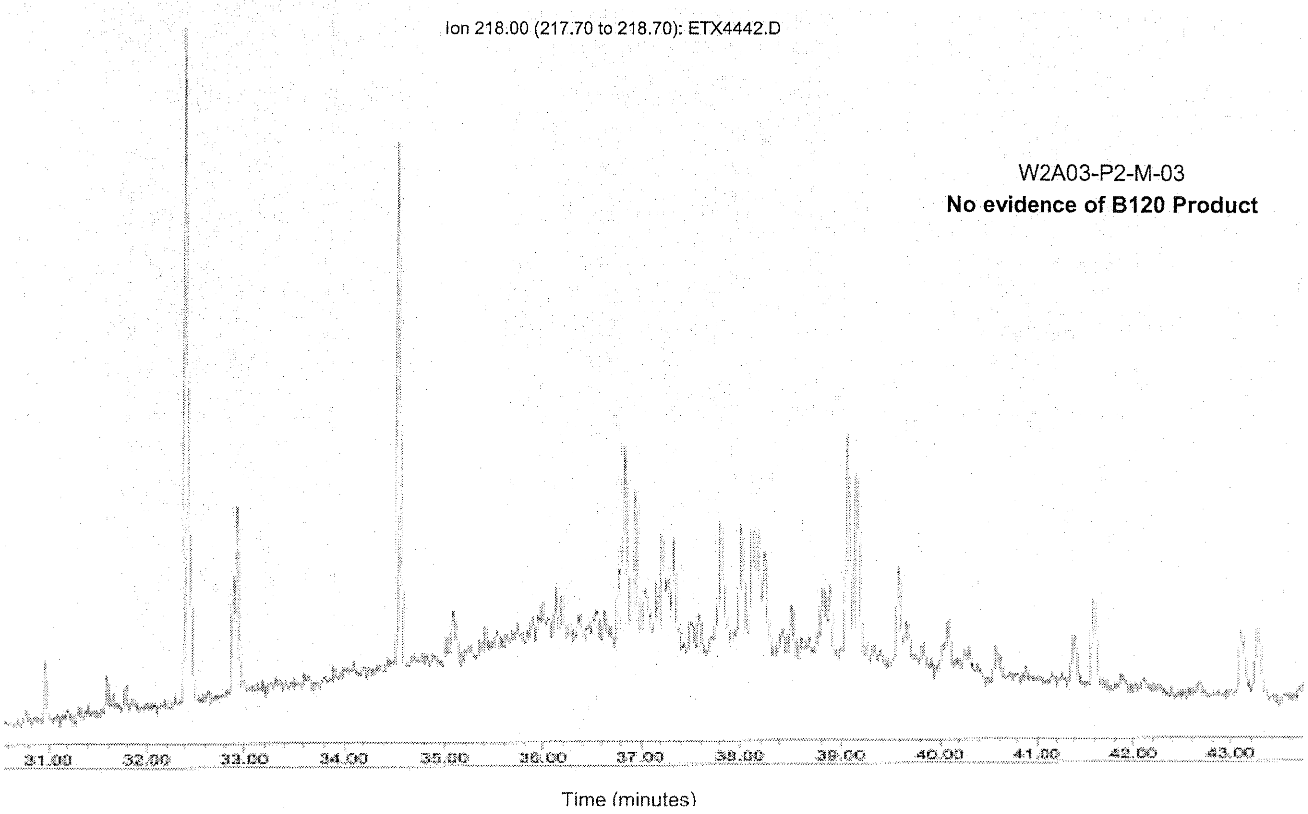
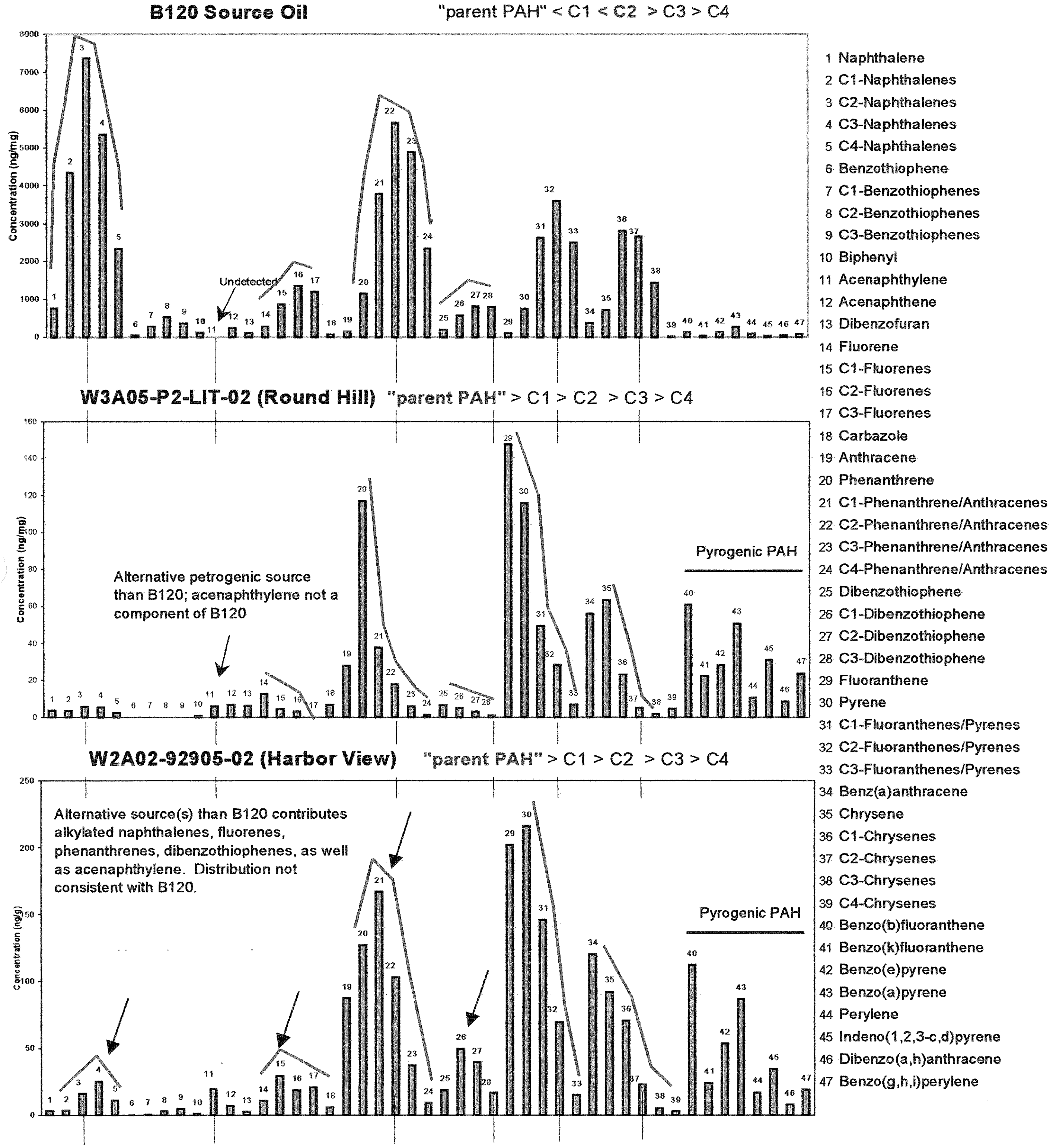


