# SPATIAL AND TEMPORAL DISTRIBUTIONS OF ORGANIC MATTER AND POLYCYCLIC AROMATIC HYDROCARBONS (PAHS) IN SURFACE WATERS OF THE YORK RIVER, VA ESTUARY

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Master of Science

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by
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APPROVAL SHEET

This thesis is submitted in partial fulfillment of
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## ABSTRACT

Models to predict the behavior of polycyclic aromatic hydrocarbons (PAHs) in the environment typically rely on total particulate organic carbon content, but do not specifically address PAH associations with organic matter pools of varying sources and reactivities. The overall objective of this study was to ascertain whether distinct groups of PAHs are associated with specific pools of particulate organic matter (POM) in estuarine surface waters. To examine the spatial and temporal variability of particulate PAHs and particulate organic matter, surface water samples were collected seasonally from six sites along the York River (VA) estuarine gradient between June 1998 and April 1999. Lipid biomarker compounds (sterols and fatty acids) were analyzed to examine associations of particulate PAHs with organic matter and to help elucidate sources of organic contaminants to the estuary.

Spatial variations in York River surface water POM were greater than temporal, and POM was dominated by autochthonous sources. Carbon-normalized total fatty acid abundances ranged from 3.61 to 61.4 $\mu g\ mg_{oc}^{-1}$, and were dominated by polyunsaturated fatty acids, biomarkers indicative of phytoplankton. Total sterol abundances varied between 1.88 and 5.39 $\mu g\ mg_{oc}^{-1}$, and were similarly dominated by the autochthonous sterols, reflecting zooplankton and phytoplankton sources. Based on carbon and nitrogen isotopic signatures and enrichments in allochthonous sterols and fatty acids relative to total organic carbon, a terrestrial source of organic matter was evident in the freshwater portion of the estuary.

The particulate PAH content of particles also exhibited more spatial than temporal variability. Total particle-associated PAH concentrations (normalized to total suspended solids, TSS) ranged from 264 to 1080 ng $g_{TSS}^{-1}$. Particulate perylene concentrations were typically the highest and most variable of all PAH compounds, ranging from 23.3 to 505 ng $g_{TSS}^{-1}$. The highest perylene concentrations were at the head of the estuary, suggesting the freshwater end-member as the dominant source of perylene in this system.

Principal component analysis (PCA) indicated that particulate PAHs could be classified into three distinct subgroups, based on their sources and physiochemical behavior: volatile PAHs, combustion-derived, predominantly particle-associated PAHs, and perylene. Isomer ratios of combustion-derived PAHs indicated that coal is the primary source of these PAHs to York River surface waters, probably the result of sediment resuspension.

During June and April the strongest positive correlations were observed between autochthonous lipid biomarkers and volatile PAHs, which may be explained by a growing pool of organic matter becoming available for PAH partitioning of PAHs entering the estuary via gaseous atmospheric flux. In contrast, strong positive correlations between all PAHs and allochthonous organic matter were observed between August and February. These relationships suggest the potential importance of sediment resuspension as a source of PAHs to surface waters, and may be driven by similarities in compound stabilities rather than true associations. The varying relationships between particular groups of PAHs and organic matter pools demonstrated in this study suggest that very specific pools of organic matter, as opposed to concentrations of organic carbon alone, can be important in the fate and transport of hydrophobic contaminants.

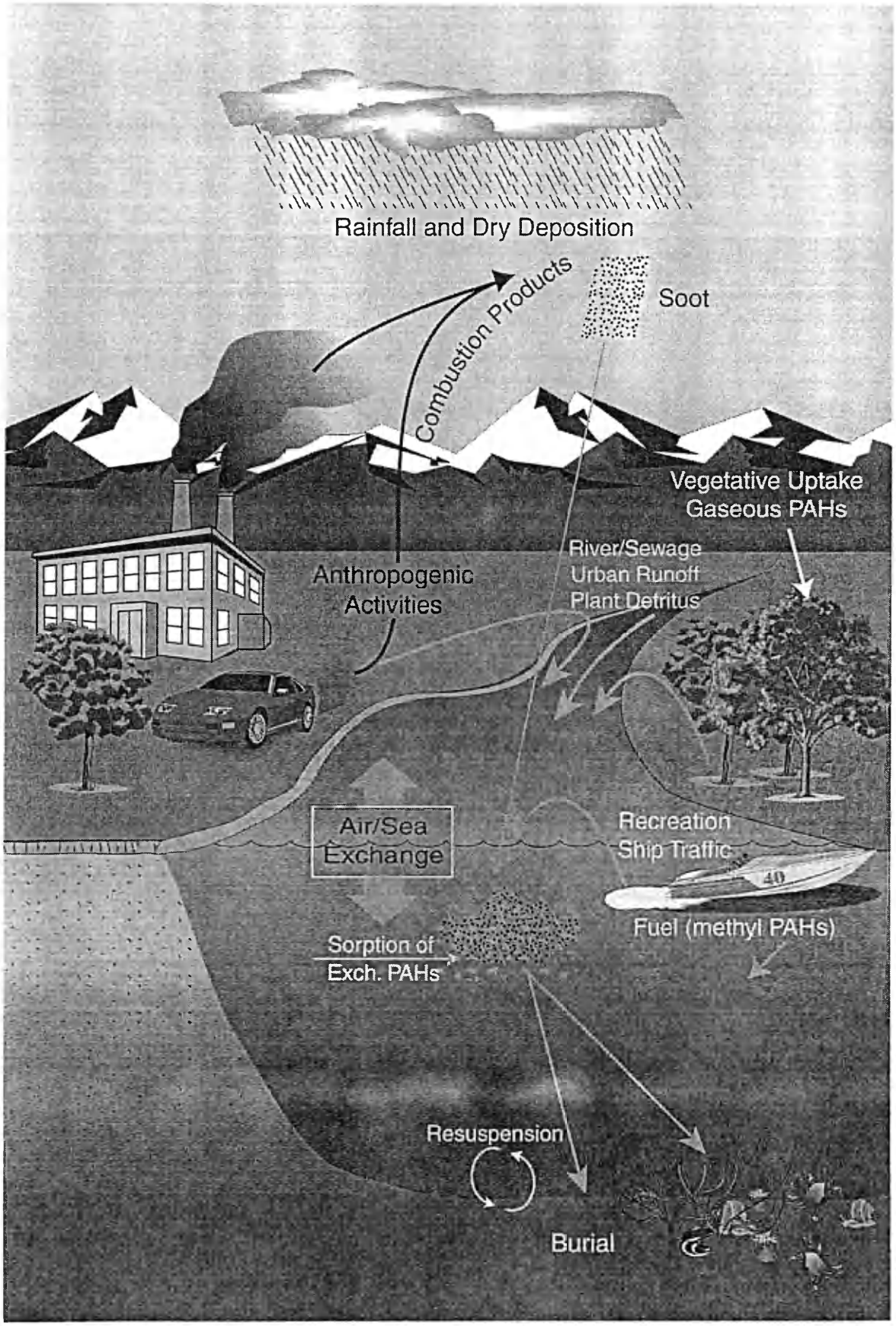
# Spatial and Temporal Distributions of Organic Matter and Polycyclic Aromatic Hydrocarbons (PAHs) in Surface Waters of the York River, VA Estuary

## INTRODUCTION

Polycyclic aromatic hydrocarbons (PAHs) are hydrophobic organic contaminants that are a natural component of uncombusted petroleum products. As well, PAHs are produced by the condensation of hydrocarbon fragments during the incomplete combustion of fossil fuels and other organic matter. PAHs are composed of two to eight aromatic rings, and thus exhibit a continuum of physical and chemical properties. PAH vapor pressures range (at 25 °C) from $10^{-12}$ to $10^{-4}$ atm (Schwarzenbach et al., 1993), resulting in variable distributions of the compounds between the vapor and particle phases in the atmosphere. For example, low molecular weight species such as phenanthrene exist almost entirely in the vapor phase in the atmosphere, while high molecular weight species such as benzo[a]pyrene (b[a]p) are almost entirely associated with particles (Lipiatou et al., 1997). Likewise, PAHs exhibit aqueous solubilities ranging from $10^{-7}$ to $10^{-1}$ mol $m^{-3}$, which result in the low molecular weight species existing predominantly in the dissolved phase and high molecular weight species occurring almost exclusively in the particulate phase (Lipiatou et al., 1997, and references therein).

PAHs may enter estuarine systems in either dissolved or particulate form via atmospheric deposition (dry deposition or associated with precipitation, or air-water gas transfer), river discharge and terrestrial runoff (Fig. 1). These contaminants also may be reintroduced into the water column by the resuspension of sediments. Primary sources of PAHs include, but are not limited to, fossil fuel combustion, waste incineration, natural fires, terrestrial runoff

Figure 1. Sources and fate of polycyclic aromatic hydrocarbons in estuarine systems. From Arzayus et al., 1999a.


Rainfall and Dry Deposition
Soot
Combustion Products
Vegetative Uptake
Gaseous PAHs
River/Sewage
Urban Runoff
Plant Detritus
Anthropogenic
Activities
Air/Sea
Exchange
Recreation
Ship Traffic
Fuel (methyl PAHs)
Sorption of
Exch. PAHs
Resuspension
Burial

(particularly road runoff), petroleum sources such as oil seepage and spills, and natural petroleum seeps in the marine environment. Removal processes from surface waters may include settling of biotic and abiotic particles containing PAHs and accumulation in bottom sediments, as well as volatilization across the air-water interface.

Whitehouse (1984) suggests that while numerous factors determine the ultimate distribution of PAHs in the aquatic environment, aqueous solubility is a major initial factor. Aqueous solubilities of hydrocarbons have been demonstrated to influence or determine their bioaccumulation, biosorption, sorption to minerals and marine sediments and transport in the marine environment. Whitehouse (1984) examined the change in solubility of six PAH compounds (phenanthrene, anthracene, 2-methylanthracene, 2-ethylanthracene, 1,2-benzanthracene and benzo[a]pyrene) in response to temperature changes from 3.7 to 25.3°C and salinities ranging from 0 to 36.7. With the exception of 1,2-benzanthracene, he found that these PAHs exhibited "normal" solubility trends: decreasing solubility with increasing temperature and with increasing salt concentration. The solubilities of these PAHs were far more sensitive to changes in temperature than salinity. For example, for anthracene, a 4°C decrease in temperature caused the same reduction in solubility as change from 0 to 33.1ppt salinity. Since the solubility of a hydrocarbon is inversely related to its organic matter/water partition coefficient (Schwarzenbach et al., 1993), it is anticipated that changes in PAH distributions along the estuarine gradient will be more affected by seasonal changes in surface water temperature than by downstream

changes in salinity. This is supported by Readman et al. (1982) who sampled surface waters of the Tamar Estuary (England) with salinities between 0 and 30, and observed no "salting-out" effects. Thus, due to the complexity of the natural environment, it is not possible to predict PAH distributions from solubility data alone (Whitehouse, 1984).

Saliot et al. (1990) point out that naturally derived and anthropogenic hydrocarbons associated with particles or in the dissolved state undergo important changes with respect to their initial composition, and suggest that in estuaries, the fate of hydrocarbons is dependent on steep gradients in physio-chemical properties such as salinity, pH, energy, tides, wave amplitude and biological processes at the water/particle interface. They suggest that one of the most important features governing hydrocarbon transport processes and their ecotoxicological impart is the partitioning between the dissolved phase, the colloidal phase and the fraction associated with suspended particles. In order to examine the biogeochemistry of organic matter in estuaries at the freshwater/seawater interface, Saliot et al. (1990) studied three river systems characterized by varying contaminant and suspended particle loads. They determined that the ratio between particulate and dissolved hydrocarbon concentrations varies with suspended matter load and season, and suggested that the ratio may be modified by biological activity of the waters.

The research presented in this thesis was conducted to further our understanding of contaminant – particulate organic matter interactions in estuaries. Specifically my research was designed to investigate the spatial and

temporal variability in PAH – organic matter associations with suspended particles in the York River estuary. In addition, dissolved phase and atmospheric (gas and aerosol) PAH data were collected in order to further examine the link between atmospheric deposition of contaminants and their incorporation into surface water particles. The first research topic is the primary subject of this thesis; however, data for evaluation of the latter question are provided in the Appendices B and C.

## RATIONALE

Estuarine regions are important coastal areas to study, as they are regions of both high pollutant input and resource use. Over 50% of the world population lives within 100 miles of the coast (Hinrichsen, 1997), and the coastal ocean (including estuaries) is thus the recipient of many anthropogenic pollutants from municipal, industrial and agricultural wastes. In spite of anthropogenic pressures, estuaries remain dynamic and productive ecosystems, and are areas of immense ecological, environmental and economic value. Their varied habitats and high rates of primary production allow estuaries to be home to a diversity of plant and animal life that supports recreational and commercial fisheries (National Science and Technology Council, 1995). Consequently, understanding the fate and transport of pollutants in estuarine environments is imperative to maintaining the health of these invaluable environments.

Polycyclic aromatic hydrocarbons (PAHs) were one of the first pollutants to be identified as being carcinogenic to humans (Baek et al., 1991). In addition to directly impacting human health, a number of PAH compounds have been

identified as either carcinogenic or mutagenic to both terrestrial and aquatic organisms (Phillips and Grover, 1994; Denissenko et al., 1996). The combustion of fossil fuels (gasoline, kerosene, diesel and coal), waste incineration, coal gasification and liquification processes, petroleum cracking, and the production of coke, carbon black, coal tar pitch and asphalt have been identified as important anthropogenic sources of PAHs (McVeety and Hites, 1988). PAHs may also be released into the marine environment via industrial wastewater, sewage, road runoff/street dust, and because PAHs are also present in uncombusted petroleum, through oil spills and ship traffic (Bouloubassi and Saliot, 1991).

Atmospheric transport is responsible for the ubiquity of many contaminants, including PAHs (LaFlamme and Hites, 1978; McVeety and Hites, 1988). LaFlamme and Hites (1978) observed not only that PAHs are distributed in marine sediments world-wide, but also that the qualitative PAH pattern is remarkably constant; a finding they determined to be consistent with anthropogenic combustion as the major source of PAHs. However, Bouloubassi and Saliot (1993) point out that although various classes of hydrocarbons (including PAHs) have been extensively studied in sediments, their transport processes from sources to sinks remain poorly understood. Assessment of the input record in surficial sediments, and the factors controlling it, requires knowledge of the sources of contaminants and their transport pathways prior to deposition to the sediment bed.

In the southern Chesapeake Bay region, absorption of atmospheric gas phase contaminants has been identified as a significant source of PAHs to

surface waters (Gustafson and Dickhut, 1997b). While some researchers have reported that PAHs in the atmosphere are mostly associated with particulate matter (Baek et al., 1991), Gustafson and Dickhut (1997a) determined that total atmospheric PAH concentrations over the southern Chesapeake Bay were dominated by the more volatile PAHs such as phenanthrene and fluorene. This resulted in the gas phase, rather than the particulate phase, having the highest levels of PAHs between January 1994 and June 1995. Gustafson and Dickhut (1997b) calculated that gas exchange fluxes of semivolatile PAHs such as phenanthrene and fluoranthene into the Chesapeake Bay are of the same magnitude as the total wet and dry atmospheric depositional fluxes for these compounds. Thus, organisms residing near the air-water interface may be exposed to high levels of these more volatile PAHs as a result of gaseous fluxes.

Although it is important to note that both aerosols and gases contribute to the total atmospheric flux of PAHs to surface waters, gas phase contaminants may have a greater impact on the pelagic biology of the estuarine system than particle-associated contaminants. While pollutants associated with aerosol particles need to desorb before they can be incorporated into organic matter such as phytoplankton, zooplankton and bacteria, gas phase contaminants can diffuse directly into phytoplankton cells and other organic matter. Research has indicated that frequently a significant fraction of high molecular weight, less volatile PAHs associated with particles appear to be irreversibly bound, and are thus unavailable for partitioning from particles to water (Readman et al., 1987; McGroddy and Farrington, 1995; McGroddy et al., 1996). In contrast, PAHs such

as phenanthrene are >90% in the gas phase in air at ambient temperatures (Bidleman, 1988). Therefore, phenanthrene and other gaseous PAHs enter surface waters largely via air-water gas exchange. Following absorption by surface waters, gaseous PAHs associate with organic matter, including phytoplankton, due to their hydrophobicity. However, gaseous PAHs may also associate with allochthonous organic matter, prior to or after its delivery to the estuarine system.

Phytoplankton can range from 3 up to 30% lipid by weight, and therefore have a high affinity for organic contaminants (Swackhamer and Skoglund, 1991). Because phytoplankton comprise the base of the food web, the partitioning of organic contaminants into phytoplankton has important implications for aquatic food web dynamics. Likewise, because the partitioning of contaminants to organic matter is a passive process, it should be noted that other sources of particulate organic matter, such as bacteria, which are often very abundant in estuarine surface waters, may play a role in the distribution of organic contaminants and their incorporation into higher trophic levels. In addition, since terrestrial organic matter comprises a significant, although less important component of the marine food web (Riera and Richard, 1996) association of organic contaminants with this carbon pool may also influence higher organisms. Thus phytoplankton, bacteria, and to a lesser extent terrestrial organic matter, may serve as the predominant sources of organic contaminants, including PAHs, derived from atmospheric gas exchange to higher trophic levels.

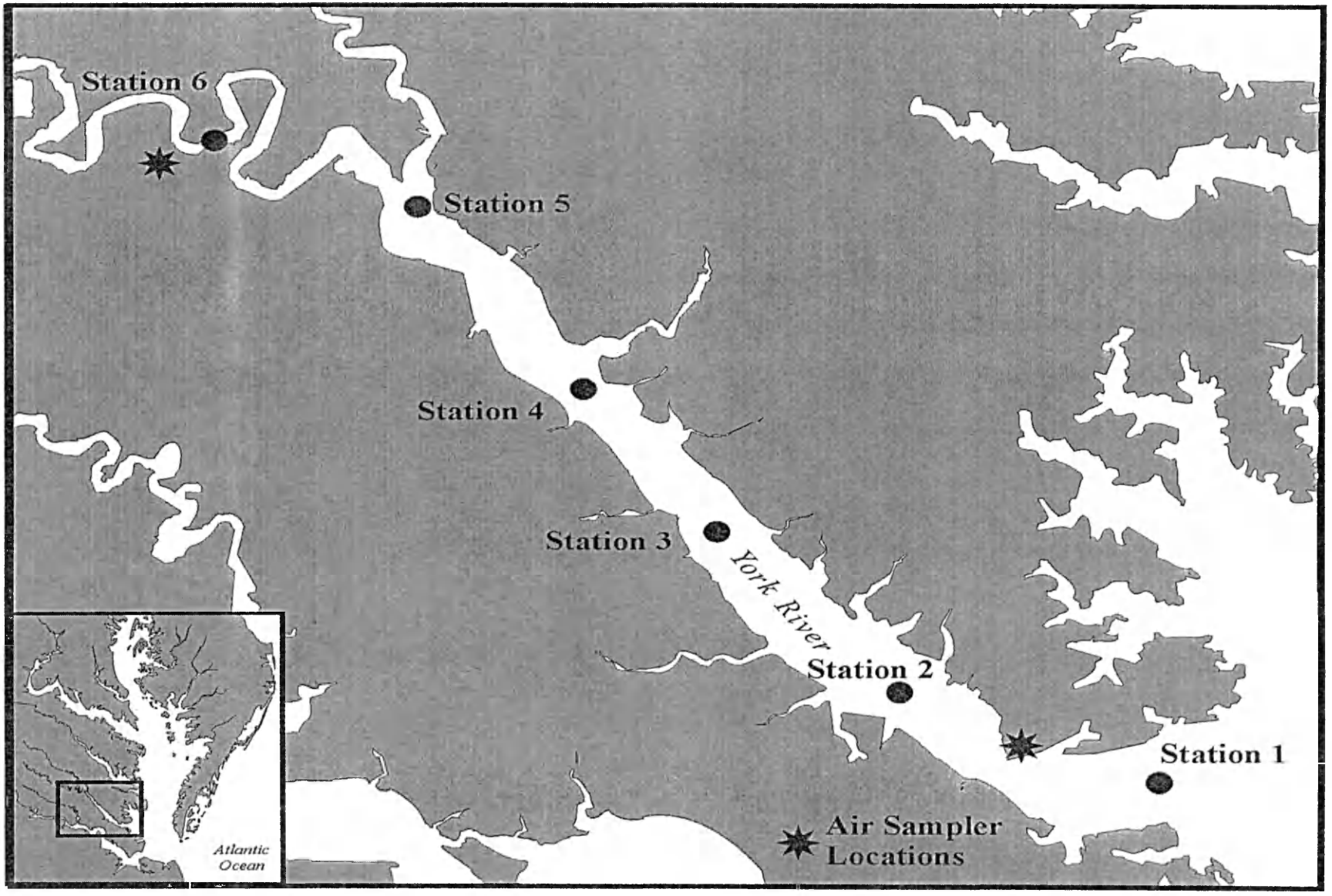
## HYPOTHESIS

The objective of this study was to ascertain whether volatile PAHs, which typically enter estuarine surface waters via gaseous atmospheric flux, are preferentially associated with autochthonous particulate organic matter. The primary hypothesis is that PAH - organic matter associations in estuarine surface waters will be dictated by the dominant mode of entry of the organic contaminants to the estuary. Thus volatile PAHs are expected to be positively correlated with phytoplankton biomarkers during periods of high productivity. In contrast, at times when gas transfer of PAHs is low, but particles indicative of terrestrial runoff/riverine inputs of organic matter are high, PAHs will be positively related to allochthonous biomarkers. This latter relationship may result from direct contaminant associations with terrestrial organic matter, from similar mechanisms of transport to the surface waters of *un*associated particulate PAHs and terrestrial matter, or as a result of similar reactivities of PAHs and terrestrial organic matter with particles in the estuary. To assess the potential relationships between PAHs and natural organic matter in the York River estuary, concentrations of PAHs in surface waters along the York River estuarine gradient, and their temporal variability were examined. In addition, the spatial and temporal distributions of organic matter in surface waters and their relationships with PAHs along the York River estuarine gradient were also investigated.

## STUDY AREA

The York River estuary (Fig. 2), a subestuary of the Chesapeake Bay, is composed of three rivers: the Pamunkey and the Mattaponi, which converge to

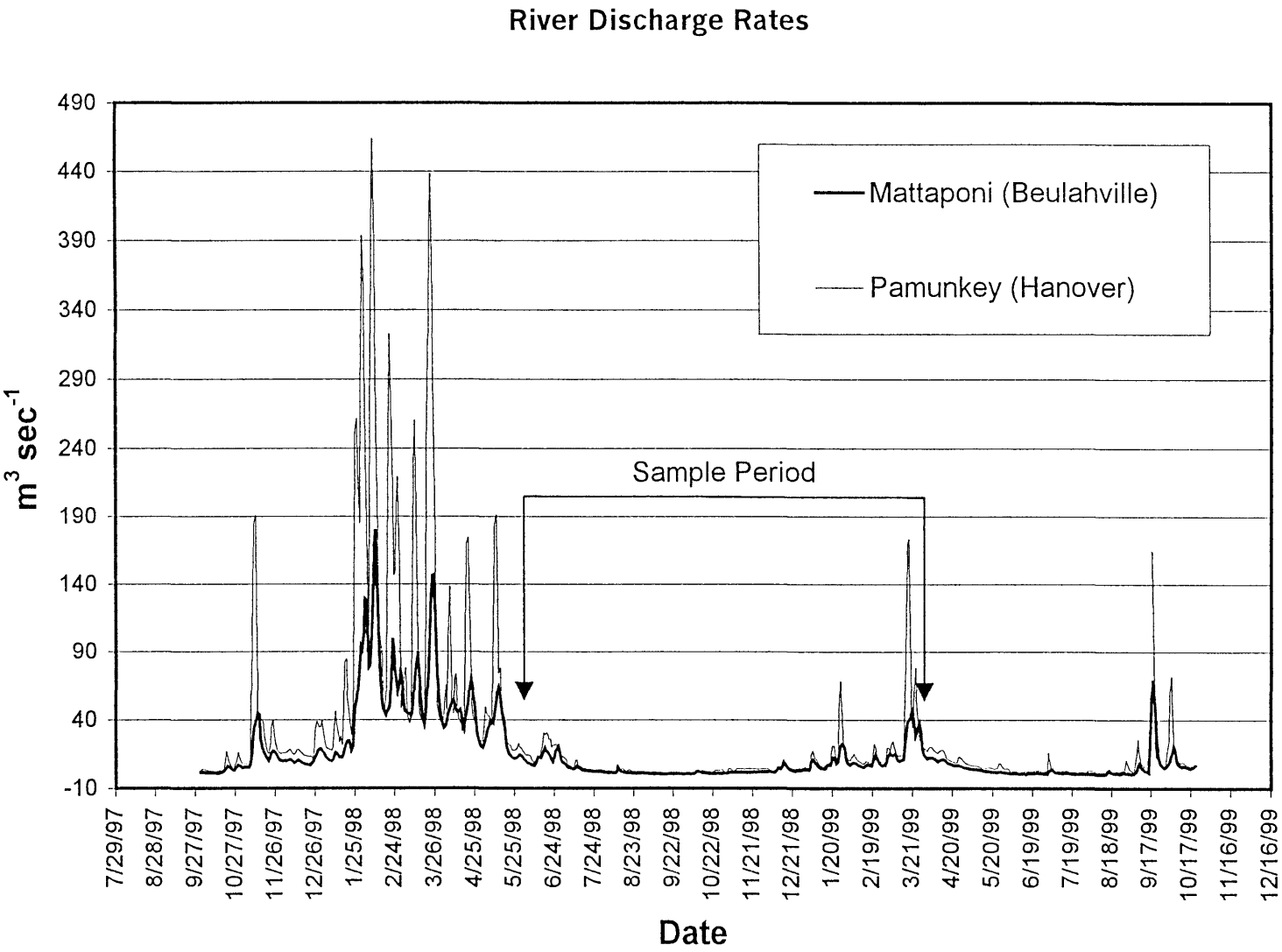
Figure 2. Surface water sampling locations in the York River, VA estuary.


