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Effects of urbanization and land use on PAH accumulation in wetland sediments

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Effects of Urbanization and Land Use on PAH Accumulation in Wetland Sediments

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In Partial Fulfillment of the
Requirements for the Degree of
Doctor of Philosophy

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by
Kimani L. Kimbrough
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APPROVAL SHEET

This dissertation is submitted in partial fulfillment of the

requirement for the degree of

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Abstract

The relationship between wetland polycyclic aromatic hydrocarbon (PAH) concentrations and adjacent land use was assessed using surface sediments, sediment cores and global information systems (GIS) in the Elizabeth River, Virginia, an urbanized subestuary of the Chesapeake Bay. Wetlands adjacent to parking lots and petroleum industrial sites exhibited the highest PAH concentrations of all land uses in surfaces sediment and historically. Automobile and coal are the dominant sources of PAHs in wetland sediments historically as determined by relative concentration, fingerprinting and source specific compounds.

An analysis of variance (ANOVA) test used to compare sixteen surface sediment sites based on land use revealed significant differences in wetland surface sediment PAH concentration. Multi-family and single-family residential, rural, undeveloped, commercial, petroleum industrial and non-petroleum industrial most accurately identified distinct land use categories in the watershed. Source assessments revealed little variability between sites, which is indicative of one atmospheric source of PAHs to wetland surface sediments. Concentration magnitude and source similarities implicate percent impervious surface and proximity to sources as having a major influences on PAH input to wetlands.

The nine sediment cores taken from wetlands adjacent to residential, rural, commercial and industrial land uses were dated using ^{210}Pb and ^{137}Cs. Wetland PAH trends were static or decreasing from past to present over the past 40 years. One commercial and one industrial site had mean core concentrations significantly higher than all other land uses. Most sediment cores had an increasing automobile PAH percentage from past to present indicating a rising significance of automobile emissions in the Elizabeth River watershed.

GIS and surfaces sediment PAH concentrations were used to assess wetland area, adjacent land use in addition to PAH storage, distribution and input at the micro (site) and macro (watershed) scales. Despite urban wetlands having the largest concentration of PAHs a disproportionately low number of associated wetlands resulted in lower PAH storage at the macro scale. Residential, urban and rural wetlands contained the largest amounts of PAHs respectively. Wetland migration and erosion make wetlands dynamic sinks that constantly release and accumulate contaminants as they migrate shoreward to keep pace with sea level rise. In the urban Elizabeth River over 75% of wetlands are not able to migrate as a result of upland development. A conceptual model depicting wetland migration with developed and undeveloped uplands, and variable PAH source in sediments indicate wetlands can act as sources or sinks of slowly degrading contamiants. PAH flux measurement determined from wetland surface sediment concentrations and accretion rates showed PAH flux to all wetlands were exponentially higher than atmospheric deposition.

Effects of Urbanization and Land Use on PAH Accumulation In Wetland Sediments

Introduction

Polycyclic aromatic hydrocarbon (PAH) characterization in the Elizabeth River watershed over the past few decades has focused on the Southern Branch where high levels of contamination are found (Bieri et al., 1986; Merrill and Wade, 1985). PAH input to the most polluted parts of the Southern Branch have been linked to point sources such as creosote spills and heavy industrialization. Although industries responsible for the pollution have closed PAH concentrations still remain high in surface sediments (Walker and Dickhut, 2001).

More recently, nonpoint source pollution such as atmospheric deposition and urban runoff have been identified as threats to aquatic systems in urban areas where the density of automobiles is high (Kennish, 2000). Runoff, which erodes particles from land, is an important vector for the movement of particle-associated contaminants from terrestrial surfaces to aquatic systems (Hoffman et al., 1982; Hoffman et al., 1984; Schueler, 1987). Consequently, runoff washes automobile emissions including brake dust, exhaust emissions deposits and crank case oil into urban aquatic systems. Thus, runoff poses a major threat to aquatic systems (Baxall and Maltby, 1997; Hoffman et al., 1982; Hoffman et al., 1984; Kennish, 2000), however little attention has been given to it in the Elizabeth River watershed.

In this study, wetlands have been used to assess the impact of urbanization/land use on the nonpoint source input of PAHs to the Elizabeth

River watershed. In doing so, it was first necessary to establish the relationship between wetland surface sediment PAH concentrations indicative of recent PAH inputs and current adjacent land use (Chapter 1). Residential, rural, commercial and industrial land uses represent the different degrees of development within the watershed making them suitable for assessing urbanization impacts at the watershed level (Anderson, 1976). Wetlands scavenge sediment and particle associated contaminants from upland runoff (Kusler, 1988). Therefore, measurements of PAH concentrations in wetland surface sediments can be used to evaluate the hypothesis that there is a relationship between land use and PAH input to wetlands.

After establishing the relationship between surface sediment PAHs and adjacent land use it is prudent to look at the relationship in a historical context (Chapter 2). Wetland sediment cores have been used to determine contaminant trends from watersheds. Hence, sediment cores were used to determine historic PAH deposition in wetlands of the Elizabeth River. Aerial photographs and Geographic Information Systems (GIS) land use coverages spanning at least 30 years were used to establish past adjacent land use for each research site. PAH trends over time were determined for sediment cores collected from nine sites to characterize the PAH depositional record with respect to residential, rural, commercial and industrial land uses.

After assessing the relationship between PAH concentrations in wetlands and adjacent land use presently and historically, an extrapolation to the watershed scale is used to identify possible policy implications (Chapter Three). Wetland and land use maps are used to categorize all watershed salt marshes by adjacent land use. Surface sediment PAH concentrations obtained from Chapter 1 were then used in conjunction with the watershed wetland distribution amount to determine the distribution of PAHs in wetland surface sediments at the watershed scale. Using the area, width and PAH concentration, a sea level rise model was produced to show the effects of wetland loss on PAH storage and scavenging. Wetlands accumulate these particles and work as storage sinks for contaminants(U.S. EPA, 1993). However, since PAHs do not readily degrade (Neff, 1979) the dynamic nature of wetlands effects their storage as wetlands migrate shoreward in response to sea level rise.

Hypotheses

The overall goal of this study was to examine whether wetland sediment PAH concentration and adjacent land use can be used to assess the impact of urbanization and nonpoint PAH input to Elizabeth River.

The following hypotheses were tested as part of this study:

Hypothesis 1 (present land use)

The abundance and source of PAHs found in Elizabeth River wetlands are influenced by adjacent land use type.

Working hypothesis

Residential, rural, commercial and industrial land uses are associated with different percentages of impervious surfaces which effect the erosion potential of particles and thus abundances of particle-associated PAHs deposited in wetlands.

Hypothesis 2 (historic land use)

The abundance and source of PAHs found in Elizabeth River wetlands are influenced by adjacent land use type historically.

Working Hypothesis

Wetlands with changes in land use over time will have significant differences in PAH concentration with time. Wetlands with no change in land use with time will have no significant changes in PAH concentration with time.

Hypothesis 3-1:

Urban (commercial and industrial) wetlands store most of the PAHs found in Elizabeth River wetlands.

Working Hypothesis

Urban wetlands which receive runoff from commercial and industrial land uses are associated with the highest concentrations of PAHs. In addition sediment in the proximity of urban areas are shown to have elevated PAH concentrations. Hence, wetlands accumulating sediments from urban areas should have higher PAH concentrations due to incorporation of polluted material.

Hypothesis 3-2:

The areal flux of PAHs to wetlands due to surface runoff is greater than that for direct atmospheric deposition alone.

Working Hypothesis

PAHs accumulated on land adjacent to wetlands through direct and indirect atmospheric deposition are eroded into wetlands. Small areas of wetlands store sediment from much larger areas of uplands

Reference

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Chapter 1

Assessment of Polycyclic Aromatic Hydrocarbon Input to Urban Wetlands in Relation to Adjacent Land Use

Abstract

The relationship between concentrations of polycyclic aromatic hydrocarbon (PAH) in wetland sediments and adjacent land use was assessed in the Elizabeth River, Virginia, an urbanized subestuary of the Chesapeake Bay. Multi-family and single-family residential, rural, undeveloped urban, commercial, petroleum industrial and non-petroleum industrial land use categories were chosen to represent different degrees of development found in land adjacent to the wetland study sites. Analysis of variance (ANOVA) revealed that adjacent land use had a significant influence on PAH levels in wetland surface sediments. Wetlands adjacent to parking lots and petroleum industrial sites exhibited the highest PAH concentrations of all land uses. Relative concentration, fingerprinting and source specific compounds were used to determine that automotive sources dominate (52-69%) PAHs input to wetland surface sediments regardless of adjacent land use. Therefore, the magnitude of PAH input to adjacent wetlands likely varies with land use relative to the traffic density and impervious surface coverage.

Introduction

Development and land use play an important role in the release of contaminants from watersheds (Hoffman et al., 1984; Hoffman et al., 1982). For example, Cundy et al. (1997) found that sediments in close proximity to urban or industrialized areas had higher concentrations of contaminants. In the Chesapeake Bay, PAH concentrations in sediments of the densely populated northern regions are generally higher than those found in the south, with the exception of the industrialized areas of the Elizabeth River (Huggett et al., 1988, Helz and Huggett, 1987). Therefore, recognizing the effects of population growth on coastal ecosystems may lead to better watershed development plans for the less populated regions.

The continuous development and construction of impervious surfaces including rooftops, roads, sidewalks, and driveways mark urbanization. Without vegetation, land runoff is far more intense and results in increased erosion (Schueler, 1987). Sediment runoff loads have increased by an order of magnitude in some urbanized areas (Novonty and Chester, 1981). The channeling of contaminants to aquatic systems, untreated release of contaminants during high flow periods, and development are causes for the increased degradation of surface waters found in urban areas. Moreover, because runoff has an intimate relationship with the land it runs over, land use is one of the factors controlling the types and concentration of various constituents of runoff in runoff.

Polycyclic aromatic hydrocarbons (PAHs) are ubiquitous hydrophobic organic contaminants that associate with particles. They represent a major problem to urban environments since they are some of the most toxic compounds in roadway runoff (Boxall and Maltby, 1997). PAHs appear on the Chesapeake Bay Toxins of Concern list (1991) and have been shown to be toxic to aquatic organisms (Boxall and Maltby, 1997). In addition, some PAHs are carcinogenic (Neff, 1979; Denissenko et al., 1996; Philips and Grover, 1994, Kennish,2000). PAHs enter the environment from both point and nonpoint sources including oil deposition, waste incineration, and fossil fuel combustion (LaFlamme and Hites, 1978). The ubiquitous nature of these contaminants in the urban environment makes PAHs an ideal suite of contaminants to track urban development at the watershed level because sources associated with automobiles and roads increase with development.

In this study, PAHs were used to assess the relationship between urbanization and contaminant input to wetlands in the Elizabeth River watershed. Geographic information systems (GIS) were used to select study sites with varying adjacent land use representing several degrees of urbanization. PAH concentrations in surface sediments collected from wetlands adjacent to various land use types were examined.

Methods

Study Area

The Elizabeth River is a tidal sub-estuary of the southern Chesapeake Bay (Figure 1-1). The watershed encompasses the city of Norfolk with an estimated population of 225,875, as well as Portsmouth (98,305), Chesapeake (20,2759) and Suffolk (64,805 - US Census, 1999). The Elizabeth River watershed also includes residential, rural, commercial and industrial land uses. Large PAH input to the Southern Branch of the Elizabeth River is historically associated with industrial sources (Bieri et al., 1986). Specifically, spills from creosote and other petroleum based manufacturing plants, which have subsequently closed, dominated PAH input to the Southern Branch. In addition to these point sources, coal has also been implicated as a major source of PAHs to the Elizabeth River (Merrill and Wade 1985; Walker and Dickhut, 2000). However, in shoal regions of the Elizabeth River atmospheric deposition and terrestrial runoff have recently been implicated as important sources of PAHs to the estuary (Walker and Dickhut, 2000).

Site Selection

Several GIS coverages were used to select sites representative of watershed attributes and present land use in the Elizabeth River watershed. The Comprehensive Coastal Inventory Tidal Marsh Inventory coverage (TMI), a compilation of United States Geological Survey (USGS) maps digitized at the Virginia institute of Marine Science was used to determine wetland availability and location. The EPA Region III land cover data set (EPALU, 1996) was used to determine land use in the watershed. By overlaying the TMI map on land use (Figure 1-2A) and USGS topographical maps (Figure 1-2B), potential sampling sites were located. Site verification (Figure 1-2C) was done to ensure the accuracy of the GIS coverages and document any land use changes. Each wetland selected for study contained 30 m or more of uplands that represented either a continuous single land use or one dominant land use (Figure 1-2A,B).

Two sets of land use categories, derived from Anderson (1976), were used. The first used four categories including: residential, undeveloped, commercial and industrial. The second set of categories was used to further refine the initial category to include eight categories (multi-family, single-family, rural, undeveloped urban, paved commercial, unpaved commercial, industrial petroleum and industrial), which divided every land use into two separate groups (Table 1-1). Detailed land use categorization was made possible by visual verification.

Sediment Sample Collection

Surface sediments were obtained from selected Elizabeth River *Spartina alterniflora* marshes by randomly selecting a section from a chart representing the wetland. The blind toss method was then used to select a specific area within each selected section. Four replicate samples were taken from marsh drainage channels that occur between hummocks at each site. The main drainage channels were not sampled. Surface sediments (upper 1.5 cm) were taken and placed in muffled (4hr at 400°C) jars that were rinsed with acetone and dried. All samples were taken within a thirteen-day period to minimize the effects of storms and the concomitant contaminant laden runoff. After collection, samples were stored in a freezer at 4 °C until analyzed.

Particulate Organic Carbon Analysis

A small fraction of each sediment sample was ground to powdery consistency using a mortar and pestle. Approximately 10 mg of sediment was treated with hydrochloric acid to remove inorganic carbon and sealed in a silver capsule that was previously ashed at 450°C for 4 hours. All samples were analyzed using a Fisons EA Model 1108 CHNS-O elemental analyzer using acetanilide and sulfanilamide as standards. Duplicate samples were analyzed for 50 % of the samples to confirm reproducibility. Sample replicate variability was ranged fro 1-4 % at all sites accept ODU where variability caused by sandy heterogeneous sediment resulted replicate variability ranges from 8-14%.

PAH Analysis

Approximately eight grams of wet sediment was Soxhlet extracted for 48 hours in 50/50 dichloromethane (DCM)/acetone (v/v). A surrogate standard composed of deuterated naphthalene, anthracene, benzo(a)anthracene, benzo(a)pyrene and benzo(ghi)perylene was added before extraction. The extract was concentrated by rotary evaporation, followed by evaporation to 1 ml using N_2, and purified over 10 g of 3% deactivated silica gel, Na_2SO_4 and copper. PAHs were eluted from the silica by adding 25 ml hexane followed by 50 ml of 20% DCM in hexane (v:v). The PAH fraction (20% DCM in hexane) was concentrated to 1 ml by rotary evaporation and an internal standard comprised of deuterated acenaphthene, phenanthrene, chrysene and perylene was added. PAHs were quantified using a gas chromatograph (GC) and an electron impact mass spectrometer (MS) operated in the selective ion monitoring (SIM) mode. All sample standards had recoveries greater than 70%.

Statistical analysis

Statistics were performed to determine whether there were significant differences in sediment PAH concentrations among wetlands with different adjacent land uses. The Cochran statistical test showed the data were homogenous. Hence, the ANOVA statistical test was used. The Fisher pairwise statistical test was also utilized to establish which land uses were significantly different. Principal component analysis (PCA) was used to determine correlations that existed within the different land uses as dictated by the associated suite of PAH variables.

Results and Discussion

Land use

PAHs are primarily associated with organic matter in sediments. Therefore, to account for between-site differences in sedimentary organic matter in the land use comparison, PAH concentrations were normalized to total organic carbon. Carbon normalization made the sandy ODU site relatively higher than without normalization, but the change had no effect on comparisons for land use sites as the commercial land use showed significant difference regardless of normalization.

Using ANOVA and the Fisher pairwise comparison statistical tests commercial land use category was the only land use with a significantly different total PAH concentration in adjacent wetland sediment (Figure 1-3B). Land use in the commercial category was comprised of three paved parking lots and site MCJ, an unpaved junkyard. Variability was demonstrated by the bimodal distribution of PAH concentrations for the various land uses shown (Figure 1-3A). In some cases intra-land use differences were greater than inter-land use differences (Figure 1-3A). The differences in the bimodal distributions proved to be significant. Therefore, a refined land use classification was developed (Table 1-1) using eight land uses (Figure 1-3C).

Refinement of the land use categories: multi-family, single family, rural, undeveloped urban, paved commercial, unpaved commercial, petroleum-industrial and non-petroleunm industrial, respectively, provided more insight into the potential effects of adjacent land use on PAH accumulation in wetlands. Commercial paved land use had the highest concentrations of PAHs in adjacent wetland surface sediment and was significantly different from all other land uses. Wetland sediments adjacent to petroleum industrial, land use had the second highest PAH concentrations with significantly different total PAH concentrations than all except wetland sediment adjacent to single family residential land uses. This, along with the aforementioned intraland use differences, shows the effectiveness of more specific division of land uses. The new land use categories reduced variability within and therefore significant differences, were recognized. A relationship between input of PAH input quantity to wetlands and land use was shown.

PAH Source Determination and Site Distinction

Principle components analysis (PCA) was used to assess between-site differences in the relative concentrations of various PAHs in the wetland sediments. PCA was run using SAS software version 8 and fractional PAH concentrations in the various wetland sediments. The suite of 16 PAHs were used as variables. Three principle components (PC1-PC3) explained 36, 21 and 12 percent of the variability in the data set, respectively.

PCA score plots for all combinations of PC 1, 2, and 3 did not reveal distinguishable groupings for the various wetland sediments (Figure 1-4). Not all combinations are represented here. In many cases, within site variability was greater than the between site variability. Therefore, the various wetland study sites and land uses were indistinguishable based on the relative concentrations of individual PAHs. This lack of distinction between sites in terms of relative PAH abundance was the first indication that few or perhaps a single source, dominates the delivery of PAHs to the sites.

Due to a lower temperature of formation, low molecular weight (LMW) PAHs, 2-3 ring compounds and methylated PAHs are more prevalent in petroleum than in pyrogenic material (Neff, 1979; Page et al., 1995). In contrast, pyrogenic PAHs, due to their high temperature of formation, have a predominance of high molecular weight (HMW) PAHs (5-6 ring compounds) and a very low abundance of alkylated compounds (Neff, 1979; Page et al., 1995). Consequently, PAH fingerprintings, which use relative abundance of HMW, LMW and methylated PAHs can be used as a means of distinguishing pyrogenic from petrogenic sources of PAHs.

