



Engineering Sciences Section – 2005

C37 Petroleum or Coal Ash: Determining the Origin of PAH Compounds in Soils

James S. Smith, Jr. OAK CREEK, Inc., Toxicology & Risk Assessment Consulting. 60 Oak Creek, Buxton, ME 04093-6616

After attending this presentation, the participant will understand how methyl aromatic ratio ("MAR") analysis may be used to determine the origin of polycyclic aromatic hydrocarbon ("PAH") compounds in soil and/or sediment. Dr. Smith will describe how MAR is applied to sites in Massachusetts, where the association of PAH compounds with coal and/or coal ash can be used to exclude them from reporting requirements under the Massachusetts Contingency Plan ("MCP"). In addition, recent research into the bioavailability of hydrophobic organic compounds ("HOC") suggests that MAR analysis may be used to support higher remediation goals for PAH compounds in sediments.

This paper has three objectives:

1. to illustrate the importance of determining the legal framework for site investigation activities;
2. to illustrate how MAR analysis may be used to exclude PAH compounds from notification requirements under the MCP and/or identify sediments with low HOC bioavailability.
3. to demonstrate how MAR analysis is applied to site to eliminate a client's environmental and financial liability for PAH compounds in soil and sediment.

The source of PAH compounds in environmental media determines whether such compounds are subject to the provisions of the Massachusetts Contingency Plan ("MCP"). The MCP contains requirements and procedures for notifying the Massachusetts Department of Environmental Protection ("MADEP") of releases and threats of release of oil and/or hazardous material ("OHM") [310 CMR 40.0300]. The release and threat of release of OHM related to coal, coal ash, or wood ash, but not wood ash resulting from the combustion of lumber or wood products, is exempt from this notification rule [310 CMR 40.0317]. As a result these same OHM may also be excluded from risk characterization. Simply stated, if PAH compounds can be shown to source from coal and/or coal ash, they are exempt from regulatory requirements under the MCP. Additionally, sediments shown to contain black carbon (e.g., coal or coal ash) have lower HOC bioavailability to benthic organisms.

Several published papers have demonstrated that analytical techniques can distinguish between sources of PAH compounds related to coal and/or coal ash from those originating from the release of petroleum. One such technique, methyl aromatic ratio ("MAR") analysis, may be used to determine the origins of PAH compounds in soil and/or sediment.

Three major types of hydrocarbon are ubiquitous in environmental media: petrogenic (i.e., crude oil and its refined products), biogenic (i.e., compounds generated by biological processes), and pyrolytic (i.e., compounds generated in combustion processes). Although gas chromatogram/mass spectra ("GC/MS") of PAH compound mixtures from these various sources may not look substantially different to the naked eye, petrogenic and pyrolytic sources of PAHs can be differentiated by relative abundance of methylated and non-methylated PAH compounds. Generally, low temperature generation of PAH compounds (i.e., temperatures below 150° Celsius), such as occurs in the natural generation of crude oil, processing of refined petroleum product and in biogenic processes, yield abundant methyl-substituted PAH compounds. In contrast, high temperature processes (i.e., those greater than 600° Celsius), like those historically associated with manufactured gas plant operations that evolved methane gas from coal, generate predominately unsubstituted non-methylated PAH compounds. This is because such high temperature processes provide the energy required to remove methyl groups from methylated PAH compounds, leaving the thermally stable non-methylated compound. The overall result of high heat processes, therefore, is a reduction in the abundance of methylated PAH compounds and an apparent increase in the abundance of heat stable non-methylated PAH compounds.

In this presentation, Dr. Smith describes how MAR is applied; illustrating the use of MAR analysis to differentiate between petrogenic and pyrolytic sources of PAH compounds.

Methyl; Ratio; Coal/Ash