

# **PS Combining Hydropyrolysis and Compound Specific Stable Isotope Measurements to Identify Sources of Biodegraded PAHs in Sediments\***

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## **Abstract**

Compound-specific  $^{13}\text{C}/^{12}\text{C}$  isotope ratio measurements have successfully been demonstrated as a useful technique for polycyclic aromatic hydrocarbons (PAHs) source apportionment in a number of studies. However, where the PAHs matrix have been subjected to heavy biodegradation, and the isotopic signatures for PAHs are overlapping for some sources, further constraints are needed for unambiguous source apportionment.

Given that stable carbon isotopic ratios ( $\delta^{13}\text{C}$ ) of PAHs are not significantly affected by biodegradation and that hydropyrolysis of asphaltenes can generate representative molecular profiles expected for non-biodegraded oils, this methodology has been used for source apportioning hydrocarbons in biodegraded environmental samples.

This protocol has been applied to river sediments, to reveal the variations in isotopic ratio ( $^{13}\text{C}/^{12}\text{C}$ ) (-24 to -28 ‰) in Clyde River sediments, suggesting that the sources of PAHs are numerous, with (petroleum and combustion sources- biomass burning, coal derived, and vehicle particulate) are providing major inputs of the parent PAHs.

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It appeared that the core samples derived their PAHs from coal, petroleum, and combustion of coal, biomass and petroleum. The historical shift in energy use, with time, from coal and coal utilization (-23 to -26‰), coal combustion (-25 to -26‰) and for values (-27 to -30‰), abundant petroleum (-27 to -29‰) and (-30‰) biomass combustion has been revealed.

The localized high level of concentrations of Benzo(a)Pyrene (BaP) and Benzo(k)fluoranthene- (32 - 4225 µg/g) generally, has been ascribed to dumping, and therefore, needs attention. Also, the exceptionally high concentrations of Benzo(k)fluoranthene and BaP with 758.4 µg/g and 846.2 µg/g respectively, in sample 608, has specifically allowed for suggesting petrol and diesel exhausts as major sources of PAHs in Glasgow area.

Finally, this combined technique has proved successful in an unambiguous source apportionment of PAHs in river and estuarine sediments in which hydrocarbons have been biodegraded.