PAH fingerprints from all of the wetland sites showed a predominance of HMW PAHs (benzo(b)fluoranthene, benzo (k)fluoranthene, benzo(e)pyrene, benzo(a)pyrene, indeno(123cd)pyrene, and benzo(ghi)perylene), and relatively low methyl and LMW PAH (fluorene, methylfluorene, phenanthrene methylphenanthrene, methylanthracene and anthracene) abundance (Figure 1-5). In contrast the petroleum fingerprints of samples run in our lab, that were used for comparison had high methyl abundance relative to all PAHs, low HMW, and high LMW abundance (Figure 1-6). The predominance of HMW PAHs at all of the wetland sites is evidence of the strong influence of pyrogenic sources for these contaminants in the Elizabeth River watershed. This conclusion is supported by previous research, which found that automobile emissions and coal dominate PAH sources in the southern Chesapeake Bay region (Arzayus et al. 2001; Dickhut et al., 2000). Qualitatively, the HMW compounds associated with each Elizabeth River wetland site exhibited a similarity in fingerprint. This fingerprint similarity between sites supports the PCA conclusion that PAH sources to wetland sediments in the Elizabeth River are similar.

Several literature sources were utilized to compare with sample fingerprints. Five compounds were used: flouranthene, pyrene, benzo(a)anthracene (baa) , benzo(a)pyrene (bap), and benzo(ghi)perylene) (bghip). Fingerprint comparisons were done using concentration compound/concentration 5 selected HMW compounds. The use of a smaller set of PAHs was necessary due to the lack of data for all compounds from various literature sources, but acceptable, as the important PAHs used for fingerprinting/distinguishing sources were included. Due to the small variability between sites, a site average was used for comparison with available literature data. Literature data included: automobile emissions (Rogge et al., 1993A; Alsberg et al. 1985; Khalili et al. 1995; Singh et al., 1993), diesel emissions (Rogge et al., 1993A; Khalili et al., 1995), tunnel air (Khalili et al., 1995; Benner et al., 1989; Colmsjö et al., 1986), road debris (Rogge et al., 1993B; Singh et al., 1993), creosote (Page et al., 1995; Kohler et al. 2000), and coal (Levendis et al.

1998; Singh et al., 1993). However, automobile emissions, diesel emissions, tunnel air and road debris, were all averaged into the auto category, which is validated by similar fingerprints for these various automotive sources of PAHs (Figure 1-7). Comparison of PAH fingerprints for automotive, coal, and creosote sources revealed differences to exploit for source differentiation (Figure 1-7).

Creosote is dominated by fluoranthene and pyrene, which had relative concentrations several orders of magnitude higher than baa, bap, and bghip. Likewise, coal has distinctly high levels of fluoranthene and pyrene with lower levels of the other HMW PAHs. In contrast, auto emissions have similar levels of fluoranthene, and pyrene, relative to bghip, and only moderately lower levels of baa and bap. Overall, there were similarities in the fractional PAH concentration between the wetland sediment studied and auto sources. However, some influence of coal and/or creosote is also evident, due to the elevated relative concentrations of fluoranthene and pyrene, as well as depressed levels of bghip in wetland sediments compared with auto sources (Figure 1-7).

Two-dimensional scatter plots of the fractional PAH concentrations demonstrate that the wetland sediment samples were most closely related to the auto signature (Figure 1-8). A mixing model was used to determine the percent contribution of auto vs. coal derived PAHs, assuming that coal rather than creosote dominates as a secondary sources of PAHs to wetland sediments. Creosote is not atmospherically-derived and therefore would not be input to the majority of the wetland sites via land-derived runoff. In addition, creosote input to the Elizabeth River has only been documented near one site (SC). Thus, although creosote cannot be distinguished from coal input to these sites a larger input of PAHs to the wetland sediments from creosote versus coal is unlikely. The two component mixing equation used to determine the relative contribution of auto and coal-derived PAHs to the wetland study sites was derived from Biddleman and Falconer (1999):

$$F_a = \frac{(R_s - R_c)(R_a + 1)}{(R_a - R_c)(R_s + 1)}$$

where F_a = fraction auto, R_s = fluoranthene/bghip ratio in the same sample, R_a = fluoranthene/bghip ratio for auto sources, and R_c = fluoranthene/bghip ratio for coal/creosote sources.

Contributions from automobile-derived PAHs ranged from 52 – 69 % for site means with an overall mean of 60% (S.E. = 1.22). ANOVA statistics resulted in no significant difference between sites (p= 0.67). These observed predominances of auto-derived PAHs in the Elizabeth River wetland sediments is in contrast to Dickhut et al. (2000) who found that PAHs in lower Chesapeake Bay sediments were 86% coal-derived and at most 14% auto-derived. Different source composition for wetland surface sediments and Chesapeake Bay sediments is evidence that wetland surface sediment PAHs are land derived not estuarine derived.

Toxicity

Published values for the effects range low (ERL) and effects range median (ERM) for PAH concentrations in sediments were used to assess toxicity (Long et al., 1995; Buchman, 1999 - Table 2). The ERL is the "lower 10th percentile concentration found to be toxic by investigators." In cases where PAH concentrations are above the ERL "toxic effects may occur in populations of sensitive organisms". The ERM is the "median concentration of the compilation of just toxic samples".

Although the total PAH level was generally low, some sites could be distinguished by the number of compounds with concentrations greater than ERL (Table 3). The rural wetland sites (DCLP, GBLP) and one of the multifamily residential sites (CC) had all PAH levels below ERL. Thus, PAH toxicity at these sites would not be expected. All other wetland sediments exhibited slightly toxic levels for one or more of the PAHs (i.e. >ERL but < ERM), with the single family residential, commercial and petro-industrial wetland surface sediments having five or more PAHs >ERL (Table 3). Sediment toxicity therefore has a relationship with land use similar to wetland surface sediment PAH concentration. Adjacent land use shows evidence of influencing toxicity in urban wetlands. Overall, however, Elizabeth River wetland sediments are not highly toxic with respect to the PAHs measured in this study.

Sediment Concentration Comparison

Surface sediment PAH concentrations from the Elizabeth River are in the same range as other marsh sites (Al-Saad and Al-Timara, 1989; Sanger et al., 1999) and estuarine sediments from urban watersheds of the Chesapeake Bay (Huggett et al., 1984; Ashley and Baker, 1999- Table 1-4). In general land use determinations were not as specific in the other studies as here however concentrations associated with greater industrial and urban development were associated with higher concentrations. Rural and residential areas were associated with lower PAH concentrations. A comparison between aquatic and wetland Elizabeth River PAH concentrations are similar except in the highly industrialized Southern Branch mouth where aquatic sediment concentrations are an order of magnitude higher. The common denominator for urban area is PAH variability in the watershed. In all of the examples there is at least an order of magnitude difference between the lower and higher sites (Table 1-4).

Conclusions

In the Elizabeth River watershed, wetlands with adjacent commercial land use had the highest PAH concentrations and highest impervious surface percentages in addition to high vehicle density in the immediate vicinity. The lowest PAH concentrations in wetland sediments were found at rural sites with low impervious surface/high vegetation percentage and low automobile traffic associated with the adjacent land. As discussed earlier, impervious surfaces allow sediment bound particles such as PAHs to be easily eroded into wetlands. In comparison, vegetation density and buffer strips slow water and decrease particle erosion potential. Hence, the difference in PAH levels found amongst wetland surface sediments are explained in part by the efficiency at which a particular surface accumulates contaminants and releases them to adjacent wetlands. The higher erosion rate of impervious surfaces (parking lots, roads, driveways) relative to vegetative surfaces (parks, undeveloped land) is manifested in the observed PAH concentrations.

Automotive sources were found to dominate PAH input to the Elizabeth River wetlands regardless of adjacent land use. Different densities of traffic are associated with commercial parking lots, driveways and multifamily residential parking lots, streets and rural roads. Therefore, the magnitude of PAH input to adjacent wetlands likely varies with land use relative to the automobile source density. Residential streets and petroleum industrial sites had high traffic and impervious surfaces, respectively, resulting in moderately high PAH wetland concentrations. The data therefore suggest source proximity and adjacent land use/impervious surfaces control PAH concentrations in urban areas.

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Table 1-1. Land use categories and associated wetland surface sediment sites in the Elizabeth River Norfolk, Virginia.

	Land use							
4 land uses	Residential		Undeveloped		Commercial		Industrial	
8 land uses	Multi-family	Single-Family	Rural	Undeveloped	Paved Commercial	Unpaved Commercial	Petro-Industrial	Non-petroleum Industrial
Sites	CC CB	GILL LVR	DCLP GBLP	GB LRP	VZP ODU PCE	MCJ	SC NC	MC SBC

Table 1-2. Published values for PAH concentrations in sediment useful for assessing toxicity. Effects range low (ERL) and effects range median (ERM) values are given for the PAHs listed (Long et al., 1995; Buchman, 1999).

Criteria	Fluor	Phen	Anth	Fluorth	Pyrene	B(a)A	Chrys	B(a)p
ERL (ng/g dry sed)	19	240	83.5	600	665	261	384	430
ERM (ng/g dry sed)	540	1500	1100	5100	2600	1600	2800	1600

Table 1-3. Numerical scaling for each of the following toxicity categories (<ERL) = 1, (>ERL) = 2, (>ERM)= 3 applied to the study sites. Note that sediments with the highest concentration in the Elizabeth River wetlands are only moderately toxic. None score above the ERM.

Site	Fluor	Phen	Anth	Fluorth	Pyrene	B(a)A	Chrys	B(a)p	Σ 1	Σ 2
CC	1	1	1	1	1	1	1	1	8	0
CB	1	1	1	2	1	2	1	1	6	2
GILL	1	2	2	2	2	2	2	2	1	7
LVR	1	2	2	2	1	2	2	2	2	6
DCLP	1	1	1	1	1	1	1	1	8	0
GBLP	1	1	1	1	1	1	1	1	8	0
GB	1	1	1	2	2	2	2	2	3	5
LRP	1	2	1	2	2	2	1	1	4	4
ODU	1	2	1	2	2	2	1	2	3	5
MCJ	1	2	1	2	2	2	1	2	3	5
VZP	1	2	1	2	2	2	2	2	2	6
PCE	1	2	1	2	2	2	2	2	2	6
SC	1	2	1	2	2	2	2	2	2	6
NC	1	2	1	2	2	2	2	2	2	6
MC	1	1	1	1	1	1	1	1	8	0
SBC	1	2	1	2	1	2	1	1	5	3

Table 1-4. Comparison of total PAH concentrations in surface sediments for various estuarine and wetland sites. Concentrations in (ug/g dry sediment). Sources: (1) Al-Saad and Al-Timara, 1989; (2) Huggett et al., 1984; (3) Ashley and Baker, 1999; (4) Sanger et al., 1999.

Site	**Low Total PAH Concentration**	**High Total PAH Concentration**
Iraq marsh[1]	0.59	2.07
South Carolina marsh[2]	109	37
Elizabeth River surface sediments[3]	~1.4	~172
Baltimore Harbor[4]	.089	30
Elizabeth River Wetlands (This Data)	1.2	22.2

Figure 1-1. Map of the Chesapeake Bay (Top) and Elizabeth River watershed land use map (Bottom). Legend depicts symbols for the sixteen wetland surface sediment sites.

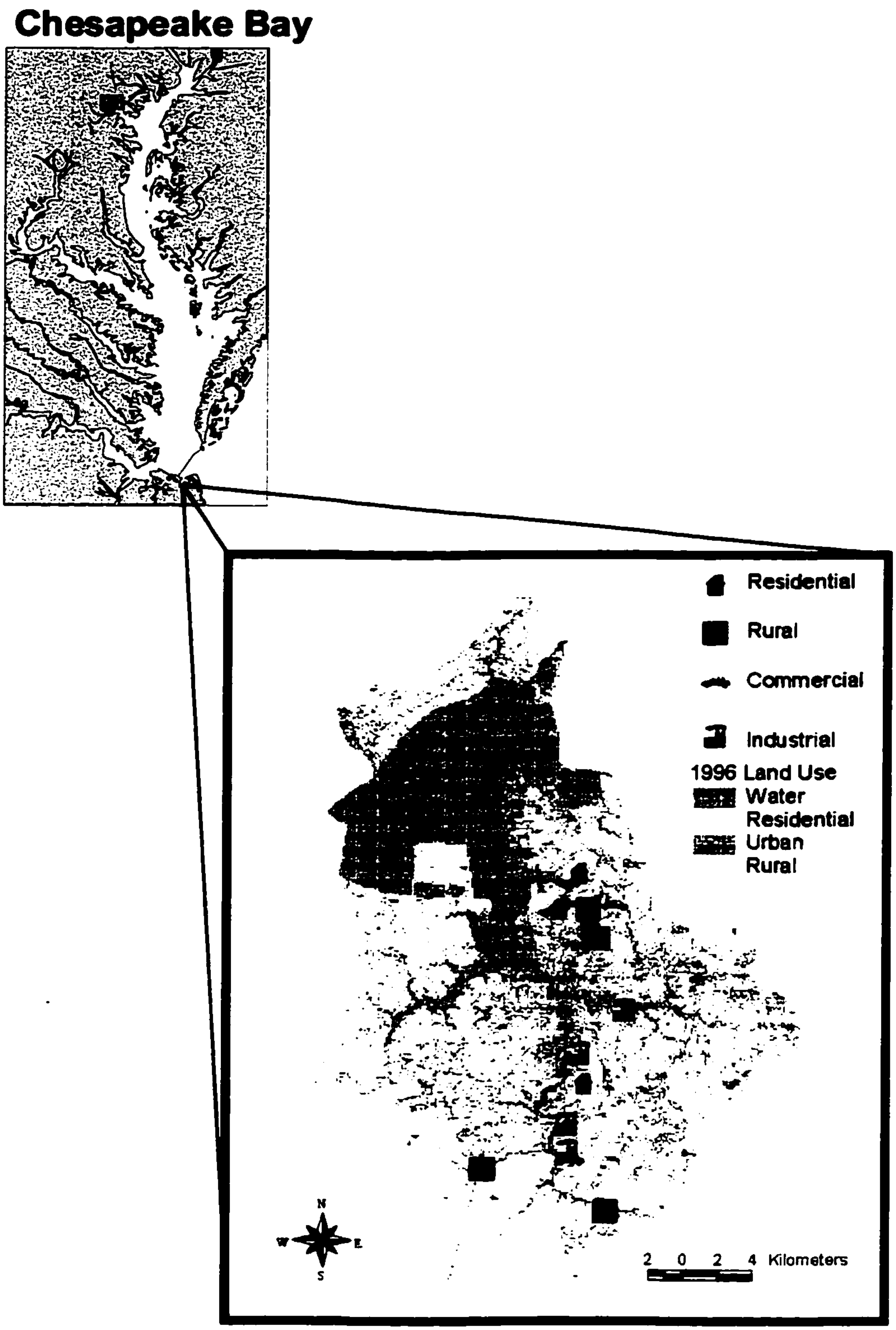
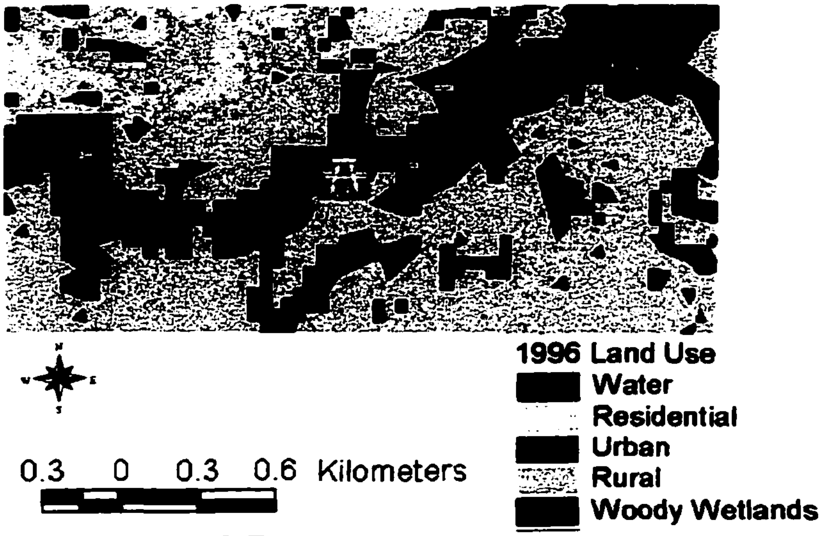
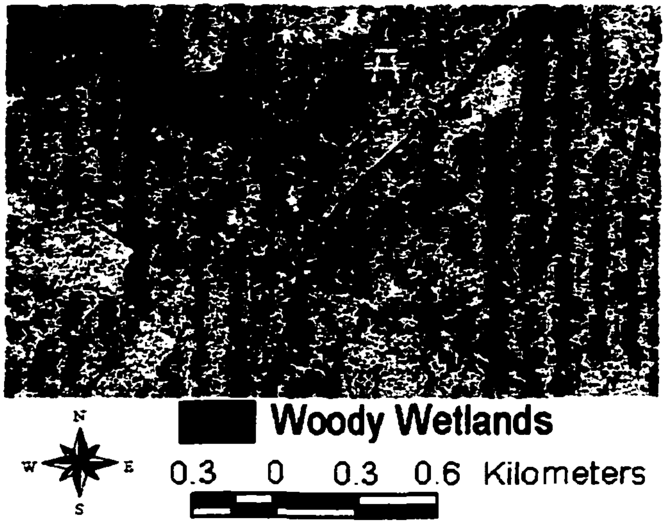

Chesapeake Bay
Residential
Rural
Commercial
Industrial
1996 Land Use
Water
Residential
Urban
Rural
N
W
E
S
2 0 2 4 Kilometers

Figure 1-2. All figures show the various resources used to find and verify possible salt marsh wetland sites based on adjacent land use. A. Example of wetland site with rural adjacent land use. B. USGS topographical map. showing site location and wetland map overlay. C. Picture/site visit used for final verification of adjacent land use.

A.


N
W
E
S
0.3 0 0.3 0.6 Kilometers
1996 Land Use
Water
Residential
Urban
Rural
Woody Wetlands

B.


N
W
E
S
Woody Wetlands
0.3 0 0.3 0.6 Kilometers

C.

Figure 1-3. A. Mean PAH concentration for each of the 16 wetland surface sediment study sites. Variability occurs within each of the four (residential, rural, commercial, and industrial) land use categories. B&C represent separate categorizations of the16 study sites. B. Graph represents 4 categories, commercial is significantly different than all other land uses. C. New categories show significance difference found by splitting the four land uses categories into eight land use categories.

