

SOURCES AND CHRONOLOGY OF POLYCYCLIC AROMATIC HYDROCARBON DEPOSITION IN SEDIMENTS FROM THE LOWER HUDSON WATERSHED.

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Introduction: Input of PAH's to estuarine and marine systems is dominantly controlled by (a) deposition of airborne particulates, (b) surface runoff from roads and land surfaces, or (c) direct inputs from industrial and sewage effluents, and fossil fuel products. It is generally accepted that virtually all the PAH emitted to the atmosphere (natural and anthropogenic) are associated with aerosols, soot and other airborne particulate matter, and that movement of these particulate is the major mechanism of PAH transport over intermediate and long distances. Because of their hydrophobic property, PAH in aquatic environments also rapidly become associated with particulate matter. Hence, particulate transport is an important control on PAH cycling in marine and estuarine environments.

PAH's in the Lower Hudson Watershed: In our ongoing investigation, sediment core samples were collected from the lower stem of the Hudson River into the New York/New Jersey (NY/NJ) Harbor complex. At each site, four cores were collected and the surface (0-2 cm) sections were composited. All composited samples contained measurable activity of Be-7 and are useful for extending chronologies to the late 1990s.



Carbon and hydrogen isotopic characterization of primary PAH sources in the lower Hudson Basin is in progress. Initial observations on primary PAH sources

are broadly consistent with the isotopic signatures for primary sources previously established by O'Malley et al. [1], except for some new ^{13}C -depleted values for power plant soot. Apart from the greater abundance of lower molecular weight and methylated PAHs in petroleum-derived PAH relative to the combustion-derived PAH, the petroleum sources are depleted in ^{13}C relative to the combustion sources [Petroleum: -25.3 to -29.7 ; Combustion: -22.0 to -25.7 ‰].

The highest levels of total PAH were found in the Western NY/NJ Harbor in Newark Bay with peak levels of about 180 ppm total PAH in the early 1950s samples. By the mid-1960s total PAH levels had dropped to about 25 ppm. A comparison of compound-specific carbon isotopic signatures of PAH in sediments representing deposition in the 1950s and 1980s in the Newark Bay has shown that 1950s sediments ($\delta^{13}\text{C}$ of 3-5 ring parentals = -22 to -25 ‰) are isotopically enriched in ^{13}C relative to their 1980s counterpart ($\delta^{13}\text{C}$ of 3-5 ring parentals = -25 to -28 ‰). Thus, an increasing participation of petroleum-related sources appears to be implicated.

Large site to site variations in $\delta^{13}\text{C}$ (>10 ‰) were observed, and likely reflects localized geographic variation of PAH sources. Therefore, a regionally well mixed atmospheric PAH sources do not appear likely to have dominated PAH input in the Lower Hudson. For example, the $\delta^{13}\text{C}$ signature ($\delta^{13}\text{C}$ of 3-5 ring parentals = -27 to -32 ‰) from the Hudson 91.8 mile marker is dramatically different when compared with samples from the NY/NJ Harbor ($\delta^{13}\text{C}$ of 3-5 ring parentals = -22 to -29 ‰). Indeed, the compound-specific $\delta^{13}\text{C}$ signature of the Jamaica ($\delta^{13}\text{C}$ of 3-5 ring parentals = -25 to -29 ‰) and Newark Bay ($\delta^{13}\text{C}$ of 3-5 ring parentals = -22 to -25 ‰) samples are also quite distinct for the 3-5 ring PAH's. Finally, the main stem Harbor (3.0W) PAH inventory appears to have $\delta^{13}\text{C}$ signatures that are intermediate between the Western Harbor PAHs (Newark Bay) and the upstream PAHs (91.8). This observation probably reflects mixing of localized sources in the mp3.0W area with upstream sources. Furthermore, the localized PAH source(s) in mp3.0W appears to bear a strong similarity to PAH sources at the Newark Bay. More refined interpretation must await on going broader isotopic ($\delta^{13}\text{C}$ and δD) characterization of PAH sources in the Hudson basin.

References: [1] O'Malley, V., Abrajano, T. A. and Hellou, J. (1994) Determination of $^{13}\text{C}/^{12}\text{C}$ Ratios of individual PAH from environmental samples: can PAH sources be source apportioned? *Organic Geochemistry* 21 (6-7), 809-822.