My Opinion on "Origins of Hydrocarbons: Northeast Cape (St. Lawrence Island) Petroleum Spill"

Zhendi Wang

Emergencies Science and Technology Division

Environmental Technology Centre, Environment Canada

335 River Road, Ottawa

Ontario, Canada, K1A 0H3

Tel: (613) 990-1597, Fax: (613) 991-9485

E-mail: zhendi.wang@ec.gc.ca

Recently I was contacted by Dr. Chiarenzelli to provide an independent opinion on the origin of hydrocarbons in samples collected from the former military installation at Northeast Cape, St. Lawrence Island of Alaska. As a scientist working in the field of forensic oil fingerprinting and spill source identification for many years, I agreed to offer my help on this important issue. I have carefully read the background information provided, and studied the analytical data and related GC chromatograms. For this case, three questions must be unambiguously answered: *(1) Were appropriate methods used for the forensic spill investigation? (2) Can the source of weathered oil (with its chemical composition having been significantly changed) be identified? (3) Can the petroleum hydrocarbons be distinguished from biogenic and/or pyrogenic hydrocarbons?*

1.   *Were appropriate methods used for the forensic spill investigation?*

Depending on the chemical/physical information needs, two types of methods, *non-specific* methods and *specific* methods, can be used for oil spill study. The non-specific methods are mainly used for hydrocarbon screening. In the non-specific methods, only groups or fractions of hydrocarbons (such as measurement of the total petroleum hydrocarbons, TPH) are measured. The non-specific methods do not provide the detailed chemical composition data needed for source identification.

However, for *defensible* oil source identification and specific hydrocarbon-contaminated site investigation needs, *specific methods are used*. A tiered analytical approach must be followed.

This approach facilitate the detailed compositional analysis by GC-MS, GC, and other analytical techniques that determine a broad range of individual oil-characteristic hydrocarbons, and determination of a variety of diagnostic ratios of target compounds. The selection of appropriate target oil analytes is dependent mainly on the type of oil spilled, the particular environmental compartments being assessed, and on expected needs for current and future data comparison. The major petroleum-specific target analytes that may need to be chemically characterized for oil source identification and environmental assessment include the following:

(1) Individual saturated hydrocarbons including n-alkanes (n-C_8 through n-C_{44}) and selected isoprenoids pristane (2,6,10,14-tetramethyl-pentadecane) and phytane (2,6,10,14-tetramethyl-hexadecane). In some cases, three other isoprenoid compounds: farnesane (2,6,10-trimethyl-C_{12}), 2,6,10-trimethyl-C_{13}, and norpristane (2,6,10-trimethyl-C_{15}) are also included;

(2) Cyclo-hexane and its alkylated (C_1 - C_{14}) homologues. This series of mono-cyclic compounds have a characteristic distribution pattern in m/z 83 mass chromatograms for different types of fuels;

(3) The volatile hydrocarbons including the BTEX group (benzene, toluene, ethylbenzene, and the 3 xylene isomers) and alkylated (C_3- to C_5-) benzenes, naphthenes, and volatile paraffins and isoparaffins;

(4) The EPA priority parent PAHs and, in particular, the petroleum-specific alkylated (C_1 to C_4) homologues of naphthalene, phenanthrene, dibenzothiophene, fluorene, and chrysene series. These alkylated PAH homologues are the backbone of chemical characterization and identification of oil spill assessments;

(5) Biomarker terpane and sterane compounds. Analysis of selected ion peaks produced by these characteristic, environmentally-persistent compounds generates information of great importance in determining source(s), weathered state and potential treatability;

(6) Measurements of bulk hydrocarbon groups including total petroleum hydrocarbons (TPH), the unresolved complex mixtures (UCM), and the total saturates and total aromatics, contents of asphaltenes and resins,