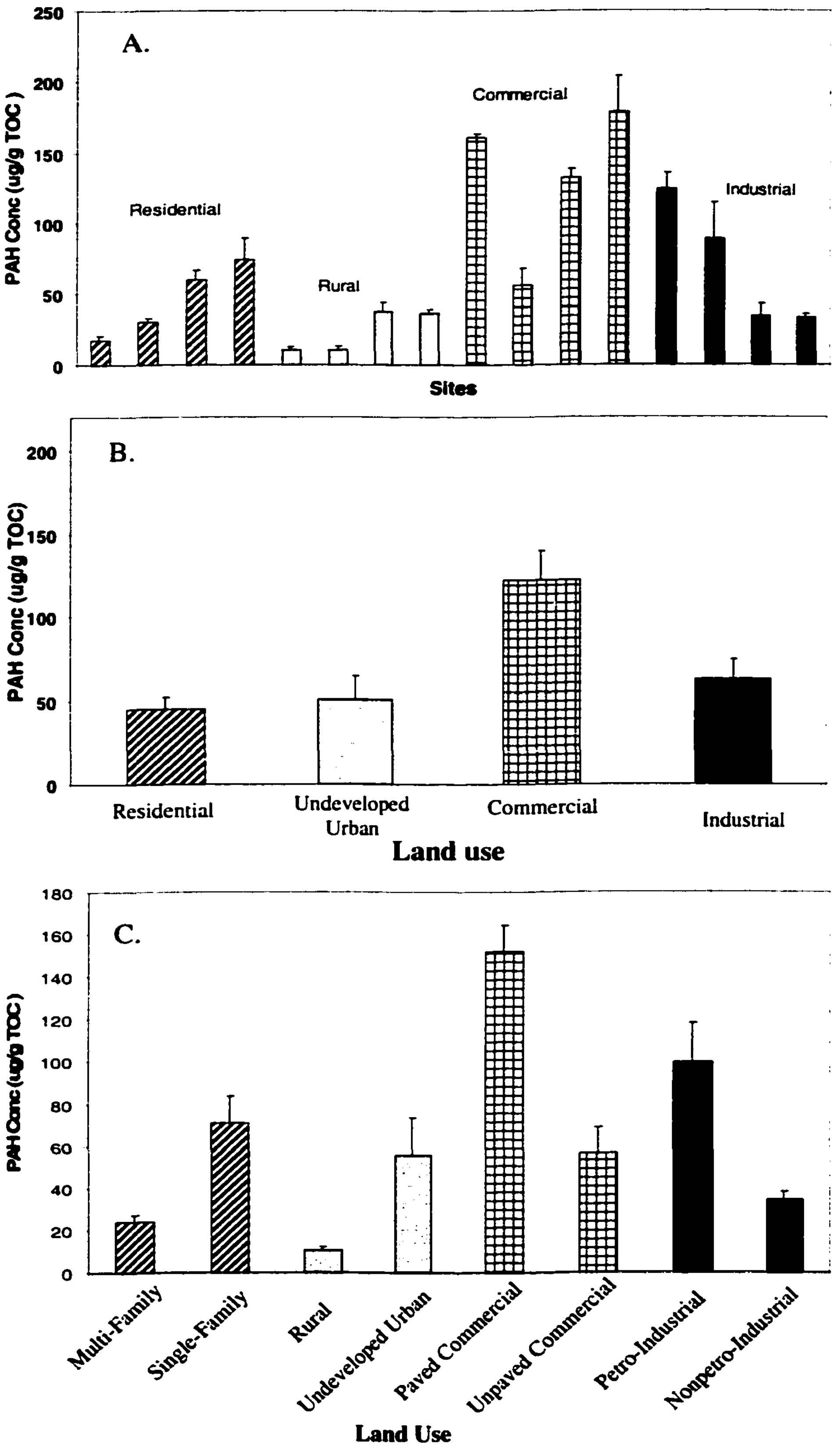

A.
PAH Conc (ug/g TOC)
250
200
150
100
50
0
Residential
Rural
Commercial
Industrial
Sites
B.
PAH Conc (ug/g TOC)
200
150
100
50
0
Residential
Undeveloped Urban
Commercial
Industrial
Land use
C.
PAH Conc (ug/g TOC)
180
160
140
120
100
80
60
40
20
0
Multi-Family
Single-Family
Rural
Undeveloped Urban
Paved Commercial
Unpaved Commercial
Petro-Industrial
Nonpetro-Industrial
Land Use

Figure 1-4. PC1- PC3 represent 69 % of the variability found in the wetland sediment samples. Principle component score plots show no distinction between land uses. Inter-land use differences are obscured by intra-land use variability.

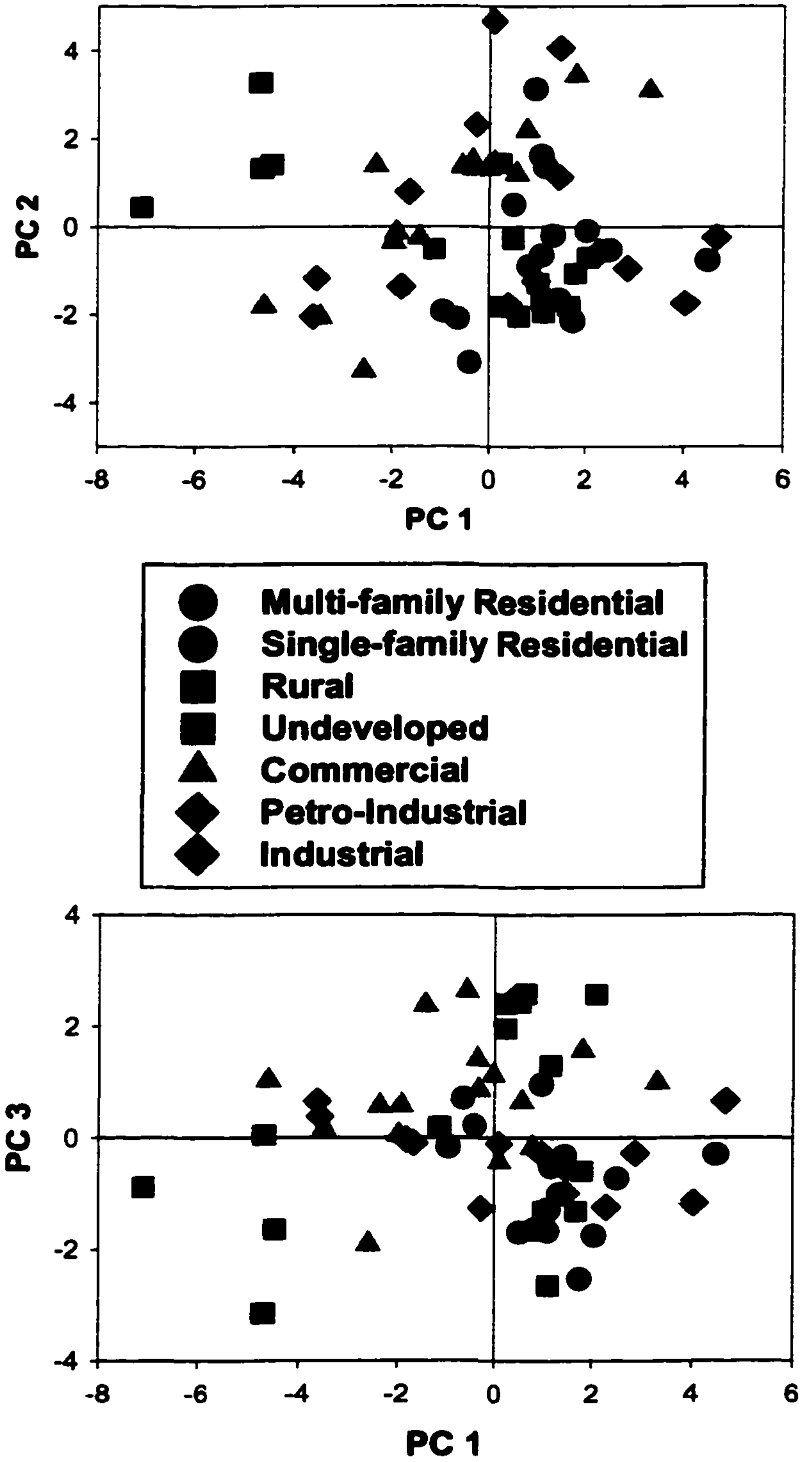
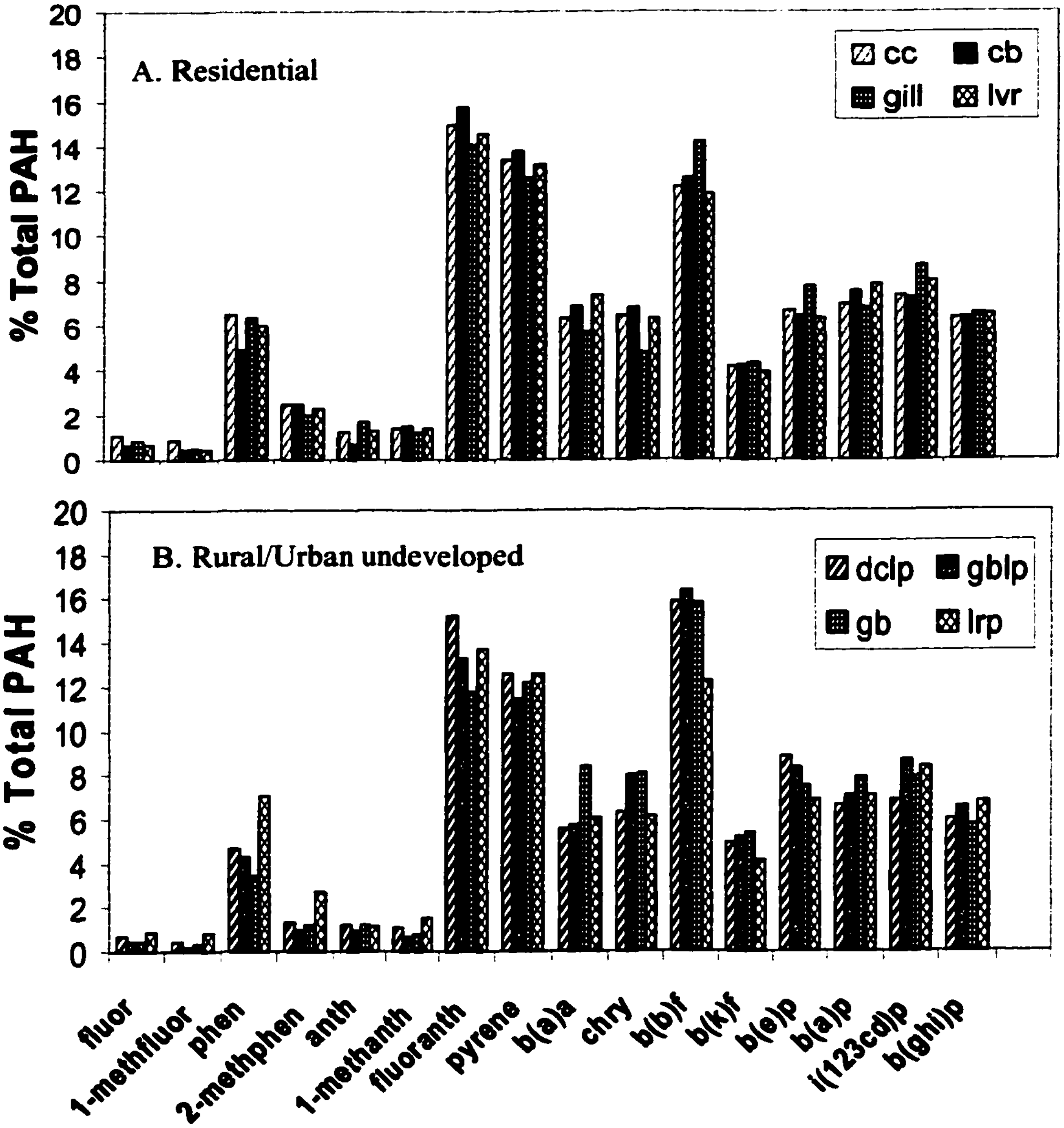

PC 2
4
2
0
-2
-4
-8
-6
-4
-2
0
2
4
6
PC 1
● Multi-family Residential
● Single-family Residential
■ Rural
■ Undeveloped
▲ Commercial
◆ Petro-Industrial
◆ Industrial
PC 3
4
2
0
-2
-4
-8
-6
-4
-2
0
2
4
6
PC 1

Figure 1-5. A-D. Relative abundance of various PAHs in wetland surface sediment (fluor = fluorene, 1-methfluor = 1-methylfluorene, phen = phenanthrene, 2-methphen = 2-methylphenanthrene, anth = anthracene, 1-methanth = 1-methylanthracene, fluoranth = fluoranthene, b(a)a = benzo(a)anthracene, chry = chrysene, b(b)f = benzo(b)fluoranthene, b(k)f = benzo(k)fluoranthene, b(e)p = benzo(e)pyrene, b(a)p = benzo(a)pyrene, I(1,2,3,c,d)p = indeno(1,2,3,c,d)pyrene, b(ghi)p = benzo(ghi)perylene). Molecular weight increases from left to right. Residential, rural/urban undeveloped, commercial and industrial all have similar fingerprints indicating similar sources for sites. High predominance of high molecular weight compounds (molecular weight greater than chrysene) indicate pyrogenic source for all sites.



% Total PAH
0
2
4
6
8
10
12
14
16
18
20
A. Residential
cc
cb
gill
lvr
B. Rural/Urban undeveloped
dclp
gblp
gb
lrp
fluor
1-methfluor
phen
2-methphen
anth
1-methanth
fluoranth
pyrene
b(a)a
chry
b(b)f
b(k)f
b(e)p
b(a)p
i(123cd)p
b(ghi)p

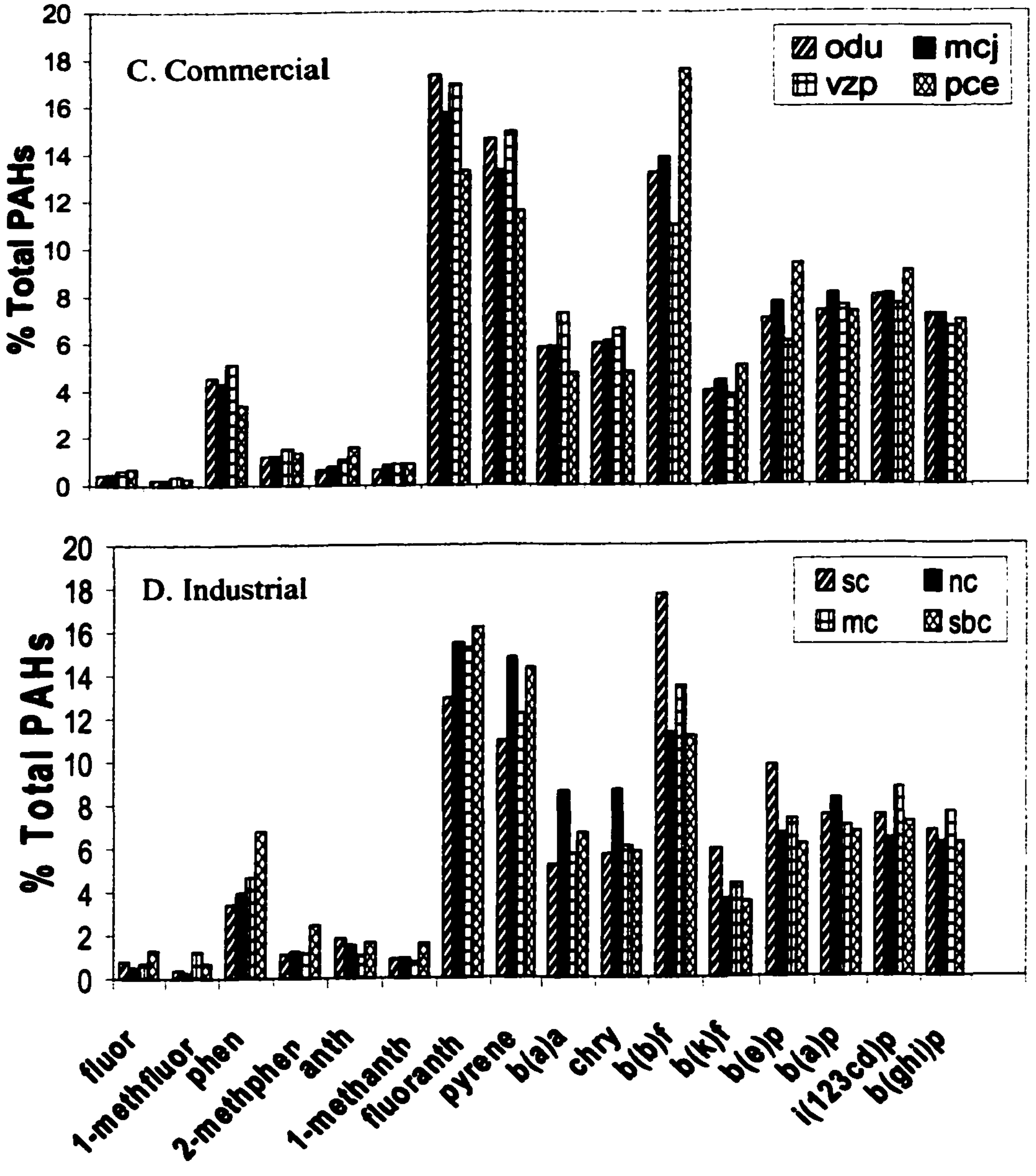
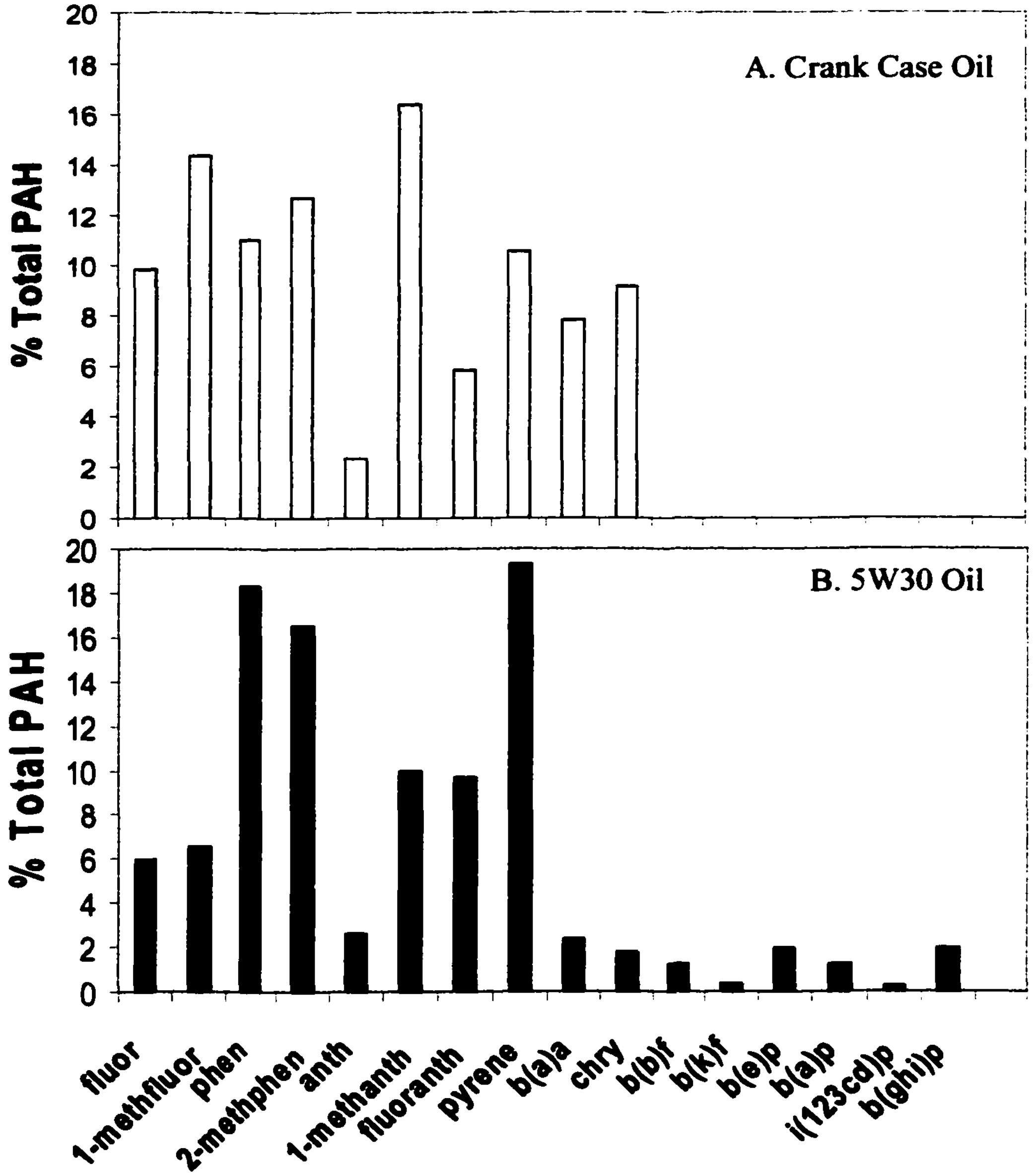

