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DEPARTMENT OF ECOLOGY

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November 30, 2022

Tracey Mulhern, Project Geologist Farallon Consulting 1201 Cornwall Ave, Ste 105 Bellingham, WA 98225 tmulhern@farallonconsulting.com

Re: Comments on Multi-Increment Sampling and Cleanup Action Report

- Site Name: Grange Supply Chehalis Cenex
- Site Address: 153 NW State Ave, Chehalis, Lewis County, WA 98532-1538
- Facility/Site No.: 1161
- Cleanup Site ID: 2882
- Agreed Order No.: DE00TCPSR-713

Dear Tracey Mulhern:

Thank you for submitting the multi-increment sampling (MIS) and cleanup action report (report) for our review.¹ The Washington State Department of Ecology (Ecology) has the following comments on the report:

General Comments

- 1. <u>Sections 3.0 and 4.0, Multi-Increment Sampling</u>: Ecology concurs with the methodology that was used for the baseline and confirmation MIS and decision units (DUs).
- Section 5.0, Forensic Sediment Analysis: Ecology appreciates your efforts use an oil-spill source identification method, including biomarkers, to determine whether elevated total extractable hydrocarbons (TEH) concentrations detected in the post-excavation confirmation sediment sample are associated with oil product released as a result of the May 2, 2016 CHS warehouse fire or are a result of historical stormwater runoff. As noted by

¹Farallon Consulting, *Multi-Increment Sampling and Cleanup Action Report, Chehalis Wetland Cleanup, Northwest Liberty Place and West Main Street, Chehalis, Washington*, June 13, 2019.

Wang et al. (2006), biological markers or biomarkers are one of the most important hydrocarbons groups for chemical fingerprinting because they can be found in crude oils, petroleum products, rocks, and sediments. Biomarkers show little or no changes in structures from their parent organic molecules or biogenic precursors and they retain all or most of the original carbon skeleton of the original natural source.² However, other than referring to the laboratory analyses reports in Appendix C, the forensic analysis in Section 5.0 did not discuss the biomarker results in any significant detail nor did it explain how these data supported the report's conclusions listed in the five bullet points on page 5-1:

- Product sample HD16154 showed a similar fingerprint to product sample HL15172.
- Product sample AA169094 showed a similar fingerprint to product sample AB16113.
- Neither of the bulk sediment samples (collected in DU1 from the 0- to 4- and the 12to 16-inch depth intervals) showed distinct similarities to the four product samples.
- The bulk sediment sample collected in DU1 from the 0- to 4-inch depth interval showed a fingerprint similar to the duplicate bulk sediment sample collected in DU1 from the 0- to 4-inch depth interval.
- The bulk sediment sample collected in DU1 from the 0- to 4-inch depth interval showed a fingerprint very different from the bulk sediment sample collected in DU1 from the 12- to 16-inch depth interval.

Instead, the report appeared to primarily rely on the polycyclic aromatic hydrocarbon (PAH) data, presented in report Figure 8 (see attached Figure 1). This figure shows bar charts of the PAH distribution for pre- and post-excavation samples from multi-increment sampling decision unit #1 (DU-1) to support the claim that the post-excavation sample is from a different source than the contaminants released from the warehouse fire.

3. Therefore, Ecology conducted a detailed review of the biomarkers laboratory analyses reports contained in Appendix C of the report.³ A data summary is shown in Table 1 and is discussed in the sections below.

² Zhendi Wang, Merv Fingas, Chun Yang, and Jan H. Christensen, *Crude Oil and Refined Product Fingerprinting: Principles*; <u>in</u>: Robert D. Morrison and Brian L. Murphy, Editors, <u>Environmental Forensics</u>, <u>Contaminant Specific</u> <u>Guide</u>, Chapter 16, pp. 339-407, Elsevier, 2006.

³ Pace Analytical Energy Services (Pace), (C8-C40) Semi-Quantitative Molecular Characterization by GC/MS – full scan mode, laboratory reports number 27832 and 18133, dated October 10, 2018.

Data Review - Biomarkers

Table 1 provides a summary of the laboratory data for selected biomarker compounds and groups and the diagnostic ratio calculations that were done to aid in interpreting the results. The table includes selected results for compounds from six biomarker groups (isoparaffins, bicyclanes, terpanes, steranes, triaromatic steranes, and monoaromatic steranes). Each biomarker group has an associated ion mass to charge ratio (m/z). For example, isoparaffins have an m/z of 113 atomic mass units. Table 1 only includes biomarker groups that had published diagnostic ratios in Wang and Christensen (2006) or Kienhuis et al. (2016) or had results above the laboratory reporting limit for the MI DU-1 samples.⁴

Diagnostic ratios are one of the traditional methods used for environmental forensics evaluations for spill/source identification, and oil correlation and differentiation (Wang and Christensen, 2006). This is because the comparison of diagnostic ratios minimizes concentration effects, induces a self-normalizing effect on the data, and in general provides a more direct analysis of the target biomarker distribution between samples.

As summarized by Wang and Christensen (2006), comparison of biomarker distribution involves the following steps:

- Whether target biomarkers detected in spill samples can be found in the same defined carbon range of suspected source candidates.
- Whether the distribution patterns and profiles of biomarkers are matching.
- Whether the abundances of target biomarkers are matching.
- Whether there are any unique or unknown biomarker compounds.
- Whether the diagnostic ratios of the major biomarkers are matching.

However, Wang et al. (2006) note that the final conclusion or whether a spill sample and suspected source is a match should rely on a "multi-criteria approach" (analysis and evaluation of more than one group of petroleum compounds; for example, terpanes, steranes, PAHs, and alkanes).

⁴ Zhendi Wang and Jan H. Christensen, 2006, *Crude Oil and Refined Product Fingerprinting: Applications; <u>in</u>: Robert D. Morrison and Brian L. Murphy, Editors, <u>Environmental Forensics, Contaminant Specific Guide</u>, Chapter 17, pp. 409-464, Elsevier, 2006, and Kienhuis, P.G.M, Hansen, A.B., Faksness, L., Stout, S.A., and Dahlmann, G., <i>CEN Methodology for Oil Spill Identification*; <u>in</u>: Scott A. Stout and Zhendi Wang, Editors, <u>Standard Handbook of Oil Spill</u> <u>Environmental Forensics</u>, Chapter 14, pp. 685-728, Elsevier, 2016.

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Evaluation Methods

Ecology's evaluation focused on comparing the pre- and post-excavation sample biomarker results to see how similar they are to each other as well as to the four product samples that were analyzed. The product samples consisted of samples of chainsaw oil and chainsaw bar oil because these products made up the largest percentage of materials stored in the warehouse (approximately 38%) at the time of the fire. However, please note that the method used by Ecology is not a substitute for a comprehensive forensic or chemometric analysis.