Station 6
Station 5
Station 4
Station 3
York River
Station 2
Station 1
Air Sampler Locations
Atlantic Ocean

form the York. The confluence of the two tributaries occurs near West Point, VA, approximately 48 km from the mouth of the York River. The salinity of the York River system is influenced by the interactions of freshwater, salt water, tidal energy and wind (Sin et al., 1999). The mean tidal range is 0.61 m at the mouth of the York River, increases to 0.88 m at West Point, and subsequently decreases (Schultz, 1999). Periods of high discharge tend to occur in winter and spring, followed by reduced flow conditions in the summer and fall (Fig. 3). During periods of low flow, salt water may extend well upriver of West Point.

Six surface water sampling stations were selected to represent the salinity range of the York River estuarine system (Fig. 2). These stations are coincident with those used by a number of other studies in the York River, in particular a study of estuarine bacterial dynamics by Schultz (1999). Station 1 (traditionally labeled WE4.2 in Chesapeake Bay Water Quality Monitoring Studies), at the mouth of the York River is considered mesohaline, with a typical surface water salinity range of 12-23 psu. Stations 2, 3, and 4 provide additional coverage of the mesohaline region. Station 3 is the same as the York River "Pod" site, where numerous seabed dynamics and sediment studies have been conducted (Wright et al., 1996; Dellapenna et al., 1998). Station 5 is located just below the confluence of the Pamunkey and Mattaponi Rivers and Station 6 is located in the tidal freshwater zone, near Sweet Hall Marsh in the Pamunkey River. Salt and freshwater marshes border the Pamunkey River throughout the study region, and continue upstream of Station 6. See Appendix A for additional station details.

Figure 3. River discharge rates from September 1997 through October 1999 of the Pamunkey and Mattaponi Rivers, which merge to form the York River (USGS Water Resources Division, 1999).


River Discharge Rates
490
440
390
340
290
240
190
140
90
40
-10
m3 sec-1
Mattaponi (Beulahville)
Pamunkey (Hanover)
Sample Period
7/29/97
8/28/97
9/27/97
10/27/97
11/26/97
12/26/97
1/25/98
2/24/98
3/26/98
4/25/98
5/25/98
6/24/98
7/24/98
8/23/98
9/22/98
10/22/98
11/21/98
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5/20/99
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7/19/99
8/18/99
9/17/99
10/17/99
11/16/99
12/16/99
Date

The region surrounding the mouth of the York River is considered semi-urban. The shores are populated, and between Stations 1 and 2 there is an oil refinery, a coal/oil-fired power plant and the Coleman Bridge (a major vehicular crossing). The only apparent industry on the Pamunkey River is a pulp and paper mill located in West Point, just upstream of Station 5. There is a second, but much smaller, vehicular crossing in this same area. Runoff from agricultural activities influence water quality of both the Pamunkey and York Rivers. Nonetheless, according to the Virginia Department of Environmental Quality (1994), the York River is one of the most pristine sub-estuarine systems in the entire Chesapeake Bay system.

## MATERIALS AND METHODS

### *Sampling Methods*

Surface water samples, from one meter below the surface, were collected at all six stations (except in August 1998 when replicate samples were collected at Stations 2, 4 and 6) off the bow of a small vessel. In order to minimize the possibility of contamination, the vessel engine was turned off during sampling and surface water samples were collected from the York River by means of a high volume peristaltic pump. Polyurethane and silicone tubing was used to avoid contamination.

Water for organic contaminant and lipid biomarker analyses was collected into 36 liter solvent-rinsed stainless steel tanks prepared by sequential rinsing with Alconox and distilled/deionized (DI) water, DI water, acetone, hexane,

dichloromethane, hexane, acetone and DI water. Approximately one to two sample volumes was passed through the pump system prior to sample collection to equilibrate tubing surfaces with ambient contaminant levels and to minimize sorptive losses from the dissolved phase. These water samples were transported back to the laboratory and filtered within 10 hours of collection.

To separate the particulate matter, the tanks were pressurized with ultra-high purity nitrogen and the sample eluted through pre-combusted (4 hours @ 450 °C) glass fiber filters (Gelman type A/E, 142 mm, nominal pore size 1μm) followed by pre-cleaned (sequential Soxhlet extractions with methanol, acetone, hexane, dichloromethane, hexane, acetone, and methanol followed by DI water rinses) Amberlite® XAD-2 resin contained in a stainless steel column (2.2 cm diameter x 35 cm long). Thus the dissolved phase was operationally defined as all materials which pass through the 1 μm filter and collect on the surface of the XAD-2 resin. Filters were stored in 75 ml of a 2:1 dichloromethane:methanol mixture and frozen (-80 °C) until extraction. The XAD-2 resin was stored submerged in methanol and refrigerated (4 °C) until extraction.

Water for bulk particle property measurements was also collected via the peristaltic pump, into pre-cleaned, sample-rinsed 2-liter high-density polyethylene jugs. Two 2-liter jugs were collected at each station and stored on ice until sample processing, within 8 hours of collection. This water was subsampled for total suspended solids (TSS), particulate organic carbon and particulate nitrogen (POC, PN), stable isotopes of carbon and nitrogen ($\delta^{13}C_{oc}$, $\delta^{15}N$), and chlorophyll-*a* measurements upon return to the laboratory. Between 250 and 500

ml, depending on particle load, was filtered onto 47 mm glass fiber filters (Gelman type A/E) for chlorophyll-*a* analysis. Pseudo-replicates were filtered for each station and filters were folded in half and stored frozen in small ziplock bags. Both POC/PN and isotope samples were filtered onto pre-combusted (4 h @ 450 °C) 13 mm glass fiber filters (Gelman type A/E). Three aliquots (25-50 ml, depending on particle load) were filtered for each measurement at each station and filters were stored frozen in acid-rinsed petri dishes until analysis. For TSS measurements, 250 to 500 ml was filtered onto numbered, pre-weighed glass fiber filters (Gelman type A/E). Filters were rinsed with DI water to remove salts and samples were stored in petri dishes until analysis. At least three aliquots were filtered for TSS from each station.

A Niskin bottle was used to collect water for measuring temperature, dissolved oxygen (DO), dissolved organic carbon (DOC) and salinity. Prior to sample collection, the bottle was allowed to soak for a few minutes at 1 meter below the surface. Water temperature was recorded immediately upon sampling the Niskin. Replicate samples were collected for DO, DOC and salinity. DO samples were fixed immediately upon collection with mangnous chloride and sodium iodide solutions. DOC samples were stored on ice until return to the laboratory. In the lab DOC samples were filtered through pre-combusted (4 h @ 450 °C) GFFs (Gelman type A/E) and the filtrate collected into pre-cleaned vials. The filtrate was acidified with several drops of 6N hydrochloric acid, and stored in the refrigerator until analysis.

### *PAH and Lipid Biomarker Analyses*

Extraction and analysis of dissolved phase PAHs are reported elsewhere (Appendix B). Particulate water samples (glass fiber filters) were extracted using a microwave-assisted solvent extraction (MASE) modification of the Bligh-Dyer extraction procedure (Bligh and Dyer, 1959). After the addition of PAH[1] and lipid[2] surrogate mixtures, the filters were extracted twice in a 2:1 solution of dichloromethane:methanol. Following each extraction the samples were centrifuged at 1800 rpm for 10 minutes at 20 °C, and the supernatant decanted into separatory funnels. This mixture was partitioned by adding methanol and 20%NaCl in hexane-extracted water such that the final solution was 1:1:0.9 dichloromethane:methanol:water (Bligh and Dyer, 1959). After collection of the organic phase, the aqueous fraction was back-extracted three times with equal amounts of hexane and hexane-extracted water. The hexane fractions were then added to the partitioned organic fraction, and the combined organic phases dried with $Na_2SO_4$ overnight. After drying, the previously combined organic phases were reduced to a total of 4 ml hexane (including rinses) by turbo-evaporation. The resulting extracts were gravimetrically divided into two sub-samples: one for subsequent PAH analyses and the other for lipid determinations. PAH samples were stored in 15 ml centrifuge vials at 4 °C. Extracts for lipid analyses were given a nitrogen headspace and frozen (-20 °C).

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[1]For all PAH analyses the surrogate standard mixture contained $d_{10}$-anthracene, $d_{12}$-benz[a]anthracene, $d_{12}$-benz[a]pyrene and $d_{12}$-benz[ghi]perylene.
[2]For all lipid analyses the surrogate standard mixture contained a $C_{19}$ fatty acid methyl ester (FAME), a $C_{19}$ alcohol and a wax ester that yielded a $C_{14}$ alcohol and a $C_{20}$ FAME following saponification.

PAH samples were purified by solid-liquid chromatography on silica gel (mesh 100-200) prior to PAH analysis in order to remove interfering compounds. Following silica gel purification, the PAH fraction was concentrated by rotoevaporation. The final extract was concentrated to approximately 150 μl under $N_2$ after the addition of an internal standard[3] containing deuterated PAHs. PAHs were quantified relative to deuterated surrogate PAHs using gas chromatography-mass spectrometry (GC-MS; Hewlett Packard 5890 Series II gas chromatograph/Hewlett Packard 5971A mass spectrometer). Compounds were separated using a 30 m x 0.25 mm DBL-XB column and peaks detected using selected ion monitoring.

The lipid subsample was blown to dryness under a gentle stream of nitrogen and subsequently dissolved in a known volume of dichloromethane. The total lipid extract (TLE) weight was determined gravimetrically by weighing aliquots of the extract following solvent evaporation with mild heat. After the determination of the TLE weight, a portion of the extract was saponified to release esterified compounds. Briefly, the extract was hydrolyzed (KOH in aqueous methanol) and re-extracted under basic (pH 12) and acidic (pH 2) conditions (Canuel and Martens, 1993). Constituent classes of neutral lipids were separated by adsorptive chromatography on silica gel. The sterol fraction was then derivatized to trimethyl silyl ethers (TMS) and analyzed by gas chromatography (Hewlett Packard 5890 Series II Plus) with flame ionization detection and a 30 m x 0.32 mm DB5 column following the addition of 5α-

[3]For all PAH analyses the internal standard mixture contained $d_{12}$-phenathrene, $d_{12}$-chrysene and $d_{12}$-perylene.

cholestane as an internal standard. After methylation with $BF_3$-methanol, the acidic lipids were purified by column chromatography (silica gel). The fatty acid methyl ester compounds (FAMEs) were then analyzed by gas chromatography (Hewlett Packard 5890 Series II) with flame ionization detection and a 30 m x 0.32 mm DB5 column, using methyl heneicosoate ($C_{21}$) as the internal standard. For both classes of lipids, identification of individual compounds was based on reference standard compounds, when available, and with verification by GC-MS (Hewlett-Packard 6890 Series GC System/Hewlett Packard 6890 mass spectrometer) using a 30 m x 0.32 mm DB5 column.

***Bulk Particle Properties Analyses***

Total suspended solids were determined by gravimetric analysis. Filters were dried overnight at 105 °C and then cooled in a dessicator. Filters were weighed repeatedly until the masses were within 5% (0.5 mg) of each other. TSS was then determined by difference. Measurements were made in triplicate, and the sample mean reported.

Particulate organic carbon and particulate nitrogen were quantified using a Fisons EA1108 CHNS-O elemental analyzer. Filters were thawed and then dried overnight at 65 °C. The filters were then acidified by placing them in a dessicator with saturated HCl fumes. After acidification the filters were again dried at 65 °C. Just prior to analysis the filters were packed into pre-combusted (4 h @ 450 °C) silver capsules. In the elemental analyzer, samples were flash-heated to 1050 °C to convert organic matter to $CO_2$, $NO_x$ and $H_2O$. Two filters for each station were analyzed.

Isotopic carbon and nitrogen ($\delta^{13}C_{oc}$ and $\delta^{15}N$) were analyzed by the Stable Isotope Facility at the University of California, Davis. Chlorophyll-*a* samples were determined by VIMS's Analytical Service Center using spectrophotometric analyses (Parsons, et al., 1984).

### *Ancillary Measurements*

The following analyses were performed by the VIMS Analytical Service Center. Salinity was measured by electrical conductance (Parsons et al., 1984). Dissolved oxygen concentrations were determined by Winkler titration (Carpenter, 1965). Dissolved organic carbon was determined by high temperature catalytic oxidation techniques using a Shimadzu TOC 5000A (Williams et al., 1993).

### *Principal Component Analyses*

Principal component analysis (PCA), a form of multivariate analysis, was used as a means of reducing the dimensionality of the PAH data set, which included 20 PAH compounds (or variables) per station. As well, PCA was used to examine the compositional similarities and differences of lipid biomarker and PAH distributions at the various stations. Briefly, the aim of PCA is to determine a few linear combinations of the original variables which can be used to summarize most of the variance, or information, contained in the original data set (Meglen, 1992). PCA output includes two matrices of information: the principal component scores and the principal component loadings. The scores matrix illustrates relationships among samples, while the loadings matrix contains information

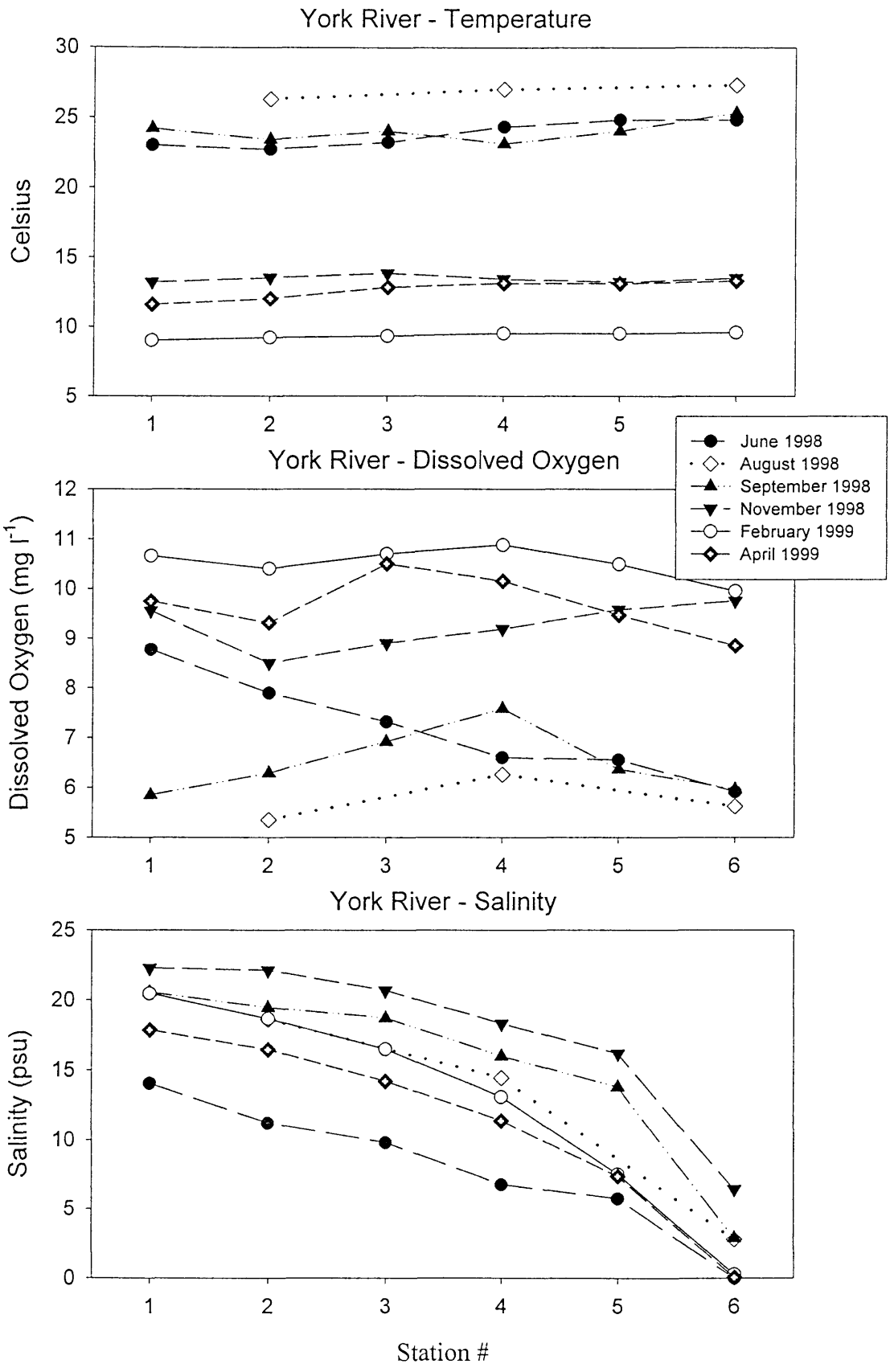
about the relationships among variables. Organic carbon-normalized fatty acid and sterol data were used in PCA analyses of lipid biomarkers, while PAH concentrations were TSS-normalized. The correlation matrix, which scales the variance of the data (often referred to as z-scoring), was used for all PCA analyses. Sterol and PAH data were analyzed using Minitab 12.1 (Minitab, Inc., 1998), while SAS System for Windows, (Release 6.12, SAS Institute, Inc.) was used to analyze fatty acid data because this software allowed the number of variables to exceed the number of samples.

## RESULTS

### *Ancillary Measurements*

There was little spatial variability in sample temperature over the course of a sampling event, with temperatures varying only 2.1 °C or less along the sample transect (Fig. 4). As expected, surface water temperatures varied seasonally, with lows of 9.0-9.6 °C in winter (February 1999) and highs of 26.3-27.3 °C in the summer (August 1998). Dissolved oxygen (DO) concentrations also exhibited very little spatial variability from month to month, except in June when steadily declining DO was observed from the mouth to the head of the estuary (Fig. 4). Surface water dissolved oxygen levels were highest in February 1999, ranging from 9.96 to 10.9 mg $l^{-1}$, and lowest in August 1998 fluctuating between 5.35 and 6.26 mg $l^{-1}$, demonstrating an inverse relationship between DO and salinity. In contrast, salinity varied both spatially and temporally throughout the year-long study period (Fig. 4). During any one sampling event salinity was always lowest

Figure 4. Surface water temperature, dissolved oxygen and salinity values, versus Station #, June 1998 through April 1999.

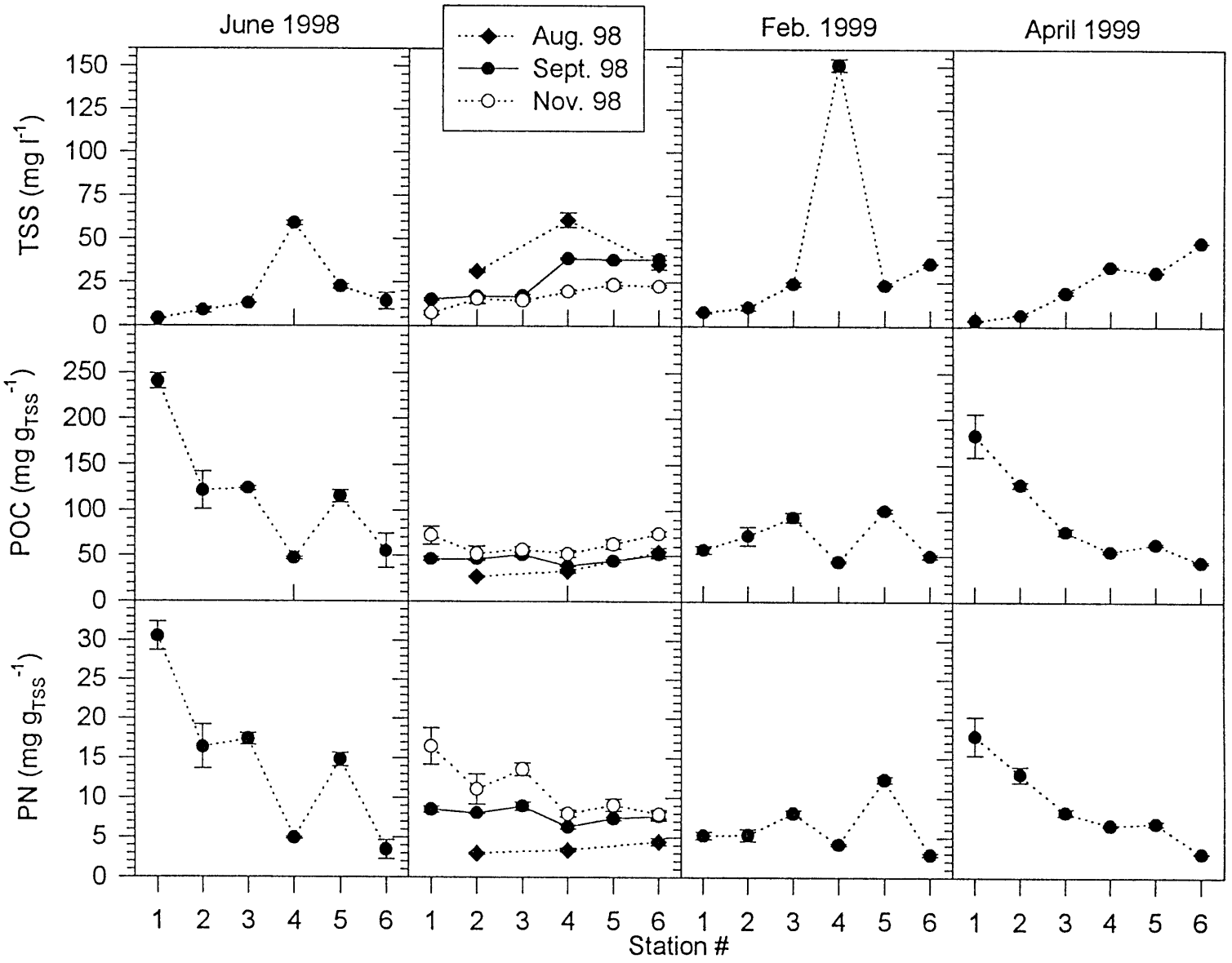

York River - Temperature
Celsius
30
25
20
15
10
5
1
2
3
4
5
York River - Dissolved Oxygen
Dissolved Oxygen (mg l-1)
12
11
10
9
8
7
6
5
1
2
3
4
5
6
June 1998
August 1998
September 1998
November 1998
February 1999
April 1999
York River - Salinity
Salinity (psu)
25
20
15
10
5
0
1
2
3
4
5
6
Station #

in the Pamunkey River at Station 6, where it ranged from a low of <0.06 in June 1998, and February and April 1999 to a high of 6.41 in November 1998. Salinity was always highest at Station 1, ranging from 14.0 in June 1998 to 22.3 in November 1998. The elevated salinities of York River surface waters in November 1998 reflect the extremely low flows of the Pamunkey and Mattaponi Rivers between June of 1998 and January 1999 (Fig. 3). The steepest gradient in salinity always occurred between Stations 5 and 6, where the absolute change in salinity varied between 5.7 and 10.9.

***Bulk Particle Properties***

Total suspended solids ranged from 3.59 to 151 mg $l^{-1}$ (April 1999, Station 1 and February 1999, Station 4, respectively), and were generally higher in the freshwater portion of the estuary than at its mouth (Fig. 5). A pronounced peak in TSS at Station 4 is apparent at most times, but most notably during February 1999 and June and August 1998. Total suspended solid concentrations (Fig. 5) were much higher in York River surface waters than those reported by Ko and Baker (1995) for the mesohaline Chesapeake Bay, which averaged only 4.1 $\pm$ 1.5 mg $l^{-1}$. The elevated York River TSS values likely result in part from the resuspension of sea-bed sediments in this highly energetic system (Dellapenna et al., 1998). The constant addition of suspended solids to surface waters at Station 4 is coincident with the fact that the York River narrows in this region of the estuary, creating the primary turbidity maximum in this system. The temporal variability in TSS is most likely the result of differences in tidal stage (ebb and

Figure 5. Surface water total suspended solids, and particulate organic carbon and particulate nitrogen content, versus Station #, June 1998 through April 1999. Lines are included to better illustrate the transect from station to station. Error bars, representing the standard error of the dependent variable, are included in all panels.


June 1998
Aug. 98
Sept. 98
Nov. 98
Feb. 1999
April 1999
TSS (mg l-1)
POC (mg gTSS-1)
PN (mg gTSS-1)
Station #

flood versus slack, spring and neap), wind stress and to a lesser degree variability in surface water primary production.