C. Commercial
▨ odu
■ mcj
⊞ vzp
⊠ pce
% Total PAHs
0
2
4
6
8
10
12
14
16
18
20
D. Industrial
▨ sc
■ nc
⊞ mc
⊠ sbc
% Total PAHs
0
2
4
6
8
10
12
14
16
18
20
fluor
1-methfluor
phen
2-methphen
anth
1-methanth
fluoranth
pyrene
b(a)a
chry
b(b)f
b(k)f
b(e)p
b(a)p
i(123cd)p
b(ghi)p

Figure 1-6. Relative abundance of PAHs in petrogenic sources. Molecular weight increases from left to right. Note that low molecular weight compounds are more abundant than high molecular weight compounds as is typical of petrogenic PAH sources.



A. Crank Case Oil
B. 5W30 Oil
% Total PAH
0
2
4
6
8
10
12
14
16
18
20
fluor
1-methfluor
phen
2-methphen
anth
1-methanth
fluoranth
pyrene
b(a)a
chry
b(b)f
b(k)f
b(e)p
b(a)p
i(123cd)p
b(ghi)p

Figure 1-7. Fractional concentrations [(PAH/ ∑5 HMW PAHs) * 100] for several PAH sources (literature derived) and Elizabeth River wetland sediments. Gas = gas engine emissions, diesel = diesel emissions, tunnel = atmospheric samples taken inside a tunnel, road = road dust, auto is a consolidation of gas, diesel, tunnel and road. Wetlands category represent all the wetland sites. The error bars represent standard error. The wetland category has small S.E. that is evidence of similar source for all wetland sites.

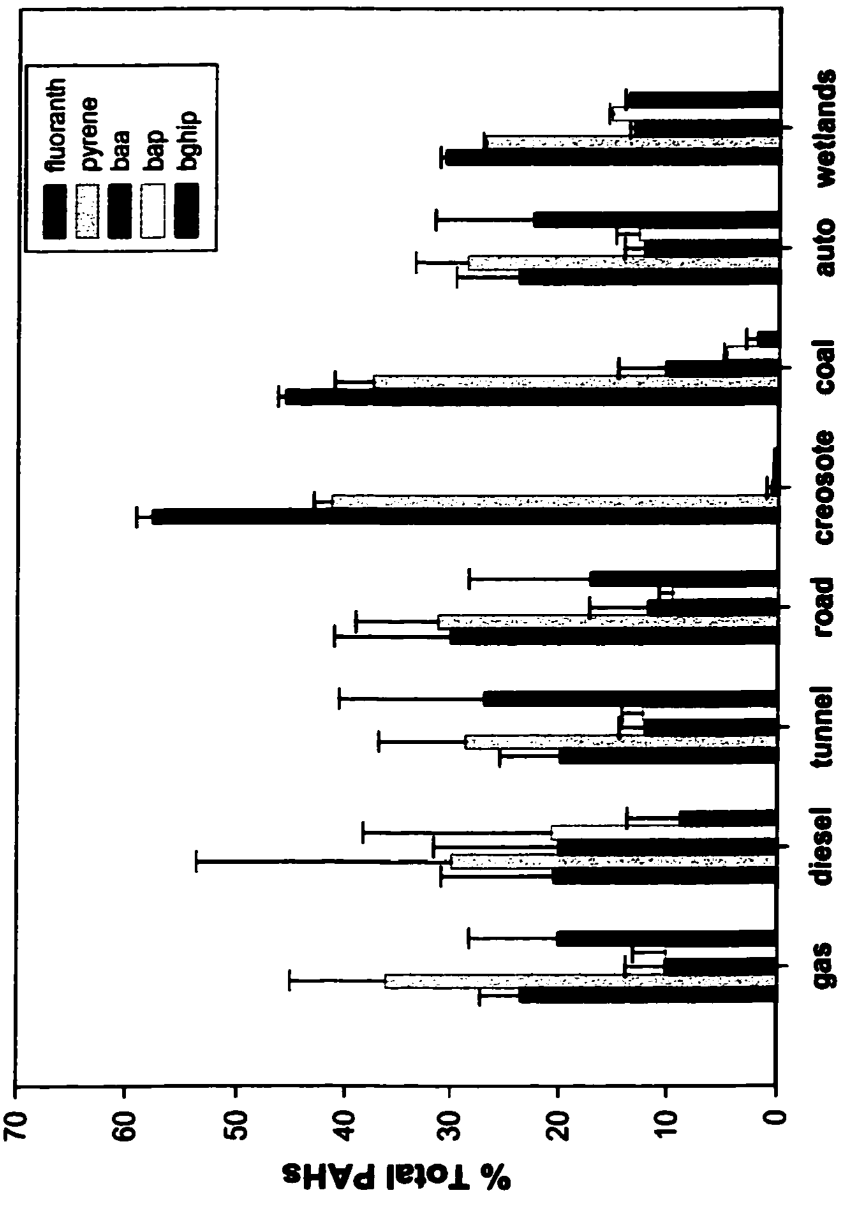
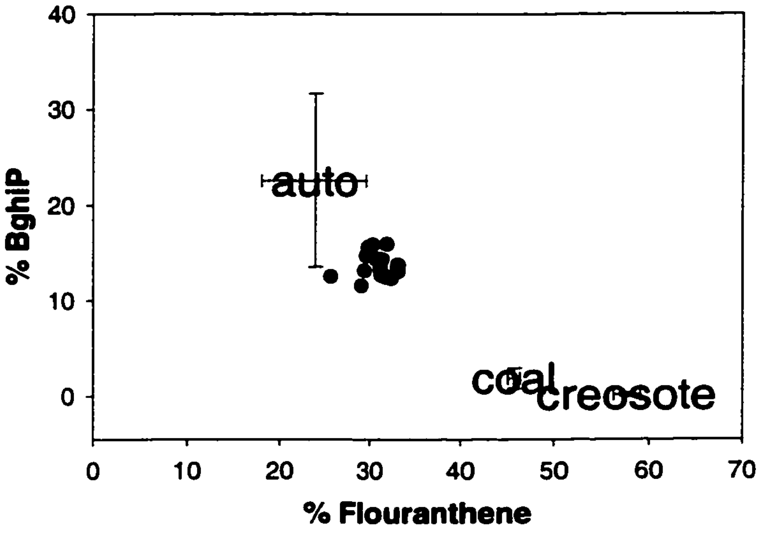
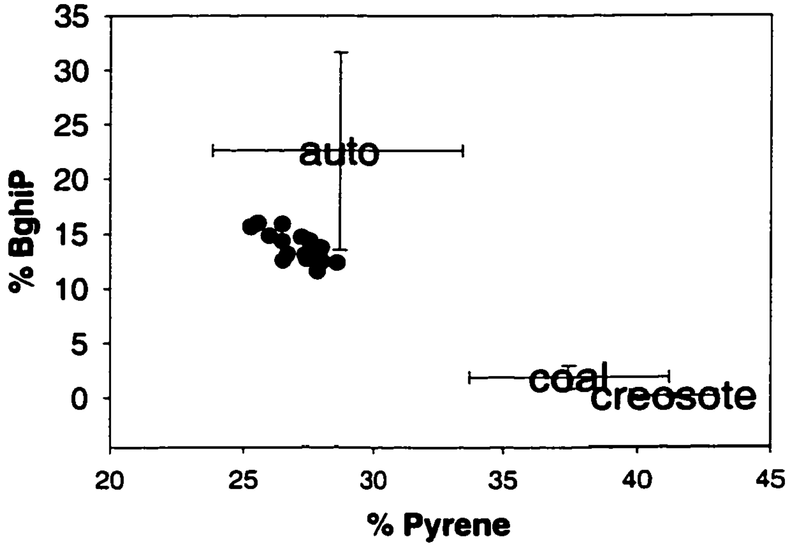
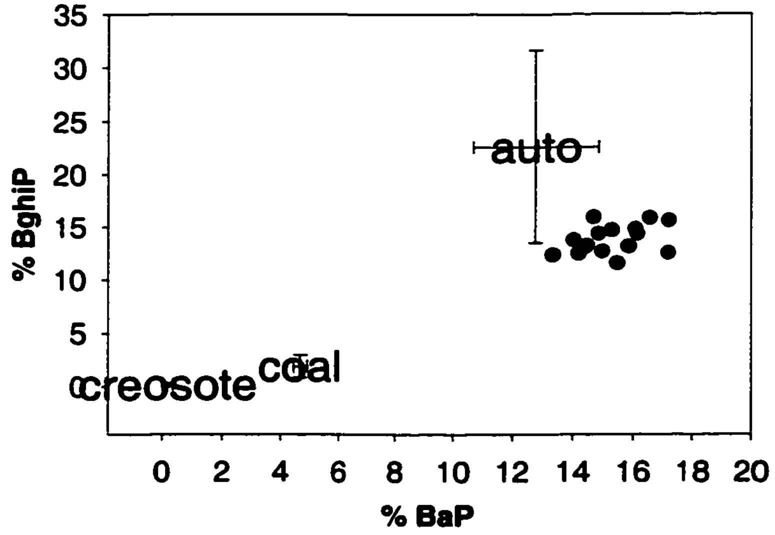

% Total PAHs
0
10
20
30
40
50
60
70
gas
diesel
tunnel
road
creosote
coal
auto
wetlands
fluoranth
pyrene
baa
bap
bghip

Figure 1-8. Two-dimensional scatter plots of PAH fractional concentrations for sources and wetland surface sediments sites(●). Sites are most similar to automobile.


% BghiP
40
30
20
10
0
auto
coal
creosote
0
10
20
30
40
50
60
70
% Flouranthene


% BghiP
35
30
25
20
15
10
5
0
auto
coal
creosote
20
25
30
35
40
45
% Pyrene


% BghiP
35
30
25
20
15
10
5
auto
creosote
coal
0
2
4
6
8
10
12
14
16
18
20
% BaP

Chapter 2

Historical PAH Deposition Assessment In The Elizabeth River, VA, Using Wetland Sediment Cores And GIS

Abstract

Historic polycyclic aromatic hydrocarbon (PAH) accumulation in wetland sediments adjacent to residential, undeveloped, commercial and industrial land uses in the Elizabeth River were assessed by characterizing nine wetland sediment cores. Wetland PAH sediment core trends were static or decreasing from past to present when observed over the past 40 years. Automobile and coal emissions were determined to be the dominant sources of PAHs in the watershed. Auto percentages varied between 21 and 76 percent, with a mean of 51 percent. Two commercial and industrial sites had significantly higher average core concentrations in addition to static profiles indicating chronically high PAH concentrations.

Introduction

PAHs are one of the most abundant pollutants in the Elizabeth River. They enter the environment from both point and nonpoint sources including automobiles, crank case oil, waste incineration, coal fired power plant emissions, and creosote spills (LaFlamme and Hites, 1978). Some PAHs are carcinogenic (Neff, 1979; Denissenko et al., 1996; Philips and Grover, 1994) and most are toxic to aquatic organisms (Boxall and Maltby, 1997).

PAH studies in the Elizabeth River have primarily been focussed in the Southern and Eastern Branches (Bieri et al., 1986), where point sources/spills from creosote plants pose a serious threat to the aquatic system (Walker and Dickhut, 2001). However, with the closing and regulation of industry (Kennish, 2000; Merril and Wade, 1985), diffuse sources are likely to have become more important (Davies, 1995). Thus, research should examine nonpoint sources of pollution in the watershed as well as continue to monitor the distribution of historic PAH contamination.

The largest nonpoint threat to the aquatic environment is urban runoff. PAHs are the predominant suite of compounds that make urban runoff toxic to aquatic organisms (Boxall and Maltby, 1997). The PAH content of runoff is related to the particular land use from which it is derived. Wetlands adjacent to urban (commercial and industrial) land uses have the highest PAH concentrations of all land uses (Chapter 1; Hoffman et al., 1982). This is likely due to the effects of impervious surfaces (roads, parking lots, highways and driveways), which increase runoff intensity causing an order of magnitude increase in sediment loads (Novonty and Chester, 1981;Schueler, 1987, Kennish, 2000). In addition, impervious surfaces are often associated with vehicular traffic, which is a major source of PAHs. Therefore, the highest concentration of PAHs were found in areas such as parking lots (Chapter 1).

Wetlands scavenge particles and associated contaminants which makes them valuable in assessing nonpoint pollution threats to aquatic systems from terrestrial land use (Schubel and Carter, 1984). Wetland sediments, because they preserve an integrated record from the surrounding watershed, are also useful for assessing historic trends of contaminants and sedimentation (French, 1993).

The Elizabeth River watershed has been urbanized for over a century and encompasses large residential, commercial, industrial and undeveloped areas. Consequently, the history of PAH contamination with potentially changing contaminant sources makes the Elizabeth River watershed ideal for assessing historic land use related PAH trends.

Examining historical patterns of PAH abundance and source information details past problems and potentially, future threats to the watershed. Sediment core data also provide time averaged PAH input that can be compared to surface sediment data to make stronger arguments regarding PAH land use associations and policy decisions. From a management perspective this research may provide information which will be valuable in determining where to focus future policy efforts and possibly wetland mitigation efforts by indirectly assessing past initiatives.

Methods

Site selection

Geographic Information Systems (GIS) land use coverages were used to select sediment wetland sampling sites representative of four land use categories (residential, rural, commercial, and industrial) in the Elizabeth River basin (Figure 2-1). Historic characterization of coring sites was done using EPA Region III land cover data set (EPALU, 1996), aerial photography, and USGS topography maps, 1981. Of all the spatial resources, the aerial photographs were preferentially utilized as they provided the most conclusive evidence of previous land use.

Sediment Core Collection and Processing

Eleven sediment core sites were chosen from the sixteen previously selected surface sediment sites in the Elizabeth River (Chapter 1). To begin the coring process a six-inch diameter PVC tube was hammered into the wetland. An airtight cap was inserted into the top of the core to prevent sediment release from the bottom during removal. Next, a deep hole was dug next to the core to facilitate easier removal of the core. The core was then removed from the wetland. The bottom was immediately sealed to stop sediment loss. Core lengths ranged from 62-102 cm. Cores were sectioned into 1.5 cm intervals to allow for comparison with previously collected surface sediments (Chapter 1). Each sediment core section was weighed to determine bulk density, homogenized and then divided into fractions that were used for chemical and geochronologic measurements.

PAH Analysis

Accelerated solvent extraction was used to extract PAHs from sediments using a method derived from Mitra et al., (1999). Hydromatrix (Dionex) was used to dry sediment. A surrogate standard composed of deuterated naphthalene, anthracene, benzo(a)anthracene, benzo(a)pyrene and benzo(ghi)perylene was added before extraction. Dichloromethane was used as the solvent for extraction. The resulting extract was concentrated by rotary evaporation, followed by evaporation to 1 ml using N_2, and purified over 10 g of 3% deactivated silica gel, Na_2SO_4 and copper in a method derived from Dickhut and Gustafson, (1995). Twenty five ml of hexane, followed by 50 ml 20% dichloromethane (DCM) in hexane (v:v) were used to elute PAHs from the silica column. The purified extract was concentrated again to 1 ml by rotary evaporation. An internal standard comprised of deuterated acenaphthene, phenanthrene, chrysene and perylene was then added. The extracts were further concentrated under high purity nitrogen to 0.5 ml. PAH analysis was performed with a gas chromatograph (GC) interfaced to an electron impact mass spectrometer (MS) operated in selective ion monitoring (SIM) mode using a 30 m DBXL column. All PAH surrogate standard recoveries were greater than 70 percent.

Geochronology

For ^{210}Pb analysis approximately 10 grams of dried finely ground sediment was used. ^{209}Po was used as a surrogate standard. Hot acid (HNO_3 and HCl) was used to leach ^{210}Po from sediment. Overnight plating of the nuclides onto 2cm x 2cm silver plates was used to harvest nuclides for counting. After alpha counting, the ^{209}Po surrogate spike and the ^{210}Po contained in the sample were used to calculate ^{210}Pb activity (Nittrouer et al., 1979).

A variation of the Constant Input Concentration (CIC) model was used to calculate ^{210}Pb sedimentation rates (Appleby and Oldfield, 1983). With this method, a least-squares regression plot of the decay region is used to obtain a slope. The slope is then used to determine the sediment accumulation rate. The basic equation that relates activity at the surface to activity at depth is:

$$C = C_0 e^{-\lambda t} \qquad (1)$$

where C_0 is excess activity at the sediment surface, and λ is the ^{210}Pb decay constant, used to solve for sediment accumulation rates recognizing that:

$$t = \frac{x}{s} \qquad (2)$$

where x is depth (cm), and s is accumulation rate (cm/time) (Ivanovich et al., 1992; Appleby and Oldfield, 1983). In this case, s is determined from the slope of a plot of log C vs x. Excess activity was estimated:

$$\text{Excess activity} = \text{uncorrected activity} - \text{supported activity} \qquad (3)$$

where uncorrected activity is the raw activity measured in core samples. Supported activity is the average activity found in the bottom of the ^{210}Pb profile where activity is constant (Figure 2-2A). With the CIC model, it is assumed that C_0 is constant and that mixing does not disturb the decay profile (Appleby and Oldfield, 1983).