Wang et al. (2006) was reviewed to understand the types of biomarkers that are likely to be present in lubricating oils (which would include chainsaw oil and chainsaw bar oil). Below is a summary of this information.

In general, lubricating oils (lube oils):

- May be divided into categories according to the type of services and applications, such as motor oil, transmission oil, hydraulic fluid, crankcase oil, cutting oil, turbine oil, heat-transfer oil, electrical oil, and many others.
- Include the carbon range of C₂₀ to C₄₀ and do not generally contain the low boiling fraction of petroleum hydrocarbons. Lube oils are largely composed of saturated hydrocarbons and their gas chromatogram (GC) trace is often dominated by a large unresolved complex mixture (UCM) with few resolved peaks. In lube oils such as hydraulic fluid, the PAH concentrations can be low, while the biomarker concentrations are, generally, high.
- Biomarkers are generally located in the high carbon number end because the refining process has removed low molecular weight biomarkers and has concentrated the high molecular weight biomarkers (for example, *n*-alkanes are usually removed by solvent extraction).
- In general, they contain high levels of target terpane and sterane compounds in comparison with most crude oils and petroleum products.
- Demonstrate significantly lower concentrations of triaromatic (TA) steranes (231 m/z) than crude oils because most aromatic hydrocarbons have been removed during the refining process. None of the four product samples analyzed had measurable TA steranes above laboratory reporting limits.
- Do not or only contain trace levels of monoaromatic (MA) steranes (253 m/z). However, all four product samples contained MA steranes.

- Sesquiterpanes (also known as bicyclanes, 123 m/z) are absent in very light kerosene and in heavy lube oils. However, bunker fuels IFO-180 (an intermediate fuel oil) and HFO-6303 (Bunker C, heavy fuel oil) have relatively high concentrations of sesquiterpanes. Sesquiterpanes are also quite abundant in diesel fuel.
- Lube oil contamination through engine exhaust and through leakage and spillage occurs everywhere. Different types of lube oils and motor exhausts were found to consistently feature distinct terpane distributions.

Microbial degradation is one of the main mechanisms by which oil and oil-related hydrocarbons are degraded from spill sites (Wang and Christensen, 2006). As summarized by Wang and Christensen (2006), biodegradation affects the oil composition in the following ways:

- Smaller hydrocarbons are degraded faster than larger hydrocarbons.
- Straight-chain *n*-alkanes degrade faster than branched alkanes.
- GC-resolved compounds are degraded more than GC UCM.
- Small aromatics are degraded faster than high molecular weight aromatics.
- Increase in alkylation level within their alkylated homologous families significantly decreases susceptibility to microbial attack.
- Microbial degradation is often isomer specific. For example, 2-/3-methyl dibenzothiophene biodegrades at the fastest rate within its isomeric series.
- A general sequence of biodegradation of oil hydrocarbon classes can be summarized as: n-alkanes > benzene, toluene, ethylbenzene, and total xylenes (BTEX) and other monoaromatic compounds > branched and cyclo-alkanes > PAHs (lighter PAHs are more susceptible than larger PAHs) > biomarker terpanes and steranes. This sequence only represents a general trend and does not mean that the more resistant class of hydrocarbons starts to be biodegraded only after the less resistant class is completely degraded.

Data Interpretation - Biomarkers

The following data interpretation comments are based on the data shown in Table 1:

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1. <u>113 m/z Isoparaffins</u>: Isoprenoids are ubiquitous in petroleum compounds and the most common and abundant of these are pristine (Pr) and phytane (Ph).⁵ The relative amounts of pristine and phytane (Pr/Ph ratio) have been used as an indicator of source rock depositional environment – the lower the ratio, the more reducing the depositional environment (Barakat et al., 2019). Also, because aerobic bacteria preferentially consume n-alkanes followed by branched alkanes (such as Pr and Ph), biodegraded oils can be recognized by their Pr/n-C17 and Ph/n-C18 ratios. Low ratios (for example < 1.0) would indicate no or low levels of biodegradation (Barakat et al., 2019). Evaporative weathering does not affect Pr/n-C17, Ph/n-C18, and Pr/Ph ratios because these compounds have about the same volatility (Wang and Christensen, 2006).</p>

Results for isoparaffins were somewhat inconsistent, even between the pre-excavation sample and its duplicate sample. This is evidenced by the fact that two out of seven biomarker results had relative percent difference (RPD) values greater than 50% with minimum and maximum values of 23% and 200%, respectively. In particular, pristine and phytane had RPD values of 44% and 23%, respectively. For non-aqueous field duplicates, it is common to use less than or equal to 50% RPD as a data quality objective.⁶

The inconsistency in the isoparaffin results may be due to removal of <C₂₀ isoalkanes and isoprenoids during the refining process. This group had a total of three calculated diagnostic ratios. Here is a summary of the difference in the ratios between pre- and post-excavation samples:

- The phytane/n-C₁₈ ratio for the post-excavation sample was slightly lower than the lowest ratio calculated for the pre-excavation samples.
- The phytane/n-C₁₆ and pristine/phytane ratios were inconclusive because the ratios for the post-excavation sample were in-between the calculated ratios for the pre-excavation sample and its duplicate.

There were also noticeable differences in the ratios between the four product samples. For example, the phytane/n- C_{18} ratios ranged from 2.46 to 4.16 and the pristine/phytane ratios ranged from 0.73 to 1.09 for the product samples.

⁵ A. O. Barakat, A. R. Mostafa, M. Sh. El-Gayar & M. F. Omar, 2019, *Organic geochemical characterization of crude oils based on alkanes and acyclic isoprenoids distribution*, Petroleum Science and Technology, 37:3, 243-254, DOI: 10.1080/10916466.2018.1539747.

⁶ For example, see: Region 1 – EPA New England, Environmental Data Review Supplement for Region 1 Data Review Elements and Superfund Specific Guidance Procedures. U.S. Environmental Protection Agency, Region 1, New England, EPA Quality Assurance Unit & TechLaw Environmental Services Assistance Team (ESAT) Contract Support, Office of Environmental Measurement and Evaluation (OEME), June 2018.

