

## **APPENDIX C**

Harbor View “Black Sediment” Source Identification Report  
And the September 29, 2005 Laboratory Analytical Report

## Harbor View “Black Sediment” Source Identification

On September 29, 2005 GeoInsight, Inc. collected a sediment sample from segment W2A-02 (Harbor View) in Mattapoisett, Massachusetts. The sediment sample was collected from the intertidal portion of the shoreline and consisted of black-colored sediment. The sample was shipped to B&B Laboratories in College Station, Texas and for polycyclic aromatic hydrocarbon (PAH) fingerprint and biomarker analyses. Analyses was conducted to determine whether or not the PAH detected in the sample could be attributed to the B-120 oil spill. The forensic evaluation of the analyses for this sample is presented below.

Figure 1 exhibits the alkane distribution of the Harbor View sample. The dominant feature of this sample is alkanes derived from terrestrial plant waxes, especially characterized by odd-numbered *n*-alkanes in the range *n*-C<sub>15</sub> to *n*-C<sub>31</sub>. The sample also has elevated concentrations identified as *n*-C<sub>24</sub> and *n*-C<sub>33</sub>. The latter compound is associated with plant wax alkanes and is elevated in this sample. The *n*-C<sub>24</sub> is also elevated out of proportion with other alkanes and the possibility of co-elution with another compound of recent biogenic origin cannot be ruled out. Such compounds can occur as single components rather than homologous series. The absence of phytane (at low parts per billion levels) and low concentrations of even-numbered alkanes does not confirm the presence of petrogenic or pyrogenic hydrocarbons.

Figure 2 compares the PAH patterns for the Harbor View sample and the B-120 product. It also compares the Harbor View sample to the Brandt tarball sample that was collected in March 2004 because the tarball sample is similar in composition to the Harbor View sample. The chemical characteristics of the Harbor View sample differs substantially from the B-120 oil, especially in regard to the heavier PAH compounds:

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- The Harbor View sample contains relatively high concentrations of parent 4-ringed PAH (e.g., pyrene, benz[a]pyrene, chrysene) when compared with PAH containing carbon side-chains. The PAH “signature” is generally consistent with a significant contribution from a combustion source (e.g. fossil fuels such as oil and coal, or renewable biogenic fuels such as wood).
- Relatively high concentrations of 5- and 6-ringed PAH compounds (benzo[b]fluoranthene and higher) compared with PAH compounds containing carbon side-chains, which is also typical of hydrocarbons with a combustion-type signature rather than the B-120 oil.
- Increased ratio of the concentration of fluoranthene and pyrene (F&P) to that of C<sub>30</sub> hopane (C<sub>30</sub>H) compared with that in the B-120 source oil (F&P:C<sub>30</sub>H ratios of 28 and 8.9, respectively). C<sub>30</sub> hopane is an extremely stable molecule compared with other PAH compounds, such as fluoranthene and pyrene. Therefore, the ratio of F&P:C<sub>30</sub>H declines over time as fluoranthene and pyrene weather. In contrast, the F&P:C<sub>30</sub>H ratio in Harbor View sample is three times higher than the F&P:C<sub>30</sub>H ratio in the source oil, indicating that the Harbor View sample had a different source that contained less C<sub>30</sub> hopane than the B-120 source oil.

In previous analyses, the F&P:C<sub>30</sub>H ratio of a B-120 tarball sample was demonstrated to be less than the F&P:C<sub>30</sub>H of the original oil in the B-120 barge, consistent with weathered oil that has “lost” some fluoranthene and pyrene relative to the C<sub>30</sub> hopane. In contrast, an increased proportion of fluoranthene and pyrene in the Harbor View sample results in a substantially higher F&P:C<sub>30</sub>H ratio than in the B-120 oil samples. This characteristic can only be accounted for by an alternative source of PAH for the Harbor View sample, one that appears to contain a proportionately higher concentration of C<sub>30</sub>-hopane than the B-120 oil, but even greater proportions of parent PAHs.

The following table highlights differences in relative concentrations of parent PAH (i.e., no carbon side-chains) as a means of distinguishing combustion (high proportion of parent PAHs) and oil-derived sources of hydrocarbons (low proportion of parent PAHs). The table also summarizes differences in the proportion of C<sub>30</sub>-Hopane in the total PAH distribution:

Parent PAH	Harbor View	B-120 Source oil
Phenanthrene	29%	6%
Fluoranthene + Pyrene	65%	9%
Chrysene	48%	9%
4-, 5-, and 6-Ring PAH <sup>1</sup>	75%	11%
C <sub>30</sub> -Hopane (as a percentage of all PAH)	0.84%	0.15%

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

The relatively high percentage of parent PAH compounds in the Harbor View sample clearly distinguishes it as containing combustion-derived material. The fingerprint could not result

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even with burning a tarball from the B-120 oil spill because fluoranthene is preferentially lost during oil burning relative to pyrene (Garrett et al. 2000),<sup>1</sup> which is the opposite of what is observed in comparing this sample with the B-120 source oil.

Therefore, chemical analyses indicate that the Harbor View “black sediment” has heavier PAH compounds than the B-120 source oil, with a signature consistent with a combustion source. However, this combustion source may be dominated by renewable fuels (e.g., wood, vegetation) based on comparison with the Brandt tarball sample, which contains PAH from combusted fossil fuel (e.g., oil, coal). Both samples contain "combustion PAH" but differences in the proportions of biomarker compounds suggest differences in the ultimate source of the fuel.<sup>2</sup> The remaining PAH signature cannot be accounted for by weathering of B-120 oil based on known processes, confirming that the Harbor View sample cannot be composed of the B-120 oil.

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<sup>1</sup> Garrett, R. M.; Guenette, C. C.; Haith, C. E.; Prince, R. C. 2000. Pyrogenic Polycyclic Aromatic Hydrocarbons in Oil Burn Residues. *Environ. Sci. Technol.* 34(10):1934-1937.

<sup>2</sup> Although the Brandt tarball sample exhibits a quite similar PAH distribution, it has a F&P:C<sub>30</sub>H ratio of 15, which is greater than the B-120 oil but still almost half that of the Harbor View sample. The Brandt tarball sample was definitely identified as containing combustion material. It is possible that the Brandt tarball contains a greater proportion of combusted fossil fuel (e.g., oil, coal) and that the Harbor View sample has a greater proportion of combusted residue from renewable fuels (e.g., wood), which in this case may have higher F&P:C<sub>30</sub>H ratios.