A low energy germanium (LEGe) detector was used to analyze ^{137}Cs by gamma spectroscopy. An energy of 661.62 keV was used to delineate ^{137}Cs. Counting times were approximately 24 hours. Seventy ml of wet sediment were packed into a vial, weighed and sealed. After counting, the sediment dry weight was determined. The final measurements resulted in plots of cumulative mass depth vs ^{137}Cs in dpm/g dry sediment.

For ^{210}Pb accumulation rate verification we used a variation of the calculation formulated by Nittrouer et al., (1983) that utilizes the major ^{137}Cs peak in the soil profile, delineating the year 1963, to assess the accuracy of the ^{210}Pb accumulation. Theoretical ^{137}Cs depth is determined by:

$$^{137}Cs_{\text{theoretical}} = {}^{210}Pb_{\text{Accum}} * Z \qquad (4)$$

where $^{137}Cs_{\text{theoretical}}$ = theoretical ^{137}Cs peak depth $^{210}Pb_{\text{Accum}}$ = ^{210}Pb accumulation rate and Z = core acquisition date –1963. The theoretical ^{137}Cs depth was then compared to the actual ^{137}Cs peak depth. An actual ^{137}Cs peak depth deeper than the theoretical ^{137}Cs depth is evidence of deep mixing. Similar ^{137}Cs peak depth are evidence of minimal mixing and were therefore used for chronological PAH studies in cores.

Results and Discussion

Site Description

Aerial photographs (Figures 2-3 and 2-4) were used to assess historical land use in the Elizabeth River watershed. At least two photos from different past decades were obtained for each of the nine study sites to assess land use. Other sources of data such as GIS land use coverages and USGS topographical maps were used to fill in the gaps between photos. Only one site (NC) had land use change during the time period studied (Figure 2-4). The land use change from undeveloped to industrial at this site occurred in the mid 1970s. For all other sites only one aerial photo is shown (Figures 2-3 and 2-4) as the adjacent land use has been constant dating back to the earliest dated photo, the last 35-40 years (Figures 2-3 & 2-4)

Sediment Accumulation rates

Since ^{137}Cs samples were not taken at every core depth interval error bars were used to represent the range in accumulation rate calculation associated with ^{137}Cs sample resolution (Figure 2-5). Cores showing signs of deep mixing were not used for PAH trend analysis. If an estimate of the 1963 ^{137}Cs peak by ^{210}Pb was within one sample interval of the actual 1963 ^{137}Cs peak the core was used for historical PAH trend analysis. Five cores fit the aforementioned criterion (CB, GC, GB, VZP and NC - Figure 2-5). The ^{210}Pb accumulation rate was used for all accumulation rate and date calculations. Core depth and accumulation rates were converted to year using equation 5.

$$\text{(Core depth interval} - \text{mixed layer depth)/accumulation rate} = \text{year} \qquad (5)$$

Site Trends and Intra-Core PAH Distribution

The Elizabeth River wetland sediment cores represent between 40 and 80 years of PAH input at each site. Of the five sediment cores that were used, three exhibited decreasing PAH concentrations with time from past to present (GCC, GB Figure 2-6, NC – Figure 2-7). In these cores, PAH concentration varied from less than one order of magnitude (NC) to more than 20-fold (GB - Figures 2-6 and 2-7). The remaining two sediment cores (CB and VZP) had one spike in concentration however the overall trend was primarily static (Figures 2-6 and 2-7). No sediment core showed a consistent increase in PAH concentration from past to present.

The decrease in PAH concentrations from past to present at site GB, where the adjacent land has remained undeveloped over the past 40 years, as well as the NC site, the only site to exhibit land use development over the past 40 years, indicates that factors other than adjacent land use are important in controlling PAH input to wetland sediments. For example, reductions in nonpoint and point source pollution over the past 40 years may well be responsible for the observed decreases in PAH inputs to many wetland sediments. In contrast, the consistently high PAH levels in the sediment cores collected from wetlands adjacent to commercial land use (VZP) may demonstrate that other factors such as increased local automobile traffic may serve to offset decreases in nonpoint source PAH inputs. The stagnant trend is likely not a result of catchment particle storage as the adjacent land use is impervious and thus not likely to store and release particles on large time scales (Hoffman et al., 1982).

Inter-site Comparison: Total PAH

ANOVA statistics along with Fisher Pairwise comparison tests were used to compare average PAH concentrations in each core. Cores encompassed samples from 40 to 80 years as calculated by ^{210}Pb. Therefore, to allow for comparison of a similar time range in the various wetland sediment cores, analysis of the average PAH concentration focused on the last 40 years.

The wetland sediment cores with the highest average PAH concentration were VZP and SC (Figure 2-8), which are adjacent to a parking lot and a petro-industrial complex, respectively. Using the Fisher Pairwise comparison test sediment cores at both of these sites (VZP & SC) were found to have significantly higher average PAH concentrations over the past 40 years compared with all other sites. This finding is consistent with what was found in the surface sediment portion of this study (Chapter 1). However one major difference was NC, a petro-industrial site, which was found to have significantly higher PAH levels in surface sediment, but significantly lower average PAH concentrations in the core profiles. This is likely the result of the high variability in wetland surface sediment PAH concentrations found at NC (Chapter 1 – Figure 1-3).

PAH Source Apportionment

PAH compound fingerprinting was used to determine probable sources for each core. The first step in source determination is to determine the general source i.e. petrogenic or pyrogenic of the PAHs. Assessing the proportions of HMW 5-6 ring compounds and LMW 2-3 ring PAHs associated with a particular sample was used to accomplish the first step. Fingerprints for two petrogenic sources, crankcase and 5w30 oil, show a dominance of LMW PAHs (Figure 2-9). Compared to the PAH fingerprints for each sampling site in this study (Figure 2-10 & 2-11) petrogenically derived PAHs are not a dominant source of input to wetland sites in the Elizabeth River. HMW PAHs are associated with pyrogenic input. Hence the sediment samples provide evidence that pyrogenic sources dominate PAH input to the Elizabeth River wetlands. One sample (CB5) had equal percentages for both LMW and HMW compounds, which distinguished it from other samples. CB5 also represented a spike in the sites core profile (Figure 2-6).

The two compounds showing the most variability between sources were benzo(ghi)perylene (bghip) and fluoranthene (Chapter 1). Thus a plot of fluoranthene and bghip was used to differentiate between PAH sources associated with wetland sediment historically (Figure 2-12 & 2-13). Relative to surface sediment sites (Chapter 1) core sites show more variability in sources (Figure 2-12 & 2-13). In general commercial is the only land use primarily associated with auto while the other land uses are distributed between the coal and automobile sources.

Sample CB5 is again differentiated from the other CB core samples and residential sample (Figure 2-12). The differentiation of CB5 by high PAH concentration (Figure 2-6), fingerprint (Figure 2-10) and compound plots (Figure 2-12) suggest CB5 is evidence of a spill or other large input of pyrogenic material.

As in Chapter 1 a mixing model based on the fluoranthene/bghip ratio was used to quantitatively determine the percentage auto relative to coal in wetland sediments for each adjacent land use category (Chapter 1). The contribution of automotive sources to PAH contamination in the wetland sediments increases with time from past to present (GCC and GB) or stayed relatively constant from past to present (Figure 2-14-VZP, NC). Only the residential core (CB) exhibits a decreasing contribution of automotive sources to PAH contamination of the sediment with time from past to present. However, when assessing the past 50 years, if the one point with significantly low auto percentage (CB5) is exclude the trend is static. Hence at the watershed level automotive PAHs are a dominant source of PAHs(Figure 2-14).

Watershed Comparison

The Elizabeth River wetland sediment cores are not indicative of what has been found in other developed watersheds. Latimer and Quinn (1996) took several cores in Narragansett Bay, RI, all but one showed increases or static PAH concentrations from past to present. In a more extensive study Van Metre (2000) took sediment cores from lakes and reservoir in watershed with differing degrees of development from five states all of which had an increasing trend of PAHs from past to present. Overall the typical trend found in urban estuaries (Latimer and Quinn 1996) and lakes (Neff, 1979; Van Metre et al., 2000) from developed areas are of increasing PAH sediment concentration from past to present. This was different from the decreasing/static PAH trends from past to present found in Elizabeth River wetlands (Figure 2-6 & 2-7).

Differences between core PAH trends found in the Elizabeth River wetlands are explained by historic pollution (Bieri, 1986; Merrill and Wade, 1995;

Mitra, 1997; Lu, 1982) PAH source changes (Figure 2-12, 2-13 and 2-14) and land use PAH relationships (Chapter 1).

Elizabeth River sediment PAH concentrations are among the highest of any urban estuary in the U.S. (Bieri, 1986) due to historic point source inputs (Merrill and Wade, 1995). However, due to regulations and plant closures point sources PAH releases have been reduced (Merril and Wade, 1985). The effect of point source reductions is recorded in wetland sediment cores. However this reduction was not found in commercial wetlands which receive direct runoff from parking lots (Figure 2-7). Point sources are easy to regulate simply by permitting effluent and using scrubbers on smokestacks.

Conclusion

PAH concentrations in the Elizabeth River wetland sediments over the past 40 years were observed to decrease form past to present or remain relatively constant, irrespective of adjacent land use. However there is room for improvement as the sites with the highest PAH concentrations, adjacent to a paved parking lot (VZP) and petroleum industrial land use (SC), are not decreasing indicating that local PAH inputs may offset decreases in PAH input at the watershed level.

In contrast to the overall level of PAHs, the automobile source percentage in various wetland sediments of the Elizabeth River ranged from static to increasing. Although, auto sources were not found to be the dominant source of

PAHs at all sites when averaged over the past 40 years, automotive sources accounted for 40-60% with coal/creosote comprising the remainder of PAH input to the study sites core, irrespective of adjacent land use. Historic trends for auto percentage were inversely related to those of PAH concentration.

These conclusions have several ramifications on future policy. Based on the increasing auto source percentage, a focus on automobile emissions of PAHs is warranted. The inverse relationship associated with the increasing automotive sources of PAHs in the watershed and decreasing PAH concentrations show that present emission controls on cars are having a positive effect. However, future policy will have to account for a possible increase in urban traffic density.

Also, due to high, chronic PAH levels, in adjacent wetland sediments, parking lots and petroleum industrial land uses should receive attention in the future. The automotive source percentage shows that parking lots were primarily affected by auto related sources. In contrast, the petroleum industrial land use showed significantly lower auto source percentages (< 40 percent).

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Figure 2-1. Sediment core study sites (11) and watershed land use in wetlands associated with the Elizabeth River estuary.

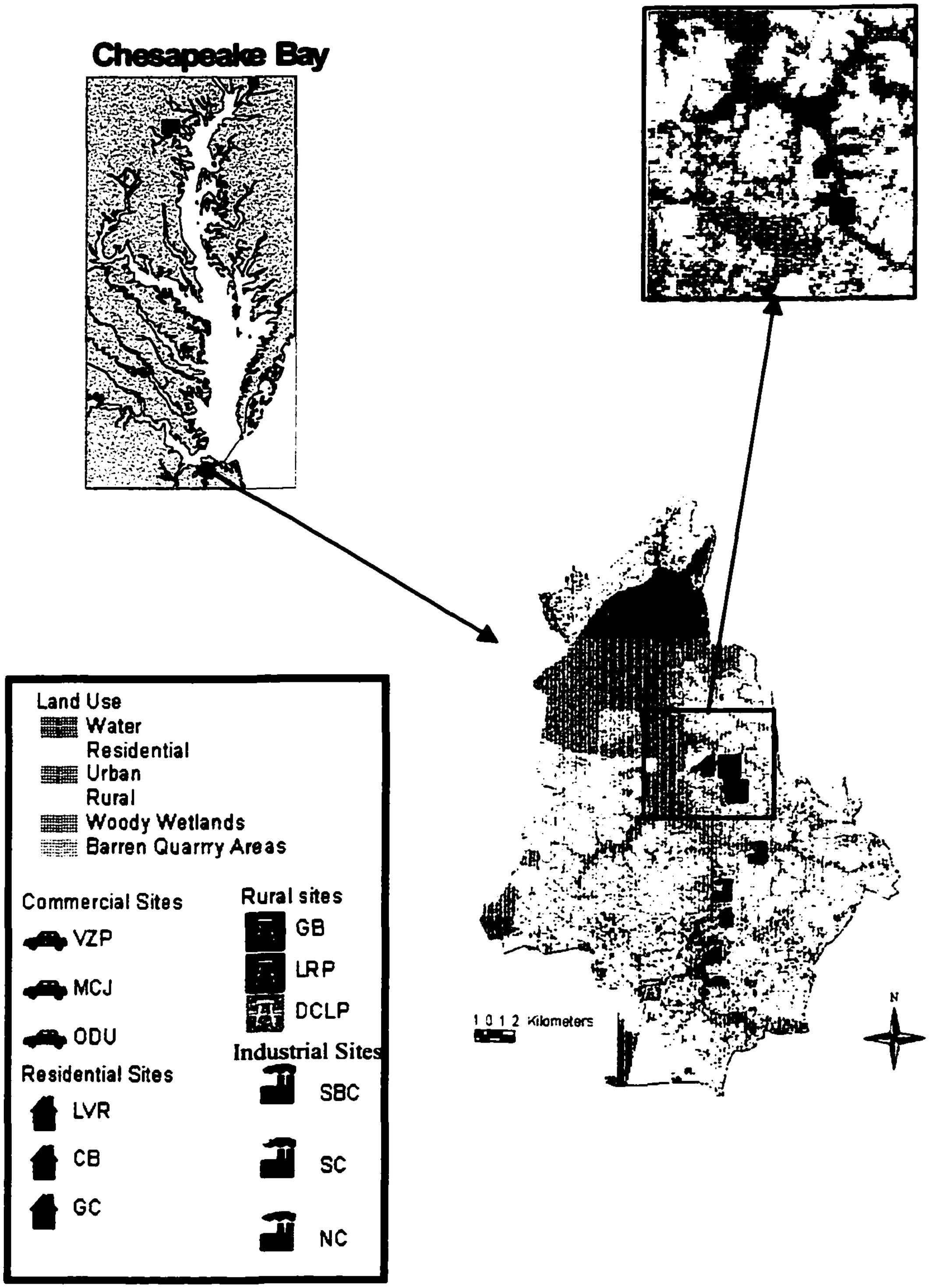
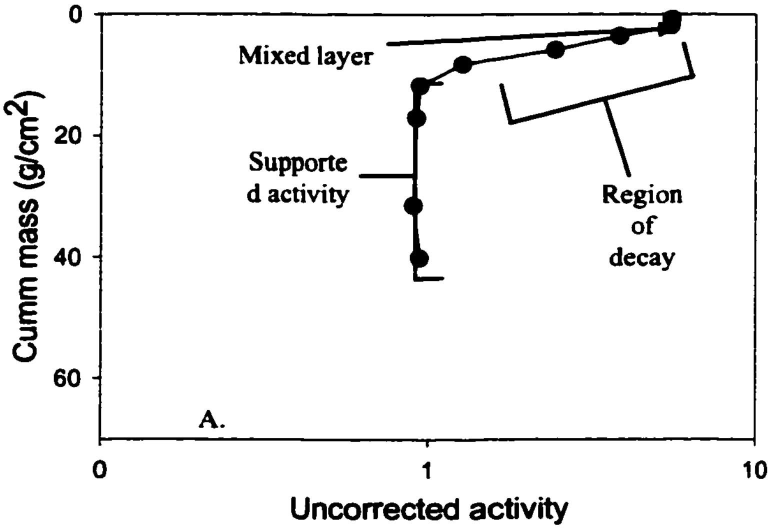

Chesapeake Bay
Land Use
Water
Residential
Urban
Rural
Woody Wetlands
Barren Quarrry Areas
Commercial Sites
VZP
MCJ
ODU
Residential Sites
LVR
CB
GC
Rural sites
GB
LRP
DCLP
Industrial Sites
SBC
SC
NC
1 0 1 2 Kilometers
N

Figure 2-2. Characteristic core profiles of ^{210}Pb (A) and ^{137}Cs (B). Panel A identifies the various parts of the profile used in calculating accumulation rates


0
20
40
60
Cumm mass (g/cm^2)
Mixed layer
Supporte d activity
Region of decay
A.
0
1
10
Uncorrected activity

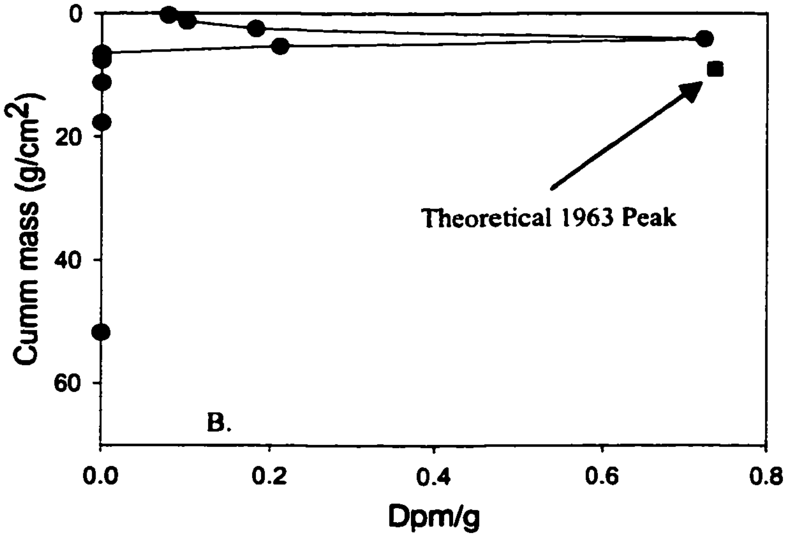
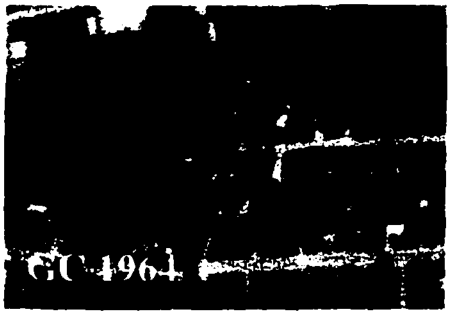

0
20
40
60
Cumm mass (g/cm^2)
Theoretical 1963 Peak
B.
0.0
0.2
0.4
0.6
0.8
Dpm/g

Figure 2-3. Aerial photographs from 1964 and 1977 of wetland sampling sites. Columns represent residential (left) and rural/undeveloped (right) study sites respectively.


