Molecular and stable isotope signatures for source apportionment of PAHs in the River Thames Sediments

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Polycyclic aromatic hydrocarbons (PAHs) are a class of persistent organic pollutants that contain two or more fused benzene rings. PAHs are generated by thermal maturation of sedimentary organic matter, by incomplete combustion of biomass and fossil fuels, and by diagenesis of biogenic precursors. Because some PAHs are carcinogens, the distribution of these compounds in the environment is of significant academic and societal interest, particularly in urbanized settings with multiple sources of PAHs.

This study focuses on investigation of PAHs in sediments in the tidal River Thames. We used a combination of molecular ratios and compound-specific carbon isotope ($\delta^{13}C$) data to determine the sources of these pollutants. We analyzed 26 samples representing the uppermost (0-10 cm) section from 26 cores taken between Richmond and Thames Barrier along the River Thames within the city limits of London. Additionally, we analyzed 24 samples at different depths (max. 1 m) from 3 cores. Molecular characterization (compound identification and concentrations) of PAHs was achieved using gas chromatography-mass spectrometry (GC-MS) and $\delta^{13}C$ values of individual PAHs were determined using a gas chromatograph/combustion/isotope ratio mass spectrometer (GC/C/IRMS).

Our molecular ratio data based on phenanthrene, anthracene, fluoranthene, and pyrene (Phen/(Phen+Anth) vs. Flrt/(Flrt+Pyr)) and benz[a]anthracene, chrysene, indeno[1,2,3-*cd*]pyrene, and benzo[*ghi*]perylene (BaA/(BaA+Chry) vs. IP/(IP+BghiP)) suggested several potential sources of PAHs: the predominance of coal combustion and coal tar material, with an addition of gasoline component. However, $\delta^{13}C$ values for phenanthrene, fluoranthene, benz[a]anthracene, and chrysene showed that PAHs are sourced primarily by coal tar, thus providing a more precise identificaiton of provenance. This study demonstrates the usefulness of an integrated approach whereby molecular characterization is used in conjunction with stable carbon isotopes for PAH source apportionment in an urban settings.