On a concentration basis (mg $l^{-1}$), particulate organic carbon and particulate nitrogen distributions in York River surface waters tended to follow the spatial and temporal trends in total suspended solids. Because particulate matter composition was the focus of this study, organic carbon and nitrogen concentrations were normalized to TSS, and are illustrated in mg $g^{-1}$ in Figure 5. The organic carbon content of surface water particles (Fig. 5) fluctuated between 27.1 mg $g^{-1}$ (August 1998, Station 2) and 241 mg $g^{-1}$ (June 1998, Station 1). In June 1998 and April 1999 a strong gradient in POC content existed between Station 1 and Station 6, with peak POC content occurring at the marine end (mouth) of the estuary. The elevated organic content of particles at the mouth of the estuary may be the result of higher primary productivity in this region. The POC gradient was not evident in August, September or November 1998, or February 1999. During August, September and November 1998, POC content of surface water particles was uniformly low at all six stations. In February 1999, POC content was slightly more variable than in the previous three sampling periods, but overall was still lower and less variable than in June 1998 or April 1999. The drop in POC content at Station 4 in February 1999, coincident with the peak in TSS, is probably to due to the dilution of organic rich particles with organic carbon-depleted particles in this region of the estuary. York River POC ranged from 2.7 to 24% (by weight TSS), and were lower and much more variable than those measured by Ko and Baker (1995) in the Chesapeake Bay

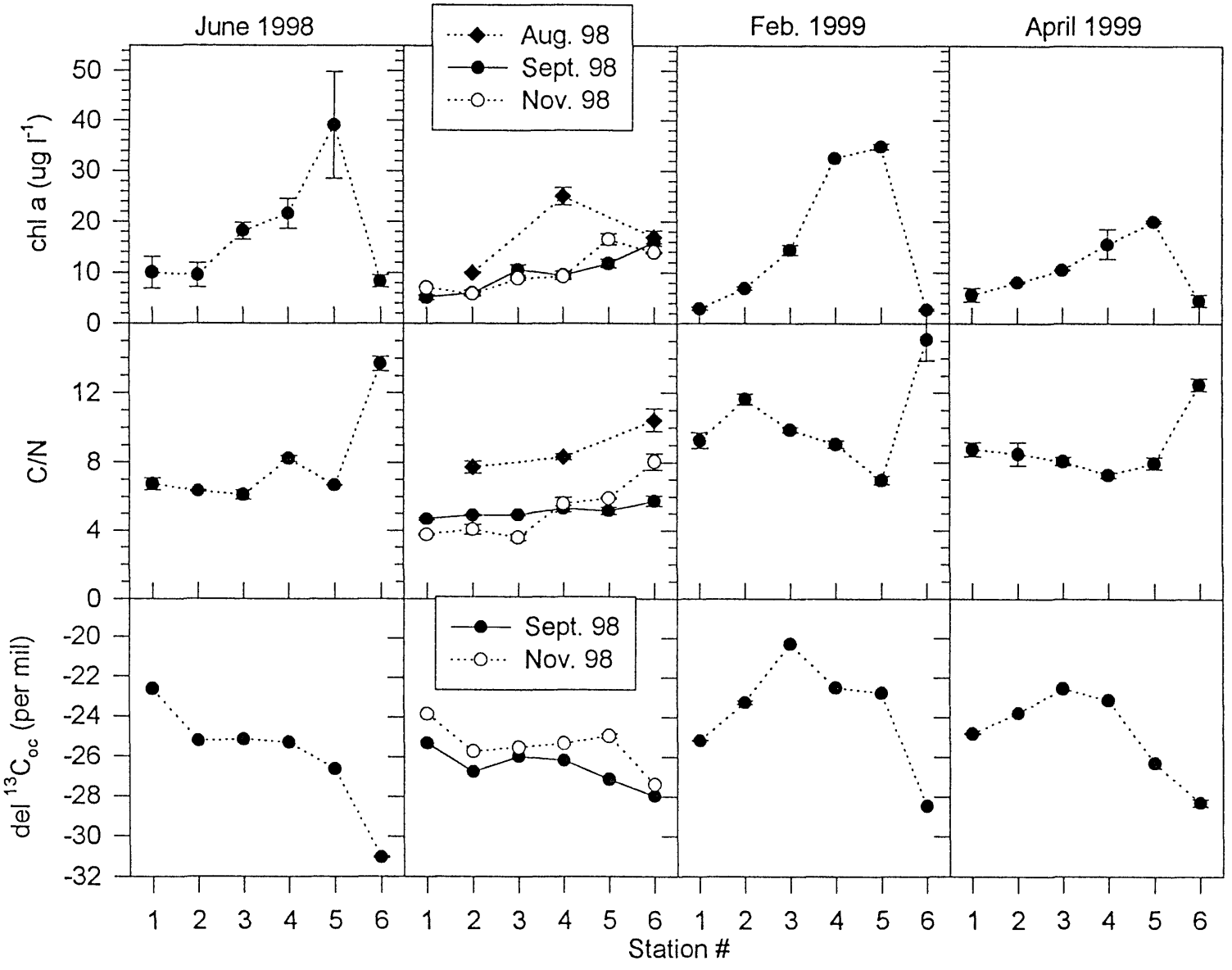
(29 ± 6%). POC was more similar to values observed by Bouloubassi and Saliot (1991 and 1993) in Rh⇔ne Delta surface waters, which varied between 4.9 and 19.1%.

Particulate nitrogen content (concentrations normalized to TSS; Fig. 5) was lowest at Station 6 in February 1999, at 2.85 mg $g^{-1}$, and highest at Station 1 in June 1998, reaching 30.5 mg $g^{-1}$. Particulate nitrogen content exhibited temporal and spatial changes in a pattern almost identical to those of organic carbon, with a strong gradient between the mouth and freshwater stations in June 1998 and April 1999, and no gradient and less variability in August and September 1998, and February 1999. Unlike POC however, there was also a gradient in PN in November 1998.

Chlorophyll-a distributions, and organic carbon quality, as indicated by C:N and $\delta^{13}C_{oc}$ values, exhibited considerable temporal and spatial variability (Fig. 6). Chlorophyll-*a* concentrations (Fig. 6) in York River surface waters ranged between 2.72 μg $l^{-1}$ (Station 6, February 1999) and 39.1 μg $l^{-1}$ (Station 5, June 1998). In June 1998, and February and April 1999, Stations 1 and 6 had similar chlorophyll-*a* concentrations, however, there was a substantial mid-estuary increase in chlorophyll-*a* indicating a mid-estuary source such as primary production, resuspension of benthic microalgae or runoff. In August, September and November 1998 there was an upstream gradient in chlorophyll-*a* between Stations 1 and 6 with a smaller mid-estuary increase.

Molar C:N ratios varied from 3.59 at Station 3 in November 1998 to 15.1 at Station 6 in February 1999 and varied markedly from station to station and

Figure 6. Surface water chlorophyll-*a* concentrations, C:N ratios and $\delta^{13}C_{oc}$ values, versus Station #, June 1998 through April 1999. Lines are included to better illustrate the transect from station to station. Error bars, representing the standard error of the dependent variable, are included in all panels.


June 1998
Aug. 98
Sept. 98
Nov. 98
Feb. 1999
April 1999
chl a (ug l-1)
C/N
del 13Coc (per mil)
Sept. 98
Nov. 98
Station #

among seasons (Fig. 6). For most sampling events there was an upstream gradient in C:N likely due to the influence of terrigenous organic matter in the freshwater reaches of the estuary. The C:N ratios tended to be lower and less variable in September and November 1998 than at other times of the year. Except for Station 6 in November 1998, the C:N ratios of York River surface waters in these two months were uniformly low, falling between 3.59 and 5.91, probably reflecting the accumulation of bacterial biomass.

$\delta^{13}C_{oc}$ was most depleted at Station 6 in June 1998 at –31.04 per mil, and most enriched at Station 3 in February 1999 at –20.29 per mil (Fig. 6). Generally, $\delta^{13}C_{oc}$ was lowest at Station 6, varying between –27.38 and –31.04 per mil over the sampling year. In June 1998 $\delta^{13}C_{oc}$ increased along the estuarine gradient, which could be explained by the mixing of two particle pools originating at the marine and freshwater ends of the estuary, respectively. It is also possible that the change in $\delta^{13}C_{oc}$ is the result of primary producers along the estuarine gradient reflecting a variation in the isotopic composition of dissolved inorganic carbon. In February and April 1999 there appears to be the addition of organic carbon with a heavier isotopic signature in the middle portion of the estuary. It is interesting to note that these two sampling periods follow freshwater flow events (Fig. 3), which may have delivered nutrients to the estuary and/or lead to water column stratification resulting in increased phytoplankton production. During September and November 1998, $\delta^{13}C_{oc}$ exhibited the least variability, but showed evidence of depletion or dilution by additional isotopically light particles near the marine end of the estuary.

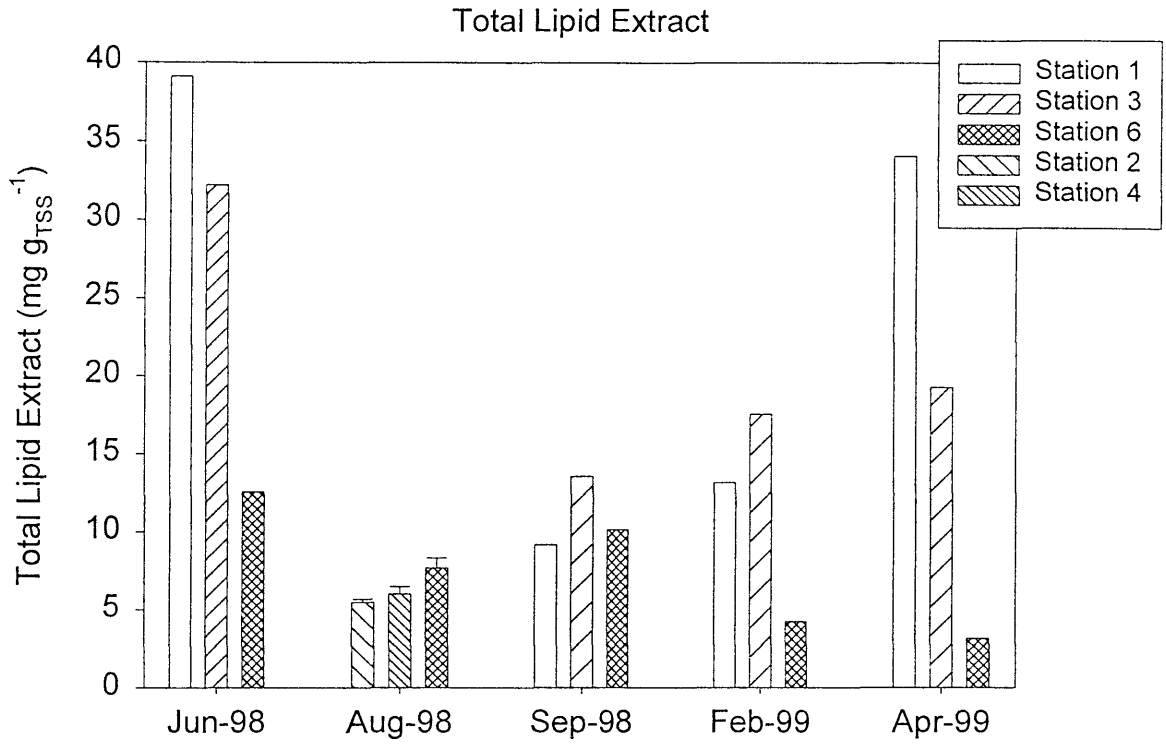
### *Organic Matter Lipid Biomarker Distributions*

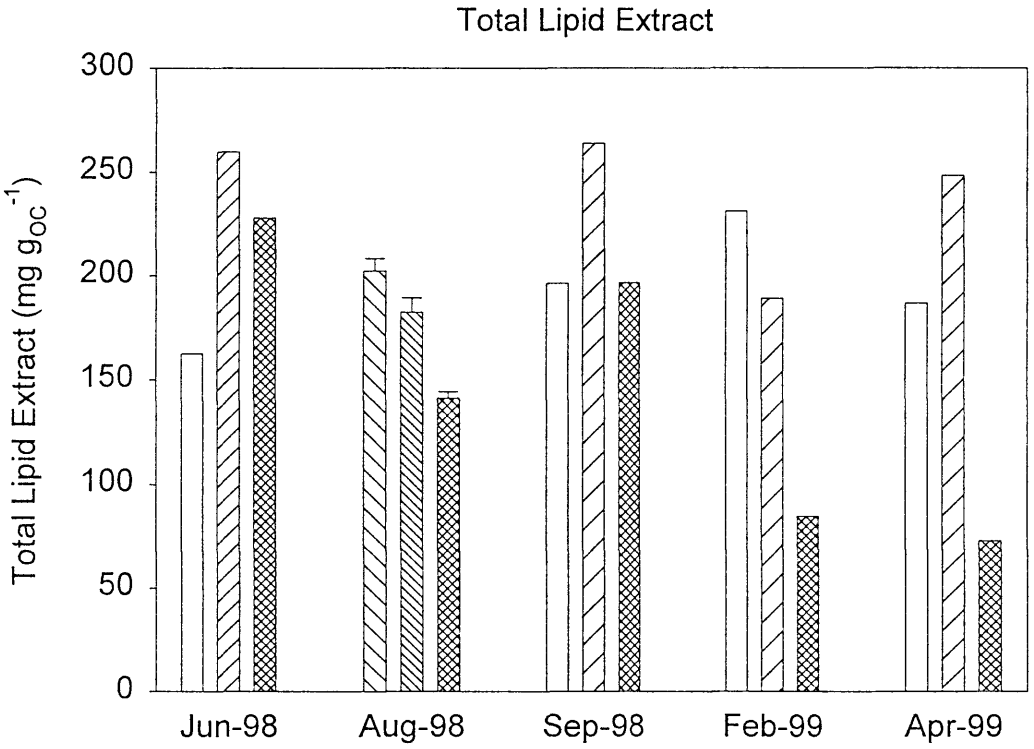
Concentrations of lipid biomarkers associated with particulate organic matter were determined for stations 1,3 and 6 in June and September 1998, and February and April 1999, as well as for replicate samples from stations 2,4 and 6 in August 1998. Lipid concentrations were not corrected for recoveries, which averaged 80 and 82% for $C_{19}$ and $C_{20}$ fatty acid methyl esters (FAMEs), respectively, and 88 and 79% for $C_{14}$ and $C_{19}$ alcohols respectively. Sample subsets were examined carefully to ensure that no bias was introduced by using uncorrected data.

#### *Total Lipid Extract*

Lipid extracts ranged from 3.2 to 39.1 mg $g_{TSS}^{-1}$ (Fig. 7), and the seasonal and spatial trends mimicked the corresponding organic carbon concentrations, with higher values and marked spatial variability in June 1998 and April 1999, and lower concentrations and less spatial variability in the intervening months. Lipid extract normalized to organic carbon (Fig. 7) suggests that there was surprisingly little temporal variability in the lipid portion of the organic carbon pool at Stations 1 and 3, averaging 19.4 ± 0.7% and 24.0 ± 0.9% lipid, respectively. However, the lipid portion of the organic carbon pool varied about three-fold at Station 6, comprising 22.8% of the organic carbon pool in June 1998 but only 8.4 and 7.2% in February and April 1999, respectively.

Figure 7. Total lipid extract concentrations, normalized to TSS and organic carbon, respectively, June 1998 through April 1999. Error bars indicate the standard error of August 1998 samples.


Total Lipid Extract
Total Lipid Extract (mg $g_{TSS}^{-1}$)
40
35
30
25
20
15
10
5
0
Jun-98
Aug-98
Sep-98
Feb-99
Apr-99
Station 1
Station 3
Station 6
Station 2
Station 4

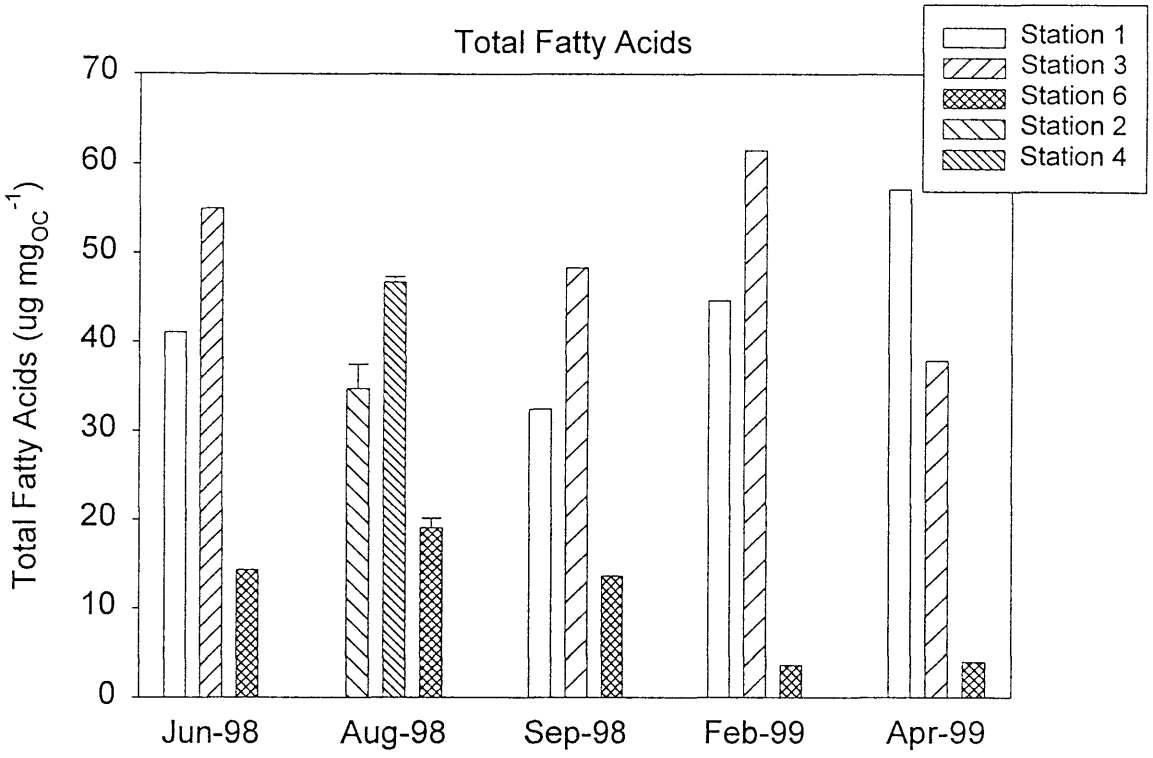

Total Lipid Extract
Total Lipid Extract (mg $g_{OC}^{-1}$)
300
250
200
150
100
50
0
Jun-98
Aug-98
Sep-98
Feb-99
Apr-99

*Fatty Acids*

The abundance of total fatty acids, normalized to organic carbon, ranged from 3.61 to 61.4 μg $mg_{oc}^{-1}$ (Fig. 8), and exhibited marked spatial variability over the course of the study. Fatty acids were always most depleted relative to organic carbon at Station 6, whereas the middle portion of the estuary (Stations 3 and 4) was typically most enriched in fatty acids, except in April 1999 when Station 1 was most enriched. Temporal variability in total fatty acids was less noticeable than the spatial component. This is particularly evident when the annual averages for each station are compared (Fig. 9); note that the standard error of the averages is much smaller than the differences among the mean concentrations for total fatty acids.

The 16:0 fatty acid consistently comprised at least 10% of the fatty acid total (Table 1). Other compounds that frequently comprised at least 10% of the total were 16:1ω7, 20:5ω3, 18:4 and 22:6ω3 fatty acids. Overall, polyunsaturated fatty acids were the dominant group of fatty acids (Fig. 9; Table 1), except at Station 6 where saturated fatty acids also dominated the fatty acid pool. Of the less abundant fatty acid groups, branched fatty acids (15:0 and 17:0 iso- and anteiso- compounds) exhibited the most temporal variability (Fig. 9), being more depleted in February 1999 than in other months (Table 1). Even-numbered long-chained fatty acids ($>C_{22}$) comprised less than 0.5% of the total fatty acid pool, but it is important to note that these compounds were enriched at Station 6 relative to total fatty acid concentrations and their concentration declined from the head to the mouth of the estuary (Fig. 9).

Figure 8. Total fatty acids and total sterol concentrations, normalized to organic carbon, June 1998 through April 1999. Error bars indicate the standard error of August 1998 samples.


Total Fatty Acids
Station 1
Station 3
Station 6
Station 2
Station 4
Total Fatty Acids (ug mg$_{OC}^{-1}$)
70
60
50
40
30
20
10
0
Jun-98
Aug-98
Sep-98
Feb-99
Apr-99

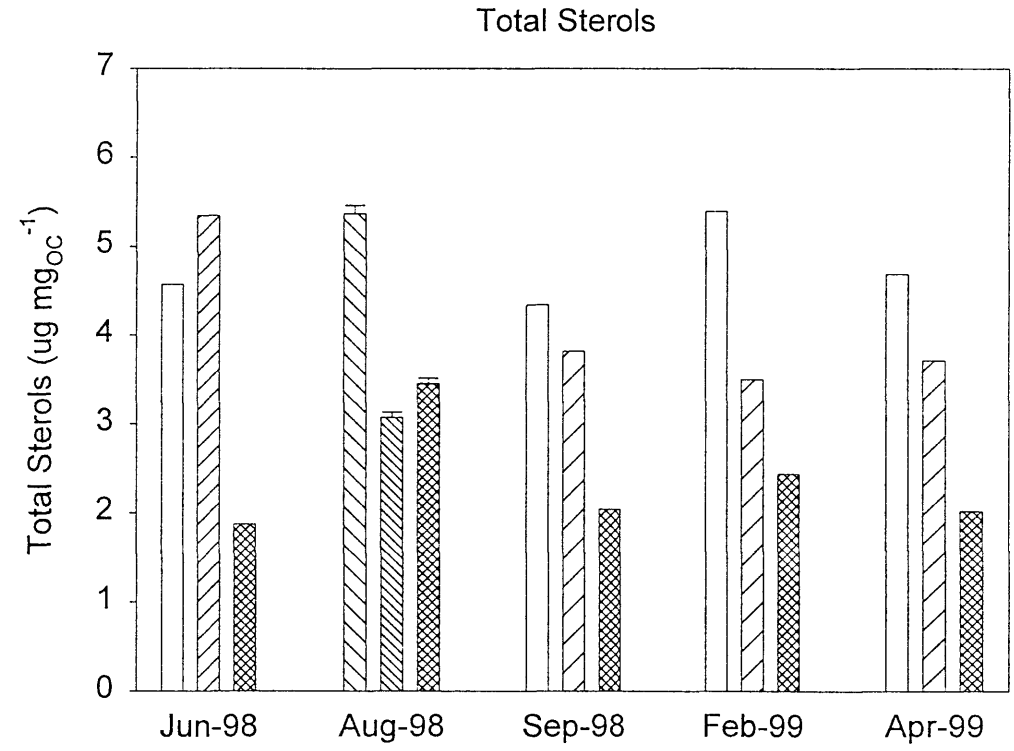

Total Sterols
Total Sterols (ug mg$_{OC}^{-1}$)
7
6
5
4
3
2
1
0
Jun-98
Aug-98
Sep-98
Feb-99
Apr-99

Figure 9. Average annual concentrations of fatty acids and sterols, normalized to organic carbon, for June 1998 through April 1999. Note the different concentration scales used in each graph. Error bars indicate the standard error of all samples for that station. Total compound class concentrations are displayed in black, autochthonous sources in grey, and allochthonous sources in white. Even-numbered long-chained fatty acids (ELCFAs) are defined by carbon chain lengths greater than $C_{22}$. Autochthonous (plankton-derived) sterols consist of: 24-norchlolesta-5,22-dien-3β-ol, cholesta-5,22-dien-3β-ol, cholest-5-en-3βol, 24-methylcholesta-5,22-dien-3β-ol, 24-methylcholesta-5,24(28)-dien-3β-ol and 24-ethylcholesta-5,24(28)-dien3β-ol. Allochthonous (vascular-plant derived) sterols include: 24-methylcholest-5-en-3β-ol, 24-ethylcholesta-5,22-dien-3β-ol and 24-ethylcholest-5-en-3β-ol.

