

The Role Of Seabed Dynamics In Controlling The Distribution And Preservation Of Polycyclic Aromatic Hydrocarbons (PAHs) In Estuarine Sediments

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LONG-TERM GOALS

Physical processes occurring at or near the water-sediment interface alter, redistribute and control the residence times and accumulation of organic contaminants. The overall objective of this study is to examine the role that energy regime and associated seabed dynamics (e.g., frequency and depths of resuspension) play in controlling the distribution of polycyclic aromatic hydrocarbons (PAHs) in estuarine sediments.

OBJECTIVES

Our objectives are to examine the effects of episodic and short-term variations in seabed erosion/deposition on: (1) the redistribution of organic contaminants between dissolved and particulate phases and (2) the advection and release of contaminants present in interstitial waters to the overlying water column. Specifically, this study is using a number of geochemical tracers to examine processes influencing the distribution of dissolved and solid-phase PAHs in estuarine sediments. These proxies will be used to quantify particle residence times in surface sediments, as well as rates of sediment accumulation and degree of disturbance. Our study is being conducted at sites representative of contrasting depositional environments in the southern Chesapeake Bay and one of its sub-estuaries, the York River.

APPROACH

Several lines of evidence indicate that distributions of polycyclic aromatic hydrocarbons (PAHs) associated with suspended particles and surface sediments collected from our York River site (high energy) differ from those observed at other sites throughout the southern Chesapeake Bay. PAH isomer ratios (an indicator of PAH source) indicate that surface water particles in the York River are largely (up to 81%) derived from coal soot (Fig. 1) and much more similar to sediments in overall composition than surface water particles from Chesapeake Bay. In contrast, surface water particles

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collected from other sites in the southern Chesapeake Bay have PAH isomer ratios indicative of automotive emission sources while sediments are dominated (80%) by signatures consistent with coal soot (Dickhut et al., in prep.). Bottom water particles have PAH isomer ratios that are intermediate in source (64% automotive and 36% coal, on average). Previous work also indicates differences in the quality of organic matter at the York River study site. Signatures of lipid biomarker compounds, stable isotope signatures and C/N ratios all suggest that the particulate organic matter and surface sediments are more refractory at our high energy site in the York River (Murray et al., in prep.).