CB 1977


DCLP 1964


GC 1964


GB 1977


LVR 1977


LRP 77

Figure 2-4. Aerial photographs from 1964-1977 of wetland and sampling sites. Columns represent commercial (left) and industrial (right) study sites, respectively.


VZP 1977


SC 1964


MCJ 1964


NC1964


NC 1985


SBC 1977

Figure 2-5. Accumulation rates calculated from ^{210}Pb and ^{137}Cs profiles for each core. ER represents a watershed averaged accumulation rate for the Elizabeth River wetland sites obtained by averaging cores from the plot. The error associated with the 1963 ^{137}Cs peak samples is represented by error bars that depict range.

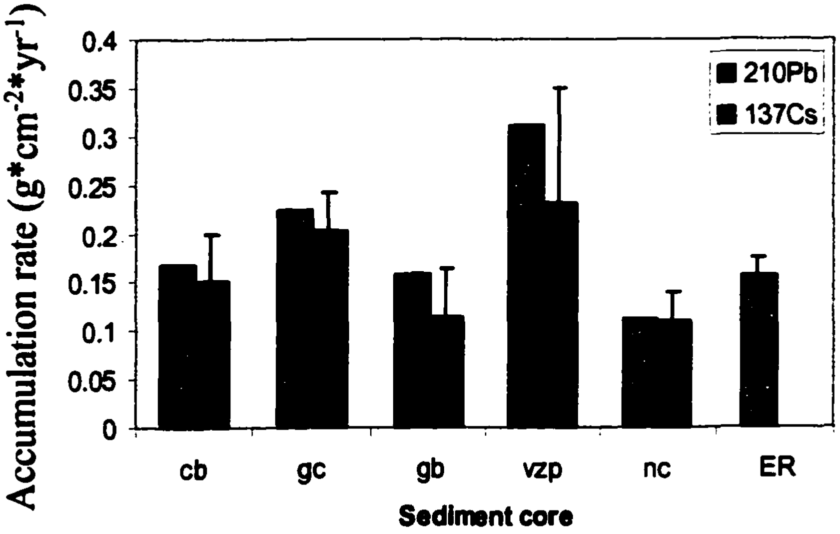

Accumulation rate (g*cm-2*yr-1)
0.4
0.35
0.3
0.25
0.2
0.15
0.1
0.05
0
■ 210Pb
■ 137Cs
cb
gc
gb
vzp
nc
ER
Sediment core

Figure 2-6. Historical PAH trends for residential and rural land use sites in Elizabeth River wetland sediment cores. Star represents sample CB5.

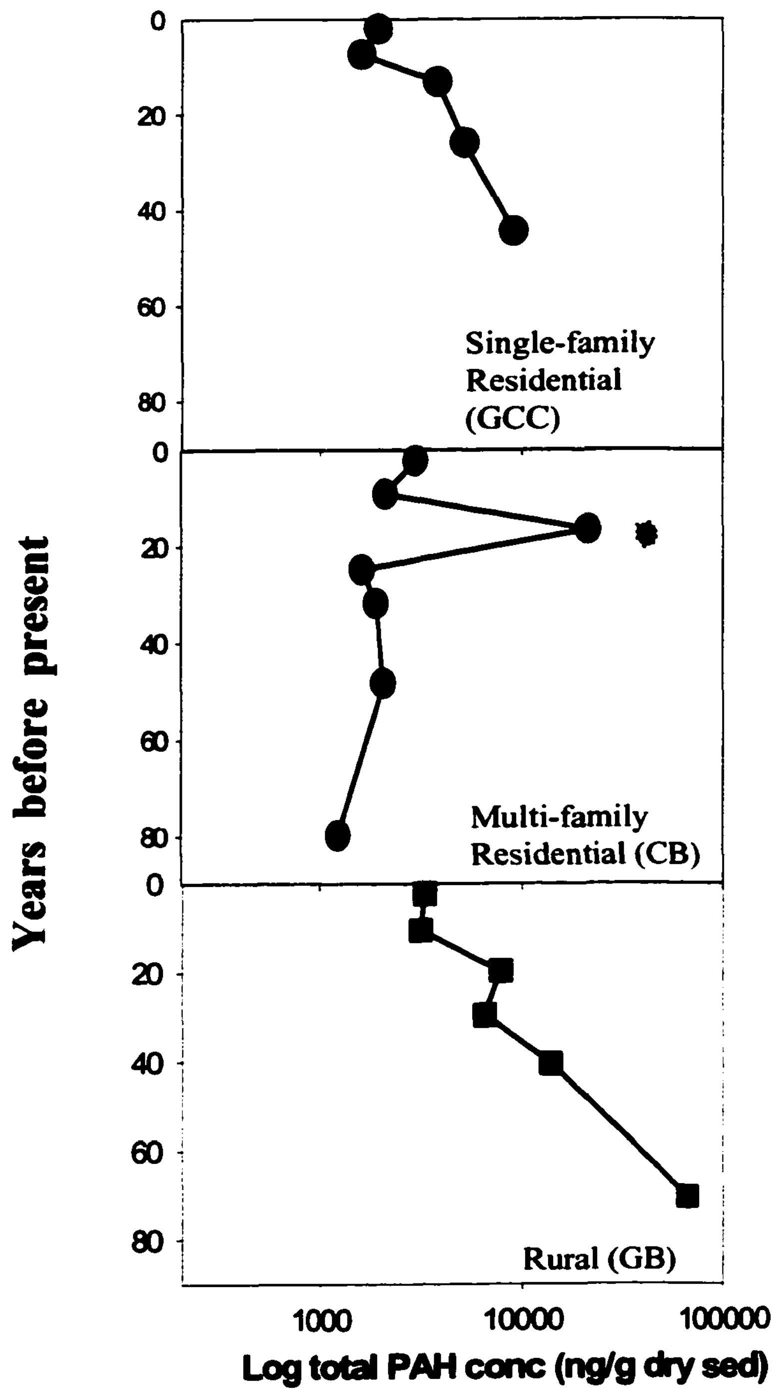

0
20
40
60
80
Single-family Residential (GCC)
Multi-family Residential (CB)
Rural (GB)
Years before present
1000
10000
100000
Log total PAH conc (ng/g dry sed)

Figure 2-7. Historical PAH trends for commercial and industrial land use sites in Elizabeth River wetland sediment cores

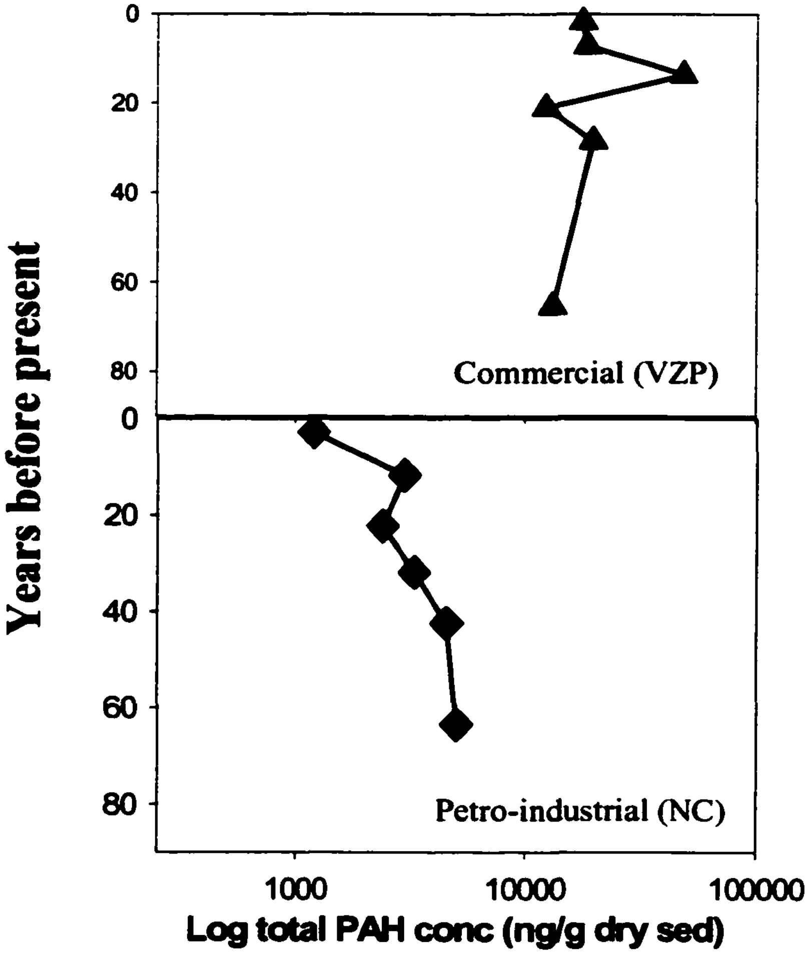

Years before present
0
20
40
60
80
Commercial (VZP)
0
20
40
60
80
Petro-industrial (NC)
1000
10000
100000
Log total PAH conc (ng/g dry sed)

Figure 2-8. Average sediment core PAH concentration for the past 40 years in Elizabeth River wetland sediment cores

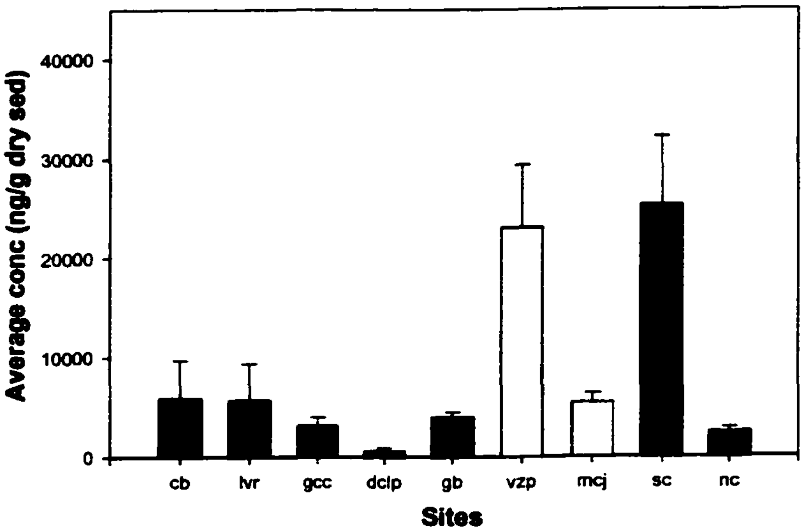

Average conc (ng/g dry sed)
40000
30000
20000
10000
0
cb
lvr
gcc
dclp
gb
vzp
mcj
sc
nc
Sites

Figure 2-9. PAH fingerprint trends for petrogenic sources are dominated by LMW compounds.

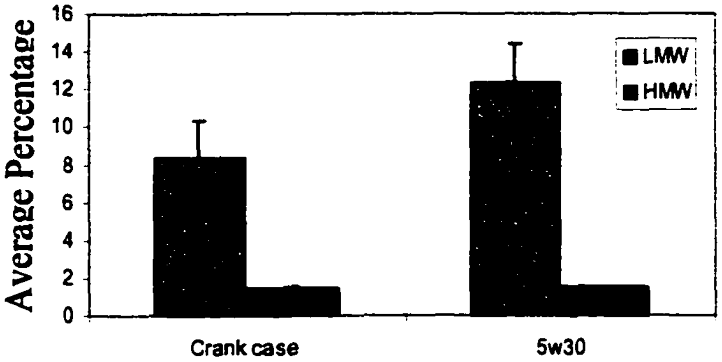

Average Percentage
16
14
12
10
8
6
4
2
0
■ LMW
■ HMW
Crank case
5w30

Figure 2-10. Relative abundance of low molecular weight (LMW) and high molecular weight (HMW) PAHs expressed as percent total PAH. Residential and undeveloped/rural site fingerprints. Greater HMW compound percentages indicate pyrogenic PAH source, while LMW compounds are indicative of petrogenic sources. Deeper samples of the same core are represented from left (surface sediments) to right (deep sediments).

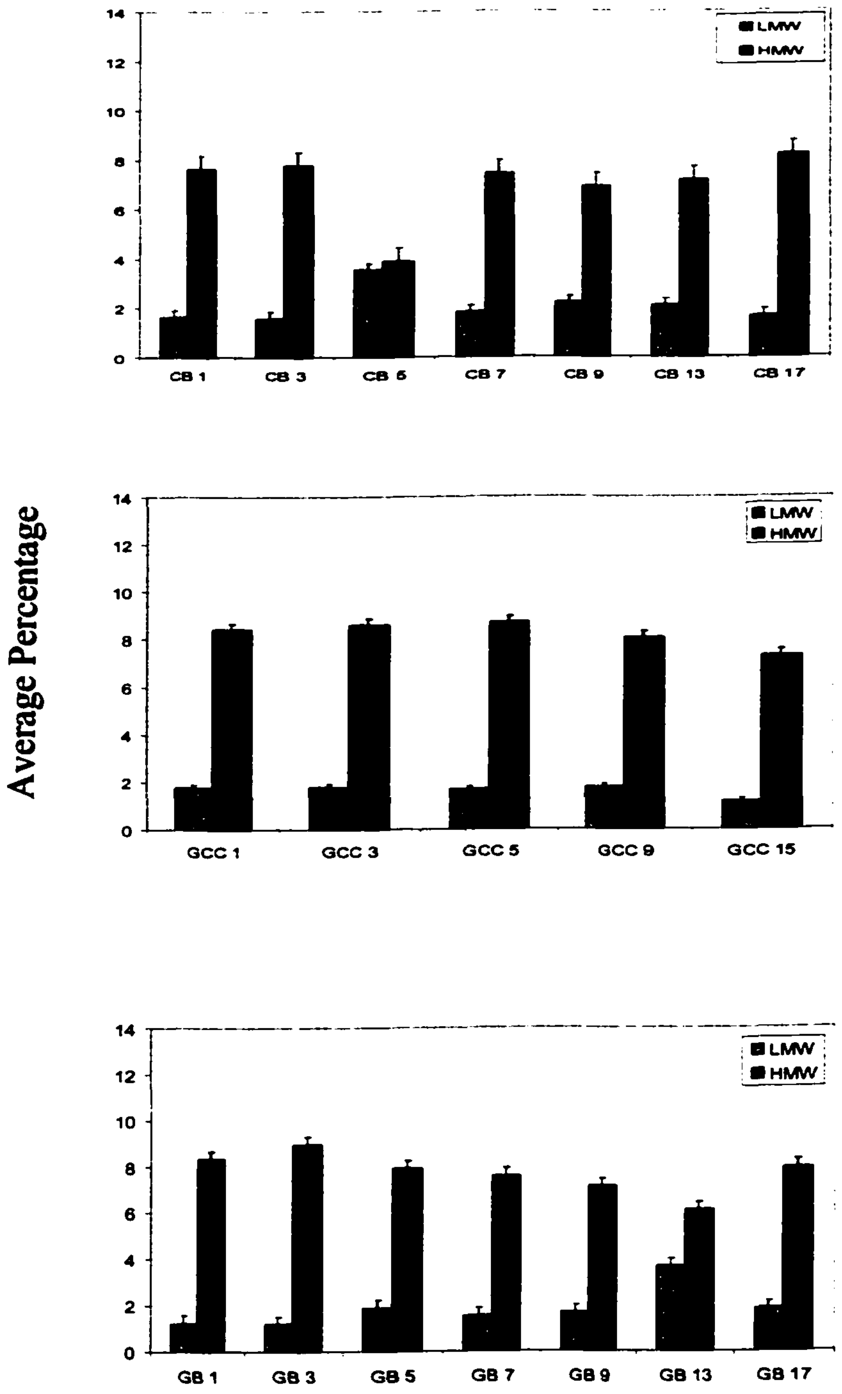

Average Percentage
14
12
10
8
6
4
2
0
LMW
HMW
CB 1
CB 3
CB 5
CB 7
CB 9
CB 13
CB 17
14
12
10
8
6
4
2
0
LMW
HMW
GCC 1
GCC 3
GCC 5
GCC 9
GCC 15
14
12
10
8
6
4
2
0
LMW
HMW
GB 1
GB 3
GB 5
GB 7
GB 9
GB 13
GB 17

Figure 2-11. Commercial and industrial site fingerprints

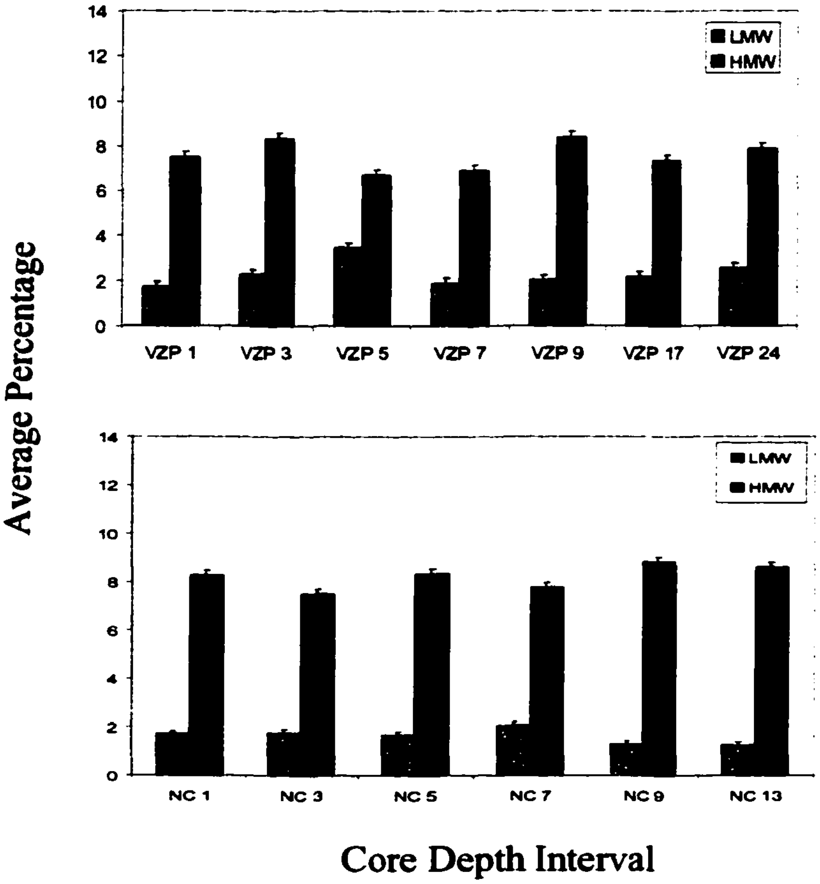
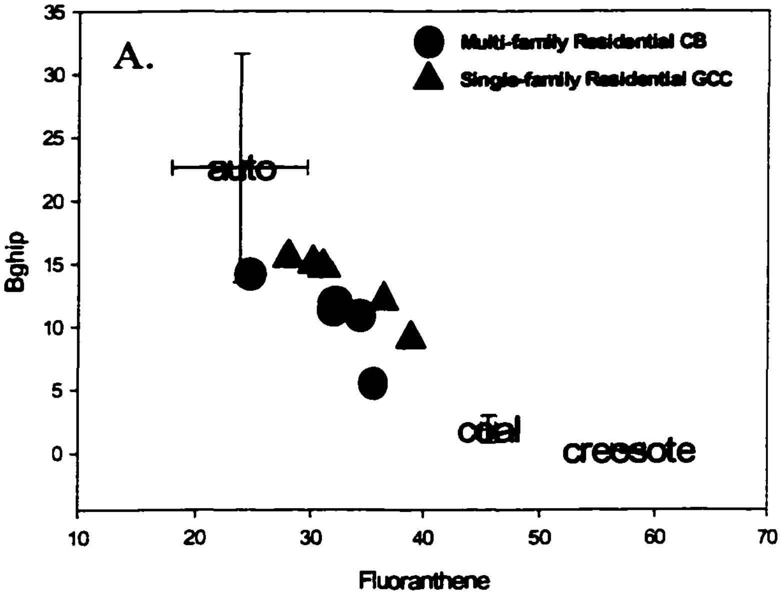

Average Percentage
14
12
10
8
6
4
2
0
■ LMW
■ HMW
VZP 1
VZP 3
VZP 5
VZP 7
VZP 9
VZP 17
VZP 24
14
12
10
8
6
4
2
0
■ LMW
■ HMW
NC 1
NC 3
NC 5
NC 7
NC 9
NC 13
Core Depth Interval

Figure 2-12. PAH sources (auto, coal, creosote) apportionment for Residential and undeveloped Elizabeth River wetland sediment cores.