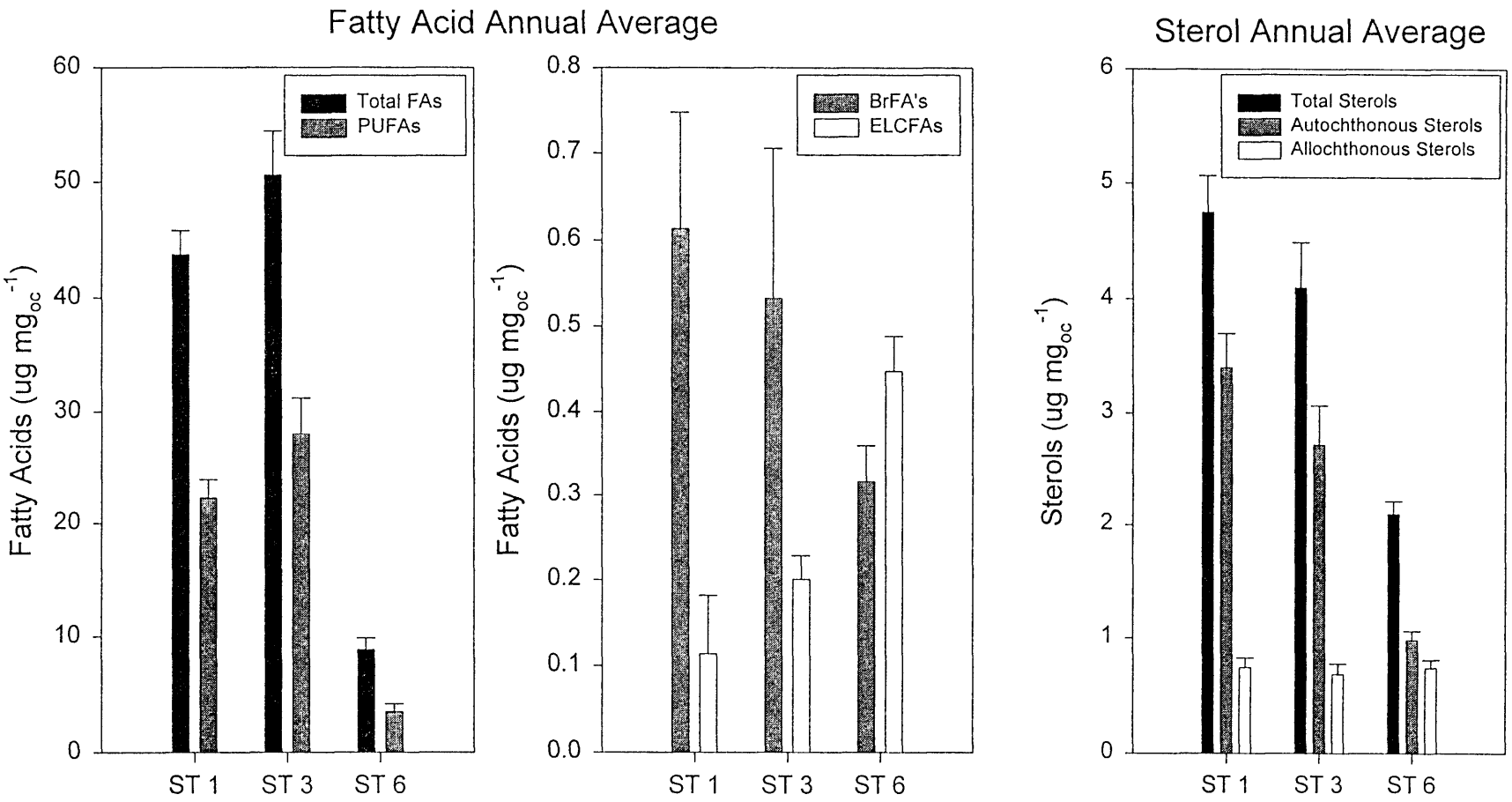

Fatty Acid Annual Average
Fatty Acids (ug mg$_{oc}^{-1}$)
Total FAs
PUFAs
BrFA's
ELCFAs
ST 1
ST 3
ST 6
Sterol Annual Average
Sterols (ug mg$_{oc}^{-1}$)
Total Sterols
Autochthonous Sterols
Allochthonous Sterols

**Table 1. Dominant Lipid Biomarker Compounds***

| | Jun-98 | | | Aug-98 | | | Sep-98 | | | Feb-99 | | | Apr-99 | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | 1 | 3 | 6 | 2 | 4 | 6 | 1 | 3 | 6 | 1 | 3 | 6 | 1 | 3 | 6 |
| **Fatty Acids (ng $mg_{OC}^{-1}$)** | | | | | | | | | | | | | | | |
| *16:1w7* | 5845 | | 2221 | 5815 | 11197 | 3836 | 4222 | 7535 | 2787 | 8079 | | 641 | 6405 | | 719 |
| 16:0 | 6625 | 7702 | 2325 | 5844 | 9637 | 3298 | 5617 | 9994 | 1997 | 5900 | 12186 | 598 | 7995 | 5906 | 653 |
| *18:4* | 3534 | 8764 | | | | | | | | | 6616 | | | 4790 | |
| 18:2 | | | | | | | | | | | 9370 | | | | |
| 20:5w3 | 6704 | 7384 | 2072 | 5768 | 6543 | | 4568 | 5816 | 1939 | 7567 | | | 9670 | 4528 | |
| 22:6w3 | 5090 | 7268 | | | | | 3461 | | | 5743 | 11370 | | 8286 | 7954 | |
| Saturated Fatty Acids | 11190 | 12786 | 4148 | 10439 | 15254 | 6372 | 9940 | 15636 | 3876 | 10559 | 19370 | 1722 | 15864 | 9732 | 1388 |
| Mono Unsaturated | 7744 | 8098 | 3287 | 8057 | 13027 | 5345 | 6508 | 10752 | 3567 | 10230 | 7207 | 1108 | 11400 | 4631 | 1132 |
| Polyunsaturated Fatty Acids | 21371 | 32881 | 6355 | 15497 | 17808 | 6672 | 15064 | 21295 | 5839 | 23604 | 34853 | 528 | 29051 | 23042 | 1222 |
| Branched Fatty Acids | 752 | 1214 | 494 | 698 | 506 | 666 | 825 | 509 | 295 | 129 | 0 | 250 | 747 | 409 | 227 |
| Even Long-chain Fatty Acids | 0 | 193 | 441 | 245 | 493 | 638 | 269 | 229 | 469 | 0 | 135 | 582 | 186 | 245 | 299 |
| Total Fatty Acids | 41057 | 54979 | 14285 | 34691 | 46594 | 19054 | 32338 | 48192 | 13577 | 44522 | 61430 | 3607 | 57062 | 37813 | 3970 |
| **Sterols (ng $mg_{OC}^{-1}$)** | | | | | | | | | | | | | | | |
| 24-norchlolesta-5,22-dien-3b-ol | | | | | | | | | | 555 | | | | 426 | |
| cholest-5-en-3b-ol | 1480 | 1175 | 595 | 1011 | 772 | 1106 | 956 | 848 | 604 | 1161 | 416 | 338 | 898 | 504 | 412 |
| 24-methylcholesta-5,22-dien-3b-ol | 998 | 1343 | | 782 | | | 722 | 713 | 217 | | | | | | |
| 24-methylcholesta-5,24(28)-dien-3b-ol | | | | 1019 | 790 | | | 719 | | 1190 | 787 | | 729 | 565 | |
| 24-methylcholest-5-en-3b-ol | | | 195 | | 336 | 417 | | | 222 | | | | | | |
| 24-ethylcholesta-5,22-dien-3b-ol | | | 202 | | | | | | | | | | | | |
| 24-ethylcholest-5-en-3b-ol | | | 322 | | 350 | 391 | 576 | 340 | 240 | | | 547 | | | 420 |
| 24-ethyl-5a(H)-cholest-3b-ol | | | | | | | | | | | 392 | | | | |
| Autochthonous Sterols | 3532 | 3878 | 965 | 3635 | 2153 | 1894 | 2876 | 3027 | 1199 | 4001 | 1776 | 936 | 3193 | 2164 | 830 |
| Allochthonous Sterols | 688 | 1099 | 718 | 1125 | 775 | 968 | 1041 | 703 | 564 | 677 | 482 | 900 | 575 | 453 | 770 |
| Total Sterols | 4573 | 5348 | 1876 | 5371 | 3080 | 3462 | 4344 | 3824 | 2048 | 5395 | 3504 | 2442 | 4686 | 3718 | 2024 |

*Note: Compounds listed comprise at least ten percent of the compound class total.

*Sterols*

Total sterol concentrations were an order of magnitude lower than total fatty acid concentrations, varying from 1.88 to 5.39 μg $mg_{oc}^{-1}$ (Fig. 8). As with total fatty acids, spatial variability was more noticeable than temporal. The relative abundances of total sterols at each of the three stations were similar to the spatial distribution of total fatty acids in June 1998 and April 1999. In contrast, during the intervening sampling periods the spatial distribution of total sterols was very different than that of total fatty acids, with sterols highest at the saline end of the estuary (Stations 1 and 2), as opposed to the middle portion of the estuary. Also in contrast to total fatty acid distributions, total sterol concentrations at Station 6 were not nearly as depleted relative to the other stations.

Cholesterol (cholest-5-en-3β-ol) always comprised at least 10% of the total sterol concentration (Table 1). Generally either cholesterol or 24-methylene cholesterol (24-methylcholesta-5,24(28)-dien-3β-ol) was the most abundant sterol, with the exception of brassicasterol (24-methylcholesta-5,22-dien-3β-ol) at Station 3 in June 1998 and β-sitosterol (24-ethylcholest-5-en-3β-ol) at Station 6 in February and April 1999 (Table 1).

At all stations, in all seasons, sterol distributions were dominated by autochthonous (plankton-derived) compounds (Yunker et al., 1995), the sum of 24-norchlolesta-5,22-dien-3β-ol, cholesta-5,22-dien-3β-ol, cholest-5-en-3βol, 24-methylcholesta-5,22-dien-3β-ol, 24-methylcholesta-5,24(28)-dien-3β-ol and 24-ethylcholesta-5,24(28)-dien3β-ol (Fig. 9; Table 1). On average these six sterol

compounds accounted for 62 ± 3.3% of total sterols concentrations. Allochthonous sterols (vascular plant-derived), 24-methylcholest-5-en-3β-ol, 24-ethylcholesta-5,22-dien-3β-ol and 24-ethylcholest-5-en-3β-ol, comprised a much smaller fraction of the total sterol pool, on average only 23 ± 2.4%. Unlike autochthonous sterols or total fatty acids, allochthonous sterols exhibited very little spatial or temporal variability, as illustrated by their nearly identical means and small error bars in Fig. 9.

***Particulate PAH Distributions***

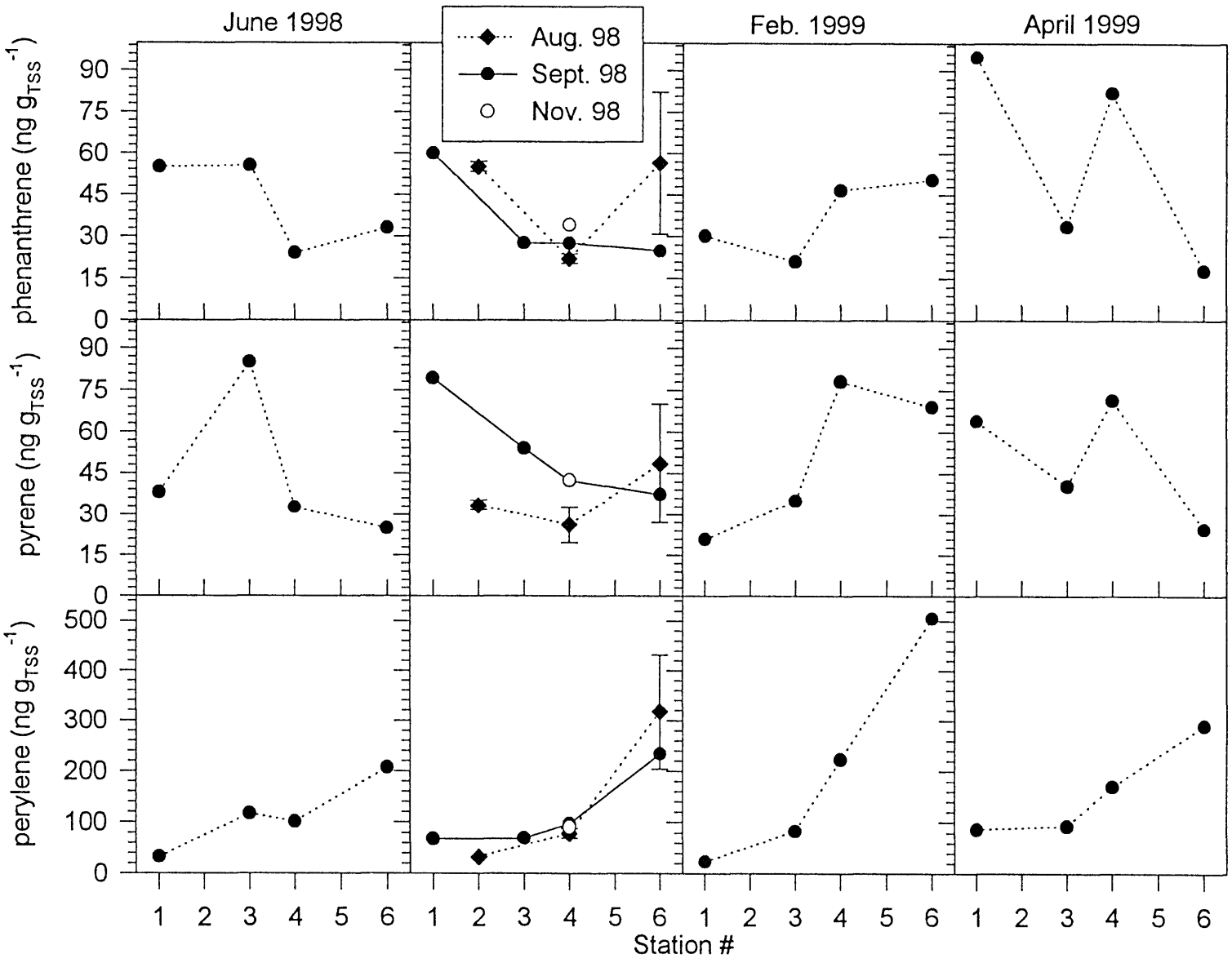
Concentrations of particulate phase PAHs were determined for stations 1,3,4 and 6 in June and September 1998, and February and April 1999; for station 4 in November 1998; and for replicate samples from stations 2,4 and 6 in August 1998. All PAH concentrations were corrected for recovery which averaged 70.3% for $d\text{-}_{10}$ anthracene, 87.7% for $d\text{-}_{12}$ benzo[a]anthracene and 74.7 % for $d\text{-}_{12}$ benzo[a]pyrene. Total particulate PAH concentrations (Table 2) ranged from 2.09 ng $l^{-1}$ at Station 1 in June 1998 to 123 ng $l^{-1}$ at Station 4 in April 1999, and averaged 20.3 ng $l^{-1}$. The peak at Station 4 in February 1999 is coincident with a spike in TSS at that site.

Concentrations of selected PAH compounds are depicted in Fig. 10. Particulate phenanthrene concentrations (normalized to TSS) were most variable in April 1999, ranging from 17.9 to 94.9 ng $g^{-1}$ at Stations 6 and 1, respectively (Fig. 10). While there was little overall temporal variability, concentrations varied markedly from station to station during any one month. Mid-estuary depletions in particulate phenanthrene were evident during most sampling periods. Particulate

**Table 2. Surface Water Particulate PAH Concentrations**

| | Jun-98 | | | | Aug-98 | | | | | | Sep-98 | | | | Nov-98 | Feb-99 | | | | Apr-99 | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | 1 | 3 | 4 | 6 | 2 | 2 SE | 4 | 4 SE | 6 | 6 SE | 1 | 3 | 4 | 6 | 4 | 1 | 3 | 4 | 6 | 1 | 3 | 4 | 6 |
| PAH (ng $l^{-1}$) | | | | | | | | | | | | | | | | | | | | | | | |
| fluorene | 0.06 | 0.18 | 0.33 | 0.10 | 0.31 | 0.02 | 0.31 | 0.01 | 0.34 | 0.13 | 0.21 | 0.10 | 0.25 | 0.19 | 0.17 | 0.06 | 0.10 | 1.38 | 0.33 | 0.09 | 0.15 | 0.47 | 0.13 |
| 1-methylfluorene | 0.06 | 0.16 | 0.22 | 0.07 | 0.31 | 0.00 | 0.31 | 0.04 | 0.28 | 0.07 | 0.17 | 0.09 | 0.22 | 0.12 | 0.14 | 0.04 | 0.08 | 0.87 | 0.22 | 0.08 | 0.10 | 0.26 | 0.10 |
| phenanthrene | 0.23 | 0.72 | 1.43 | 0.47 | 1.73 | 0.06 | 1.35 | 0.10 | 2.00 | 0.91 | 0.91 | 0.47 | 1.07 | 0.96 | 0.67 | 0.24 | 0.51 | 7.04 | 1.81 | 0.34 | 0.64 | 2.81 | 0.86 |
| anthracene | 0.03 | 0.16 | 0.35 | 0.06 | 0.19 | 0.01 | 0.32 | 0.03 | 0.36 | 0.14 | 0.16 | 0.09 | 0.25 | 0.18 | 0.14 | 0.03 | 0.12 | 1.90 | 0.38 | 0.06 | 0.15 | 0.38 | 0.14 |
| 2-methylphenanthrene | 0.11 | 0.32 | 0.58 | 0.16 | 1.15 | 0.07 | 0.67 | 0.03 | 0.73 | 0.24 | 0.42 | 0.24 | 0.46 | 0.30 | 0.28 | 0.09 | 0.22 | 2.09 | 0.61 | 0.14 | 0.23 | 0.67 | 0.30 |
| 2-methylanthracene | 0.02 | 0.07 | 0.01 | 0.03 | 0.09 | 0.01 | 0.06 | 0.06 | 0.10 | 0.10 | 0.07 | 0.04 | 0.01 | 0.06 | 0.01 | 0.04 | 0.05 | 0.06 | 0.13 | 0.03 | 0.06 | 0.01 | 0.10 |
| 1-methylanthracene | 0.07 | 0.18 | 0.38 | 0.08 | 0.72 | 0.03 | 0.39 | 0.01 | 0.49 | 0.15 | 0.23 | 0.16 | 0.32 | 0.20 | 0.21 | 0.05 | 0.15 | 1.44 | 0.32 | 0.07 | 0.15 | 0.40 | 0.20 |
| 1-methylphenanthrene | 0.07 | 0.24 | 0.39 | 0.10 | 0.73 | 0.02 | 0.46 | 0.02 | 0.49 | 0.16 | 0.29 | 0.14 | 0.31 | 0.20 | 0.18 | 0.05 | 0.14 | 1.65 | 0.54 | 0.12 | 0.16 | 0.42 | 0.19 |
| fluoranthene | 0.16 | 1.19 | 2.08 | 0.43 | 1.17 | 0.10 | 1.90 | 0.22 | 2.42 | 0.98 | 1.33 | 0.88 | 1.75 | 1.61 | 0.91 | 0.21 | 0.94 | 13.66 | 2.91 | 0.27 | 0.92 | 2.97 | 1.35 |
| pyrene | 0.16 | 1.10 | 1.93 | 0.35 | 1.05 | 0.06 | 1.60 | 0.40 | 1.71 | 0.76 | 1.20 | 0.92 | 1.63 | 1.43 | 0.83 | 0.17 | 0.85 | 11.81 | 2.49 | 0.23 | 0.78 | 2.45 | 1.19 |
| benz[a]anthracene | 0.07 | 0.44 | 0.98 | 0.16 | 0.45 | 0.02 | 0.84 | 0.06 | 0.79 | 0.23 | 0.44 | 0.31 | 0.77 | 0.58 | 0.38 | 0.08 | 0.42 | 5.39 | 1.19 | 0.10 | 0.40 | 1.05 | 0.55 |
| chrysene | 0.07 | 0.39 | 0.78 | 0.16 | 0.41 | 0.04 | 0.70 | 0.06 | 0.71 | 0.23 | 0.42 | 0.30 | 0.67 | 0.56 | 0.33 | 0.08 | 0.34 | 3.82 | 1.15 | 0.11 | 0.38 | 1.00 | 0.56 |
| benzo[b]fluoranthene | 0.16 | 0.91 | 2.01 | 0.37 | 0.84 | 0.07 | 1.72 | 0.13 | 1.50 | 0.49 | 0.93 | 0.79 | 1.55 | 1.17 | 0.79 | 0.21 | 0.97 | 10.40 | 2.42 | 0.22 | 0.97 | 2.13 | 1.41 |
| benzo[k]fluoranthene | 0.06 | 0.30 | 0.65 | 0.12 | 0.29 | 0.04 | 0.55 | 0.05 | 0.45 | 0.13 | 0.33 | 0.25 | 0.49 | 0.37 | 0.26 | 0.07 | 0.32 | 3.27 | 0.83 | 0.07 | 0.35 | 0.71 | 0.43 |
| benzo[e]pyrene | 0.10 | 0.52 | 1.08 | 0.20 | 0.49 | 0.03 | 0.96 | 0.08 | 0.83 | 0.26 | 0.51 | 0.48 | 0.88 | 0.66 | 0.43 | 0.12 | 0.52 | 5.38 | 1.21 | 0.13 | 0.50 | 1.25 | 0.73 |
| benzo[a]pyrene | 0.09 | 0.50 | 1.02 | 0.17 | 0.47 | 0.03 | 0.94 | 0.06 | 0.74 | 0.22 | 0.50 | 0.48 | 0.84 | 0.56 | 0.41 | 0.10 | 0.49 | 4.94 | 1.05 | 0.13 | 0.50 | 1.19 | 0.60 |
| perylene | 0.14 | 1.52 | 5.99 | 2.94 | 1.03 | 0.00 | 4.79 | 0.56 | 11.24 | 4.02 | 1.03 | 1.18 | 3.77 | 8.97 | 1.78 | 0.19 | 2.01 | 33.61 | 18.19 | 0.31 | 1.79 | 5.85 | 13.98 |
| indeno[123cd]pyrene | 0.12 | 0.57 | 1.31 | 0.26 | 0.55 | 0.08 | 1.46 | 0.07 | 1.26 | 0.44 | 0.54 | 0.69 | 0.94 | 0.88 | 0.47 | 0.12 | 0.81 | 7.02 | 1.45 | 0.14 | 0.62 | 1.49 | 1.10 |
| benzo[ghi]perylene | 0.16 | 0.54 | 1.14 | 0.23 | 0.50 | 0.04 | 1.04 | 0.06 | 0.83 | 0.27 | 0.51 | 0.63 | 0.92 | 0.79 | 0.44 | 0.11 | 0.65 | 5.63 | 1.24 | 0.15 | 0.66 | 1.24 | 0.85 |
| dibenz[ah]anthracene | 0.09 | 0.14 | 0.20 | 0.09 | 0.29 | 0.00 | 0.36 | 0.02 | 0.24 | 0.07 | 0.13 | 0.16 | NQ | 0.21 | 0.12 | 0.06 | 0.20 | 1.51 | 0.32 | 0.04 | 0.43 | 0.42 | 0.20 |
| Total PAH | 2.09 | 10.23 | 22.88 | 6.60 | 12.78 | 0.20 | 20.73 | 0.77 | 27.50 | 4.41 | 10.36 | 8.40 | 17.11 | 20.05 | 8.94 | 2.11 | 9.90 | 122.85 | 38.85 | 2.88 | 9.99 | 27.18 | 24.99 |
| **TSS (mg $l^{-1}$)** | 4.24 | 12.97 | 59.10 | 14.20 | 31.42 | | 61.06 | | 35.34 | | 15.17 | 17.06 | 38.63 | 38.39 | 19.64 | 7.99 | 24.16 | 150.92 | 35.99 | 3.59 | 19.19 | 34.26 | 48.22 |
| **POC (mg $l^{-1}$)** | 1.02 | 1.61 | 2.79 | 0.78 | 0.85 | | 2.02 | | 1.92 | | 0.71 | 0.88 | 1.51 | 1.98 | 1.03 | 0.45 | 2.24 | 6.60 | 1.81 | 0.65 | 1.49 | 1.91 | 2.12 |

Figure 10. Particulate phase concentrations of the PAHs phenanthrene, pyrene and perylene, versus Station #, June 1998 through April 1999. Phenanthrene illustrates the behavior of volatile PAHs; pyrene, that of combustion-derived, particle associated PAHs; and perylene, is a PAH with anthropogenic and natural sources (Venkatesan, 1988; Bouloubassi and Saliot, 1993). Lines are included to better illustrate the transect from station to station. Error bars indicate standard error of August 1998 samples.


June 1998
Aug. 98
Sept. 98
Nov. 98
Feb. 1999
April 1999
phenanthrene (ng $g_{TSS}^{-1}$)
pyrene (ng $g_{TSS}^{-1}$)
perylene (ng $g_{TSS}^{-1}$)
0
15
30
45
60
75
90
0
15
30
45
60
75
90
0
100
200
300
400
500
1 2 3 4 5 6 1 2 3 4 5 6 1 2 3 4 5 6 1 2 3 4 5 6
Station #

pyrene concentrations were lowest in February 1999 at Station 1, and highest in June 1998 at Station 3, ranging from 20.9 to 85.1 ng $g^{-1}$ (Fig. 10). As with phenanthrene, mid-estuary depletions in particulate pyrene were evident in August and September 1998. However, in June 1998 and February 1999 mid-estuary maxima in particulate pyrene were evident, indicating an additional source of combustion-derived particulate PAH to York River surface waters at these times. Particulate perylene concentrations varied the greatest of all PAHs, from 23.3 to 505 ng $g^{-1}$ at Stations 1 and 6, respectively, in February 1999 (Fig. 10). While the magnitude of change varied among months, particulate perylene concentrations were always highest at Station 6, and decreased downstream toward Station 1, suggesting the freshwater region of the estuary as the dominant source of perylene.

## Discussion

In some respects, the June 1998 – April 1999 field season for the York River may be considered atypical. For example, the low flow period extended through the fall, well into the winter, and the rate of freshwater discharge in winter and spring was well below the previous year (Fig. 3). However, conditions typical of a phytoplankton bloom, such as elevated chlorophyll-*a* concentrations, were captured during several sampling events (Fig. 5). The range is of chlorophyll-*a* concentrations observed in this study is similar to the monthly mean concentrations for the years 1985-1994 compiled by Sin (1998), which ranged from 5 to 30 $\mu g\ l^{-1}$. For the purposes of this study, there appears to be sufficient

variability in both organic carbon quantity and quality to assess PAH-organic matter associations.

### *Organic Matter in Estuarine Surface Waters*

A variety of tools are used to determine sources of organic matter in estuarine systems, including chlorophyll-*a*, ratios of bulk particulate organic carbon to particulate nitrogen, bulk stable isotope determinations and various classes of lipid biomarkers. Sources of organic matter in estuaries include allochthonous inputs originating in the surrounding watershed and delivered by river inflow and terrestrial runoff, as well as autochthonous sources including phytoplankton, zooplankton and other organic matter produced within the system (Canuel et al., 1995). In an estuarine system however, organic matter such as phytoplankton produced in the freshwater reaches may be considered allochthonous to the estuary. Canuel and Martens (1993) compiled from the literature a summary of source indicators (stable carbon isotopes, fatty acids, sterols and hydrocarbons) for algae, terrestrial vascular plants, bacteria and seagrasses. Ratios of carbon to nitrogen (C:N) and stable nitrogen ratios (Cifuentes et al., 1988) can also be used in identifying organic matter sources. While bulk parameters and single biomarker compounds may not individually identify specific sources of organic matter, when used together it is often possible to identify likely sources of organic matter.