(7) Additives to petroleum products. They include alkyl lead additives (tetramethyl lead and trimethylethyl lead at m/z 253 and 223, dimethyldiethyl lead at m/z 267 and 223, methyltriethyl lead at m/z 281 and 223, tetraethyl lead at 295 and 237); oxygenates including ethanol, methanol, methyl tertiary butyl ether (MTBE), ethyl tertiary butyl ether (ETBE), and

tertiary amyl methyl ether (TAME); fuel dyes used for differentiation among fuel grades; and anti-oxidant compounds, called inhibitors, such as aromatic amines and alkyl-substituted phenols added to fuels to retard autooxidation;

(8) Measurement of stable carbon isotope ratio (δ^{13}C) of hydrocarbon groups, sometimes measurement of the isotopic composition of individual compounds by GC-IRMS for correlating spills with suspected sources is also included in many oil spill studies.

In my opinion, during the Phase IV remedial investigation:

(1) Only non-specific methods for analysis of certain hydrocarbon groups (such as DRO and RRO) were used;

(2) An extremely fast GC program (only 0-1.5 minutes!) was used for characterization of oil hydrocarbons, by which many compounds co-eluted;

(3) No fingerprints and quantitative data of oil characteristic n-alkanes, alkylated PAH homologues, and biomarkers are reported (are these characterizations performed?);

(4) The report indicated that *"The laboratory project manager reviewed the tentatively identified compounds (TICs) from the library search and the DRO/RRO chromatograms to comment on whether petroleum hydrocarbons were the likely source of the reported DRO and RRO concentrations"*. I am puzzled how can compounds can be identified from such chromatograms. The identification and characterization of major components should be achieved by recognition of mass spectral data and comparison with the library mass spectra, comparison of GC retention data with reference standards, and calculation of retention index (RI) values and comparison with literature RI values.

Even though only non-specific methods were used, the profile and distribution pattern of the GC chromatograms and the UCM (unresolved complex mixture of hydrocarbons) indicate that the majority of compounds in sediment samples analysed are petrogenic hydrocarbons.

2.   *Can the source of weathered oil (with its chemical composition having been significantly changed) be identified?*

When crude oil or petroleum products are accidentally released to the environment, whether on water or land, they are immediately subject to a wide variety of changes in physical and chemical properties that in combination are termed "weathering". The most important weathering processes include (1) evaporation, (2) emulsification, (3) natural dispersion, (4) dissolution, (5) microbial degradation, (6) photooxidation, and (7) other processes such as sedimentation, adhesion, and oil-fine interaction. The rate of weathering of oil is very dependent on a number of spill conditions (such as temperature, and natural processes such as the type of oil spilled, the local environmental conditions during and after spillage, and natural population of indigenous microbial and microbiological activities during and after spill. In the first few days following a spill, the loss of hydrocarbons is largely caused by evaporation. For heavy or residual oils the losses are only about several percentages of volume. For lighter fuels, evaporation can remove more than half the spill. Biodegradation of petroleum hydrocarbons is generally much longer term process, whose quantitative and qualitative aspects depend on the type, nature, and amounts of the oil present, the environmental conditions (such as temperature, oxygen, nutrients, water activity, salinity, and pH), and composition of microbial community. However, even with all of these weathering processes, large amounts of petroleum hydrocarbons can remain many years after spills (such as the Arrow spill, BIOS spill, and Nipisi spill)

Major chemical compositional changes due to weathering are summarized in the following:
(1) For lightly weathered oils and refined products (less than 15% mass loss), the abundances of low end n-alkanes are significantly reduced. However, the ratios of n-C_{17}/pristane and n-C_{18}/phytane are found to be virtually unaltered. The losses of BTEX and C_3-benzene compounds are also significant, and the most abundant 2-ring alkylated naphthalene series appear to be slightly enriched.
(2) For moderately weathered oils and refined products (e.g., ~15-30% weathered), significant losses occur in n-alkanes and relatively low-molecular-weight isoprenoid compounds. The volatile aromatic compounds are almost completely removed. The loss of C_0 and C_1-naphthalenes can be significant. The ratio of GC-resolved peaks to UCM can be considerably decreased due to the preferential loss of resolved hydrocarbons over the unresolved complex hydrocarbons. The biomarker compounds are enriched.