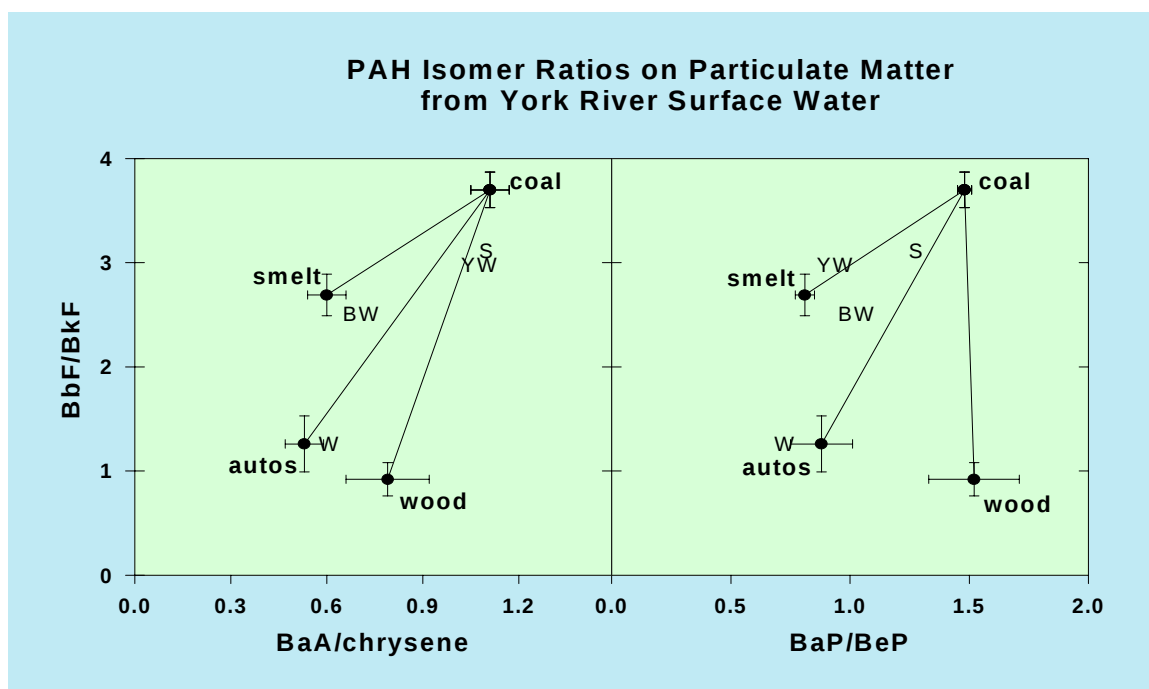


Fig. 1. Ratios of benzo[b]fluoranthene to benzo[k]fluoranthene (BbF/BkF) plotted against ratios of benzo(a)anthracene(BaA)/chrysene and benzo(a)pyrene/benzo(e)pyrene (BaP/BeP) for various sources of PAHs (coal, smelters, auto emissions and wood). Average ratios for surface particles (1m) collected from the water column of the York River (YW), Chesapeake Bay (W), bottom water particles (BW) and sediments (S).

These observations lead us to hypothesize that the high physical energy and deep seabed mixing characteristic of the York River site (Dellapenna et al., 1998) contribute to the observed differences in PAH composition. Frequent physical disturbance can promote degradation of organic matter through the concomitant oxygenation of porewaters (e.g., Aller et al., 1996). Since PAHs encompass a wide range of physical-chemical properties (e.g., solubility), individual compounds partition to differing degrees between dissolved and solid phases. For example, lower molecular weight compounds with relatively low K_{ow} , and thus decreased affinity for particulate and colloidal organic matter, more readily partition into the interstitial waters than higher molecular weight compounds. Consequently, we predict that episodic flushing events associated with storms and periods of increased tidal energy (i.e. neap-spring tidal energy oscillations) will result in renewal of interstitial fluids and exchange of dissolved and/or colloidal associated contaminants with the overlying water column. Given the properties of this compound class, we predict that these processes will preferentially remove, and possibly promote degradation of low MW PAHs and to a lesser extent high MW PAHs. This is

supported by our observation that low MW PAHs including fluorene, 1-methylfluorene and phenanthrene are depleted in sediments from the high energy York River study site compared to sediments from Chesapeake Bay.

WORK COMPLETED

Our goals in the initial phase of this project were to quantify sediment mobility at our physically dynamic (POD) site over spring-neap and episodic (storm) forcings and to identify a steady-state accumulation site within the York River subestuary. Several cores were collected along transects both within and just outside the York river during January and February in an effort to identify a steady state accumulation site. Cs-137 activity was measured in order to screen cores and identify potential high accumulation sites. Pb-210 analysis was conducted at sites where Cs-137 profiles indicated high sediment accumulation rates. To examine the role of tidal and storm forcings in sediment disturbance, we collected a series of kasten cores (3 m) from shoal and channel sites within the York River estuary at two-week intervals and following energetic wind events. A current meter was deployed throughout this sampling period to document changes in energy regime. The timeseries measurements were discontinued in May and resumed in August. Between August and October we have continued to collect cores representing the seabed under neap-spring tidal forcings. In addition to capturing variations in tidal energy, our timeseries includes samples collected during a moderate storm event when we experienced sustained winds >20 kts over a 24-hour period and following Hurricane Floyd (September 1999).

During August and October, sediment cores were collected to document downcore changes in dissolved and solid-phase PAHs at sites representing contrasting energy regimes (i.e., steady-state accumulation and physically disturbed). For this work, a pair of cores (box core with ~40 cm penetration and kasten core with ~3 m penetration) were collected from the study sites. The focus of this effort was to capture an intact sediment-water interface (box core) as well as a historical record of PAH inputs to this region (kasten core). Horizons subsampled from these core will be used to document downcore changes in the concentration of dissolved and solid-phase PAHs in sediments characterized by contrasting energy regimes.