The C:N stoichiometry of fresh phytoplankton is 6.7, (Redfield, 1934) and its carbon isotopic signature is heavier than that of terrestrial upland plants, with reported $\delta^{13}C_{oc}$ values for phytoplankton ranging from –18 to –22 per mil

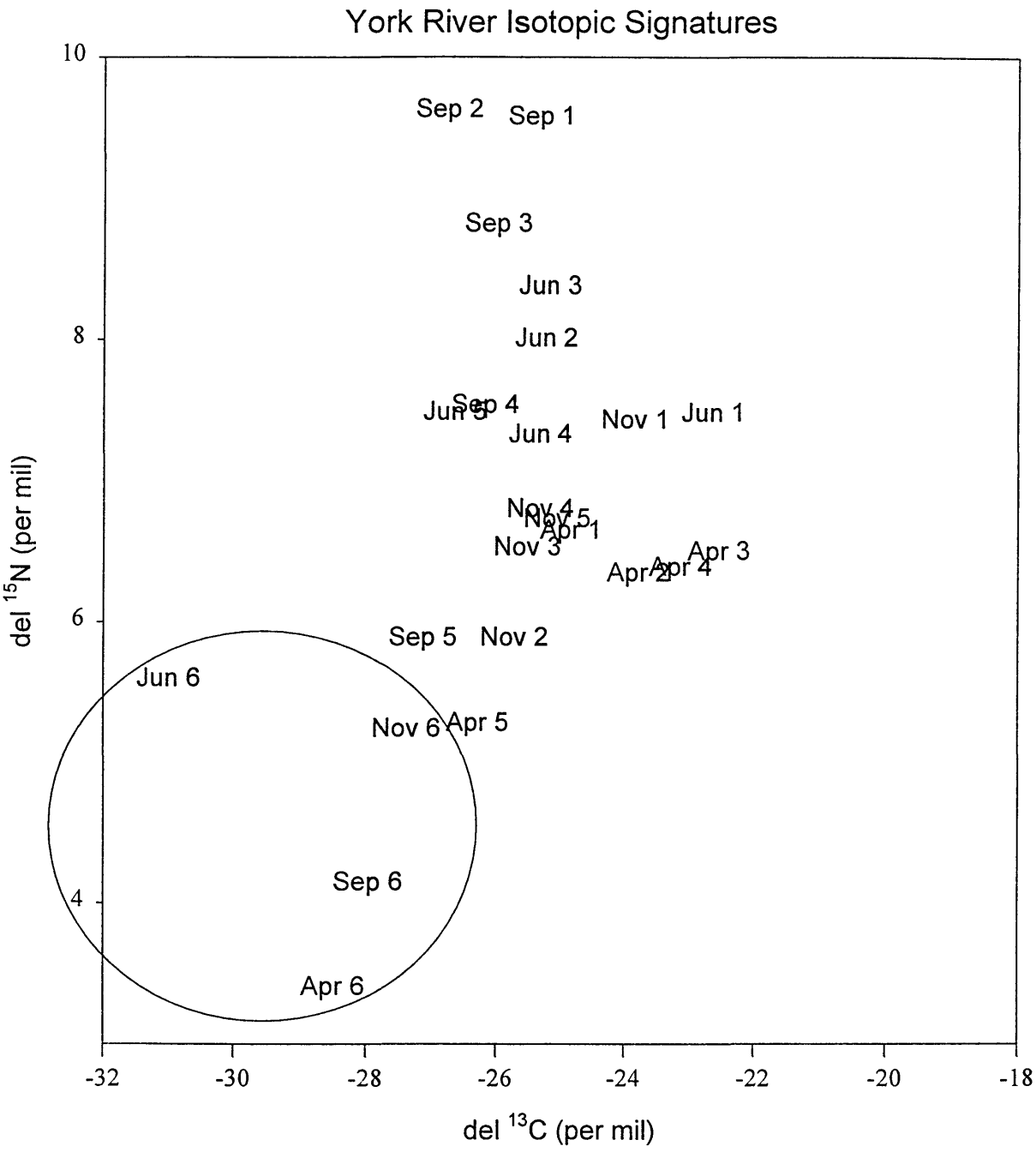
(Peterson et. al, 1985; Cifuentes et al., 1988; Canuel and Martens, 1993). Molar C:N ratios dropped and carbon isotopic signatures were less negative toward the middle and the mouth of the York River estuary during June 1998, and February and April 1999, suggesting that phytoplankton dominated the organic matter pool (Fig. 6). The coincident mid-estuary increases in chlorophyll-*a* support the dominance of phytoplankton during these months. In contrast, the unusually low C:N ratios observed in surface waters during September and November 1998, which ranged between 3.76 and 5.92, and the low levels of chlorophyll-*a* in the estuary at these times, may be the result of the accumulation of bacterial biomass (C:N typically less than 6, Goldman et al., 1987; Lee and Fuhrman, 1987) throughout the estuary following the warm summer months and lack of freshwater flow. It should be noted, however, that bacteria would probably have to be the only surface water particles in order to attain C:N ratios between 4 and 5.

At the head of the York River estuary both elevated C:N ratios and depleted $\delta^{13}C_{oc}$ measurements suggest that terrigenous organic matter dominates (Fig. 6). While the C:N ratios in the freshwater region of the estuary were lower than the 20-100 typical range for vascular plants, they were higher than those of fresh phytoplankton (6.7) and aquatic bacteria (typically <6; Goldman et al., 1987; Lee and Fuhrman, 1987). The stable carbon isotopic signature of –31.08 to –27.38 per mil measured at Station 6 is also very similar to the –26 to –28 per mil reported for vascular plants (Peterson et. al, 1985; Cifuentes et al., 1988; Canuel and Martens, 1993). Moreover, when isotopic

carbon and nitrogen signatures are combined, the differing organic matter composition at the head of the estuary (Station 6) becomes evident (Fig. 11). Station 6 samples, regardless of time of year, are distinct in terms of their stable isotopic N and C signals. This indicates that the mixture of particulate organic matter at this station is unique relative to the other sites sampled with in the York River estuary. Overall, the combined isotopic values were similar to the envelope of values reported by Cifuentes et al. (1988) as indicative of terrestrial and/or sewage-derived organic matter.

The uniqueness of the organic matter pool in the freshwater region of the York River is further exemplified by the lipid biomarker distributions. Careful categorization of fatty acids and sterols as autochthonous or allochthonous was an important step in making this distinction. Polyunsaturated fatty acids (PUFAs) and branched fatty acids (BrFAs) are typically used as biomarkers for fresh phytoplankton and some sulfate reducing bacteria, respectively (Nichols et al., 1983; Volkman et al., 1989 and Perry et al., 1979; Parkes and Taylor, 1985, respectively), and were considered to be indicators of autochthonous organic matter in this system. Even-numbered long-chained fatty acids (ELCFAs), components of higher plants (Cranwell, 1974; Canuel and Martens, 1993), are typically used as indicators of allochthonous organic matter, as was done here. However, allochthonous and autochthonous classification of sterols was a bit more complicated. The groupings chosen are almost identical to those reported by Yunker et al. (1995). In this study sterols, indicative of phytoplankton and zooplankton sources, were selected to represent autochthonous sources and

Figure 11. Surface water particulate isotopic signatures, as a function of Station #, June 1998 through April 1999. Samples are denoted by the month during which they were collected and Station number. $\delta^{13}C_{oc}$ are relative to PDB, and $\delta^{15}N$ relative to air.


York River Isotopic Signatures
10
8
6
4
Sep 2
Sep 1
Sep 3
Jun 3
Jun 2
Jun 5
Sep 4
Jun 4
Nov 1
Jun 1
Nov 4
Nov 5
Apr 1
Nov 3
Apr 3
Apr 2
Apr 4
Sep 5
Nov 2
Jun 6
Nov 6
Apr 5
Sep 6
Apr 6
-32
-30
-28
-26
-24
-22
-20
-18
del $^{15}$N (per mil)
del $^{13}$C (per mil)

allochthonous sterols represented vascular plant sources. While the three allochthonous sterols have traditionally been used as indicators of terrestrial material (Killops and Killops, 1993), Volkman (1986) noted that there are many environments, removed from terrigenous sources, where 24-ethylcholest-5-en-3β-ol is a dominant sterol, and therefore this compound must also be derived from other sources, such as cyanobacteria and freshwater algae (Volkman, 1986; Volkman et. al, 1999). However, because the bulk particle property analyses indicate a source of terrestrial organic matter to this system, and because freshwater algae would be considered allochthonous to the estuary, 24-ethylcholest-5-en-3β-ol was included as an allochthonous biomarker.

Autochthonous fatty acids, in the form of PUFAs, exceeded those indicating allochthonous sources in the surface waters of the York River estuary at all stations, in all seasons, and autochthonous sterol concentrations were always greater than allochthonous sterol concentrations (Fig. 9; Table 1). While large temporal variability in POC content was observed at Station 1, where it ranged approximately 5-fold (Fig. 5), the annual variability in lipid biomarker concentration and composition was quite low at all stations, including Station 1 (Fig. 9). The relatively low temporal variability in polyunsaturated fatty acids is somewhat surprising, as this is typically considered an indicator of "fresh" algal organic matter, as these compounds are particularly reactive (Shaw and Johns, 1985). These fatty acid and sterol distributions suggest that relatively fresh phytoplankton and zooplankton were always the dominant sources of suspended organic matter in York River surface waters.

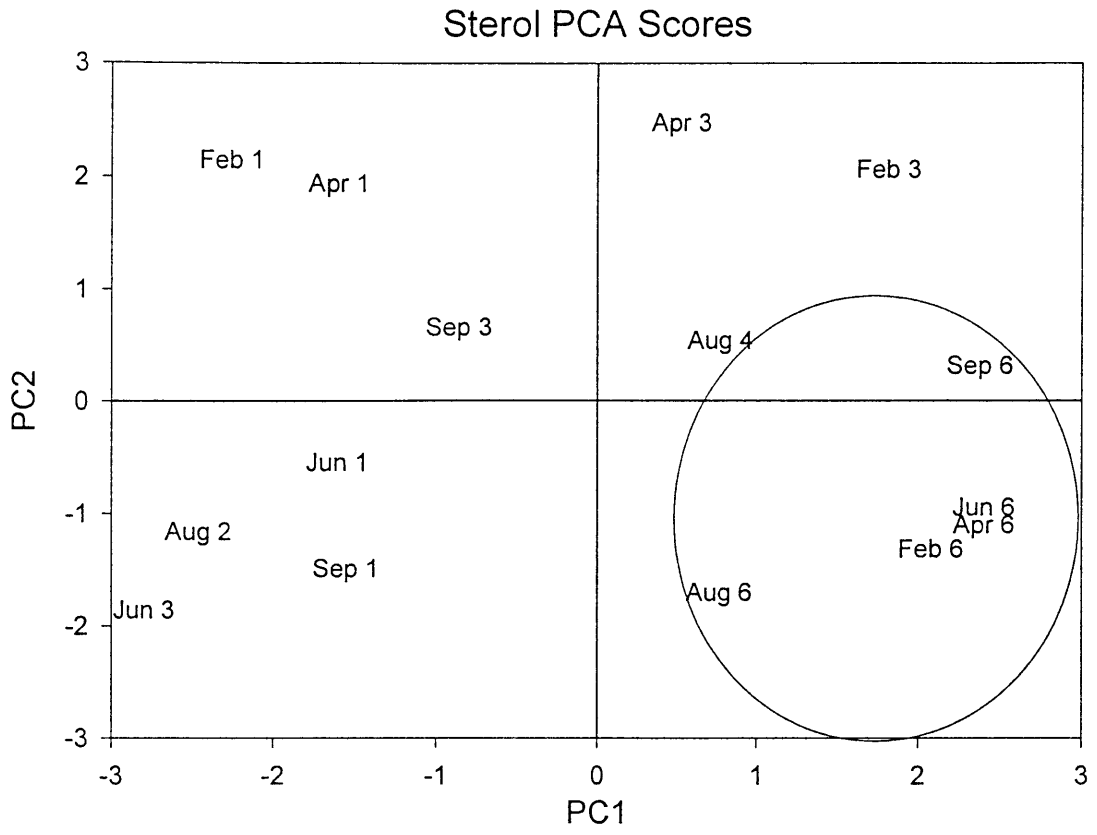
However, there were subtle and important differences in lipid biomarker composition at the head of the estuary. Biomarkers indicative of terrestrial organic matter, such as ELCFAs and allochthonous sterols comprised greater fractions of the total organic carbon pool at Station 6 than at other stations in the estuary (Fig. 9). The average percent distribution of autochthonous and allochthonous sterols at Station 6 was 46.8 and 35.2%, respectively, while it was 66.2 and 16.7% at Station 3 and 71.6 and 15.7% at Station 1 (Fig. 9; Table 1). This substantial contribution of allochthonous material at the head of the estuary is consistent with the bulk particulate matter interpretation discussed earlier.

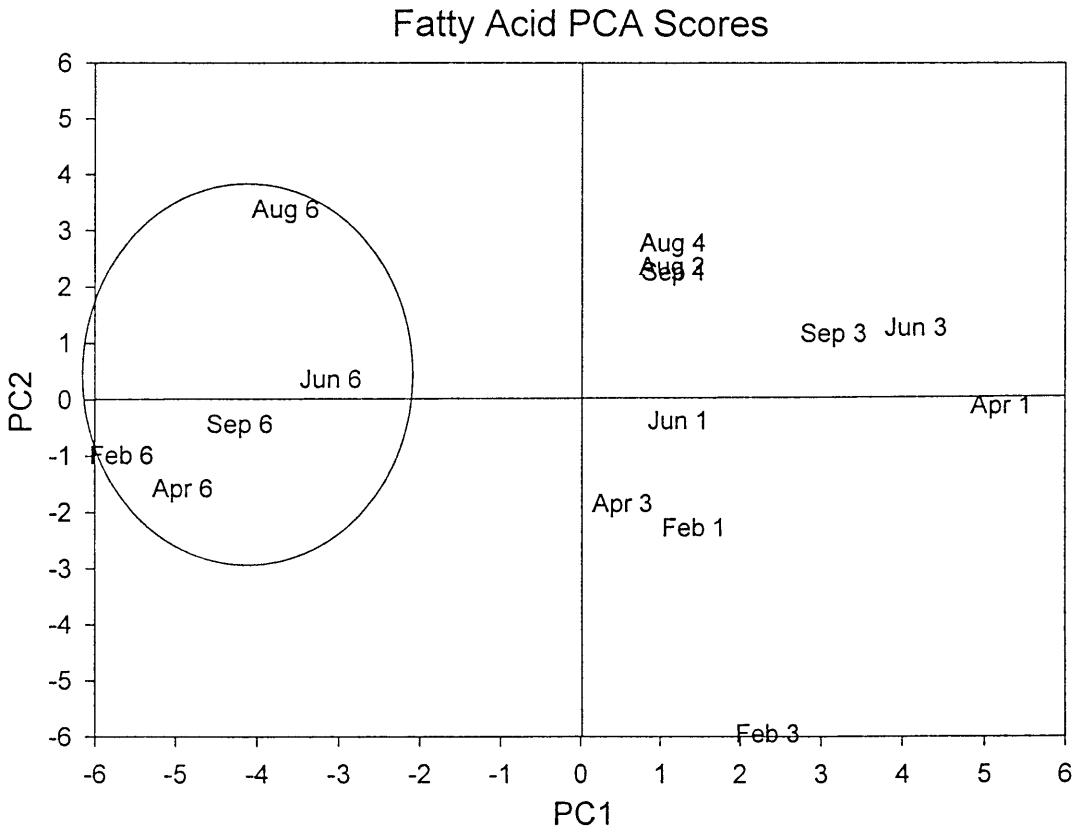
In addition to these observational differences, principal component analysis (PCA) of fatty acid and sterol concentrations in surface waters of the York River illustrates the different organic matter composition at Station 6 as compared to the rest of the estuary (Fig. 12). Both fatty acid and sterol compositions at the head of the estuary were different from the rest of the estuary; Station 6 samples cluster distinctly apart from the other stations, with little seasonal variability. For fatty acid compounds, principal component 1 (PC1) accounted for 39.2% of the variance, and principal component 2 (PC2) for 19.2% of the variance. Sterol PC1 accounted for 42.5% of the variance, and PC2 for 26.7%.

### *Particulate PAHs in Estuarine Surface Waters*

Mean individual and total concentrations of particulate PAHs from all York River surface water sites (ng $l^{-1}$) measured in this study were higher than those determined by Gustafson and Dickhut (1997c) for a single site near the York

Figure 12. Principal component analysis (PCA) scores for fatty acids and sterols. Fatty acid analysis includes all fatty acids detected, while sterol analysis was limited to the 9 sterols identified in the text as autochthonous and allochthonous. Samples noted by date of collection and Station number. PCA score results indicate unique organic matter composition at Station 6 relative to other sites.


Sterol PCA Scores
PC2
PC1
Feb 1
Apr 1
Sep 3
Apr 3
Feb 3
Aug 4
Sep 6
Jun 1
Aug 2
Sep 1
Jun 3
Jun 6
Apr 6
Feb 6
Aug 6

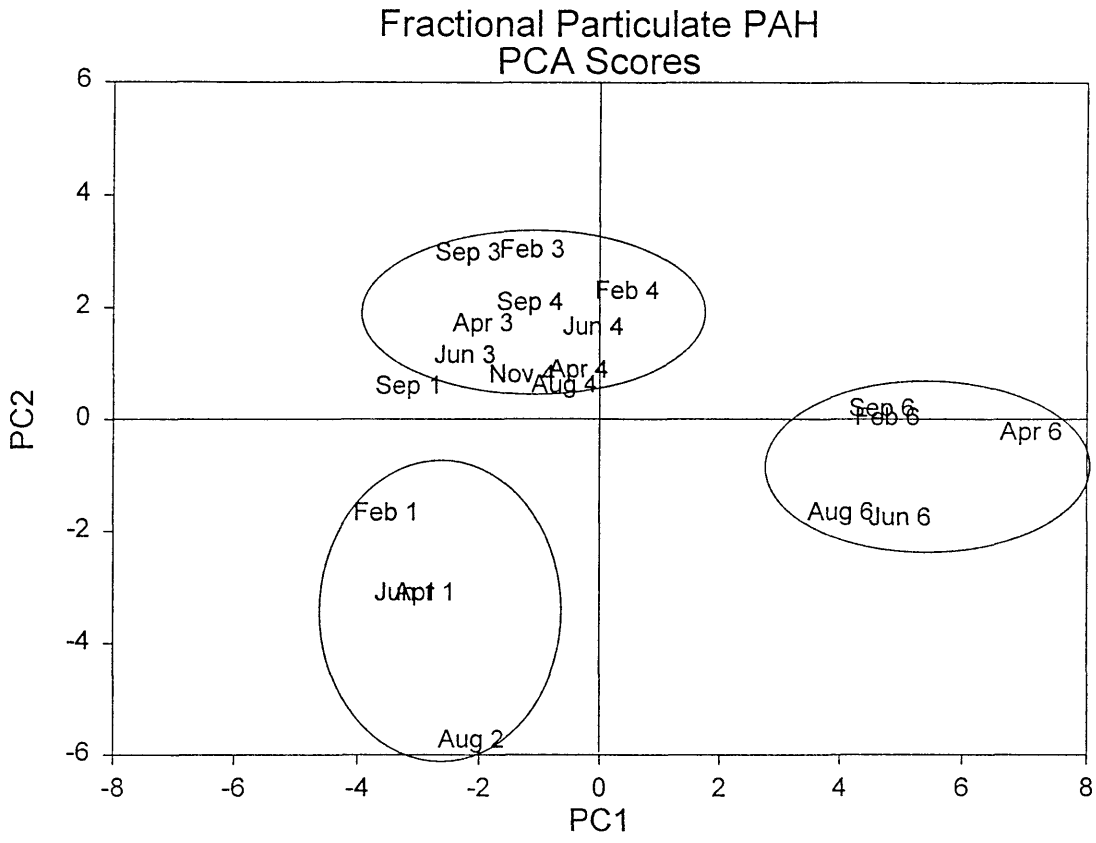

Fatty Acid PCA Scores
PC2
PC1
Aug 6
Jun 6
Sep 6
Feb 6
Apr 6
Aug 4
Sep 3
Jun 3
Jun 1
Apr 1
Apr 3
Feb 1
Feb 3

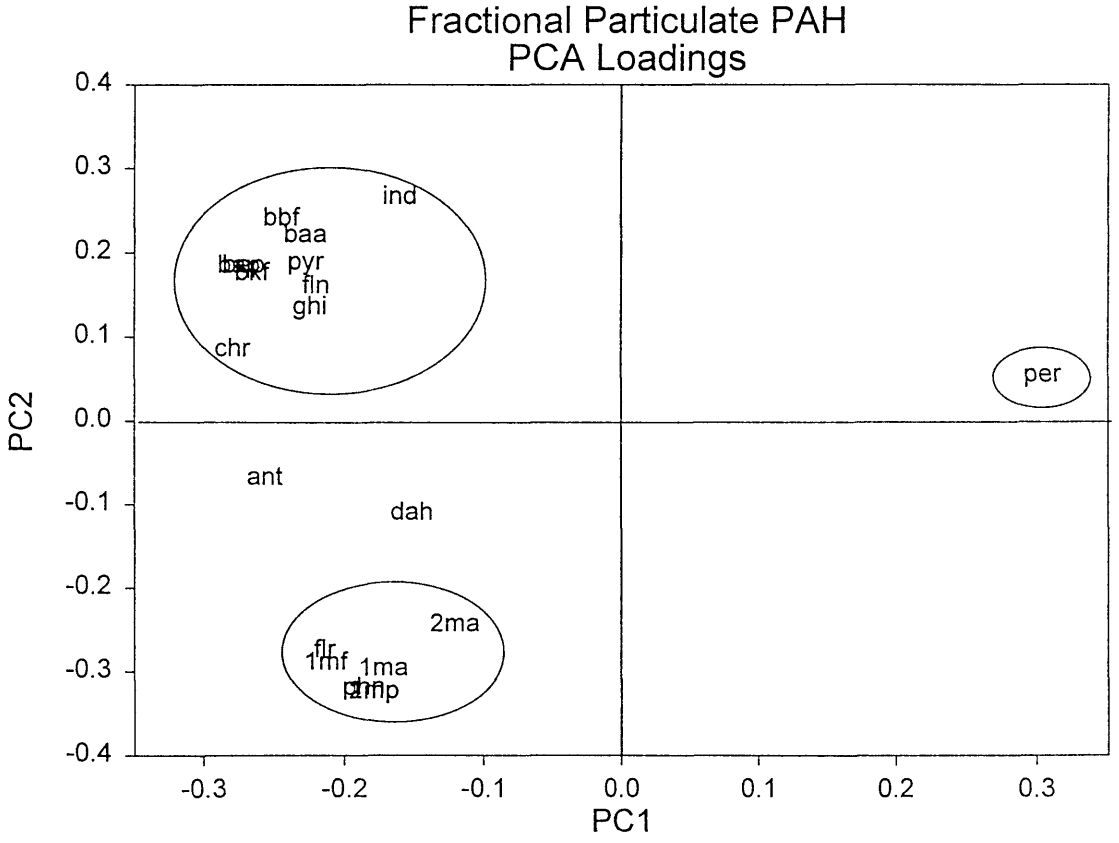
River mouth. However, mean individual and total concentrations of PAHs at this particular site were very similar for both studies, underscoring the importance of spatial variability in PAH concentrations in the York River estuary. Ranges of concentrations of phenanthrene, fluoranthene, pyrene and benzo[a]pyrene (ng $g^{-1}$) were within those measured by Ko and Baker (1995) in mesohaline Chesapeake Bay surface waters. Concentrations in surface waters of the York River were, however, lower than those determined for surface waters of the Rhône Delta (Bouloubassi and Saliot, 1991).

A plot of the principal component analysis scores (Fig. 13) indicates that compositional patterns of particulate PAHs in the York River Estuary fall into three distinct clusters, again emphasizing the spatial element of PAH distributions in this environment. The first two principal components from the analysis account for 52.9 and 25.6% of the variance in the data set, respectively. Samples from the Pamunkey River (Station 6) grouped separately from the marine end-member samples (Stations 1 & 2), while Station 3 and 4 samples clustered in a third region of the graph.

Principal component analysis (Fig. 13) also provides a means of reducing the complexity of the total PAH data set, originally comprised of 20 individual PAH compounds per sample. Values of loadings from the PCA analysis contain information about the relationships among the variables (Meglen, 1992), or here, the PAH compounds. Principal component one loadings illustrated a difference between perylene (positive 0.3) and the remaining 19 PAH compounds, which ranged between -0.1 and -0.3. This may be a function of natural versus

Figure 13. Principal component analysis (PCA) scores and loadings for particulate PAHs. The scores illustrate relationships among samples, while the loadings contain information about the relationships among variables. PCA score results (samples noted by date of collection and Station number) indicate unique distributions of PAHs at the head (Station 6), middle (Stations 3 and 4) and mouth (Stations 1 and 2) of the York River estuary. PCA loadings illustrate 3 distinct groups of PAHs: perylene - per; volatile PAHs – fluorene (flr), 1-methylfluorene (1mf), phenanthrene (phn), 2-methylphenanthrene (2mp), 2-methylanthracene (2ma), 1-methylanthracene (1ma), and 1-methylphenanthrene (1mp); and combustion-derived particle associated PAHs – fluoranthene (fln), pyrene (pyr), benz[a]anthracene (baa), chrysene (chr), benzo[b]fluoranthene (bbf), benzo[k]fluoranthene (bkf), benzo[e]pyrene (bep), benzo[a]pyrene (bap), indeno[123cd]pyrene (ind) and benzo[ghi]perylene (ghi). Anthracene (ant) and dibenz[ah]anthracene (dah) do not coincide with these groupings.