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(3) For severely weathered oils and refined products, not only n-alkanes but branched and cyclo-alkanes are heavily or completely lost, the UCM becomes extremely pronounced, resulting in significant increase in relative ratios of UCM/GC-TPH and in substantial decrease in relative ratios of resolved peaks to GC-TPH. The BTEX and alkyl benzene compounds are completely absent. Pronounced decrease in the alkylated naphthalene series relative to other alkylated PAH homologous series is clearly observed. In each alkylated PAH family, a distribution profile of C_0- $< C_1$- $< C_2$- $< C_3$- is clearly developed. The alkylated chrysene series is significantly enhanced relative to other PAH series. Biomarker compounds are concentrated because of their refractory nature and high resistance to biodegradation.

All these chemical composition distributions and their characteristic changes due to weathering can be used for weathering checks and spill source identification. Generally speaking, GC-FID traces, including the quantitative n-alkane distribution and the relative size of UCM in the GC chromatograms, are useful only for estimation of general weathering trends and identification of the carbon range of remaining hydrocarbons. They are not source-specific. The alkylated PAH homologues (specifically, the C0- to C4-, naphthalenes, phenanthrenes, dibenzothiophenes, fluorenes, and chrysenes must be characterized for source identification), and the biomarker terpanes and steranes are highly degradation-resistant and can be used effectively and defensively for fingerprinting weathered oils and for source identification of spilled oils.

Furthermore, a number of diagnostic ratios of alkylated PAHs and biomarkers have been developed and successfully used for spill source identification and differentiation. A benefit of comparing diagnostic ratios of spilled oil and suspected source oils is that any concentration effects are minimized. In addition, the use of diagnostic ratios to correlate and differentiate oils tends to reduce the influence of variations due to instrument operating conditions, operators, and matrix effects. For characterization of spilled oil residues and identification of unknown spill samples, many researchers utilized a number of diagnostic ratios of selected source-specific alkylated PAHs in combination with determination of ratios of selected paired biomarkers. These ratios are very sensitive tools for source identification and differentiation, determination of weathering extent and degree of surface and subsurface samples, and distinguishing between composition changes due to physical weathering and biodegradation.

To summarize,

(1) Source identification can not be based on visual comparison of GC chromatograms between the weathered samples and the reference "fresh" oil. This practice can be very misleading.

(2) The source identification of weathered oils is best made by quantitative characterization of alkylated PAHs and biomarkers and determination of diagnostic ratios of target hydrocarbons. However, I did not see any of these data in the report. Are these data available?

3. *Can the petroleum hydrocarbons be distinguished from biogenic and/or pyrogenic hydrocarbons?*

After being spilled, oil hydrocarbons often mix with other background hydrocarbon sources in the impacted area. Therefore, the unambiguous differentiation of petrogenic hydrocarbons from biogenic and/or pyrogenic hydrocarbons is critically important for source identification and allocation of different sources of hydrocarbons.

One of the potential sources of hydrocarbons contributing to the background is biogenic hydrocarbons. Hydrocarbons from both anthropogenic and natural sources including biogenic source are very common in the marine and inland environments. Biogenic hydrocarbons are generated either by biological processes or in the early stages of diagenesis in recent marine sediments. Most soils and sediments contain some fraction of organic matter derived from biological sources including land plants, phytoplankton, animals, bacteria, macroalgae and microalgae. The biogenic hydrocarbons have the following chemical composition characteristics:

(1)   n-Alkanes show a distribution pattern of odd carbon-numbered alkanes being much more abundant than even carbon-numbered alkanes in the range of n-C_{21} to n-C_{33}, resulting in unusually high carbon preference index (CPI) values, which is defined as the sum of the odd carbon-numbered alkanes divided by the sum of the even carbon-numbered alkanes. Petroleum oils characteristically have CPI values around 1.0.