A.
Multi-family Residential CB
Single-family Residential GCC
auto
coal
creosote
Bghip
35
30
25
20
15
10
5
0
10
20
30
40
50
60
70
Fluoranthene

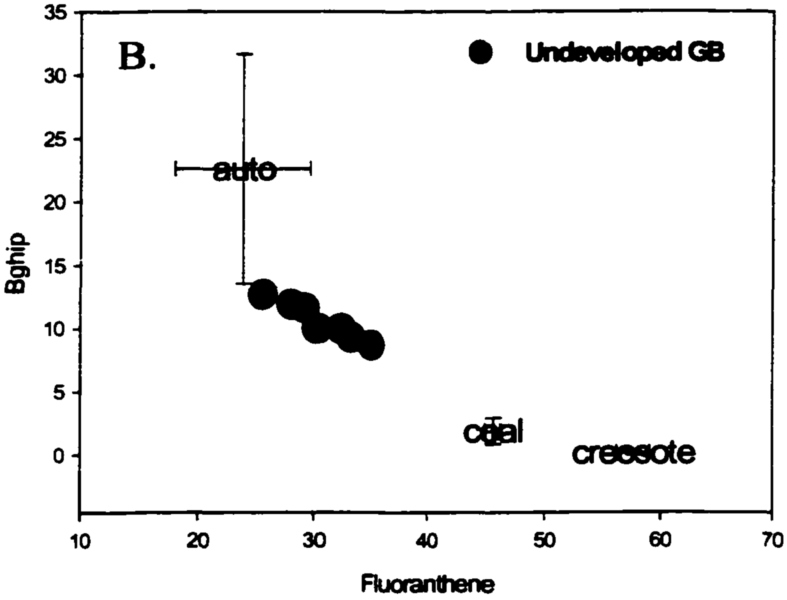
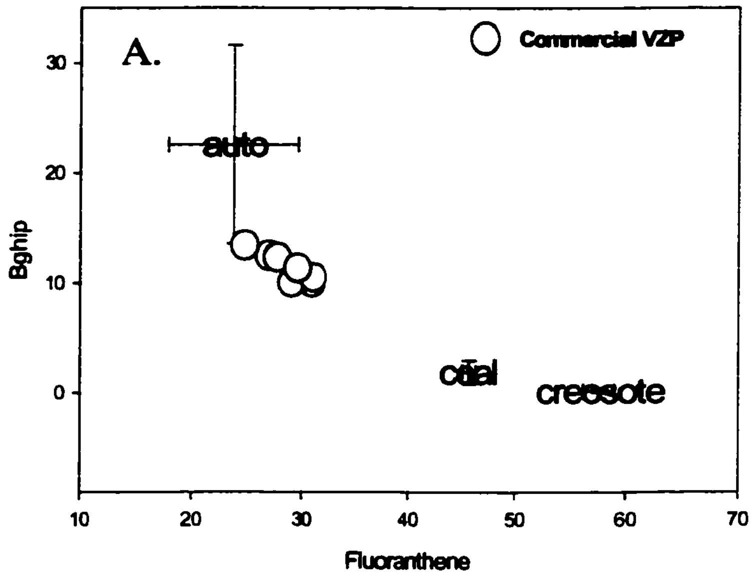

B.
Undeveloped GB
auto
coal
creosote
Bghip
35
30
25
20
15
10
5
0
10
20
30
40
50
60
70
Fluoranthene

Figure 2-13. PAH sources (auto, coal, creosote) apportionment for commercial and industrial Elizabeth River wetland sediment cores.


A.
○ Commercial VZP
auto
coal
creosote
Bghip
30
20
10
0
10
20
30
40
50
60
70
Fluoranthene

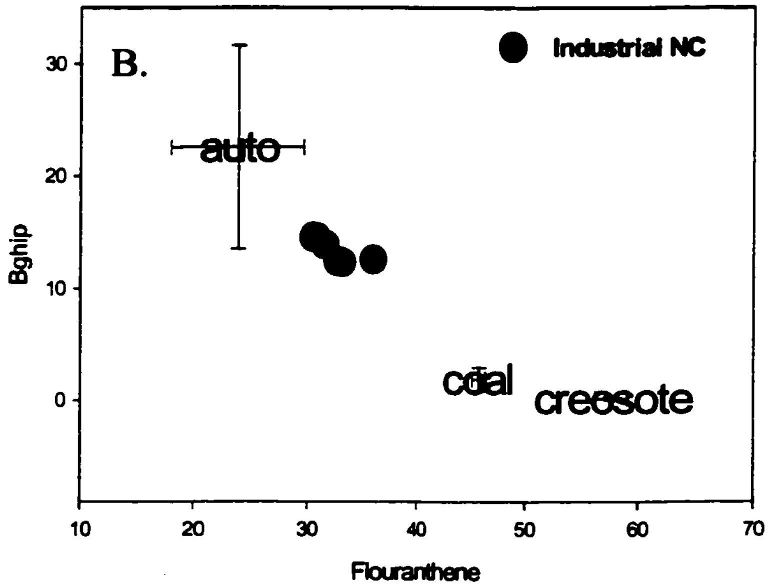
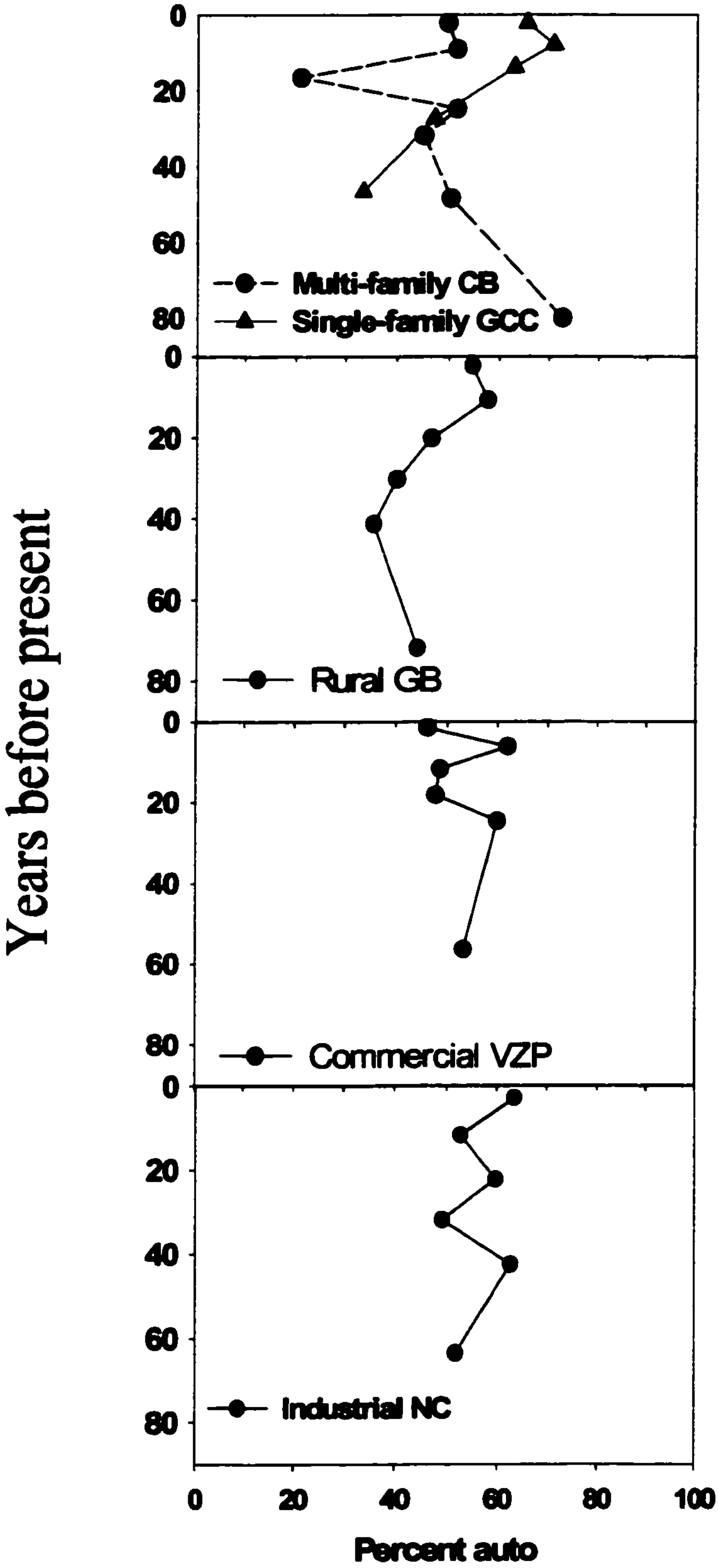

B.
● Industrial NC
auto
coal
creosote
Bghip
30
20
10
0
10
20
30
40
50
60
70
Flouranthene

Figure 2-14. Wetland sediment core plots showing change in percent automobile derived PAHs


Years before present
0
20
40
60
80
Multi-family CB
Single-family GCC
Rural GB
Commercial VZP
Industrial NC
0
20
40
60
80
100
Percent auto

Chapter 3

PAH and Wetland Distribution in the Elizabeth River Watershed

Abstract

Wetland area, adjacent land use and PAH input were assessed at the micro (site) and macro (watershed) scales in the Elizabeth River, Virginia, USA. Sixteen wetland sites were used to assess PAH storage and distribution in wetlands of the watershed. Extrapolation to the macro scale showed the largest amounts of PAHs were stored in wetlands with residential, urban and rural adjacent land uses, respectively. Wetland area rather than PAH concentration differences were responsible for storage differences between the different river branches. Urban land use had smaller areas of associated wetland and higher PAH concentration in the sediments relative to residential wetlands. Smaller urban wetlands face diminished function and possible total loss due to the effects of upland development and sea level rise (SLR). Slow degradation rates along with wetland migration and erosion result in wetlands being both sinks and sources of particle associated PAHs.

Introduction

In many urban areas, marshes have been drained for development due to the scarcity of land (Holland et al., 1995; Kusler, 1988). For this reason urban wetlands have been lost at a higher rate than rural wetlands. Moreover, further loss of urban wetlands will likely occur because adjacent development restricts their shoreward migration rendering them more susceptible to loss due to SLR (Titus, 1988).

Sea level rise occurs as a result of the global warming associated with atmospheric insulation by greenhouse gasses (Broecker, 1987; Peltier and Tushingham, 1989). Expected rates of global sea level rise vary greatly (Titus. 1988). In the Chesapeake Bay, estimates of sea level rise range between 2.6 and 3.1 mm/year (Davis, 1987; Titus, 1988). Therefore based on current measurements marshes can keep pace with sea level rise. A more chronic problem will be the loss of wetlands to migration or as a result of small increases in sea level rise (Titus,1988; Hill, 1992). In the Elizabeth River wetland loss is especially important because disposal of potentially toxic dredge spoils has occurred in marshes and shoal areas (Nichols and Howard-Strobel, 1986). Erosion of dredge spoils associated with wetlands could release contaminated sediments.

In this study, I address several of the issues put forth by Kusler (1988) regarding future strategies for dealing with urban wetlands. Possible strategies include enhancement of present wetlands, enlargement, pollution control, flood management, habitat, water quality management and offsite versus onsite restoration. The focus of this paper is on water quality management and pollution control.

To determine the status of wetlands in addition to their relationship with PAHs in the Elizabeth River wetland distribution, PAH storage, and PAH flux to wetlands were assessed at the watershed scale. We extrapolate from the site scale to the watershed scale using surface sediment data from 16 sites associated with urban, residential and rural land uses (Chapter 1 & 2). Previous research revealed a link between land use and PAH concentration in wetland surface sediments (Chapter 1). In extrapolating to the watershed scale we use global information systems (GIS), digitized wetland coverages and land use maps to analyze wetland and PAH data spatially.

The aim of this study is not to conclude whether wetland PAH storage is positive or negative as wetlands are dynamic and do not represent permanent repositories for contaminants, especially for compounds such as PAHs that do not readily degrade. However, this evaluation may provide managers with information that will help in determining whether wetlands should be protected from runoff and degradation or used for water quality enhancement. This work also gives a blueprint that can be built upon to characterize contaminant storage in other urban watersheds.

Methods

GIS

The EPA Region III land cover data set (EPALU, 1996) was used to assess land use in the Elizabeth River watershed (Figure 3-1). A wetland coverage digitized at VIMS from USGS topographical maps was used to determine wetland type, distribution and dimensions (Table 3-1). To quantify upland land use, a 200 m buffer of all salt marsh communities was made for the Elizabeth River watershed. The 200 m salt marsh buffer was then used to cut the EPA land use map resulting in a grid (10 m resolution) coverage of adjacent salt marsh upland land use. Land use categories were restricted to residential, urban (commercial and industrial) and rural to reflect the categories in the land cover map legend. The original legend had categories that were low intensity urban, high intensity urban, and rural. Comparison with other land use coverages, aerial photographs, and topographic maps, substantiates the nomenclature change. Percent land use for all salt marsh uplands was quantified using the size and number of grid cells representing each land use.

Wetland PAH Distribution

PAH wetland surface sediment concentrations were determined by random sampling of Elizabeth River salt marshes. Four replicate surface sediment (upper 1.5 cm) samples were collected from 16 wetland sites. Samples were taken within a thirteen-day period to minimize the effects of storms and associated contaminant laden runoff (Chapter 1).

Surface sediments were collected from four sites within each land use (residential, commercial, industrial and rural) category (Chapter 1). The surface sediment sites were verified visually making the categories more specific than possible with land use maps. Subsequently, the land use categories were distilled down to residential, urban and rural for this part of the research. A mean sediment PAH concentration was determined for wetlands within each of three adjacent land uses using the 4 residential, 8 urban (commercial and industrial) and 4 rural sites (Figure 3-2). Details of the sediment PAH analysis are described elsewhere (Chapter 1).

Areal concentrations of total PAH were calculated for wetlands representing each of the three adjacent land uses:

$$\text{PAH (ng/g)*Depth (cm)*dry density (g/cm}^3\text{)} = \text{PAH areal conc (ng/cm}^2\text{)} \quad (1)$$

where dry density (0.56 g/cm^3, standard error = 0.06) was the average sediment density calculated from surface sediment of nine sediment cores collected from the nine wetland core sampling sites (Chapter 2). Depth is 1.5 cm (Chapter 1). The total PAH stored in wetland surface sediments with rural, residential, and urban adjacent land uses was then calculated by multiplying the PAH areal concentration by the wetland area in each land use category. PAH concentrations were taken from Chapter 1. The PAH flux to wetlands with different adjacent land uses was also calculated as follows:

$$\text{PAH conc (ng/g)} * \text{accumulation rate } (\text{g*cm}^{-2}\text{*yr}^{-1}) = \text{PAH flux } (\text{ng*cm}^{-2}\text{*yr}^{-1}) \quad (2)$$

using a watershed sediment accumulation rate (mean = 0.188 $\text{g*cm}^{-2}\text{*yr}^{-1}$, S.E. = 0.028) obtained by averaging the accumulation rate from sediment cores used for PAH trend assessment (Chapter 2). The small standard error associated with the bulk density and accumulation rates justifies their usage for extrapolation to the watershed scale.

Results and Discussion

Watershed Land Use

On average, the Elizabeth River watershed (Figure 3-1) is comprised of 39% residential, 19% urban and 42% rural land uses. Residential and urban land uses dominate the intensely urbanized Eastern Branch and Lafayette River (Figure 3-3 A and 3-3C). The Southern Branch is dominated by urban land use in the north and rural land use in the south (Figure 3-3 D). The least urbanized of all the branches, the Western Branch, is primarily composed of residential and rural land uses (Figure 3-3B). Each river branch has a unique land use mixture that reflects the extent of urbanization and therefore potential contaminant input to wetlands.

Industrialization in the Elizabeth River is focussed in the main stem and the mouths of each river branch (Figure 3-3). Urbanization and the occurrence of associated impervious surfaces generally decreases in each branch from mouth to headwaters (Figure 3-3). The exception is the Lafayette River, which has intensive industry utilization at the mouth and along the river towards the south (Figure 3-3D). Overall, the Elizabeth River watershed is comprised of heterogeneous land use with intense urbanization in the north and increased rural acreage in the south (Figure 3-1 and 3-3). However, watershed land use is not indicative of the type of land use found adjacent to wetlands.

Wetland Characterization

Wetland area for the watershed (5.47×10^6 m^2) was 1.9 percent of the total watershed area (2.88×10^8 m^2). The Lafayette River, Western, Eastern, and Southern Branch wetland areas represented 1194 km^2, 1765 km^2, 832 km^2, and 1681 km^2, respectively. As a percentage of the total watershed wetland areas, these regions were 54% residential, 17% urban and 30% rural (Figure 3-4).