Fractional Particulate PAH
PCA Scores
PC2
PC1
Sep 3
Feb 3
Feb 4
Sep 4
Apr 3
Jun 4
Jun 3
Nov 4
Apr 4
Aug 4
Sep 1
Sep 6
Feb 6
Apr 6
Feb 1
Aug 6
Jun 6
Aug 2


Fractional Particulate PAH
PCA Loadings
PC2
PC1
ind
bbf
baa
pyr
fln
ghi
chr
per
ant
dah
2ma
1ma

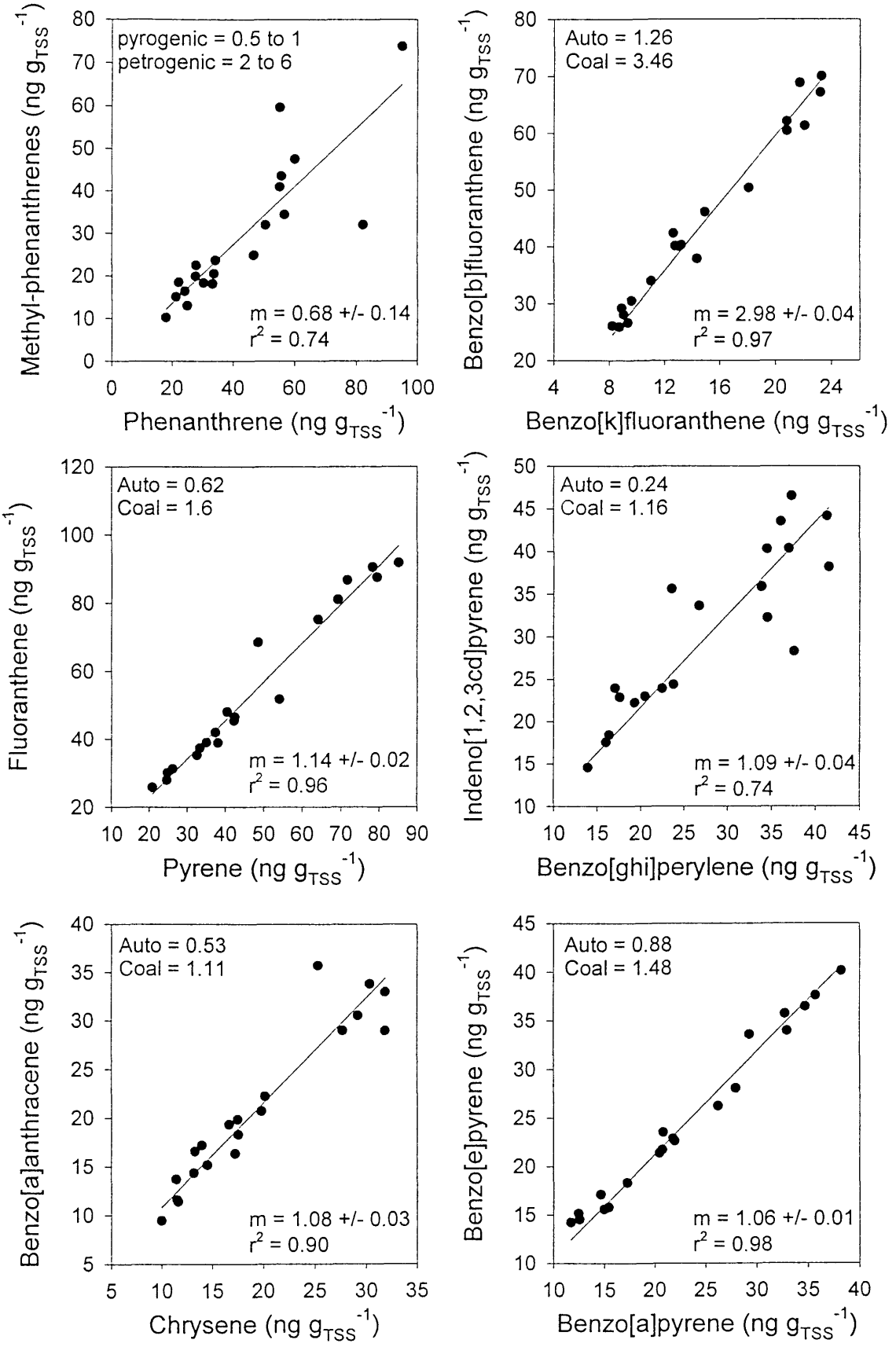
anthropogenic sources of these compounds. Principal component 2 loadings separated the compounds into two distinct clusters (Fig. 13). These groupings appear to be a function of physio-chemical behavior of the PAHs, with volatile compounds having the most negative PC2 values, and cluster in the lower left-hand quadrant, while heavier, predominantly particle associated combustion-derived particles cluster in the upper left-hand quadrant. Although perylene has a PC2 loading that would place it with the combustion-derived PAHs it is observed to stand alone to the right on the PCA loadings graph, suggesting that this compound has a unique source. The unique behavior of perylene (Figs. 10 and 13) relative to other PAHs suggests that the predominant source of this PAH to the York River estuary is natural rather than anthropogenic. Several authors have used relative abundances of perylene compared to anthropogenic PAHs to discern between anthropogenic and diagenetically derived perylene (Venkatesan, 1988; Bouloubassi and Saliot, 1993). The subsequent analyses of organic matter - PAH associations will be categorized using these three subgroups of PAHs: volatile, combustion-derived and perylene. Readman et al. (1982) determined a similar grouping of PAHs in the Tamar Estuary, based on observed environmental behavior: “Group I” was low molecular weight PAHs incorporating naphthalene, phenanthrene and anthracene and “Group 2” was the larger molecular weight compounds fluoranthene, pyrene, chrysene, benz[a]anthracene, benzo[b]fluoranthene, benzo[k]fluoranthene and benzo[a]pyrene. In their study, Group 1 PAHs exhibited no significant correlations with either salinity or suspended particles while Group 2 PAH

concentrations were highly correlated with suspended particles. This led Readman et al. (1982) to propose volatilization as an important process in determining the fate of Group I compounds, and sediment burial as the principal fate of Group 2 PAHs. No attempt was made however, to correlate these groups of PAHs with any specific pool of suspended particles.

### *Sources of Particulate PAHs*

Distinguishing among different sources and behavior of PAHs is of fundamental interest in assessing their transport and bioavailability. Most PAHs in the environment can be considered to be from one of two anthropogenic sources: petrogenic (oil-derived) or pyrogenic (combustion-derived). However, as noted above, certain PAHs such as perylene are also believed to be diagenetic products of natural organic matter (Venkatesan, 1988; Bouloubassi and Saliot, 1993). PAHs formed due to combustion at high temperatures are dominated by unsubstituted species, while lower temperatures of formation favor a higher degree of alkylation (LaFlamme and Hites, 1978; Colombo et al., 1989). For example, in petroleums, the ratio of methylphenanthrenes to phenanthrene (MP/P) ranges from 2 to 6, while in typical combustion mixtures the ratio is between 0.5 and 1.0 (Youngblood and Blumer, 1975; Prahl and Carpenter, 1983). The ratio of methylphenanthrenes to phenanthrene in York River surface waters is less than 1 (first panel of Fig. 14; slope of the regression line represents the average ratio of the compounds), suggesting that PAHs in this system are the result of combustion processes, rather than uncombusted petroleum.

Figure 14. Particulate PAH ratios for all samples. The slope of the regression line, b, represents the average ratio of the compounds (first panel) or isomers (remaining five panels) across all samples in space and time. Representative ratios for automobile and coal sources (pyrogenic and petrogenic sources in the first panel), are included in the upper right-hand corner of each graph.


pyrogenic = 0.5 to 1
petrogenic = 2 to 6
m = 0.68 +/- 0.14
r2 = 0.74
Methyl-phenanthrenes (ng gTSS-1)
Phenanthrene (ng gTSS-1)
Auto = 1.26
Coal = 3.46
m = 2.98 +/- 0.04
r2 = 0.97
Benzo[b]fluoranthene (ng gTSS-1)
Benzo[k]fluoranthene (ng gTSS-1)
Auto = 0.62
Coal = 1.6
m = 1.14 +/- 0.02
r2 = 0.96
Fluoranthene (ng gTSS-1)
Pyrene (ng gTSS-1)
Auto = 0.24
Coal = 1.16
m = 1.09 +/- 0.04
r2 = 0.74
Indeno[1,2,3cd]pyrene (ng gTSS-1)
Benzo[ghi]perylene (ng gTSS-1)
Auto = 0.53
Coal = 1.11
m = 1.08 +/- 0.03
r2 = 0.90
Benzo[a]anthracene (ng gTSS-1)
Chrysene (ng gTSS-1)
Auto = 0.88
Coal = 1.48
m = 1.06 +/- 0.01
r2 = 0.98
Benzo[e]pyrene (ng gTSS-1)
Benzo[a]pyrene (ng gTSS-1)

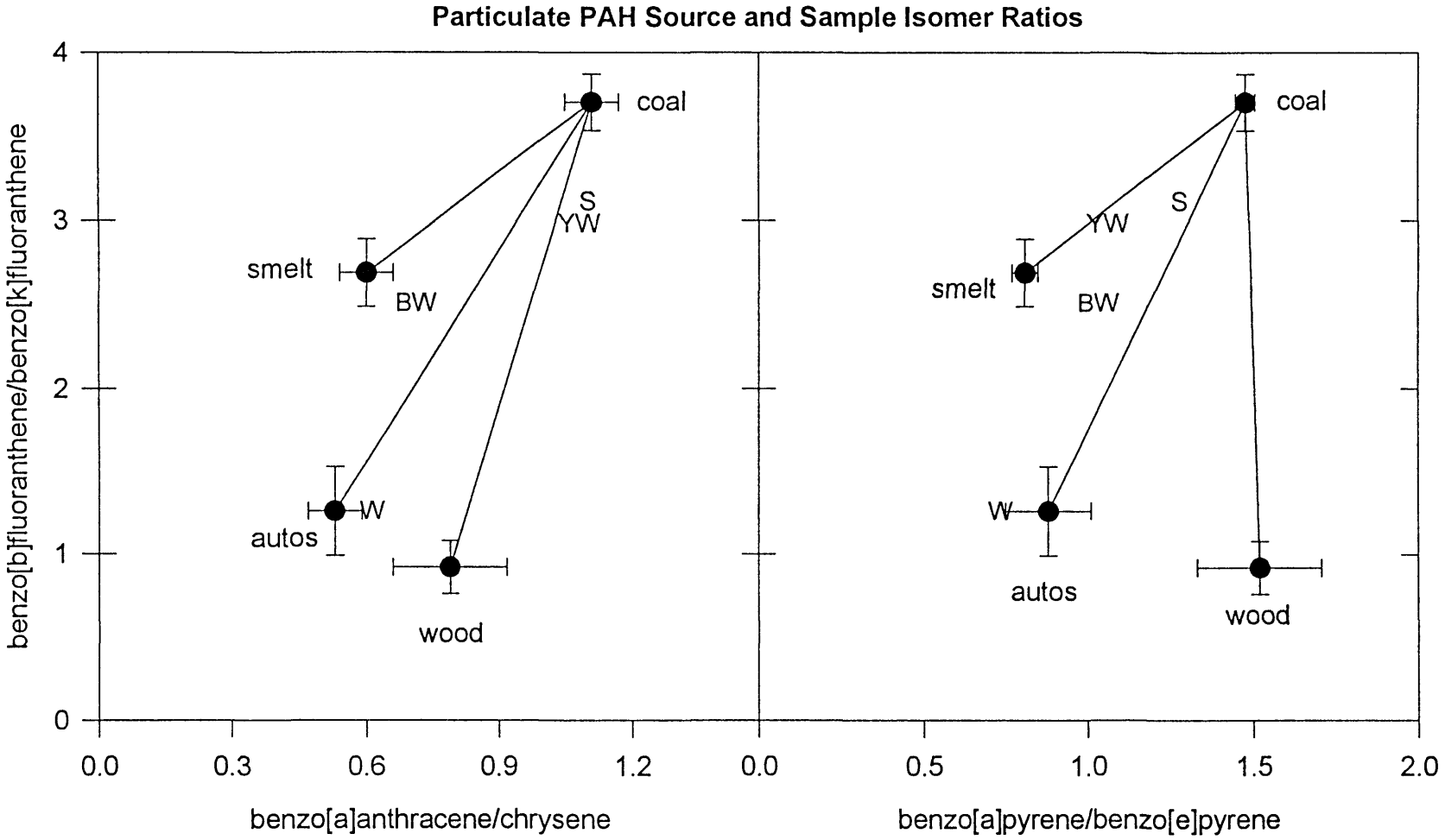
Environmental concentrations of PAHs can also be related to contributing sources by comparing them with emission patterns of potential sources. In order to evaluate the compositional differences in PAH profiles, the concentrations of PAHs are typically standardized into a ratio with a specific PAH (Baek et al., 1991). Ratios of PAH isomer pairs are often used as source indicators rather than specific compound abundances, because isomers will partition similarly to other phases in the environment since their thermodynamic partitioning and kinetic mass transfer coefficients are comparable (Dickhut et al., in prep.). Ratios of selected PAH isomers were examined to determine if there were significant PAH compositional differences among particulate samples at each of the sampling sites. Ratios were chosen based on the availability of previously reported values as indicators of potential sources of PAHs and differences in photoreactivity of the compounds. Uniform isomer ratios for PAHs in York River surface waters should indicate similar PAH sources along the estuarine gradient. In contrast, variations in isomer ratios among sites or with time may be due to differences in PAH source material composition, transport pathways, and potentially, geochemical reactivity between isomers. Thus, variable ratios of PAH isomers should be a tracer of PAH transformation during transport from their origin to the time of sample collection, or may simply reflect differences in PAH sources between sites or seasons (Sporstol et al., 1983; Colombo et al., 1989; Zeng and Vista, 1997). PAH isomer ratios such as phenanthrene/anthracene, pyrene/fluoranthene, and benzo[e]pyrene/benzo[a]pyrene have been used

indirectly to infer differential transport mechanisms of particle associated PAHs (Liu and Dickhut, 1997).

PAH isomer ratios were calculated for five pairs of PAHs (Fig. 14) and compared to discrete source values available in the literature (Dickhut et al., in prep.). In these figures the slope of the regression line represents the average ratio of the isomers across all samples in space and time. Isomer ratios were very homogenous, both throughout the estuary and over the year, as suggested by the extremely strong correlation coefficients and low standard errors for the isomer ratios. Ratios of fluoranthene/pyrene, benz[a]anthracene/chrysene, benzo[b]fluoranthene/benzo[k]fluoranthene and indeno[1,2,3cd]pyrene/benzo[ghi]perylene indicate PAHs in York River surface waters are more compositionally similar to combusted coal than automobile exhaust. Using two component mixing models, these four isomer pairs indicate that particulate PAHs in York River surface waters are up to 80 ± 10% coal derived. However, benzo[e]pyrene/benzo[a]pyrene ratios were more indicative of automobile than coal source materials.

To help elucidate this seemingly conflicting information, multiple isomer ratios were plotted together (Fig. 15). Added to this were sample values for York River surface waters (YW) and surface water, bottom water and surface sediments of samples from the Chesapeake Bay (W, BW, and S respectively; Dickhut et al., in prep). These graphs clearly illustrate that PAHs in York River surface waters are more similar in overall composition to Chesapeake Bay sediments and bottom water than to Chesapeake Bay surface waters. The

Figure 15. Particulate PAH source and sample isomer ratios. Sample abbreviations are as follows: YR – York River surface waters, this study; W – Chesapeake Bay surface waters; BW – Chesapeake Bay bottom waters; S – Chesapeake Bay surface sediments.


Particulate PAH Source and Sample Isomer Ratios
benzo[b]fluoranthene/benzo[k]fluoranthene
4
3
2
1
0
coal
S
YW
smelt
BW
W
autos
wood
0.0
0.3
0.6
0.9
1.2
benzo[a]anthracene/chrysene
0.0
0.5
1.0
1.5
2.0
benzo[a]pyrene/benzo[e]pyrene

different source signature of PAHs in York River versus Chesapeake Bay surface waters is likely due to greater sediment suspension in the physically energetic York River estuary (Dellapenna et al., 1998).

### *Particulate Organic Matter – Particulate PAH Relationships*

An understanding of the sorption properties of contaminants such as PAHs is crucial, as it can impact the physical transport and the chemical reactivity of the compounds (Karickhoff, 1984). However, there has been much less work regarding contaminant-organic matter associations in surface waters than for estuarine sediments. Prahl & Carpenter (1983) pointed out that PAH-organic matter associations may reflect sources of PAHs, and definitely affect dispersal patterns, bioavailability and ultimate impact of these compounds on aquatic organisms. Ko and Baker (1995) observed elevated concentrations of PAHs and other hydrophobic contaminants in the large particle fraction (>202 μm) of Chesapeake Bay surface waters and speculated that zooplankton played an important role in the accumulation of contaminants. Analysis of PAH-organic matter associations in sediments from southern Chesapeake Bay (including two York River sites) suggest that the distribution of methylated and volatile PAHs is influenced by uptake by lipid-rich surface water particles and subsequent delivery to the sediments (Arzayus et al., 1999b, in prep.).

Initial assessment of relationships between particulate PAHs and organic matter in York River Estuary surface waters were discouraging, as there was not even a significant relationship between PAH concentration and organic carbon content. A basic geochemical tool used for assigning a quantitative value to

contaminant–organic matter associations is the distribution coefficient (Olsen et al., 1982). The magnitude of hydrophobic organic contaminant-particle association varies directly with contaminant hydrophobicity, as parameterized by the octanol-water partition coefficient, $K_{ow}$, or aqueous solubility (Baker et al., 1991). Because of the importance of organic carbon in the sorption of uncharged organic compounds, PAH distributions are typically modeled using the partition coefficient reduced to a form containing only organic matter - $K_{oc}$, the ratio of particulate carbon bound and dissolved contaminant concentrations (Karickhoff, 1984). However, a major assumption in this partitioning paradigm is that contaminants have equal affinities for all particulate organic matter. The lack of correlation between PAHs and organic carbon in York River surface waters suggested that PAHs may be associated with specific pools within the total organic carbon pool, which may vary both temporally and spatially. As such, perhaps this lack of correlation should not have been surprising, given the temporal focus of the study. Organic carbon partitioning models have typically been applied to sediments (Karickhoff et al., 1979), which integrate PAH and organic carbon concentrations over much longer timescales than the monthly "snapshots" examined in this study.

Reassessment of characteristics of organic carbon in York River surface waters revealed substantial variability in carbon quantity (mg $g^{-1}$), carbon quality (chlorophyll-*a* concentrations, C:N ratios and $\delta^{13}C_{oc}$ values, Figs. 5 and 6 ) and carbon source as reflected by fatty acid and sterol distributions (Fig. 9). There were steep gradients in POC content in June 1998 and April 1999 (Fig. 5), which

were similar to the gradients in PAH concentration, with the exception of perylene (Fig. 10). However, overall concentrations of particulate organic carbon varied very little from August 1998 through February 1999 (Fig. 5); during this same time-period, the variability in PAH concentrations was no less than at other times of the year (Fig. 10). Obviously, changes in PAH concentration are not related to carbon content alone.

For the analyses of organic matter – PAH associations, it was determined that in months when organic carbon quantity and quality co-varied (June 1998 and April 1999), lipid biomarker and PAH concentrations could be normalized to mass (i.e. TSS), but not POC, as normalizing to POC would remove the largest component of the variability of the organic carbon pool. In the intervening months, August 1998 through February 1999, organic carbon concentrations were less variable, and by normalizing to organic carbon it was possible to assess specific relationships between PAH and lipid biomarker concentrations. The resulting correlations among the three PAH groups previously described and various lipid biomarkers are summarized in Table 3.

During June 1998 and April 1999, when both the quantity and quality of carbon changed throughout the estuary, volatile PAHs were significantly related to organic carbon content of the particles ($n=7$, $p<0.01$), but combustion-derived particulate PAHs were not (Table 3). In addition, perylene concentrations were inversely related to POC. However, volatile and combustion PAHs correlated significantly with TLE and both autochthonous and allochthonous lipid biomarkers (Table 3). The correlation between combustion-derived PAHs and

**Table 3. Particulate Organic Matter - PAH Correlations[a,b]**

| | June '98 & Apr. '99 (TSS normalized) | | | Aug. '98-Feb. '99 (OC normalized - except OC &TLE) | | |
|---|---|---|---|---|---|---|
| | Volatile PAHs[c] | Combustion PAHs[d] | Perylene[e] | Volatile PAHs[c] | Combustion PAHs[d] | Perylene[e] |
| Organic Carbon (OC) | 7/7 ** | 1/10 * | (-) | ns | ns | ns |
| Total Lipid Extract (TLE) | 6/7 **<br>1/7 * | 7/10 * | (-) | ns | ns | (-) |
| Polyunsaturated FAs | 7/7 ** | 1/10 **<br>9/10 * | (-) | ns | ns | (-) |
| Even Long-Chained FAs | 5/7 **<br>1/7 * | ns | ns[f] | ns | ns | *** |
| Autochthonous Sterols | 7/7 ** | 1/10 **<br>9/10 * | (-) | ns | ns | (-) |
| Allochthonous Sterols | 2/7 **<br>5/7 * | 1/10 * | (-) | 7/7 *** | 8/10 **<br>2/10 * | ns |

[a] Fractions signify number of compounds within each group exhibiting significant correlations.

[b] ns, *, **, *** indicate not significant, $p<0.05$, $p<0.01$ and $p<0.001$, respectively

[c] Volatile PAHs include the following 7 compounds: fluorene, 1-methylfluorene, phenanthrene, 2-methylphenanthrene, 2-methylanthracene, 1-methylanthracene, and 1-methylphenanthrene.

[d] Combustion PAHs include the following 10 compounds: fluoranthene, pyrene, benz[a]anthracene, chrysene, benzo[b]fluoranthene, benzo[k]fluoranthene, benzo[e]pyrene, benzo[a]pyrene, indeno[123cd]pyrene and benzo[ghi]perylene.

[e] (-) denotes significant negative correlation ($p<0.05$)

[f] Significant at $p<0.05$ when OC normalized.

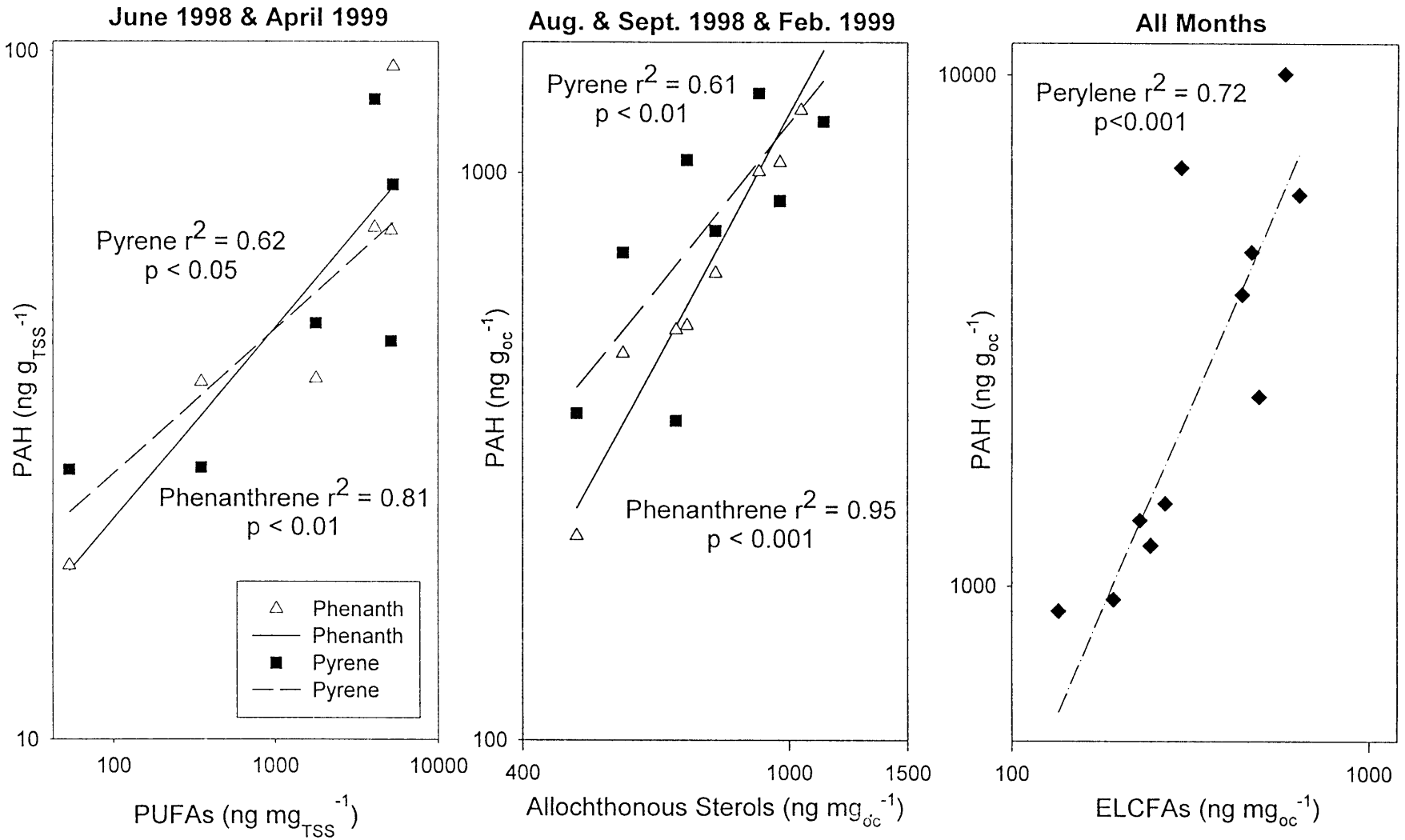
TLE but not organic carbon may be because TLE is particularly hydrophobic pool of organic carbon, providing a "sticky" surface area to capture combustion-derived PAHs.

In June and April the strongest relationships were observed between volatile PAHs, such as phenanthrene, and autochthonous organic matter, both polyunsaturated fatty acids ($n=7$, $p<0.01$; Fig. 16 and Table 3) and autochthonous sterols ($n=7$, $p<0.01$; Table 3). Correlations between volatile PAH compounds and allochthonous sterols were slightly weaker ($n=2$, $p<0.01$; $n=5$, $p<0.05$; Table 3). The relationships of volatile PAHs with both autochthonous and allochthonous organic matter suggests the absorption of these compounds into all lipid pools during these months. The stronger relationships between volatile PAHs and autochthonous organic matter may be the result of a growing pool of phytoplankton available for PAH partitioning during the spring and early summer. In effect, phytoplankton may be acting as a biological pump of PAHs from the atmosphere to estuarine surface waters. Uptake of gaseous atmospheric PAHs would also explain the relationship between volatile PAHs and allochthonous organic matter. Adsorption of hydrophobic organic contaminants by terrestrial vegetation is well-documented (Simonich and Hites, 1994 and 1995), and thus volatile PAHs may be adsorbed by allochthonous organic matter prior to or during its residence in estuarine surface water.