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2. <u>123 m/z Bicyclanes (Sesquiterpanes)</u>: Bicyclanes, also known as sesquiterpanes, can be particularly useful for the chemical fingerprinting of lighter petroleum products. Bicyclic biomarker sesquiterpanes with the drimane skeleton are ubiquitous components of crude oils and ancient sediments and their original sources included higher plants, algae, and bacteria (Wang et al., 2006). However, the sesquiterpane distribution and concentrations vary between oils from different source countries and/or American Petroleum Institute (API) gravity ranges, and in different refined products. In lighter to middle petroleum products like jet fuel and diesel, the lower molecular weight bicyclic sesquiterpanes are generally concentrated and useful (Kienhuis et al., 2016). However, as with any other low-boiling compounds, the sesquiterpanes are subject to evaporative weathering and this should be considered before using them for ratio comparison (Kienhuis et al., 2016).

Results for this group were consistent between the pre-excavation sample and duplicate – none of the four results shown in Table 1 exceeded 50% RPD. This group had a total of three calculated diagnostic ratios (8 β (H) drimane/Total C₁₅ bicyclic sesquiterpane, 8 β (H) Homodrimane/Total C₁₅ Bicyclic Sesquiterpane, and 8 β (H) Homodrimane/8 β (H) drimane). Here is a summary of the difference in the ratios between pre- and post-excavation samples and the observations of the product sample ratios:

- For two ratios, the post-excavation sample was higher than the highest ratio calculated for the pre-excavation samples.
- The 8β (H) Homodrimane/8β (H) drimane showed the highest amount of variability between the four product samples. The post-excavation sample had a lower ratio than the pre-excavation samples.
- There were significant differences in all three ratios between the Site samples (preand post-excavation) and the product samples.
- There was no consistent similarity in the ratios between the four product samples. For example, product samples HL15172 and AA16094 had the same 8β (H) drimane/Total C₁₅ bicyclic sesquiterpane ratios but had very different ratios for 8β (H) Homodrimane/Total C₁₅ Bicyclic Sesquiterpane.
- <u>191 m/z Terpanes</u>: Results for this group were consistent between the pre-excavation sample and duplicate – only one result out of a total of 38 shown in Table 1 exceeded 50% RPD. This group had a total of 15 calculated diagnostic ratios. Here is a summary of the difference in the ratios between pre- and post-excavation samples:
 - a. Four ratios showed increases.

- b. Five ratios showed decreases.
- c. Six ratios had no discernable change.
- d. Wang and Christensen (2006) note that the 22R epimers of the 17α, 21β(H)homohopanes are more susceptible to biodegradation than their 22S configuration homohopanes. The results of the C₃₁ homohopane (22S)/C₃₁ homohopane (22R) ratio do not appear to show any change between the pre- and post-excavation samples. Therefore, this particular ratio does not appear to indicate any significant biodegradation effect.
- e. Within the terpane and sterane groups, studies have suggested that norhopanes are the most biodegradation resistant and the C30 $\alpha\beta$ hopane was more sensitive to weathering than its higher homologues (Wang and Christensen, 2006). The post-excavation C29 $\alpha\beta$ -30-norhopane/C30 $\alpha\beta$ hopane ratio was 0.68, slightly less than the ratios in the pre-excavation sample and duplicate (0.72 and 0.70, respectively). This is the opposite of what might be expected if biodegradation and weathering had an effect on the ratio.

Although 9 of 15 post-excavation samples showed differences compared to the preexcavation samples, it is difficult to evaluate the significance of this because 6 of 15 sample ratios showed no change and there was a noticeable amount of variation between the four product samples. Therefore, for terpanes, the pre- and postexcavation samples did not show a consistent difference and these samples did not seem to match any particular product sample. According to Wang and Christensen (2006), biomarker terpanes and steranes are not depleted during evaporative weathering.

- 4. <u>217 m/z Steranes</u>: The results for this group were generally consistent between the preexcavation sample and duplicate – only one of the 22 results in Table 1 exceeded 50% RPD. This group had a total of eight calculated diagnostic ratios. Here is a summary of the observations in the ratios of the pre- and post-excavation samples and product samples:
 - a. Five of the diagnostic ratios (C₂₇αα/C₂₇ββ, C₂₈αα/C₂₈ββ, C29ααS/C29ααR, sum C₂₇/sum C₂₉, and C₂₇-C₂₈-C₂₉ steranes/17α,21β-Hopane) appear to show a slight increasing trend (median of product samples < pre-excavation sample < post-excavation sample). However, there seemed to be no obvious such trend among the samples for the C₂₉αα/C₂₉ββ, C27ββ/C29ββ, or 13β,17α-Diacholestane (20S+R)/14α,17α-Cholestane (20S+R) ratios.
 - b. The product sample ratios for C_{27} - C_{28} - C_{29} steranes/17 α ,21 β -Hopane showed considerable variation.

<u>Interpretation</u>: Steranes degrade in the order of C_{27} first, then C_{28} , then C_{29} (Wang and Christensen, 2006). Therefore, if degradation was significant, it would be expected that the sum $C_{27}/sum C_{29}$, and $C_{27}\beta\beta/C_{29}\beta\beta$ ratios in the post-excavation sample would show a decrease compared to the pre-excavation samples. However, this was not observed. Instead, there was either no discernable change or there was an increase in the post-excavation sample.

<u>Uhler et al</u>. (2016) notes that there is diversity in the occurrence and relative amounts of terpane and sterane biomarkers in lubricating oils because of the many sources of crude oil used in the refining and blending process of these oils. This may be part of the reason for the variation in the ratios for the product samples.

- 5. <u>231 m/z Triaromatic Steranes</u>: Results for triaromatic (TA) steranes were inconclusive for two reasons:
 - a. TA steranes were detected in the pre- and post-excavation samples but were not detected in any of the product samples.
 - b. Only one of the 6 pre- and post-excavation samples ratios showed a discernable difference.
- 6. <u>253 m/z Monoaromatic Steranes</u>: Monoaromatic (MA) steranes were present in all of the samples (pre- and post-excavation and product) even though they are not typically seen above trace levels in lubricating oils according to Wang et al. (2006). Results for MA steranes were consistent between the pre-excavation sample and duplicate none of the 13 results in Table 1 exceeded 50% RPD. This group had a total of three calculated diagnostic ratios. Here is a summary of the difference in the ratios between pre- and post-excavation samples:
 - a. One ratio showed an increase.
 - b. One ratio showed a decrease.
 - c. One ratio had no discernable change.

Regarding the product sample diagnostic ratios, there was considerable variation between the four product samples. Therefore, the median product ratio was used for comparison to the pre- or post-excavation ratios. However, neither the pre- or post-excavation ratios appeared to correlate with the median product ratios.