(2)   The notable absence of the "unresolved complex mixture (UCM)" hump in the chromatograms.

(3)   Pristane is often more abundant than phytane in biogenic materials, suggesting a phytoplankton input.

(4)   The presence of a "biogenic cluster" (identified as olefinic hydrocarbons of biogenic origin) in the gas chromatograms of the aromatic fractions.

(5)   A high abundance of the biogenic PAH perylene, an unsubstituted PAH produced in subtidal sediments by a process known as early diagenesis.

(6)   The presence of plant terpenoid biomarker compounds on occasion.

As residues from burning, PAH distributions are the most useful tool in distinguishing pyrogenic hydrocarbons from petrogenic hydrocarbons. Petrogenic materials (crude oils and refined products), in general, exhibit alkylated PAH distribution patters where the C_1-, C_2-, and C_3-PAHs are more abundant than the parent (C_0-) and C_4-PAHs. This kind of characteristic PAH distribution profile has been termed as "*bell shaped*". By weathering or degradation, the "bell-shaped" distribution can be readily modified to the distribution profile of C_0- < C_1- < C_2- < C_3- (*inverse-sloped*) in most alkylated PAH homologous families. In contrast, pyrogenic materials generally exhibit alkylated PAH homologue distribution patterns in which the parent PAHs are often the most abundant. The composition features of pyrogenic PAHs can be summarized as the follows:

(1)   The dominance of the unsubstituted compounds over their corresponding alkylated homologues. This kind of PAH distribution profile of $C_0 >> C_1 > C_2 > C_3 > C_4$ has been generically termed as *skewed* or *sloped*.

(2)   The dominance of the high molecular mass 4-6 ring PAHs over the low molecular mass 2-3 ring PAHs.

(3)   On the gross level, PAH comprise a much higher mass percentage in most pyrogenic source materials than in most petrogenic source materials.

Numerous quantitative diagnostic ratios have been defined to differentiate pyrogenic PAHs from other hydrocarbon sources. Recently, a new "Pyrogenic Index" was proposed by Wang et al. as a quantitative indicator for identification of pyrogenic PAHs and for differentiation of pyrogenic and petrogenic PAHs. The Pyrogenic Index (PI) is defined as the ratios of the total of the other EPA priority unsubstituted 3-6 ring PAHs to the total of 5 target alkylated PAH homologues:

$$PI = \Sigma(\text{other 3 - 6 ring EPA PAHs}) / \Sigma(\text{5 alkylated PAHs})$$

Compared to other diagnostic ratios obtained from individual compounds, this index ratio has its own distinct advantages: (1) determination of the changes in this ratio more truly reflects the difference in the PAH distribution between these two sets of hydrocarbons; (2) this ratio offers better accuracy with less uncertainty than those relative ratios determined from individual PAH compounds; and (3) this ratio shows great consistency from sample to sample and is subject to little interference from the concentration fluctuation of individual components within the PAH series. Also, long-term natural weathering and biodegradation only slightly alter the values of this ratio, but the ratio will be dramatically altered by input of pyrogenic PAHs. This index ratio can be used and has been successfully used as a general and effective criterion to unambiguously differentiate pyrogenic PAHs and petrogenic PAHs in a number of spill case studies.

In conclusion,

(1)   From the example chromatograms provided, it is apparent that *the majority of hydrocarbons in sediment samples are petrogenic hydrocarbons*.

(2)   Biogenic compounds may be present in spill samples and this should be confirmed by a well-designed analytical approach. There are no defensible fingerprinting evidences, however, to support the suggestion that majority of compounds found in the spill samples are of biogenic origin.

(3)   Input of pyrogenic hydrocarbons should be confirmed by additional characterizations as described above.