Combustion PAHs such as perylene were also significantly correlated with PUFAs ($n=1$; $p<0.01$; $n=9$, $p<0.05$; Fig. 16) and autochthonous sterols ($n=1$; $p<0.01$; $n=9$, $p<0.05$) in June 1998 and April 1999 (Table 3). However, only one

Figure 16. Particulate PAH – Lipid biomarker Associations. Phenanthrene illustrates volatile PAH behavior and pyrene exemplifies combustion-derived PAH behavior. June 1998 and April 1999 represent periods when organic carbon quantity and quality of surface water particles co-varied along the York River estuarine gradient, and so the PAH and lipid biomarker compounds are TSS-normalized. During August and September 1998 and February 1999, organic carbon quality varied while organic carbon quantity of surface water particles was constant, and thus PAH and lipid biomarkers were organic carbon-normalized.

**Particulate PAH-Lipid Biomarker Associations in York River Surface Waters**



combustion PAH compound, not pyrene, was significantly correlated with allochthonous sterols during these months ($p<0.05$; Fig. 16 and Table 3). Assuming that combustion-derived PAHs in York River surface waters are derived from sediment resuspension, the associations between these PAHs and autochthonous organic matter biomarkers may simply be the result of the co-existence of the two particle pools in surface waters rather than adsorption of combustion-derived PAHs by the lipid pool. Thus, the relationship between combustion PAHs and autochthonous, but not with allochthonous organic biomarkers, may result from autochthonous compounds dominating the organic matter pool. However, the increased supply of lipids during spring and early summer (Fig. 8) likely provides hydrophobic (i.e. "sticky") surface area to capture combustion-derived PAHs, and autochthonous organic matter and combustion-derived PAH particles may be associated.

From August 1998 to February 1999, when the quality of carbon varied much more than the quantity (Figs. 5 and 6), it was possible to examine relationships between organic carbon normalized lipid biomarkers and PAHs to determine whether PAH associations with specific lipid pools existed. During this period PAHs correlated only with allochthonous sterols (Table 3). Again, the volatile PAH relationship with allochthonous sterols ($n=7$, $p<0.001$; Fig. 16 and Table 3) was stronger than that of combustion PAHs ($n=8$, $p<0.01$; $n=2$, $p<0.05$; Fig. 16 and Table 3). These relationships may result from the direct vegetative uptake of PAHs prior to or during allochthonous organic matter residence in surface waters, or the PAHs and organic matter may be unassociated but have

comparably slow degradation rates. This latter explanation is consistent with the fact that PAH source indicators point to sediment resuspension as a dominant source of combustion-derived PAHs to York River surface waters. Because fatty acids are more reactive than sterols, the association of PAHs with allochthonous sterols but not fatty acids also supports the theory that PAHs and organic matter are unassociated but co-exist in surface waters due to their comparably slow degradation rates. Prahl and Carpenter (1983) hypothesized that the similarities in the distributions of plant wax *n*-alkanes and combustion PAHs in coastal Washington sediments was the result of roughly similar size and density characteristics rather than interactions interaction between the two particle pools.

Particulate perylene associations with organic matter were distinctly different than those observed for volatile and combustion PAHs. The only significant (positive) correlation between perylene and organic biomarkers was with even-numbered long-chained fatty acids, ELCFAs ($n=13$, $p<0.05$; Fig. 16), and this relationship was valid during all months. Prahl and Carpenter (1983) observed similar distributional patterns between perylene and plantwax hydrocarbons, but did not speculate on a mechanism for this relationship due to "a lack of understanding of processes producing perylene." It is again apparent that the source of perylene in the York River is different than that of the other PAHs, and its correlation with ELCFAs in all sampling periods suggests that this source is supplied from the freshwater end of the estuary and that it does not vary seasonally (Fig. 10). Furthermore, because perylene is correlated with ELCFAs, but not allochthonous sterols, both relatively refractory pools of organic

matter, there may be a specific terrestrial source of perylene to the estuary. As discussed earlier, allochthonous sterols may be confounded by freshwater algae, while even-numbered long-chained fatty acids are derived solely from vascular plants. Thus, the relationship between ELCFAs and perylene also suggests that perylene may be the product of diagenetic processes occurring in soils, with subsequent delivery to estuarine surface waters by terrestrial run-off.

## CONCLUSIONS

Autochthonous organic matter, primarily fresh phytoplankton as indicated by polyunsaturated fatty acids, dominates surface waters of the York River estuary. However a strong terrestrial organic matter signature is evident at the head of the estuary. In this energetically dynamic system, surface water PAHs associated with particles are more similar in composition to PAHs in Chesapeake Bay sediments than in Bay surface waters, and appear to be predominantly coal derived.

While particulate organic matter – PAH correlations may not indicate true associations between the compounds, the varying relationships between distinct groups of PAHs and lipid biomarkers demonstrated in this study suggest that very specific pools of organic matter, as opposed to concentrations of organic carbon alone, can be important in the fate and transport of hydrophobic contaminants. The combined analyses of organic matter biomarkers and PAHs suggest that delivery processes, such as atmospheric deposition, sediment resuspension and terrestrial runoff, and the physio-chemical behavior of individual PAH compounds, are important in predicting their distribution in the

environment (Table 4). For example, the June 1998 and April 1999 PAH associations with autochthonous organic matter (PUFAs and sterols) may be explained by a growing pool of this organic matter becoming available for partitioning, with simultaneous uptake of volatile PAHs, as well as the "sticking" of combustion-derived particulate PAHs to this fresh organic matter. The allochthonous particulate organic matter – volatile PAH correlations observed from August 1998 through February 1999 may also be the result of direct vegetative uptake of volatile PAHs by allochthonous organic matter residing in surface waters. However, the more likely mechanism of association between volatile PAHs and allochthonous sterols in the fall and winter months is terrestrial vegetative uptake of volatile PAHs prior to delivery by run-off to estuarine surface waters. Combustion-derived particulate PAHs are also positively correlated with allochthonous sterols during the fall and winter months. This relationship, coupled with isomer ratios indicative of coal, indicates that sediment resuspension is the dominant mode of entry to York River surface waters of combustion-derived particulate PAHs during these months, with these PAHs and allochthonous sterols unassociated but possessing comparably slow degradation rates. Sediment resuspension could also reintroduce associated volatile PAHs and allochthonous organic matter to the surface waters.

Finally particulate perylene behavior suggests a distinct source of this PAH to the estuary, which is probably natural rather than anthropogenic. The association of perylene with even-numbered long-chain fatty acids suggests that the source of this PAH is terrestrial, or a product of terrestrial diagenetic

**Table 4. PAH - Lipid Biomarker Correlations and their Implications**

| PAH Group[a] | Model PAH | Correlated Lipids | Months Correlated[b] | Apparent dominant mode of entry | Proposed Mechanism of Association |
|---|---|---|---|---|---|
| Volatiles | Phenanthrene | PUFAs | June & April** | air-water gas exchange | phytoplankton uptake |
| | | autochthonous sterols | June & April** | air-water gas exchange | phytoplankton uptake |
| | | ELCFAs | June & April** | air-water gas exchange | vegetative uptake - terrestrial or *in situ* |
| | | allochthonous sterols | June & April* | air-water gas exchange or terrestrial run-off | vegetative uptake - terrestrial or *in situ* |
| | | | August - February*** | terrestrial runoff or sediment resuspension | vegetative uptake - terrestrial or *in situ* |
| Combustion-derived particulate | Pyrene | PUFAs | June & April* | atmospheric deposition or sediment resuspension | PAH particles sticking to organic matter particles |
| | | autochthonous sterols | June & April* | atmospheric deposition or sediment resuspension | PAH particles sticking to organic matter particles |
| | | allochthonous sterols | August - February** | sediment resuspension | unassociated, co-occurring refractory particles |
| Naturally-derived | Perylene | ELCFAs | All*** | terrestrial runoff | unassociated, refractory particles entering estuary concomitantly |

[a] See Table 3 for specific PAHs in each group.

[b] *, **, *** indicate $p<0.05$, $p<0.01$ and $p<0.001$, respectively, for most PAHs in the group (Table 3)

processes in soils. Overall, the observed relationships between PAHs and lipid biomarkers in surface waters of the York River estuary support the hypothesis that PAH-organic matter associations in estuarine surface waters will be dictated by the dominant mode of entry of the contaminants to the estuary.

## FUTURE WORK

Future work will include calculating the magnitude of volatile flux of PAHs entering York River surface waters, using atmospheric and dissolved phase PAH data collected concurrently with the particulate data presented in this thesis (see Appendices B and C). This information will be used to link PAH transport between the atmosphere and surface waters to the accumulation of PAHs in Chesapeake Bay sediments (Arzayus et al., 1999b, in prep.).

# APPENDIX A: SURFACE WATER STATION DETAILS

**Table 5. Station Location, Time of Arrival and Water Depth**

| Date | Station # | Latitude (N) | Longitude (W) | Time Arrived | Water Depth (feet) |
|---|---|---|---|---|---|
| 5-Jun-98 | 1 | 37 14.40 | 76 23.20 | 7:47 | 39 |
| | 2 | 37 16.72 | 76 33.34 | 8:49 | 42 |
| | 3 | 37 21.01 | 76 38.03 | 10:16 | 17 |
| | 4 | | | 10:52 | 12 |
| | 5 | 37 30.80 | 76 47.20 | 11:32 | 11 |
| | 6 | 37 32.82 | 76 53.32 | 12:36 | 24 |
| 20-Aug-99 | 2 | 37 16.74 | 76 33.39 | 7:58 | 43 |
| | 4 | 37 25.57 | 76 42.60 | 13:01 | 10 |
| | 6 | 37 32.80 | 76 53.35 | 11:06 | 28 |
| 10-Sep-98 | 1 | 37 14.29 | 76 23.19 | 8:54 | 36 |
| | 2 | 37 16.65 | 76 33.33 | 9:55 | 42 |
| | 3 | 37 21.11 | 76 38.04 | 16:07 | 18 |
| | 4 | 37 25.55 | 76 42.61 | 15:23 | 10 |
| | 5 | 37 30.84 | 76 47.19 | 14:27 | 13 |
| | 6 | 37 32.80 | 76 53.35 | 13:14 | 30 |
| 19-Nov-98 | 1 | 37 14.42 | 76 23.22 | 8:52 | 40 |
| | 2 | 37 16.76 | 76 33.36 | 9:40 | 46 |
| | 3 | 37 21.01 | 76 38.05 | 11:00 | 20 |
| | 4 | 37 25.60 | 76 42.58 | 11:49 | 14 |
| | 5 | 37 30.79 | 76 47.22 | 12:33 | 13 |
| | 6 | 37 32.81 | 76 53.33 | 13:40 | 29 |
| 4-Feb-99 | 1 | 37 14.40 | 76 23.19 | 7:59 | 40 |
| | 2 | 37 16.78 | 76 33.33 | 8:44 | 45 |
| | 3 | 37 21.03 | 76 38.01 | 9:58 | 19 |
| | 4 | 37 25.58 | 76 42.62 | 10:40 | 10 |
| | 5 | 37 30.79 | 76 47.20 | 11:18 | 13 |
| | 6 | 37 32.78 | 76 53.30 | 12:22 | 28 |
| 1-Apr-99 | 1 | 37 14.40 | 76 23.20 | 7:55 | 42 |
| | 2 | 37 16.70 | 76 33.34 | 8:40 | 41 |
| | 3 | 37 21.02 | 76 38.03 | 12:58 | 18 |
| | 4 | 37 25.58 | 76 42.62 | 12:30 | 12 |
| | 5 | 37 30.81 | 76 47.21 | 11:39 | 11 |
| | 6 | 37 32.83 | 76 53.32 | 10:44 | 24 |

# APPENDIX B: DISSOLVED PHASE PAHS

## *Sampling Methods*

Collection and separation of dissolved phase PAHs was as described in Sampling Methods of the Materials and Methods section in the main portion of this document.

## *Dissolved PAH Analyses*

The XAD-2 resin, with deuterated PAH surrogate standard added, was Soxhlet extracted for 24 hours each in acetone and hexane. The acetone extracts were then back-extracted three times with equal amounts of hexane and hexane-extracted water. The resulting hexane fractions (from Soxhlet extraction and back-extraction) were combined and the solvent volume was reduced using rotoevaporation and ultimately concentrated to one milliliter by evaporation under pure nitrogen. This extract was cleaned by solid-liquid chromatography on silica gel (mesh 100-200) prior to PAH analysis in order to remove interfering compounds. Following silica gel purification, the PAH fraction was again concentrated by rotoevaporation. The final extract was concentrated to approximately 150 μl under $N_2$ after the addition of an internal standard containing deuterated PAHs. PAHs were quantified relative to deuterated surrogate PAHs by gas chromatography-mass spectrometry (GC-MS, Hewlett Packard 5890 Series II gas chromatograph/Hewlett Packard 5971A mass spectrometer) using a 30 m x 0.25 mm DBL-XB column and selected ion monitoring.

Table 6. Surface Water Dissolved PAH Concentrations

| | Jun-98 | | | | | | Aug-98** | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | 1 | 2 | 3 | 4 | 5 | 6 | 2 | 2 SE | 4 | 4 SE | 6 | 6 SE |
| **PAH (ng $l^{-1}$)** | | | | | | | | | | | | |
| naphthalene | 12.8600 | NQ | 10.0119 | NQ | NQ | 13.1223 | 10.7257 | 0.0000 | NQ | 0.0000 | 10.1820 | 0.1466 |
| acenaphthylene | 0.3725 | NQ | 0.1828 | NQ | NQ | 0.2953 | 0.3322 | 0.0000 | NQ | 0.0000 | 0.1591 | 0.0407 |
| acenaphthene | 2.3178 | NQ | 1.5608 | NQ | NQ | 1.7961 | 3.6321 | 0.0000 | NQ | 0.0000 | 1.4201 | 0.0894 |
| fluorene | 1.9734 | 2.4447 | 1.6022 | 1.2545 | 1.6941 | 1.6840 | 1.6803 | 0.7352 | 1.2741 | 0.0850 | 1.4701 | 0.0531 |
| 1-methylfluorene | 0.9867 | 1.0054 | 0.8967 | 0.7530 | 1.0258 | 0.9223 | 0.8445 | 0.0774 | 0.7483 | 0.0077 | 0.8326 | 0.0625 |
| phenanthrene | 2.5899 | 4.5292 | 1.9323 | 1.1881 | 1.5527 | 2.1457 | 3.7632 | 0.0304 | 1.7213 | 0.0194 | 1.7469 | 0.0173 |
| anthracene | 0.0578 | 0.3217 | 0.0595 | 0.0481 | 0.0718 | 0.0304 | 0.2313 | 0.0193 | 0.0452 | 0.0001 | 0.0393 | 0.0022 |
| 2-methylphenanthrene | 0.3364 | 0.4655 | 0.2454 | 0.1540 | 0.2111 | 0.2587 | 0.5867 | 0.0944 | 0.2624 | 0.0152 | 0.2751 | 0.0072 |
| 2-methylanthracene | 0.0254 | 0.0588 | 0.0173 | 0.0147 | 0.0267 | NQ | 0.0563 | 0.0089 | 0.0234 | 0.0009 | 0.1453 | 0.1453 |
| 1-methylanthracene | 0.3184 | 0.4989 | 0.2977 | 0.2135 | 0.3015 | 0.2416 | 0.4287 | 0.0740 | 0.2254 | 0.0139 | 0.1277 | 0.1129 |
| 1-methylphenanthrene | 0.1935 | 0.3132 | 0.1808 | 0.1332 | 0.1883 | 0.1513 | 0.3468 | 0.0498 | 0.1649 | 0.0076 | 0.1854 | 0.0063 |
| 9-methylanthracene | 0.0106 | 0.0613 | 0.0175 | 0.0214 | 0.0625 | NQ | NQ | 0.0000 | 0.0328 | 0.0027 | 0.0239 | 0.0003 |
| fluoranthene | 0.6802 | 3.0543 | 0.6236 | 0.5569 | 1.0109 | 0.3078 | 3.1053 | 0.3171 | 0.3531 | 0.0057 | 0.6980 | 0.1976 |
| pyrene | 0.5142 | 1.9772 | 0.4713 | 0.5345 | 0.8624 | 0.2740 | 2.2117 | 0.1948 | 0.3211 | 0.0102 | 0.4953 | 0.1354 |
| benz[a]anthracene | 0.0422 | 0.0902 | 0.0203 | 0.0631 | 0.1083 | 0.0075 | 0.1179 | 0.0066 | NQ | 0.0000 | NQ | 0.0000 |
| chrysene | 0.0391 | 0.0502 | 0.0136 | 0.0425 | 0.0903 | 0.0094 | 0.0579 | 0.0032 | 0.0063 | 0.0063 | 0.0119 | 0.0001 |
| benzo[b]fluoranthene | 0.0543 | 0.0337 | 0.0203 | 0.1263 | 0.2316 | 0.0173 | 0.0667 | 0.0099 | 0.0169 | 0.0018 | 0.0156 | 0.0004 |
| benzo[k]fluoranthene | 0.0301 | 0.0145 | 0.0120 | 0.0421 | 0.0750 | 0.0089 | 0.0109 | 0.0109 | 0.0074 | 0.0074 | NQ | 0.0000 |
| benzo[e]pyrene | 0.0322 | 0.0201 | 0.0112 | 0.0596 | 0.0989 | 0.0111 | 0.0464 | 0.0070 | 0.0125 | 0.0004 | 0.0127 | 0.0008 |
| benzo[a]pyrene | 0.0287 | 0.0103 | 0.0072 | 0.0583 | 0.1145 | NQ | 0.0246 | 0.0055 | NQ | 0.0000 | NQ | 0.0000 |
| perylene | 0.0165 | 0.0097 | 0.0114 | 0.2220 | 0.5042 | 0.1035 | 0.0294 | 0.0056 | 0.0286 | 0.0003 | 0.0860 | 0.0150 |
| 7-methylb[a]p | 0.0118 | ND | NQ | 0.0177 | 0.0271 | NQ | NQ | 0.0000 | ND | 0.0000 | 0.0030 | 0.0030 |
| indeno[123cd]pyrene | 0.0158 | 0.0054 | 0.0107 | 0.0829 | 0.1498 | 0.0063 | NQ | 0.0000 | NQ | 0.0000 | NQ | 0.0000 |
| benzo[ghi]perylene | 0.0453 | 0.0113 | 0.0109 | 0.0736 | 0.1249 | 0.0111 | 0.0259 | 0.0130 | 0.0033 | 0.0033 | 0.0127 | 0.0018 |
| dibenz[ah]anthracene | 0.0346 | NQ | 0.0087 | 0.0147 | 0.0135 | NQ | 0.0237 | 0.0000 | NQ | 0.0000 | 0.0035 | 0.0035 |
| Total PAH* | 8.0254 | 14.9754 | 6.4710 | 5.6570 | 8.5188 | 6.1910 | 13.6463 | 0.8389 | 5.2471 | 0.0917 | 6.1820 | 0.3140 |

* Total PAH does not include napthalene, acenaphthylene or acenaphthene, since these PAHs were not always quantifiable due to low recoveries (<40%).

** August data are the mean and standard error of two replicate samples at Stations 2, 4 and 6.

**Table 6 (cont.). Surface Water Dissolved PAH Concentrations**

| | Feb-99 | | | | | | Apr-99 | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | 1 | 2 | 3 | 4 | 5 | 6 | 1 | 2 | 3 | 4 | 5 | 6 |
| **PAH (ng $l^{-1}$)** | | | | | | | | | | | | |
| naphthalene | 9.5620 | 7.3961 | 7.0059 | 9.1673 | 7.8367 | NQ | NQ | 10.8239 | 8.4197 | NQ | NQ | 6.6448 |
| acenaphthylene | 0.3449 | 0.2423 | 0.1940 | 0.2465 | 0.2476 | NQ | NQ | 0.2798 | 0.1950 | NQ | NQ | 0.1450 |
| acenaphthene | 1.4968 | 1.1414 | 0.7235 | 0.7129 | 1.4192 | NQ | NQ | 2.0654 | 1.4049 | NQ | NQ | 0.6158 |
| fluorene | 0.9262 | 0.8530 | 0.6435 | 0.5348 | 0.8224 | 0.3363 | 0.6938 | 1.2318 | 0.8802 | 0.6805 | 1.1110 | 0.3609 |
| 1-methylfluorene | 0.2710 | 0.2630 | 0.1894 | 0.1805 | 0.2683 | 0.1618 | 0.3062 | 0.3698 | 0.2561 | 0.2564 | 0.2627 | 0.1549 |
| phenanthrene | 1.6874 | 1.5298 | 1.0132 | 1.0250 | 1.3631 | 0.6856 | 2.0841 | 2.6918 | 1.5265 | 1.3659 | 1.5102 | 0.6248 |
| anthracene | 0.0300 | 0.0356 | 0.0258 | 0.0448 | 0.0709 | 0.0240 | 0.0537 | 0.0488 | 0.0391 | 0.0458 | 0.0636 | 0.0186 |
| 2-methylphenanthrene | 0.2070 | 0.1912 | 0.0980 | 0.1370 | 0.1952 | 0.1529 | 0.3212 | 0.2713 | 0.1582 | 0.1723 | 0.1400 | 0.0961 |
| 2-methylanthracene | NQ | NQ | NQ | 0.0210 | 0.0178 | 0.0159 | 0.0199 | 0.0194 | 0.0089 | 0.0142 | 0.0125 | 0.0112 |
| 1-methylanthracene | 0.1149 | 0.0998 | 0.0601 | 0.0998 | 0.1394 | 0.0921 | 0.1551 | 0.1459 | 0.0907 | 0.1035 | 0.0901 | 0.0530 |
| 1-methylphenanthrene | 0.1161 | 0.1124 | 0.0643 | 0.0875 | 0.1194 | 0.0945 | 0.2281 | 0.1926 | 0.1321 | 0.1595 | 0.0988 | 0.0767 |
| 9-methylanthracene | 0.0155 | 0.0340 | 0.0482 | 0.1102 | 0.2528 | 0.0145 | 0.0333 | 0.0385 | 0.0305 | 0.0718 | 0.1550 | NQ |
| fluoranthene | 0.5298 | 0.4867 | 0.3063 | 0.3828 | 0.4470 | 0.1658 | 0.5127 | 0.5938 | 0.4540 | 0.4360 | 0.5351 | 0.1909 |
| pyrene | 0.3110 | 0.2690 | 0.1901 | 0.2816 | 0.3124 | 0.1667 | 0.2534 | 0.4115 | 0.2871 | 0.3068 | 0.3766 | 0.2123 |
| benz[a]anthracene | NQ | NQ | NQ | 0.0630 | NQ | 0.0174 | 0.0170 | 0.0084 | 0.0123 | 0.0182 | 0.0178 | 0.0147 |
| chrysene | 0.0103 | 0.0072 | NQ | 0.0443 | 0.0098 | 0.0189 | 0.0167 | 0.0085 | 0.0094 | 0.0276 | 0.0129 | 0.0145 |
| benzo[b]fluoranthene | 0.0121 | 0.0076 | 0.0059 | 0.0995 | 0.0119 | 0.0339 | 0.0290 | 0.0207 | 0.0134 | 0.0590 | 0.0205 | 0.0303 |
| benzo[k]fluoranthene | 0.0058 | 0.0021 | NQ | 0.0329 | NQ | 0.0145 | 0.0112 | 0.0089 | NQ | 0.0233 | 0.0153 | 0.0142 |
| benzo[e]pyrene | 0.0143 | 0.0053 | 0.0050 | 0.0578 | 0.0087 | 0.0195 | 0.0282 | 0.0281 | 0.0129 | 0.0356 | 0.0162 | 0.0241 |
| benzo[a]pyrene | 0.0071 | 0.0036 | NQ | 0.0525 | NQ | 0.0144 | 0.0147 | 0.0101 | 0.0051 | 0.0129 | 0.0138 | 0.0164 |
| perylene | 0.0041 | 0.0082 | 0.0104 | 0.1797 | 0.0377 | 0.1351 | 0.0240 | 0.0149 | 0.0198 | 0.0380 | 0.0476 | 0.1474 |
| 7-methylb[a]p | NQ | ND | ND | NQ | ND | 0.0140 | ND | NQ | 0.0020 | 0.0048 | 0.0119 | 0.0150 |
| indeno[123cd]pyrene | 0.0051 | NQ | ND | 0.0636 | NQ | 0.0078 | 0.0164 | 0.0104 | NQ | 0.0114 | 0.0118 | 0.0213 |
| benzo[ghi]perylene | 0.0238 | 0.0067 | NQ | 0.0540 | NQ | 0.0289 | 0.0193 | 0.0240 | 0.0085 | 0.0184 | 0.0175 | 0.0434 |
| dibenz[ah]anthracene | 0.0094 | ND | ND | 0.0306 | NQ | 0.0222 | 0.0056 | 0.0057 | 0.0064 | 0.0159 | 0.0424 | 0.0519 |
| Total PAH* | 4.3007 | 3.9153 | 2.6602 | 3.5571 | 4.0720 | 2.2228 | 4.8438 | 6.0943 | 3.9512 | 3.8730 | 4.5234 | 2.1777 |

* Total PAH does not include napthalene, acenaphthylene or acenaphthene, since these PAHs were not always quantifiable due to low recoveries (<40%).