Polycyclic Aromatic Hydrocarbon (PAH) Diagnostic Ratios

As mentioned above, one of the report's conclusions was that the comparison of the bar charts shown in Figure 1 (report Figure 8) support the claim that the post-excavation sample is from a different source than the contaminants released from the warehouse fire. To further evaluate the PAH data, Ecology used a diagnostic ratio method from Douglas et al. (1996) that included source ratios.⁷ However, please note that this method is not a substitute for a comprehensive PAH source/forensics analysis.

As explained by Douglas et al. (1996), source ratios retain the initial oil signature until they degrade below detection. Two source ratios were developed by them): C2-dibenzothiophenes/C2-phenanthrenes (D2/P2) and C3-dibenzothiophenes/C3-phenanthrenes (D3/P3). Their study concluded that the D2/P2 and D3/P3 ratios are useful in the 30-70% (moderate degradation) total petroleum depletion range in both marine and terrestrial environments. Above 70% total hydrocarbon depletion, there was a trend to slightly higher ratios due to the slightly faster biodegradation of the phenanthrenes.

In general, useful PAHs for diagnostics only occur sporadically and at low concentrations in lubricating oils because they have been refined to remove aromatic compounds to improve the oil's performance characteristics (Uhler et al., 2016).⁸ However, Uhler et al. (2016) shows an example of an instance where low but detectable quantities of PAHs of forensic interest (such as alkylated dibenzothiophenes and phenanthrenes) were observed in a heavy-duty diesel oil lubricant.

PAH Data Review and Interpretation

To create the PAH values in Table 1 for calculating the source ratios, the relative amounts of selected PAH constituents were read from the PAH bar charts that were included in the Pace (2018) laboratory reports (Figures 1 through 6). The key for identifying PAHs on the bar charts is also included in Figure 7. These PAH values were then used in the source ratio calculations. Ecology has the following comments on the calculated PAH diagnostic ratios shown in Table 1:

1. Source Ratio (D2/P2):

 ⁷ Douglas, G.S., A. E. Bence, R.C. Prince, S.J. McMillen, and E.L. Butler, 1996, *Environmental Stability of Selected Petroleum Hydrocarbon Source and Weathering Ratios*, Environmental Science & Technology, 30: 2332-2339.
 ⁸ Uhler, A.D., Stout, S.A., Douglas, G.S., Healey, E.M., and Emsbo-Mattingly, S.D., *Chemical Character of Marine Heavy Fuel Oils and Lubricants*; <u>in</u>: Scott A. Stout and Zhendi Wang, Editors, <u>Standard Handbook of Oil Spill Environmental Forensics</u>, Chapter 13, pp. 641-683, Elsevier, 2016.

- a. The post-excavation ratio (0.3) is lower than the lowest pre-excavation sample ratio (0.4) and the lowest product sample ratio.
- b. The product sample ratios range from 0.4 to 0.9 with a median value of 0.7.
- 2. <u>Source Ratio (D3/P3)</u>:
 - a. The pre-excavation sample ratios (0.03 and 0.04) are an order of magnitude below the post-excavation sample ratio (0.4). The very low pre-excavation sample ratio is due to the very high C3-phenanthrenes result in the pre-excavation sample.
 - b. The product sample ratios range from 0.3 to 0.7 with a median value of 0.6.
 - c. This source ratio appears to be inconclusive because of the large difference between the pre-excavation sample and the product and post-excavation samples.

Petrogenic/Pyrogenic PAHs

Research regarding PAHs in the environment has shown that they originate from three potential sources:^{9, 10}

- *Petrogenic* fossil fuels
- *Pyrogenic* high temperature natural and anthropogenic processes (including combustion of fossil fuels in internal combustion engines, coal gas processes, and wood burning)
- Biogenic transformation of natural organic precursors in the environment by relatively rapid chemical/biological (diagenic) processes. Biogenic PAHs generally do not contribute much to the total mass of PAH in sediments that have been contaminated by anthropogenic sources.

As summarized by Boehm (2006), the types of PAHs that are formed during fossil fuel production include a complex variety of parent (unsubstituted, such as C₀-phenanthrene) and alkylated PAHs. Therefore, series of PAHs that are composed of parent and substituted PAHs form many families or homologous series of PAHs. For example, the phenanthrene

⁹ Boehm, Paul D., 2006, *Polycyclic Aromatic Hydrocarbons (PAHs)*; <u>in</u>: Robert D. Morrison and Brian L. Murphy, Editors, <u>Environmental Forensics, Contaminant Specific Guide</u>, Chapter 15, pp. 313-338, Elsevier, 2006.

¹⁰ Neff, J.M, S.A. Tout, and D.G. Gunster, 2005, *Ecological Risk Assessment of Polycyclic Aromatic Hydrocarbons in Sediments: Identifying Sources and Ecological Hazard*. Integrated Environmental Assessment and Management, vol. 1, no. 1, pp. 22-33.

homologous series includes phenanthrene itself (C₀-phenanthrene), plus a series of alkylated homologues of phenanthrene with many alkyl substitutions (for example phenanthrene-C₁, phenanthrene-C₂, phenanthrene-C₃, and phenanthrene-C₄). As a general rule, these alkyl PAHs are more abundant that the parent compounds in petroleum and homologues with two to four alkyl carbons are usually more abundant than the less or more highly alkylated homologes (Neff et al. 2005, Boehm 2006). In pyrogenic PAH assemblages, the main compound in each homologous series is the unalkylated parent compound or a homologue with only one or two alkyl substituents (Neff et al. 2005). The below figure from Emsbo-Mattingly and Litman (2016) illustrates how the relative abundance of parent and alkylated PAHs changes with temperature, causing the petrogenic "bell shaped" profile to transform into a progressively more skewed profile.¹¹



(Figure from Emsbo-Mattingly and Litman, 2016)

¹¹ Emsbo-Mattingly, S.D. and E. Litman, *Polycyclic Aromatic Hydrocarbon Homolog and Isomer Fingerprinting*, <u>in</u>: Scott A. Stout and Zhendi Wang, Editors, <u>Standard Handbook of Oil Spill Environmental Forensics</u>, Chapter 5, pp. 255-312, Elsevier, 2016.

Petrogenic/Pyrogenic PAHs in Site Data

The PAH bar charts in Figure 1 for the pre- and post-excavation samples were examined to see if there were any patterns to indicate petrogenic or pyrogenic source. The pre-excavation sample bar chart does not show any skewing to the left (C_0 parent) for any of the PAHs and therefore appears to be more consistent with a petrogenic source. The product sample bar charts (Figures 3 through 6) also do not show any obvious left skewing.