For the study designed to assess the role of neap-spring fluctuations in tidal energy, cores were characterized using x-radiography, water content, elemental analysis and radioisotope distributions (Be-7, Pb-210, Cs-137). On several occasions, pore waters were isolated using centrifugation, filtered and analyzed for PAHs. However, concentrations of dissolved PAHs at the POD site have been below our detection limits. Additional measurements were performed on the cores collected in August (POD) and October (steady-state). These include Eh, dissolved and particulate organic carbon, and dissolved and solid-phase PAHs. Analysis of these cores is underway.

RESULTS

PAH-Organic Matter Associations

A portion of our efforts in the past year have been directed towards synthesizing results obtained from our previously-supported study in which lipid biomarker compounds were used to examine specific interactions between PAHs and discrete organic matter sources. We have employed a form of the Freundlich Isotherm model: $y = ax^n$, where a is the sorption frequency factor and n is the non-linearity factor, y is the sorbed PAH concentration and x is the PAH concentration in water (Schwarzenbach et

al., 1993). This model has typically been used to approximate sorption behavior of a given sorbate in aqueous solution in equilibrium with a sorbent characterized by heterogeneous sites.

A modification of the Freundlich model, where x = the concentration of a specific lipid biomarker, was most useful in predicting associations between lipid biomarker compounds and volatile and methylated PAHs in sediments. Moreover, the sorption frequency factor, differed for the three types of PAHs (volatile, methylated and high molecular weight). The sorption frequency factor represents the amount of contact a given lipid molecule has with the PAH and suggests that PAH relationships with source-specific lipid biomarkers are influenced by the mode of entry of the PAH to the sediments. We found that the sorption frequency factor for volatile and methylated PAHs increased with air-water gas exchange rates. Whereas this factor was constant for high MW PAHs. We propose that a gas exchange mechanism drives volatile and methyl PAH associations with plant and plankton derived organic matter, while the heavier combustion derived PAHs are trapped within a soot matrix, unable to partition with organic matter via a gas exchange mechanism.

Results from this work indicate that PAH behavior is influenced by source and physical chemical behavior. Gas exchange of volatile and methyl PAHs can result in specific PAH-POM associations. OM production within an estuary can thus affect the degree to which an estuary can serve as a “biological pump” for volatile and gaseous PAHs. In contrast, we propose that PAHs introduced as soot particles associate with OM particulates via a different mechanism (i.e., sticking and staying with the particles with which they mix).

Sediment Dynamics

Previous studies of the York River (Dellapenna et al., 1998, Dellapenna) suggested that deep physical reworking dominates the upper York (in particular the area near the POD site) in contrast to the lower York which is characterized by relatively limited physical mixing and some areas of steady-state accumulation. Nearly uniform Pb-210 activity profiles in the upper York suggested mixing to depths as great as ~1 m, and the focus of the current POD-site studies is to quantify the mixing frequency and depths. A time-series of X-radiographs during 1999 show marked variations in the seabed surface, suggesting erosion/deposition on the order of 10 cm in response to spring-neap cycles and wind events. This is supported by seabed measurements of Cs-137 which show varying penetration depths in accord with spring and neap cycles; depths are typically ~10 cm greater during neap (deposition) than spring (erosion). Our preliminary conclusion is that seabed mixing on decimeter scales occurs frequently in response to tidal forcing and wind events, but meter-scale mixing observed from Pb-210 profiles occurs only during major storm events (such as Hurricane Agnes in 19__). Near the York River mouth, steady-state accumulation sites have been found on the channel flanks, with little evidence of extensive physical mixing. The reduced mixing in the lower York may, in part, reflect the general reduction in tidal energy in this area.

IMPACT/APPLICATIONS

Our research has shown the importance of physical and biological processes in determining distributions of PAHs associated with suspended particles and surficial sediments of southern Chesapeake Bay. Results from this study provide insights useful in developing models for predicting contaminant behavior in the environment and assessing the risks PAHs deposited in sediments pose to organisms.

TRANSITIONS

Results from this study complement other studies funded through the ONR Harbor Processes in the lower Chesapeake Bay and Elizabeth River, VA. Our investigation into the role of physical energy in influencing sediment distributions of PAHs also complements ONR-supported work in the Hudson River estuary (Geyer and colleagues).

RELATED PROJECTS

A research grant funded through VA Sea Grant and EPA (to R.M.D.) will support related work in the urbanized Elizabeth River, VA estuary.

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