Tracking a Petrogenic Source with Pyrogenic Compounds: Forensic PAH Apportionment at a Site with Severely Weathered Crude Oil

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Background/Objectives. In support of a "No Further Action" decision, the contribution of spilled crude oil from a pipeline breach to polycyclic aromatic hydrocarbons (PAHs) in floodplain soil was quantified several years after initial cleanup. Challenges included pre-existing urban PAH contamination, advanced weathering of the crude oil from years of surface exposure, and the need to determine whether exceedances of a benzo(a)pyrene (BAP) human health risk criterion were attributable to the spilled crude oil.

Approach/Activities. Using upstream floodplain soil and site crude oil samples collected in a range of weathering states as end members, a PAH apportionment model was developed which was robust to a wide range of oil weathering stages and sensitive to cases where relatively small amounts of crude oil were present.

Anthropogenic PAH sources are generally divided into petrogenic (from fossil fuels and refined petroleum products) and pyrogenic (from combustion of organic matter or fossil fuels) categories. Relative amounts of individual PAHs and other hydrocarbons are used for forensic distinction between these sources. Conventionally, petroleum biomarkers and alkylated PAHs are favored for forensic evaluation of petrogenic sources. At this site, however, the residual crude oil was so altered by years of surface exposure that biomarkers and alkylated PAHs alone were not reliable for crude oil quantification. A site-specific forensic approach was needed to provide quantitative apportionment under conditions of advanced weathering. The high molecular weight, non-alkylated 5- and 6-ring PAHs (5+PAH) are strongly associated with pyrogenic PAH sources and have low concentrations in petrogenic sources, so are generally not used for petrogenic source forensics. However, the 5+PAH were relatively unweathered in the most weathered oil samples at the site and had a distinct fingerprint from background. These qualities led us to develop an apportionment model based on 5+PAHs. To increase sensitivity to small amounts of oil, the model included a biomarker and alkylated PAHs that were most resistant to weathering at the site.

Results/Lessons Learned. Model results had an excellent fit to floodplain soil samples from the spill area, providing confidence in apportionment of BAP to the crude oil. PAH source mixtures in spill area samples with BAP exceedances varied from predominantly crude oil to all background. Soil concentrations of BAP attributed to crude oil ranged from none to 1.3 mg/kg while concentrations of BAP attributable to background sources ranged from 0.1 to 48 mg/kg, demonstrating that no BAP exceedance was due solely to spilled crude oil and that most benzo(a)pyrene at the site originated from other PAH sources. A notable observation was that, in contrast to the general 'rule' that petroleum biomarkers are more resistant to weathering than PAHs, 5+PAHs were more resistant to weathering than biomarkers under site conditions. Therefore, despite their relatively low abundance in crude oil, these 'pyrogenic' PAHs provided a reliable forensic tracer of a petrogenic source at this site. This experience underscores the need to account for PAH source weathering using site-specific data when possible to improve accuracy of source apportionment.