However, the post-excavation sample shows obvious skewing for phenanthrenes (PHEN), pyrenes/fluoranthenes (PY), and the chrysenes (CHR) and therefore appears to be consistent with a pyrogenic source.

Biomarkers and PAH Data Interpretation Conclusions Summary

Based on the data review that is described above, Ecology has the following data interpretation conclusions:

- 1. Differences in diagnostic ratios were observed for some biomarkers between the pre- and post-excavation samples. Specifically, these include:
 - a. <u>113 m/z isoparaffins</u>: one of three ratios (phytane/n- C_{18}).
 - b. <u>123 m/z sesquiterpanes</u>: two of three ratios (to varying degrees).
 - c. <u>191 m/z terpanes</u>: 9 of 15 ratios (increase or decrease).
 - d. <u>231 m/z steranes</u>: five of the eight ratios showed differences. There appeared to be a slight increasing trend in these samples (median of product samples < pre-excavation sample < post-excavation sample).
 - e. <u>253 m/z MA steranes</u>: two of three ratios (one increase and one decrease).
- 2. There were inconclusive differences in the diagnostic ratios for 231 m/z TA steranes.
- 3. There was considerable variation in the product sample ratios. The amount of correlation of the product samples with the pre- and/or post-excavation sample ratios was also not consistent.
- 4. PAH Bar Charts Analysis:
 - a. The post-excavation sample D2/P2 source ratio is less than both the pre-excavation sample ratio and the lowest product sample ratio. This may support the conclusion that

the post-excavation sample may be from a different source than the contaminants released from the warehouse fire.

- b. The D3/P3 source ratio was inconclusive because of the large difference between the pre-excavation sample and the product and post-excavation samples.
- c. The shapes of the PAH bar chart profiles suggest that the post-excavation samples may have originated from more of a pyrogenic source. Neither the pre-excavation nor product sample bar charts show any skewing that would suggest a pyrogenic source. Therefore, these appear to be from more of a different, and likely petrogenic, source.

Overall Conclusion: Based on the results of the biomarkers diagnostic ratios, PAH source ratios, and PAH bar charts analysis, Ecology's conclusion is that the pre-excavation sediment sample collected in DU1 from the 0- to 4-inch depth is more likely than not from a different contamination source than the post-excavation sediment sample collected in DU1 from the 12-to 16-inch depth interval. It is Ecology's determination that the interim action wetlands sediment excavation work sufficiently removed the petroleum contamination that was released from warehouse fire. Therefore, no further sediment characterization or remediation is necessary in the wetlands area in response to the warehouse fire petroleum release.

If you have any questions, please contact me at 360-890-0059 or <u>steve.teel@ecy.wa.gov</u>.

Sincerely,

SSTeel

Steve Teel, LHG Cleanup Project Manager/Hydrogeologist Toxics Cleanup Program Southwest Region Office

Enclosure: Table and Figures

cc: Jerry Eide, Cenex Harvest States Cooperative, jerry.eide@chsinc.com
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Enclosure