Table 6 (cont.). Surface Water Dissolved PAH Concentrations

| | Feb-99 | | | | | | Apr-99 | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | 1 | 2 | 3 | 4 | 5 | 6 | 1 | 2 | 3 | 4 | 5 | 6 |
| PAH (ng $l^{-1}$) | | | | | | | | | | | | |
| naphthalene | 9.5620 | 7.3961 | 7.0059 | 9.1673 | 7.8367 | NQ | NQ | 10.8239 | 8.4197 | NQ | NQ | 6.6448 |
| acenaphthylene | 0.3449 | 0.2423 | 0.1940 | 0.2465 | 0.2476 | NQ | NQ | 0.2798 | 0.1950 | NQ | NQ | 0.1450 |
| acenaphthene | 1.4968 | 1.1414 | 0.7235 | 0.7129 | 1.4192 | NQ | NQ | 2.0654 | 1.4049 | NQ | NQ | 0.6158 |
| fluorene | 0.9262 | 0.8530 | 0.6435 | 0.5348 | 0.8224 | 0.3363 | 0.6938 | 1.2318 | 0.8802 | 0.6805 | 1.1110 | 0.3609 |
| 1-methylfluorene | 0.2710 | 0.2630 | 0.1894 | 0.1805 | 0.2683 | 0.1618 | 0.3062 | 0.3698 | 0.2561 | 0.2564 | 0.2627 | 0.1549 |
| phenanthrene | 1.6874 | 1.5298 | 1.0132 | 1.0250 | 1.3631 | 0.6856 | 2.0841 | 2.6918 | 1.5265 | 1.3659 | 1.5102 | 0.6248 |
| anthracene | 0.0300 | 0.0356 | 0.0258 | 0.0448 | 0.0709 | 0.0240 | 0.0537 | 0.0488 | 0.0391 | 0.0458 | 0.0636 | 0.0186 |
| 2-methylphenanthrene | 0.2070 | 0.1912 | 0.0980 | 0.1370 | 0.1952 | 0.1529 | 0.3212 | 0.2713 | 0.1582 | 0.1723 | 0.1400 | 0.0961 |
| 2-methylanthracene | NQ | NQ | NQ | 0.0210 | 0.0178 | 0.0159 | 0.0199 | 0.0194 | 0.0089 | 0.0142 | 0.0125 | 0.0112 |
| 1-methylanthracene | 0.1149 | 0.0998 | 0.0601 | 0.0998 | 0.1394 | 0.0921 | 0.1551 | 0.1459 | 0.0907 | 0.1035 | 0.0901 | 0.0530 |
| 1-methylphenanthrene | 0.1161 | 0.1124 | 0.0643 | 0.0875 | 0.1194 | 0.0945 | 0.2281 | 0.1926 | 0.1321 | 0.1595 | 0.0988 | 0.0767 |
| 9-methylanthracene | 0.0155 | 0.0340 | 0.0482 | 0.1102 | 0.2528 | 0.0145 | 0.0333 | 0.0385 | 0.0305 | 0.0718 | 0.1550 | NQ |
| fluoranthene | 0.5298 | 0.4867 | 0.3063 | 0.3828 | 0.4470 | 0.1658 | 0.5127 | 0.5938 | 0.4540 | 0.4360 | 0.5351 | 0.1909 |
| pyrene | 0.3110 | 0.2690 | 0.1901 | 0.2816 | 0.3124 | 0.1667 | 0.2534 | 0.4115 | 0.2871 | 0.3068 | 0.3766 | 0.2123 |
| benz[a]anthracene | NQ | NQ | NQ | 0.0630 | NQ | 0.0174 | 0.0170 | 0.0084 | 0.0123 | 0.0182 | 0.0178 | 0.0147 |
| chrysene | 0.0103 | 0.0072 | NQ | 0.0443 | 0.0098 | 0.0189 | 0.0167 | 0.0085 | 0.0094 | 0.0276 | 0.0129 | 0.0145 |
| benzo[b]fluoranthene | 0.0121 | 0.0076 | 0.0059 | 0.0995 | 0.0119 | 0.0339 | 0.0290 | 0.0207 | 0.0134 | 0.0590 | 0.0205 | 0.0303 |
| benzo[k]fluoranthene | 0.0058 | 0.0021 | NQ | 0.0329 | NQ | 0.0145 | 0.0112 | 0.0089 | NQ | 0.0233 | 0.0153 | 0.0142 |
| benzo[e]pyrene | 0.0143 | 0.0053 | 0.0050 | 0.0578 | 0.0087 | 0.0195 | 0.0282 | 0.0281 | 0.0129 | 0.0356 | 0.0162 | 0.0241 |
| benzo[a]pyrene | 0.0071 | 0.0036 | NQ | 0.0525 | NQ | 0.0144 | 0.0147 | 0.0101 | 0.0051 | 0.0129 | 0.0138 | 0.0164 |
| perylene | 0.0041 | 0.0082 | 0.0104 | 0.1797 | 0.0377 | 0.1351 | 0.0240 | 0.0149 | 0.0198 | 0.0380 | 0.0476 | 0.1474 |
| 7-methylb[a]p | NQ | ND | ND | NQ | ND | 0.0140 | ND | NQ | 0.0020 | 0.0048 | 0.0119 | 0.0150 |
| indeno[123cd]pyrene | 0.0051 | NQ | ND | 0.0636 | NQ | 0.0078 | 0.0164 | 0.0104 | NQ | 0.0114 | 0.0118 | 0.0213 |
| benzo[ghi]perylene | 0.0238 | 0.0067 | NQ | 0.0540 | NQ | 0.0289 | 0.0193 | 0.0240 | 0.0085 | 0.0184 | 0.0175 | 0.0434 |
| dibenz[ah]anthracene | 0.0094 | ND | ND | 0.0306 | NQ | 0.0222 | 0.0056 | 0.0057 | 0.0064 | 0.0159 | 0.0424 | 0.0519 |
| Total PAH* | 4.3007 | 3.9153 | 2.6602 | 3.5571 | 4.0720 | 2.2228 | 4.8438 | 6.0943 | 3.9512 | 3.8730 | 4.5234 | 2.1777 |

* Total PAH does not include napthalene, acenaphthylene or acenaphthene, since these PAHs were not always quantifiable due to low recoveries (<40%).

## APPENDIX C: ATMOSPHERIC PAHS

### *Sampling Methods*

Atmospheric samples, both vapor and particulate, were collected using high-volume air samplers (General Metal Works model GPYN1123). Atmospheric particles were collected onto a pre-combusted (4 h @ 450 °C), pre-weighed glass fiber filter (8 in x 10 in Gelman type A/E). Following removal of particulate contaminants by the filter, the air passes through two solvent-extracted (Soxhlet extracted with acetone followed by petroleum ether, each for 24 h; dried for 2 h @ 60 °C) polyurethane foam (PUF) plugs (8 cm diameter x 7.6 cm long) in order to collect the vapor phase PAHs. Air samples were collected coincident with surface water sampling for approximately 10 hours. One air sampler was equipped with a flow controller to maintain constant flow rates during sampling, regardless of particulate loading. This feature was unavailable on the VIMS Oyster Pier sampler, but minimal differences in flow rates were detected between the beginning and end of each sample period, as determined by manometer readings. The sample media was collected as soon as possible the following day in order to minimize desorptive losses of PAHs due to changes in air temperature. PUF plugs and glass fiber filters were stored in a freezer (-20 °C) until extraction.

### *Atmospheric PAH Analyses*

Prior to solvent extraction, atmospheric total suspended solid (TSS) loads were determined by the change in mass of the pre-weighed GFF per unit volume

of air sampled. PUF plugs and glass fiber filters were then analyzed for PAHs by Soxhlet extracting the materials with the appropriate solvents (24 hours each - acetone and petroleum ether for PUFs; acetone and dichloromethane for filters) after the addition of deuterated PAH surrogate standards. For each sample media the two extracts were combined, concentrated via rotoevaporation, solvent exchanged into hexane, and concentrated to one milliliter by evaporation under pure nitrogen. This extract was cleaned by solid-liquid chromatography on silica gel (mesh 100-200) prior to PAH analysis in order to remove interfering compounds (Dickhut and Gustafson, 1995). Following silica gel purification, the PAH fraction was again concentrated by rotoevaporation. The final extract was concentrated to approximately 150 μl under $N_2$ after the addition of an internal standard containing deuterated PAHs. PAHs were quantified relative to deuterated surrogate PAHs by gas chromatography-mass spectrometry (GC-MS, Hewlett Packard 5890 Series II gas chromatograph/Hewlett Packard 5971A mass spectrometer) using a 30 m x 0.25 mm DBL-XB column and selected ion monitoring.

**Table 7. Air Sample Details**

| PUF Sample ID | Filter Sample ID | Filter # | Sample Location | Date | Time | Manometer (in.) Start | Manometer (in.) Finish | TSP (mg) |
|---|---|---|---|---|---|---|---|---|
| YR49 | YR95 | lab blank | NA | NA | NA | NA | NA | NA |
| YR53 | YR104 | lab blank | NA | NA | NA | NA | NA | NA |
| YR64 | YR121 | lab blank | NA | NA | NA | NA | NA | NA |
| YR29 | YR96 | YR1 | Sweet Hall | 6/5/98 | 0800-1800 | 1.50 | 1.75 | 0.03006 |
| YR30 | YR117 | YR3 | VIMS | 6/5/98 | 0850-1936 | 1.40 | 1.25 | 0.02016 |
| YR31 | YR103 | YR2 | Sweet Hall | 8/20/98 | 0800-1800 | 1.80 | 2.00 | 0.027252 |
| YR46 | YR102 | YR4 | VIMS | 8/20/98 | 0730-1823 | 2.30 | 2.10 | 0.023453 |
| YR47 | YR97 | YR5 | Sweet Hall | 9/10/98 | 0800-1800 | 3.20 | 3.05 | 0.023368 |
| YR48 | YR118 | YR6 | VIMS | 9/10/98 | 0742-1946 | 2.20 | 2.15 | 0.027852 |
| YR50 | YR119 | YR7 | Sweet Hall | 11/19/98 | 0800-1800 | 3.00 | 3.00 | 0.032855 |
| YR51 | YR101 | YR8 | VIMS | 11/19/98 | 0925-2058 | 2.25 | 1.90 | 0.055795 |
| YR52 | YR120 | YR10 | Sweet Hall | 2/4/99 | 0800-1800 | 1.85 | 2.00 | 0.023097 |
| YR61 | YR100 | YR11 | VIMS | 2/4/99 | 0816-1940 | 2.10 | 2.10 | 0.041508 |
| YR62 | YR98 | YR9 | Sweet Hall | 4/1/99 | 0800-1800 | 3.20 | 3.00 | 0.026992 |
| YR63 | YR99 | YR12 | VIMS | 4/1/99 | 0705-1902 | 1.30 | 1.60 | 0.031953 |

Table 8. Atmospheric Particulate PAH Concentrations

| | | | Jun-98 | | Aug-98 | | Sep-98 | |
|---|---|---|---|---|---|---|---|---|
| | Blank 1 | Blank 2 | Sweet Hall | VIMS | Sweet Hall | VIMS | Sweet Hall | VIMS |
| | YR95 | YR121 | YR96 | YR117 | YR103 | YR102 | YR97 | YR118 |
| **PAH (ng)** | | | | | | | | |
| naphthalene | NQ | NQ | NQ | NQ | NQ | NQ | NQ | NQ |
| acenaphthylene | NQ | NQ | NQ | NQ | NQ | NQ | NQ | NQ |
| acenaphthene | NQ | NQ | NQ | NQ | NQ | NQ | NQ | NQ |
| fluorene | 0.2265 | NQ | 2.4360 | 1.4630 | 1.6971 | 2.8571 | 1.8863 | 6.8877 |
| 1-methylfluorene | NQ | ND | NQ | NQ | NQ | NQ | NQ | NQ |
| phenanthrene | 0.8956 | 1.1892 | 26.0667 | 15.8661 | 15.2065 | 30.3053 | 17.8511 | 66.0083 |
| anthracene | NQ | ND | 1.1107 | 0.8581 | 0.8544 | 2.7432 | 1.0950 | 4.2331 |
| 2-methylphenanthrene | 0.2947 | 0.4696 | 6.2324 | 4.2730 | 4.8630 | 7.4797 | 5.4868 | 12.9906 |
| 2-methylanthracene | ND | NQ | NQ | NQ | NQ | NQ | 0.4440 | NQ |
| 1-methylanthracene | 0.1342 | NQ | 2.8377 | 2.1006 | 2.3632 | 3.2815 | 2.7127 | 4.6653 |
| 1-methylphenanthrene | 0.1414 | NQ | 3.2281 | 2.5944 | 2.4977 | 3.4262 | 2.7886 | 5.6405 |
| 9-methylanthracene | ND | ND | ND | ND | ND | ND | ND | NQ |
| fluoranthene | 0.2755 | 0.3443 | 37.8994 | 29.2647 | 23.3831 | 60.2089 | 41.3589 | 130.4008 |
| pyrene | 0.2522 | 0.2420 | 23.1671 | 20.3750 | 15.4438 | 39.3419 | 30.1099 | 79.3292 |
| benz[a]anthracene | ND | NQ | 7.9884 | 5.2668 | 7.4466 | 9.3875 | 7.4711 | 15.8192 |
| chrysene | ND | NQ | 16.4206 | 15.4689 | 10.5909 | 22.2666 | 23.0447 | 58.9922 |
| benzo[b]fluoranthene | NQ | NQ | 20.7001 | 22.4868 | 25.5595 | 41.1024 | 36.6021 | 59.7513 |
| benzo[k]fluoranthene | NQ | NQ | 5.5141 | 6.2206 | 4.9793 | 8.7960 | 11.5600 | 17.6315 |
| benzo[e]pyrene | NQ | NQ | 10.4002 | 11.5791 | 14.2136 | 24.1186 | 17.5747 | 28.7127 |
| benzo[a]pyrene | NQ | NQ | 4.8958 | 8.2441 | 4.4480 | 8.2308 | 11.9917 | 21.0051 |
| perylene | NQ | ND | NQ | NQ | NQ | NQ | 1.7770 | NQ |
| 7-methylb[a]p | ND | ND | NQ | NQ | NQ | NQ | NQ | NQ |
| indeno[123cd]pyrene | NQ | ND | 8.4873 | 10.2684 | 9.8108 | 19.6235 | 17.3050 | 27.3269 |
| benzo[ghi]perylene | NQ | NQ | 8.3037 | 10.4642 | 9.3082 | 25.3704 | 14.7737 | 31.9751 |
| dibenz[ah]anthracene | ND | ND | NQ | NQ | NQ | NQ | NQ | NQ |

Table 8 (cont.). Atmospheric Particulate PAH Concentrations

| | Nov-98 | | Feb-99 | | Apr-99 | |
|---|---|---|---|---|---|---|
| | Sweet Hall | VIMS | Sweet Hall | VIMS | Sweet Hall | VIMS |
| | YR119 | YR101 | YR120 | YR100 | YR98 | YR99 |
| **PAH (ng)** | | | | | | |
| naphthalene | NQ | NQ | NQ | NQ | NQ | NQ |
| acenaphthylene | NQ | NQ | NQ | NQ | NQ | NQ |
| acenaphthene | NQ | NQ | NQ | NQ | NQ | NQ |
| fluorene | ND | 6.1898 | 0.9811 | 5.0169 | 1.4279 | 1.7044 |
| 1-methylfluorene | 1.3844 | 2.0693 | ND | NQ | NQ | NQ |
| phenanthrene | 18.9116 | 72.0527 | 9.1083 | 53.6766 | 11.1075 | 36.9317 |
| anthracene | 0.8088 | 3.4532 | 0.4288 | 2.2501 | 0.5257 | 2.3417 |
| 2-methylphenanthrene | 8.0785 | 15.7442 | 2.8727 | 12.9229 | 4.9560 | 9.7382 |
| 2-methylanthracene | NQ | 0.9805 | NQ | 0.8832 | NQ | 0.6253 |
| 1-methylanthracene | 3.3202 | 6.0714 | 1.1679 | 4.8095 | 2.3403 | 3.7374 |
| 1-methylphenanthrene | 4.0000 | 7.1651 | 1.5163 | 5.7422 | 2.3890 | 4.2409 |
| 9-methylanthracene | ND | ND | NQ | 1.2858 | ND | ND |
| fluoranthene | 26.9066 | 95.5961 | 13.1356 | 95.5649 | 16.2330 | 61.7949 |
| pyrene | 21.2759 | 50.6574 | 13.0166 | 50.2725 | 13.0801 | 29.7356 |
| benz[a]anthracene | 11.1658 | 13.8198 | 5.1767 | 12.3137 | 7.3839 | 9.4064 |
| chrysene | 20.8103 | 39.2916 | 9.5781 | 35.7097 | 8.7606 | 21.0823 |
| benzo[b]fluoranthene | 45.5176 | 58.3474 | 20.2817 | 56.0826 | 9.8851 | 26.0534 |
| benzo[k]fluoranthene | 9.1910 | 14.7398 | 4.5125 | 14.5458 | 2.5798 | 6.8674 |
| benzo[e]pyrene | 26.0778 | 30.9721 | 9.7656 | 29.1309 | 5.3267 | 12.9526 |
| benzo[a]pyrene | 8.0697 | 16.4407 | 7.3118 | 14.6892 | 2.5681 | 4.2272 |
| perylene | NQ | 3.0219 | NQ | 2.7256 | NQ | NQ |
| 7-methylb[a]p | NQ | ND | NQ | NQ | NQ | NQ |
| indeno[123cd]pyrene | 22.5205 | 33.6276 | 13.5178 | 30.8875 | 5.7532 | 11.9255 |
| benzo[ghi]perylene | 35.7939 | 37.1051 | 12.4312 | 37.8945 | 6.4753 | 14.6261 |
| dibenz[ah]anthracene | NQ | NQ | NQ | NQ | NQ | NQ |

Table 9. Atmospheric Gaseous PAH Concentrations

| | | | | Jun-98 | | Aug-98 | | Sep-98 | |
|---|---|---|---|---|---|---|---|---|---|
| | Blank 1 | Blank 2 | Blank 3 | Sweet Hall | VIMS | Sweet Hall | VIMS | Sweet Hall | VIMS |
| | YR49B | YR53 | YR64B | YR29 Avg | YR30B | YR31B | YR46B | YR47B | YR48B |
| **PAH (ng)** | | | | | | | | | |
| naphthalene | NQ | 7.3560 | 6.9911 | 124.2847 | 143.9721 | NQ | NQ | NQ | NQ |
| acenaphthylene | NQ | 0.3077 | 1.1079 | 8.4536 | 18.6372 | NQ | NQ | NQ | NQ |
| acenaphthene | NQ | 1.0674 | 2.8809 | 273.9734 | 588.7685 | NQ | NQ | NQ | NQ |
| fluorene | 1.5727 | 1.0587 | 2.4404 | 320.1391 | 241.5662 | 372.0642 | 731.2999 | 80.2560 | 4678.3596 |
| 1-methylfluorene | 0.2828 | NQ | ND | 238.2986 | 140.5474 | 151.9161 | 234.3368 | 57.5151 | 353.4892 |
| phenanthrene | 18.3735 | 4.3047 | 15.7492 | 2039.6570 | 915.3777 | 2307.6698 | 7189.9651 | 363.3287 | 17818.4025 |
| anthracene | 0.8831 | NQ | 0.5221 | 32.9161 | 20.8262 | 48.8612 | 354.2793 | 5.8198 | 1351.0162 |
| 2-methylphenanthrene | 2.0576 | 1.3495 | 2.5094 | 401.2843 | 281.4353 | 305.5270 | 999.6994 | 137.9136 | 2317.1654 |
| 2-methylanthracene | NQ | NQ | NQ | NQ | NQ | NQ | NQ | NQ | NQ |
| 1-methylanthracene | 0.8634 | 0.8190 | 1.1896 | 344.7865 | 270.7073 | 173.9423 | 702.7117 | 125.3509 | 1052.1874 |
| 1-methylphenanthrene | 0.9859 | 0.6363 | 1.1711 | 285.9758 | 220.5999 | 192.1120 | 624.4213 | 107.9571 | 1117.2139 |
| 9-methylanthracene | ND | ND | NQ | ND | ND | ND | NQ | NQ | 31.9384 |
| fluoranthene | 3.4264 | 1.0476 | 3.0123 | 489.3000 | 196.8793 | 487.1938 | 2095.2465 | 90.7694 | 8471.0053 |
| pyrene | 1.8240 | 0.6769 | 1.2487 | 445.4486 | 126.5343 | 181.5637 | 1013.6750 | 62.8068 | 4443.0159 |
| benz[a]anthracene | NQ | NQ | NQ | 105.3373 | 6.7956 | 10.1013 | 10.4293 | 6.4182 | 32.2503 |
| chrysene | 0.1664 | NQ | 0.3730 | 118.0330 | 9.9064 | 8.4149 | 18.9511 | 5.1929 | 84.1598 |
| benzo[b]fluoranthene | 0.1019 | NQ | 0.2993 | 24.5990 | 4.5729 | 4.2914 | 2.9288 | 2.7252 | 3.9217 |
| benzo[k]fluoranthene | NQ | NQ | 0.1563 | NQ | 1.3252 | 0.7162 | 0.6914 | 0.4322 | 1.4216 |
| benzo[e]pyrene | 0.0839 | NQ | 0.1655 | 47.4782 | 3.4497 | 1.8279 | 1.9393 | 1.2308 | 2.1495 |
| benzo[a]pyrene | NQ | NQ | 0.1325 | 8.9538 | 1.4018 | NQ | 0.5243 | NQ | 1.1726 |
| perylene | NQ | NQ | 0.1111 | NQ | NQ | ND | NQ | ND | 0.8861 |
| 7-methylb[a]p | ND | ND | NQ | ND | ND | ND | ND | ND | 1.2176 |
| indeno[123cd]pyrene | ND | ND | ND | 8.2279 | 1.8831 | NQ | NQ | 0.5743 | 1.7403 |
| benzo[ghi]perylene | 0.2496 | NQ | NQ | 20.9658 | 1.8632 | 0.6437 | 0.9991 | 0.9842 | 3.2263 |
| dibenz[ah]anthracene | 0.0917 | NQ | NQ | 7.2280 | 0.7394 | ND | ND | ND | 3.1229 |

**Table 9. Atmospheric Gaseous PAH Concentrations**

| | | | | Jun-98 | | Aug-98 | | Sep-98 | |
|---|---|---|---|---|---|---|---|---|---|
| | Blank 1 | Blank 2 | Blank 3 | Sweet Hall | VIMS | Sweet Hall | VIMS | Sweet Hall | VIMS |
| | YR49B | YR53 | YR64B | YR29 Avg | YR30B | YR31B | YR46B | YR47B | YR48B |
| **PAH (ng)** | | | | | | | | | |
| naphthalene | NQ | 7.3560 | 6.9911 | 124.2847 | 143.9721 | NQ | NQ | NQ | NQ |
| acenaphthylene | NQ | 0.3077 | 1.1079 | 8.4536 | 18.6372 | NQ | NQ | NQ | NQ |
| acenaphthene | NQ | 1.0674 | 2.8809 | 273.9734 | 588.7685 | NQ | NQ | NQ | NQ |
| fluorene | 1.5727 | 1.0587 | 2.4404 | 320.1391 | 241.5662 | 372.0642 | 731.2999 | 80.2560 | 4678.3596 |
| 1-methylfluorene | 0.2828 | NQ | ND | 238.2986 | 140.5474 | 151.9161 | 234.3368 | 57.5151 | 353.4892 |
| phenanthrene | 18.3735 | 4.3047 | 15.7492 | 2039.6570 | 915.3777 | 2307.6698 | 7189.9651 | 363.3287 | 17818.4025 |
| anthracene | 0.8831 | NQ | 0.5221 | 32.9161 | 20.8262 | 48.8612 | 354.2793 | 5.8198 | 1351.0162 |
| 2-methylphenanthrene | 2.0576 | 1.3495 | 2.5094 | 401.2843 | 281.4353 | 305.5270 | 999.6994 | 137.9136 | 2317.1654 |
| 2-methylanthracene | NQ | NQ | NQ | NQ | NQ | NQ | NQ | NQ | NQ |
| 1-methylanthracene | 0.8634 | 0.8190 | 1.1896 | 344.7865 | 270.7073 | 173.9423 | 702.7117 | 125.3509 | 1052.1874 |
| 1-methylphenanthrene | 0.9859 | 0.6363 | 1.1711 | 285.9758 | 220.5999 | 192.1120 | 624.4213 | 107.9571 | 1117.2139 |
| 9-methylanthracene | ND | ND | NQ | ND | ND | ND | NQ | NQ | 31.9384 |
| fluoranthene | 3.4264 | 1.0476 | 3.0123 | 489.3000 | 196.8793 | 487.1938 | 2095.2465 | 90.7694 | 8471.0053 |
| pyrene | 1.8240 | 0.6769 | 1.2487 | 445.4486 | 126.5343 | 181.5637 | 1013.6750 | 62.8068 | 4443.0159 |
| benz[a]anthracene | NQ | NQ | NQ | 105.3373 | 6.7956 | 10.1013 | 10.4293 | 6.4182 | 32.2503 |
| chrysene | 0.1664 | NQ | 0.3730 | 118.0330 | 9.9064 | 8.4149 | 18.9511 | 5.1929 | 84.1598 |
| benzo[b]fluoranthene | 0.1019 | NQ | 0.2993 | 24.5990 | 4.5729 | 4.2914 | 2.9288 | 2.7252 | 3.9217 |
| benzo[k]fluoranthene | NQ | NQ | 0.1563 | NQ | 1.3252 | 0.7162 | 0.6914 | 0.4322 | 1.4216 |
| benzo[e]pyrene | 0.0839 | NQ | 0.1655 | 47.4782 | 3.4497 | 1.8279 | 1.9393 | 1.2308 | 2.1495 |
| benzo[a]pyrene | NQ | NQ | 0.1325 | 8.9538 | 1.4018 | NQ | 0.5243 | NQ | 1.1726 |
| perylene | NQ | NQ | 0.1111 | NQ | NQ | ND | NQ | ND | 0.8861 |
| 7-methylb[a]p | ND | ND | NQ | ND | ND | ND | ND | ND | 1.2176 |
| indeno[123cd]pyrene | ND | ND | ND | 8.2279 | 1.8831 | NQ | NQ | 0.5743 | 1.7403 |
| benzo[ghi]perylene | 0.2496 | NQ | NQ | 20.9658 | 1.8632 | 0.6437 | 0.9991 | 0.9842 | 3.2263 |
| dibenz[ah]anthracene | 0.0917 | NQ | NQ | 7.2280 | 0.7394 | ND | ND | ND | 3.1229 |

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