Figure G-8. Comparison of B120 Source Oil and Selected W3A and W2A Sediment Samples



B120 Source Oil "parent PAH" < C1 < C2 > C3 > C4

Undetected

W3A05-P2-LIT-02 (Round Hill) "parent PAH" > C1 > C2 > C3 > C4

Alternative petrogenic source than B120; acenaphthylene not a component of B120

Pyrogenic PAH

W2A02-92905-02 (Harbor View) "parent PAH" > C1 > C2 > C3 > C4

Alternative source(s) than B120 contributes alkylated naphthalenes, fluorenes, phenanthrenes, dibenzothiophenes, as well as acenaphthylene. Distribution not consistent with B120.

Pyrogenic PAH

Note: The red line indicates the change in the distribution of "parent" and alkylated PAH for each PAH group (e.g., naphthalenes, phenanthrenes, chrysenes). Oils tend to have relatively low "parent" PAH concentrations and high alkylated PAH concentrations, peaking for example, in B120 at C2-alkylated forms to give a characteristic bell-shaped curve. In contrast, pyrogenic sources tend to have high "parent" PAH concentrations with consistently declining alkylated PAH concentrations or almost no alkylated PAH.

Figure G-9. *n*-Alkane Distributions in Sediment Sample W2A02-92905-02 from Harbor View