Table and Figures

				Peak Heig	ht or Ratio of	Peak Heights	;			
	Pace Lab Symbol	Sample ID (Lab ID) Pre-Excavation Samples Results		Relative	Excavation Sample Results	Product Sample ID (Lab ID) Product Samples Results				
Identity or Ratio		DU1-0-4-<2mm (27832-1)	DU1-0-4-<2mm Duplicate Sample (27832-1 Dup)	Difference (RPD)	DU1-EX1- 0.4<2mm (27832-2)	HD16154 (28133-1)	HL15172 (28133-2)	AA16094 (28133-3)	AB16113 (28133-4)	Median Diagnostic Ratio
Biomarkers	Т			[r	1	1
123 m/z Bicyclanes (Sesquiterpanes)		5330	C 401	21	5000	2004	2620	2220	4757	N1.0
C ₁₅ Bicyclic Sesquiterpane	m	5228	0481 13261	21	5890 15225	2064	3620	2329	1/5/	NA NA
C Bicyclic Sesquiternane	0	7603	7647	11	7604	1893	5775 2973	1041 887	1056	ΝΔ
8β (H) Homodrimane (C ₁₂)	r	33686	36189	7	35936	6891	14653	3054	2292	NA
		33000	50105	,	33330	0051	14055	5054	2252	
113 m/z Isoparaffins										
Iso-alkane w/13 Carbon Atoms	I-13	0	690	200	740	0	195	2044	1643	NA
Iso-alkane w/14 Carbon Atoms	I-14	1609	999	47	3622	0	280	4867	3784	NA
Frarnesane (isoprenoid - C15)	I-15	1880	1069	55	6655	0	308	3299	2760	NA
Iso-alkane w/16 Carbon Atoms	I-16	4241	2667	46	13015	478	699 2275	3624	2556	NA
Pristane (isoprepoid - C19)	1-18 Pr	5382 21/29	3215	50	20743	1048 3654	2375 6740	1433 3061	792 2421	NA NA
Phytane (isoprenoid - C20)	Ph	13917	11043	23	52896	3345	6246	3528	3297	NA
		10017		20	02000	00.0	02.0	0020	0107	
191 m/z Terpanes										
C ₂₁ -Tricyclic Terpane	1	53480	80089	40	57868	2941	4979	3741	3680	NA
C ₂₂ -Tricyclic Terpane	2	0	2752030	200	12232	0	0	0	0	NA
C ₂₃ -Tricyclic Terpane	3	887814	758634	16	722649	36249	47714	50671	49953	NA
C ₂₄ -Tricyclic Terpane	4	117896	160800	31	141569	7283	10138	11309	11500	NA
C ₂₅ -Tricyclic Terpane	5(S+R)	84280	91117	8	88785	5114	6859	6701	5946	NA
C ₂₄ -Tetracyclic Terpane	Z4	52440	62584	18	62526	7601	6349	8982	7810	NA
C ₂₆ -Tricyclic Terpane	6a*	61855	65488	6	72032	5662	4263	7820	5830	NA
C ₂₆ -Tricyclic Terpane	6b	62602	67600	8	77519	4101	6113	7666	6350	NA
C ₂₈ -Tricyclic Terpane #1	A	63669	67416	6	68232	3984	8775	10047	8824	NA
C ₂₈ -Tricyclic Terpane #2	В	75056	68240	10	70974	9268	6960	9568	9392	NA
C ₂₉ -Tricyclic Terpane #1	С	78840	74272	6	78536	5564	5361	10992	9504	NA
C_{29} -Tricyclic Terpane #2	D	75328	76144	1	79784	5408	5722	9736	9984	NA
18α -22,29,30-Trisnorheonopane (TS)	E	122568	115560	6	105728	15082	13889	22624	20864	NA
17 u-22,23,30-mishomopane (mi)	г 10э*	63824	58160	G	62184	/928	5076	9216	2011	NA NA
C_{30} Tricyclic Terpane #2	100 10b	71/180	68664	1	70952	6/87	6/11	9210	8078	ΝΔ
17α -28.30-Bisnorhopane	100	73248	63288	- - 15	76784	0	1808	3656	0	NA
C ₂₁ -Tricyclic Terpane #1	11a''	36810	30509	19	33291	0	3072	5514	5056	NA
17α -25 Norhopane	J	57638	48368	17	50088	5917	3841	6365	5592	NA
C ₃₁ -Tricyclic Terpane #2	11b	56024	48368	15	50088	5954	4190	6180	5592	NA
17 α,21β-30 Norhopane	к	364038	321820	12	333883	27272	25468	71325	59708	NA
18α-30 Norneohopane	C29Ts	100584	79364	24	80824	6232	5486	16025	15016	NA
17α-Diahopane	C30*	31552	29536	7	27984	0	0	3820	3746	NA
17β ,21 α -30 Normoretane	L	46656	42224	10	46056	3072	2728	7280	6595	NA
18α+18β-Oleanane	Ma+Mb	51864	45000	14	55616	3114	2842	5136	4024	NA
170,21p-Hopane	N	506872	461040	9	488578	30/20	27225	2006	71596	NA
$225-17\alpha$ 21B-30-Homohopane	P	149472	141160	6	139048	12240	11139	35528	28584	NA
$22R-17\alpha$, 21β -30-Homohopane	Q	103712	101481	2	97368	8496	7796	25880	22416	NA
Gammacerane	R	29200	28920	1	29692	3256	0	5316	5424	NA
22S-17α,21β-30-Bishomohopane	т	72088	70984	2	69288	7595	6096	18793	14380	NA
22R-17α,21β-30-Bishomohopane	U	52872	48968	8	47216	3192	4624	13176	11143	NA
22S-17α,21β-30-Bishomohopane	WS	41064	41600	1	42160	3315	2766	10197	9933	NA
22R-17 α ,21 β -Trishomohopane	WR	26464	27936	5	22214	2533	1931	6104	6398	NA
$225-1/\alpha$, 21β -Tetrahomohopane	XS	13077	17879	31	14488	0	0	5549	5595	NA
$228-17\alpha$, 21β -Pentahomohonane		8024 108/0	0450 12/01	13	9020 8760	0	0	3030	3000	NA NA
$228-17\alpha$, 21β -Pentahomohopane	YR	6176	5620	9	6545	0	0	3204	2515	NA
				-		-	-			
217 m/z Steranes										
13 β ,17 α -Diacholestane (20S)	1	169104	158992	6	180288	7923	9897	13769	12855	NA
$13\beta,17\alpha$ -Diacholestane (20R)	2	103772	97590	6	110277	5705	7296	9037	9245	NA
13α , 17β -Diacholestane (20S)	3	51600	50320	3	55856	3520	3659	5317	3983	NA
130,179-Diacholestane (20R)	4	46773	43693	/ 6	48496 124495	2162	3333	4464	5521	NA
24 -methyl-13B 17 α -Diacholestane (203)	6	88296	37051	82	90528	0	2980	0	0	NA
24 -methyl- 13α , 17β -Diacholestane (20S)	7D	26288	25032	5	23188	1778	2340	3217	2691	NA
14α,17α-Cholestane (20S)	7	45523	46270	2	53150	1881	3072	3316	2594	NA
24-ethyl-13 β ,17 α -Diacholestane (20S)+14 β ,17 β -	0,00	160425	149002	o	149506	90EE	10775	15009	12120	NA
Cholestane (20R)	οτου	100425	140003	0	140320	6035	10112	13308	12120	INA
14β,17β-Cholestane (20S)	9	77584	79000	2	76104	4501	5964	10652	9188	NA
[24-methyl-13α,17β-Diacholestane (20R)	9D	37624	30862	20	36904	1538	1277	2871	2805	NA
144,1/a-Unoiestane (20K)	10	103492	8/248	17	102544	5516	5641	11/57	9521	NA
24-ethyl-13a.17B-Diacholestane (20K)	17	59772	10430U 54720	14 10	60473	3031	0597 4625	6980	52/9 52/9	NA NA
24-ethyl-13 α .17 α -Diacholestane (205)	13	54280	49488	9	53208	1190	025	4439	4007	NA
24-methyl-14β,17β-Cholestane (20R)	14	84136	73296	14	90792	2973	3030	7214	6169	NA
24-methyl-14β,17β-Cholestane (20S)	15	129372	115696	11	128288	4656	5042	10446	8689	NA
24-methyl-14 α ,17 α -Cholestane (20R)	16	80000	71312	11	84440	2597	2620	6187	4903	NA
24-ethyl-14 α -Cholestane (20S)	17	91976	78760	15	87848	4287	4748	9655	8263	NA
24-ethyl-14β,17β-Cholestane (20R)	18	99920	96487	3	100403	7439	7296	13434	13760	NA
[24-ethyl-14β,17β-Cholestane (20S)	19	130288	118757	9	117112	7348	8510	14505	13455	NA
24-ethyi-14 α ,1/ α -Cholestane (20R)	20	78784	72304	9	81464	5067	5900	11709	10213	NA
231 m/z Triaromatic Steranes										
C ₂₀ Triaromatic Sterane	T1	18416	18632	1	19848	ND	ND	ND	ND	NA
C ₂₁ Triaromatic Sterane	T2	21245	20913	2	25496	ND	ND	ND	ND	NA

