C31 Effects of Analytical Variability for Calibrated vs. Uncalibrated PAH on Hydrocarbon Source Recognition Methods

Jeffrey W. Short, MS, Auke Bay Laboratory, National Marine Fisheries Service, NOAA, 11305 Glacier Highway, Juneau, AK 99801-8626*

After attending this presentation, attendees will learn of implicit limitations of hydrocarbon analytical data used for identifying hydrocarbon source contributions when applied to determining natural resource damage assessment following accidental release of petroleum hydrocarbons.

This presentation will impact the forensic community and/or humanity by demonstrating that the limitations inherent in the usual GCMS method used for analyzing environmental samples for evidence of contamination by petroleum products are rarely recognized by experts who interpret these data. The analytical reliability of the alkyl-substituted polycyclic aromatic hydrocarbons (PAH), which contain most of the information for identifying hydrocarbon sources within the PAH class of hydrocarbons, is substantially lower than for the parent homologues, but these data are usually interpreted on the implicit assumption of equal reliability. This presentation will demonstrate how this lower reliability constrains valid interpretations of these data, which should help practitioners to avoid invalid conclusions regarding hydrocarbon source contributions in natural resource or property damage assessments from chronic or catastrophic releases of petroleum products.

Hydrocarbon source identification for samples contaminated by petroleum products usually relies on data produced by gas-chromatograph/mass spectrometer (GCMS) systems. A single GCMS analysis produces a wealth of data, and may include results for dozens of hydrocarbon analytes in each of three classes: the polycyclic aromatic hydrocarbons (PAH); the normal and branched alkanes; and the alicyclic hydrocarbons, or biomarkers. Analysis of the biomarkers is often definitive, because these compounds are environmentally persistent and are characteristic of the geologic age and conditions during formation of the petroleum products in question. However, the concentrations of biomarkers in crude oil is low compared with the PAH or other alkanes, and they may be absent entirely from the more volatile fractions of refined petroleum products. This limits the utility of the biomarkers for hydrocarbon source resolution to environmental samples that are heavily polluted by crude oil or its less volatile refined products, such as the bunker oils. In other cases, useful information for source identification may be limited to the PAH and the other alkanes, and these may be altered by weathering processes following introduction into the environment.

Weathering processes often lead to rapid degradation of the alkanes, especially the normal alkanes, while alteration of PAH concentrations is usually slower and more predictable. Hence the PAH are often the primary focus of efforts to deduce hydrocarbon source contributions in samples that are not heavily contaminated. Analytically, the quality of PAH results may distinguished according to the availability and use of authentic calibration standards. These standards are available for many unsubstituted and for some alkyl-substituted PAH, permitting fairly rigorous identification and measurement of these PAH in environmental samples. Unfortunately, the most abundant and persistent PAH in crude and refined oils are the more substituted PAH, which comprise multiple isomers for which authentic calibration standards are rarely available. The identification, measurement and detection limits of these alkyl-substituted PAH is therefore less certain, and their measurement usually relies on response factors that are assumed to be identical to either the un-substituted parent PAH or the most similar alkyl-substituted PAH for which a calibration standard is available. Actual detection limits for these uncalibrated alkyl-substituted PAH are necessarily higher than those of corresponding un-substituted homologues, because the analytical signal is spread among numbers of isomers that increase sharply with increasing alkyl substitution. The limitations imposed by these considerations on efforts to deduce hydrocarbon source contributions to contaminated environmental samples are largely unknown.

In this presentation I compare the variability of calibrated and uncalibrated PAH in a large series of reference samples for the Exxon Valdez oil spill, to evaluate how differences in data quality between calibrated and un-calibrated PAH affect methods for assessing hydrocarbon source contributions. The reference samples were all analyzed by the same method at the same laboratory. Coefficients of variation for the calibrated PAH are typically 10% - 15% for the calibrated PAH, increasing to as much as 50% for the most substituted PAH. This increasing variability constrains the resolution of both analyte ratio methods and of multivariate statistical methods for deducing hydrocarbon source contributions. These limitations are illustrated by comparison with results for hydrocarbons in benthic and riparian sediments from the northeast Gulf of Alaska (GOA). The hydrocarbons in these GOA sediments may be from a collection of closely related sources that preclude weathering alterations following introduction to the environment, and so provide a rigorous test of hydrocarbon source discrimination methods. Analyte ratio results from the reference sample set are compared directly with those from the GOA sediments. Comparison of results for a multivariate statistical approach, which makes much fuller use of the available information than do analyte ratio methods, is accomplished by combining the Aitchison metric applied to hydrocarbon concentration pattern differences among samples, with hierarchical cluster analysis. Results of these comparisons provide an example of the inadequacy of these approaches (especially the ratio methods) to detect hydrocarbon source contribution differences that actually exist in the field, when these sources are closely related geologically and the hydrocarbon analytes are limited to the PAH.

Hydrocarbon Source Identification, Polycyclic Aromatic Hydrocarbon, Oil Spill