Table 1 - Data Summary and Diagnostic Ratios

	Pace Lab	Pre-Excavation	re-Excavation Samples Results		Excavation Sample Results	Product Samples Results				
Identity or Ratio	Symbol	DU1-0-4-<2mm (27832-1)	DU1-0-4-<2mm Duplicate Sample (27832-1 Dup)	Difference (RPD)	DU1-EX1- 0.4<2mm (27832-2)	HD16154 (28133-1)	HL15172 (28133-2)	AA16094 (28133-3)	AB16113 (28133-4)	Median Diagnostic Ratio
20S C ₂₆ Triaromatic Sterane	Т3	63208	48648	26	57526	ND	ND	ND	ND	NA
20R C26 + 20S C ₂₇ Triaromatic Steranes	T4	222109	169824	27	204168	ND	ND	ND	ND	NA
20S C_{28} Triaromatic Sterane	15 T6	81000	65424	21	76448	ND ND	ND	ND ND	ND	NA
20R C_{27} Triaromatic Sterane	то т7	64293	51208	23	60474	ND	ND	ND	ND	NA
253 m/z Monoaromatic Steranes										
20S, 5β C27-MAS	a	53617	54954	2	54948	1177	959	2182	1884	NA
205, dia C27-MAS 20R. 5B C27-MAS + 20R C27 dia MAS	a 2	64288	62232	3	46206 56144	2485 1877	623	3691	3420	NA NA
20S, 5α C27-MAS	d	46114	45811	1	42184	0	1282	1071	983	NA
20R, 5β C28-MAS + 20S C28 dia MAS	е	143138	135411	6	132261	2111	2161	5759	5471	NA
20R, 5α C27-MAS 20S Εα C28 MAS	f	45808	34344	29	57856 85572	1873	2213	2006	2369	NA
203, 56 C28-MAS + 20S C28 dia MAS	в h	119825	101735	18	109384	2194	2434	5771	4660	NA
20S, 5β C29-MAS + 20S C29 dia MAS	i	93856	82134	13	78291	3257	4121	6795	6652	NA
20S, 5α C29-MAS	j	50672	41608	20	48952	839	1434	1640	2783	NA
20R, 5α C28-MAS	k	75504	61220	21	77016	1142	0	2362	2053	NA
20R, 5β C29-MAS + 20R C29 dia MAS 20R 5α C29-MAS	l m	60448 34112	51522 29170	16 16	48358	2247	2510	4790	4669	NA NA
		54112	23170	10	52504	Ŭ	Ŭ	1517	1700	
Biomarker Diagnostic Ratios Bicyclanes (Sesquiterpanes)										
8β (H) Drimane/Total C ₁₅ Bicyclic Sesquiterpane		0.93	0.94	NA	1.14	0.67	0.57	0.57	0.47	0.57
8β (H) Homodrimane/Total C ₁₅ Bicyclic		2 62	2 56	NIA	2 66	1 74	ว วา	0.05	0.01	1.25
Sesquiterpane 8β (H) Homodrimane/8β (H) Drimane		2.05	2.30	NA	2.00	2.59	3.88	1.66	1.75	2.17
Isoparaffins										
phytane/n-C ₁₆		3.28	4.14	NA	4.06	7.00	8.94	0.97	1.29	4.14
phytane/n-C ₁₈		2.59	3.43	NA	2.55	3.19	2.63	2.46	4.16	2.91
pristine/phytane		1.54	1.25	NA	1.33	1.09	1.08	0.87	0.73	0.97
Terpanes Cod/Coa tricyclic terpane		0.06	0.11	NA	0.08	0.08	0.10	0.07	0.07	0.08
C_{23}/C_{24} tricyclic terpane		7.53	4.72	NA	5.10	4.98	4.71	4.48	4.34	4.59
C_{23} tricyclic terpane/ C_{30} $\alpha\beta$ hopane		1.75	1.65	NA	1.48	1.18	1.75	3.16	0.70	1.47
C_{24} tricyclic terpane/ C_{30} $\alpha\beta$ hopane triplet ratio:		0.23	0.35	NA	0.29	0.24	0.37	0.71	0.16	0.30
C ₂₄ tetracyclic/C ₂₆ tricyclic (S)/C ₂₆ tricyclic (R) terpane		1.35E-05	1.41E-05	NA	1.12E-05	3.27E-04	2.44E-04	1.50E-04	2.11E-04	2.27E-04
Ts/Tm C ₂₂ bisnorhopane/C ₂₂ αβ hopane		1.12 0.14	1.12 0.14	NA NA	0.97 0.16	2.64 0.00	2.35 0.07	1.19 0.23	1.36 0.00	1.85 0.03
$C_{29} \alpha\beta$ -30-norhopane/ $C_{30} \alpha\beta$ hopane		0.72	0.70	NA	0.68	0.89	0.94	4.45	0.83	0.91
oleanane/C ₃₀ $\alpha\beta$ hopane		0.10	0.10	NA	0.11	0.10	0.10	0.32	0.06	0.10
moretane/C ₃₀ $\alpha\beta$ hopane		0.12	0.12	NA	0.12	0.16	0.08	0.51	0.10	0.13
gammacerane/ $C_{30} \alpha \beta$ hopane		0.06	0.06	NA	0.06	0.11	0.00	0.33	0.08	0.09
tricyclic terpanes $(C_{19}-C_{26})/C_{30} \alpha\beta$ nopane		2.34	2.46	NA NA	2.19	1.83	2.69	5.07	1.08	2.26
C_{31} homohopane (22S)/ C_{31} homohopane (22S)/ C_{32} bishomohopane		1.44	1.55	NA	1.45	1.44	1.45	1.57	1.20	1.40
(22R)		1.36	1.45	NA	1.47	2.38	1.32	1.43	1.29	1.37
Sum C_{31} to $C_{33}/17\alpha$,21 β -Hopane		0.88	0.94	NA	0.85	1.22	1.26	6.84	1.30	1.28
Steranes		0.59	0.59	NA	0.70	0.42	0.52	0.31	0.28	0.36
C ₂₂ αα/C ₂₂ ββ		0.37	0.38	NA	0.39	0.34	0.32	0.31	0.33	0.34
C ₂₉ αα/C ₂₉ ββ		0.34	0.34	NA	0.37	0.34	0.37	0.42	0.38	0.37
C29ααS/C29ααR		0.58	0.64	NA	0.65	0.37	0.52	0.28	0.25	0.33
$C_{27}\beta\beta/C_{29}\beta\beta$		1.03	1.05	NA	1.03	0.85	1.06	0.95	0.82	0.90
Sum C_{27} /Sum C_{29}		0.94	0.98	NA	1.03	0.91	1.03	0.83	0.82	0.87
13β,17α-Diacholestane (20S+R)/14α,17α- Cholestane (20S+R)		1.82	1.92	NA	1.85	1.84	1.90	1.51	1.82	1.83
Triaromatic Steranes										
$C_{20} TA/(C_{20} TA + C_{21} TA)$		0.46	0.47	NA	0.44	ND	ND	ND	ND	NA
C ₂₆ TA (20S)/sum of C ₂₆ TA (20S) through C ₂₈ TA (20R)		0 12	0.12	NΔ	0.12	ND	ND	ND	ND	NΔ
(20R) C₂₂ TA (20R)/C₂₀ TA (20R)		1.56	1.42	NA	1.50	ND	ND	ND	ND	NA
C ₂₈ TA (20R)/C ₂₈ TA (20S)		0.79	0.78	NA	0.79	ND	ND	ND	ND	NA
C ₂₆ TA (20S)/{(C ₂₆ TA (20S) + C ₂₈ TA (20S)}		0.44	0.43	NA	0.43	ND	ND	ND	ND	NA
C ₂₈ TA (20S)/{(C ₂₆ TA (20S) + C ₂₈ TA (20S)}		0.56	0.57	NA	0.57	ND	ND	ND	ND	NA
Monoaromatic Steranes		1 47	1 57	NΔ	1 26	0 98	1 63	1 71	0 96	1 09
total 203, 027/total 208, 027		0.63	0.68	NA	0.64	1.36	1.34	0.83	0.81	1.03
totai C28/totai C29		1.70	1.00	INA	1.34	0.00	0.09	1.04	0.00	0.67
Selected PAHs From Bar Charts			l			 				
C ₃ -naphthalenes		1 २	1 २	0	13.7 100	9.5 9.5	14 8 7	5.5 5	7 77	
		J	5	U U	100	5.5	0.7		1.2	INA I
C₁-phenanthrenes		2.5	2.5	0	47.5	11	15	6	7.5	NA

Table 1 - Data Summary and Diagnostic Ratios

	Pace Lab	Pre-Excavation Samples Results		Relative	Excavation Sample Results		Product Samples Results			
Identity or Ratio	Symbol	DU1-0-4-<2mm (27832-1)	DU1-0-4-<2mm Duplicate Sample (27832-1 Dup)	Difference (RPD)	DU1-EX1- 0.4<2mm (27832-2)	HD16154 (28133-1)	HL15172 (28133-2)	AA16094 (28133-3)	AB16113 (28133-4)	Median Diagnostic Ratio
C ₃ -phenanthrenes		100	100	0	26.5	14	16.5	20.5	27	NA
C ₄ -phenanthrenes		2.5	2.5	0	19	17	19.5	15.5	14	NA
C ₂ -dibenzothiophenes		1.5	1.7	13	11	9	7	9	7.2	NA
C ₃ -dibenzothiophenes		3	3.5	15	11.5	10	9	13.5	9	NA
PAH Diagnostic Ratios										
- Source Ratio (D2/P2) C ₂ -dbenzothiophenes/C ₂ -phenanthrenes		0.5	0.4	NA	0.3	0.8	0.4	0.8	0.9	0.7
- Source Ratio (D3/P3) C3-dbenzothiophenes/C3-phenanthrenes		0.03	0.04	NA	0.4	0.7	0.5	0.7	0.3	0.6

Notes

PAH = polycyclic aromatic hydrocarbon

"0" or ND in result columns = Not Detected

NA = Not Applicable

Values shown above are Pace Analytical Energy Services laboratory report results for peak height (for biomarkers) or relative amount from PAH bar chart.

Biomarkers diagnostic ratios from Wang and Christensen (2006), Table 17.2.1 or Kienhuis et al. (2016), Tables 14.4 and 14.6.

PAH source ratios from Douglas et al. (1996).

Ratios were not calculated for biomarkers that had RPD >50%

Table and Figures

Table 1	Data Summary and Diagnostic Ratios.
Figure 1	Figure 8 from Farallon (2019).
Figure 2	Pre-excavation duplicate sample PAH bar chart.
Figure 3	Product sample HD16154 PAH bar chart.
Figure 4	Product sample HL15172 PAH bar chart.
Figure 5	Product sample AA16094 PAH bar chart.
Figure 6	Product sample AB16113 PAH bar chart.
Figure 7	Bar chart key for identifying aromatic hydrocarbons.









Aromatic Hydrocarbon Distribution 28133-1 [HD16154] 1/10



Aromatic Hydrocarbon Distribution 28133-2 [HL15172] 1/10



Aromatic Hydrocarbon Distribution 28133-3 [AA16094] 1/10



Figure 6: Product sample AB16113 PAH bar chart

Aromatic Hydrocarbon Distribution 28133-4 [AB16113] 1/10





Key for Identifying Aromatic Hydrocarbons

No	m/z	Abbreviation	Compound
1	120	AB	C ₃ -alkylbenzenes
2	134		C ₄ -alkylbenzenes
3	148		C₅-alkylbenzenes
4	162		C ₆ -alkylbenzenes
5	128	NAPH	C ₀ -naphthalene
6	142		C ₁ -naphthalenes
7	156		C ₂ -naphthalenes
8	170		C ₃ -naphthalenes
9	184		C₄-naphthalenes
10	166	FL	C ₀ -fluorene
11	180		C ₁ -fluorenes
12	194		C ₂ -fluorenes
13	208		C ₃ -fluorenes
14	222		C ₄ -fluorenes
15	154	BP	C ₀ -biphenyl
16	168		C ₁ -biphenyls + dibenzofuran
17	182		C ₂ -biphenyls + C1 Dibenzofuran
18	178	PHEN	C ₀ -phenanthrene
19	192		C ₁ -phenanthrenes
20	206		C ₂ -phenanthrenes
21	220		C ₃ -phenanthrenes
22	234		C₄-phenanthrenes
23	202	РҮ	C ₀ -pyrene/fluoranthene
24	216		C ₁ -pyrenes/fluoranthenes
25	230		C ₂ -pyrenes/fluoranthenes
26	244		C ₃ -pyrenes/fluoranthenes
27	258		C ₄ -pyrenes/fluoranthenes
28	228	CHR	C ₀ -chrysene
29	242		C ₁ -chrysenes
30	256		C ₂ -chrysenes
31	270		C₃-chrysenes
32	284		C ₄ -chrysenes
33	148	ВТ	C ₁ -benzothiophenes
34	162		C ₂ -benzothiophenes
35	176		C ₃ -benzothiophenes
36	190		C ₄ -benzothiophenes
37	204		C₅-benzothiophenes



Key for Identifying Aromatic Hydrocarbons – Cont.

No	m/z	Abbreviation	Compound
38	184	DBT	C ₀ -dibenzothiophene
39	198		C ₁ -dibenzothiophenes
40	212		C ₂ -dibenzothiophenes
41	226		C ₃ -dibenzothiophenes
42	240		C ₄ -dibenzothiophenes
43	234	NBT	C ₀ -naphthobenzthiophene
44	248		C ₁ -naphthobenzthiophenes
45	262		C ₂ -naphthobenzthiophenes
46	276		C ₃ -naphthobenzthiophenes
47	290		C ₄ -naphthobenzthiophenes
48	253	MAS	Monoaromatic steranes
49	267		Monoaromatic steranes
50	239		Monoaromatic steranes
51	231	TAS	Triaromatic steranes
52	245		Triaromatic steranes