In contrast to watershed land use, residential wetlands dominate in all branches of the Elizabeth River except the Southern Branch where rural wetlands comprise the largest percentage (Figure 3-4). Most of the rural wetlands are found in the Western and Southern Branches comprising 24% of the total watershed wetland area, whereas in the urbanized Lafayette River and Eastern Branches rural wetlands only comprise 6% of the total wetland area

(Figure 3-4). Urban wetlands have the lowest percentages of all land uses comprising less than 17% of the total watershed wetland area and no more than 22 percent of wetland area in any branch (Figure 3-4). No material characterizing wetland loss in the Elizabeth River was found in the literature. Due to the small size of the wetlands and low resolution of aerial photography no estimations of wetland loss could be calculated.

PAH Assessment

The sixteen surface sediment sites were grouped and averaged resulting in residential, urban and rural PAH concentrations of 4973 ± 985, 7078 ± 584, and 3401 ± 845 ng/cm^2, respectively (Figure 3-2). These PAH concentrations were used to determine watershed scale PAH storage in Elizabeth River wetlands. At the micro scale an obvious but nonetheless important variable for assessing PAH storage in the Elizabeth River wetlands is wetland size, which ranges from 480 m^2 to 85,508 m^2. In general, the least contaminated sites (rural areas) are associated with the largest wetlands, whereas sites located in intensely urbanized areas, especially the northern watershed, had smaller wetlands. Residential wetlands had moderate sizes that were similar to one another (Table 3-1).

Total watershed wetland area and PAH concentration both affect the PAH storage in wetlands relative to land use. Overall, PAH storage in residential, urban and rural wetland surface sediments (Figure 3-5) reflects the wetland distribution, composition and area (Figure 3-4). For example, wetlands adjacent to residential land use store the largest amount of PAHs in surface sediments due to the larger wetland area. However, in comparison to the wetland distribution (Figure 3-4), PAH storage in wetland surface sediments is elevated for urban wetlands and much lower in the cleaner, rural areas (Figure 3-5), reflecting the levels of PAH contamination in these areas. Consequently, slight increases in wetland size in more contaminated, urban wetlands would result in much greater PAH storage. Overall, most of the PAHs are found in the Western Branch, Southern Branch, Lafayette River and Eastern Branch respectively (Figure 3-6).

PAH Flux to Wetlands

When averaged, the total watershed PAH flux to wetlands of the Elizabeth River is 1.08 g/(m^{2*}yr). PAH fluxes to residential, rural, and urban wetlands are 1.06 ± 0.18, 0.72 ± 0.10 and 1.46 ± 0.16 g/(m^{2*}yr), respectively, with the only significant difference occurring between urban and rural fluxes as determined by the Fisher Pairwise comparison test (Figure 3-7). Compared to direct atmospheric deposition of PAHs, which was ~10^{-4} g/(m^{2*}yr) (Dickhut & Gustafson, 1995) in the Chesapeake Bay PAH, input to wetlands due to land-derived runoff is several orders of magnitude (10,000x) higher (Figure 3-7). This is expected as runoff, focuses atmospheric deposition from a larger surface area and incorporates it into marsh sediment. It may also include PAHs from oil spillage, tire and brake wear, and direct deposition of automobile emissions not included in atmospheric deposition.

Wetland accumulation and Erosion

Sea level rise is a major threat to wetland survival in urbanized watersheds, where wetland shoreward migration is negated by developed adjacent land use (Titus, 1988). A conceptual model was created to assess the outcome of wetland loss and migration due to sea level rise. The model assumed the rate of erosion is equal to the rate of shoreward migration in addition to a constant sediment PAH concentration throughout the wetland. Thus, PAH concentration on eroding sediment is equal to concentration on accreting sediment. Migrating marshes, with constant PAH concentrations, are “dynamic sinks” of PAHs that store a constant amount of contaminant (Figure 3-8B)

Migrating wetlands due to development are not allowed to migrate into adjacent uplands (Figure 3-8A). Erosion occurs at the same rate as the migrating wetland however, no concomitant wetland building takes place at the landward side. Hence, wetland surface area, as it erodes becomes increasingly smaller resulting in less of the constant PAH flux from uplands being scavenged. PAH accumulation in the shrinking wetland decreases as a result of wetland loss until runoff is released directly into the aquatic system (Figure 3-8A). The non-migrating wetland, as it erodes becomes a net source of PAHs to the aquatic system.

In wetlands with variable PAH concentrations at depth, where shore line erosion is equal to wetland marsh accretion, the concentration of the eroding and accreting sediment is no longer constant. Wetland sites where PAH concentrations decrease from past to present (higher PAH concentrations at depth) have PAH erosional flux that is greater than PAH accreting flux of PAHs from adjacent land use (Figure 3-9B). Hence, they are net sources for PAHs. As deeper higher concentration sediment is eroded input of lower concentration material occurs on the wetland surface. The opposite effect is true of sites with increasing PAH concentration from past to present, they are net sinks of PAHs

When assessing Elizabeth River wetlands in the context of this model the constant PAH concentration assumption is not valid. Sediment core trends in the Elizabeth River were decreasing or static from past to present (Chapter 2). Therefore, deeper sediments in Elizabeth River wetlands have higher PAH concentrations. These sites will behave like net sources to the aquatic system. In addition, over 75 % of Elizabeth River wetlands have developed uplands (residential, commercial or industrial) and are not able to migrate. This exacerbates the problem because the highest concentration sites associated with commercial and industrial land uses are not migrating regardless of their historic PAH trend. The majority of Elizabeth River wetlands may release all of their stored PAHs with time.

In contrast most developing watersheds have an increasing PAH concentration from past to present (Metre et al., 2000; Latimer and Quinn, 1996) and are therefore net sinks for PAHs. Clearly the flux of PAHs in or out of wetlands does not drive watershed management of PAHs. However increasing wetland area in appropriate watersheds would be beneficial. Increasing PAH levels are not acceptable and should be lowered. Although Elizabeth River wetlands are sources it is a more important to focus on the evidence that PAH concentrations are not increasing in the watershed. These models are useful as they show the dynamic nature of wetlands and how they effect storage of contaminants and are only apart of the management puzzle in any watershed.

Conclusions

Elizabeth River wetlands were categorized by adjacent land use including residential, rural and urban. PAH concentrations in wetland surface sediment revealed significantly higher PAH concentrations in urban relative to rural land uses. GIS was used in conjunction with specific wetland measurements to spatially characterize wetland area, location, and PAH storage at the watershed scale. Extrapolation to the watershed scale elucidated spatial ramifications associated with heterogeneous wetland, land use, and PAH distribution in the watershed. Specifically, the GIS analysis indicated urban wetland area was disproportionately low, rural wetlands were heterogeneously distributed and residential wetlands dominated percent area in all river branches.

Fluxes of PAHs to Elizabeth River wetland sediments calculated using watershed accretion rates and surface sediment concentrations were exponentially higher than direct atmospheric deposition. Higher fluxes were attributed to closer proximity to sources and increased impervious surface coverage in urban, residential and rural land uses respectively.

Urban wetlands are associated with the greatest PAH flux relative to rural and residential wetlands. However, spatial GIS measurements indicate rural wetlands, which are primarily located in the Southern and Western branches of the Elizabeth River, are most likely to survive SLR. The greatest threat to PAH storage from land-derived runoff in the Elizabeth River is dwindling wetlands adjacent to urban land uses.

Efforts to address the problem should focus on increasing marsh area and creating buffer zones to allow for marsh shoreward migration. If not addressed models show that the Elizabeth River wetlands could become a major source of PAHs and other stored contaminants in the long term. Wetlands without anywhere to migrate may simple be totally eroded resulting in direct release of runoff into the aquatic system. At present Elizabeth River are minor source of PAHs to the aquatic system because the historical sediment being eroded has a higher concentration than present accumulating sediments. This could become even greater problem in the Elizabeth River if dredge material begins to erode.

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Titus, G. T. 1988. Sea level rise and wetland loss: an overview. EPA-230-05-86-013 Greenhouse Effect Sea Level Rise and Coastal Wetlands. 1-33.

Table 3-1. Dimensions of the 16 wetland sediment sites used for extrapolating to the watershed scale.

Land use	**Site**	**Width (m)**	**Area (m^2)**	**Length (m)**
Residential	cc	68.00	19090	280.74
Residential	cb	20.00	16235	811.75
Residential	gill	45.00	17761	394.69
Residential	lvr	52.50	19090	363.62
Rural	dclp	96.67	46400	480.00
Rural	gblp	71.67	85508	1193.13
Rural	gb	20.00	7473	373.65
Rural	lrp	43.33	4801	110.79
Commercial	odu	20.00	16235	811.75
Commercial	vzp	96.67	45041	465.94
Commercial	pce	15.00	7900	526.67
Commercial	mcj	33.33	5116	153.48
Industrial	sc	20.00	6726	336.30
Industrial	nc	75.00	21824	290.99
Industrial	mc	26.67	9273	347.74
Industrial	sbc	33.33	14961	448.83

Figure 3-1. Locations of the Elizabeth River study site and wetland land use at the watershed scale.

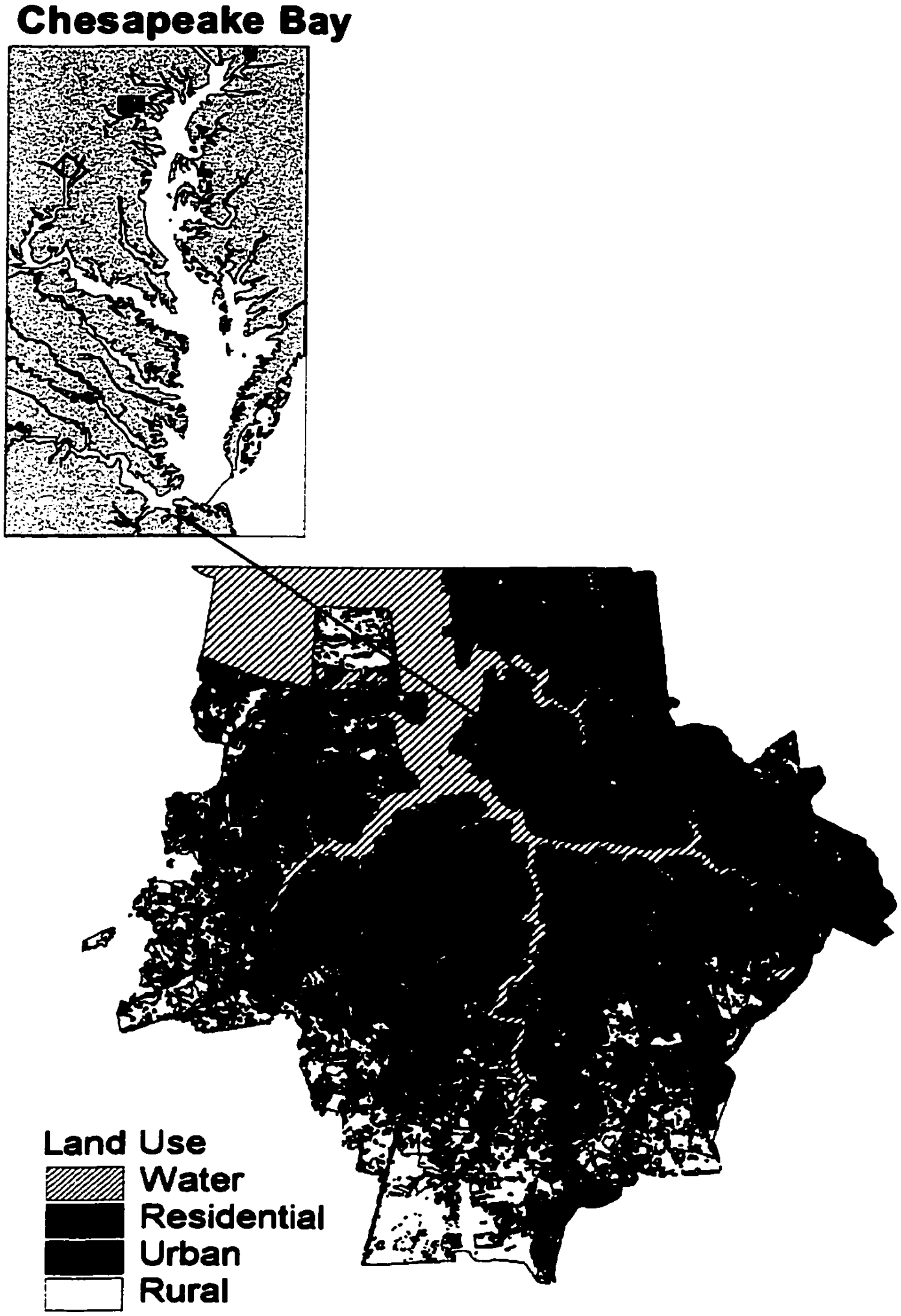


Figure 1 Wetland land use at the watershed scale.

Figure 3-2. Total PAH concentration for each type of wetland land use sediment.

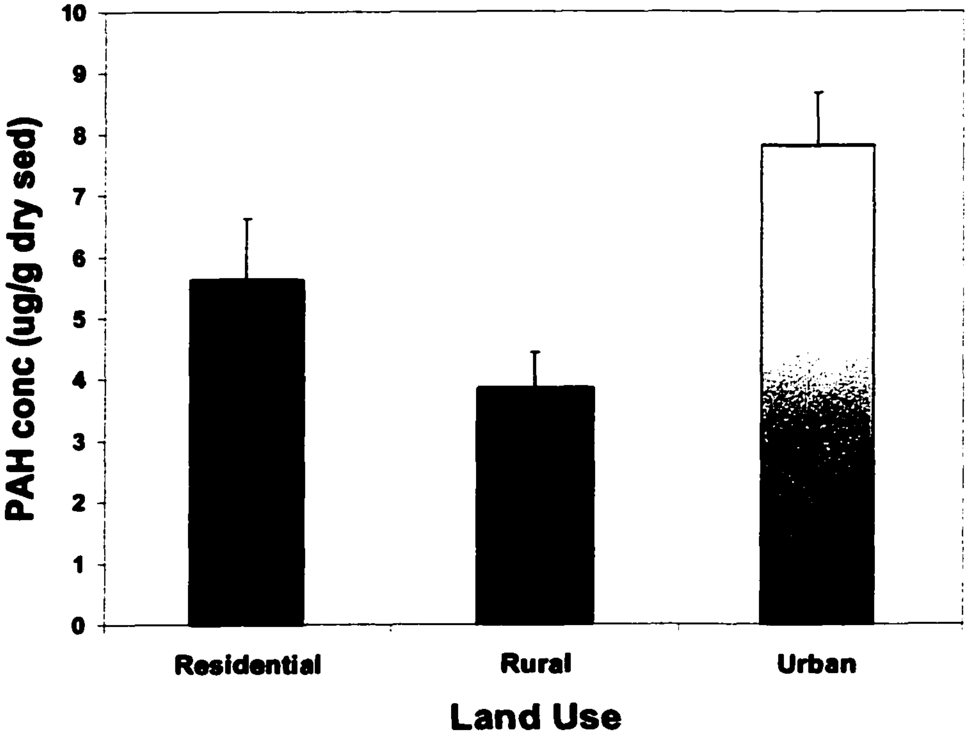
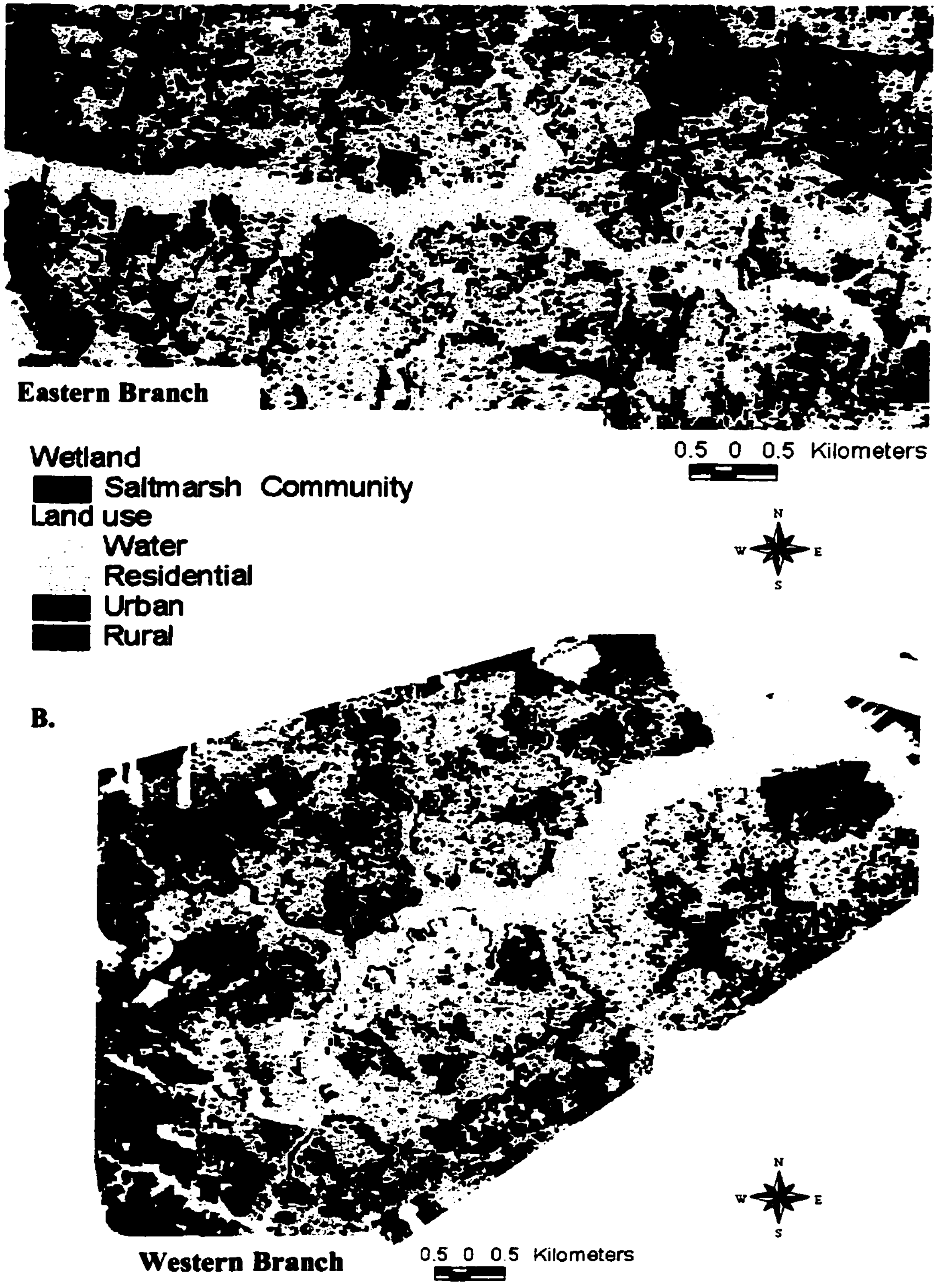
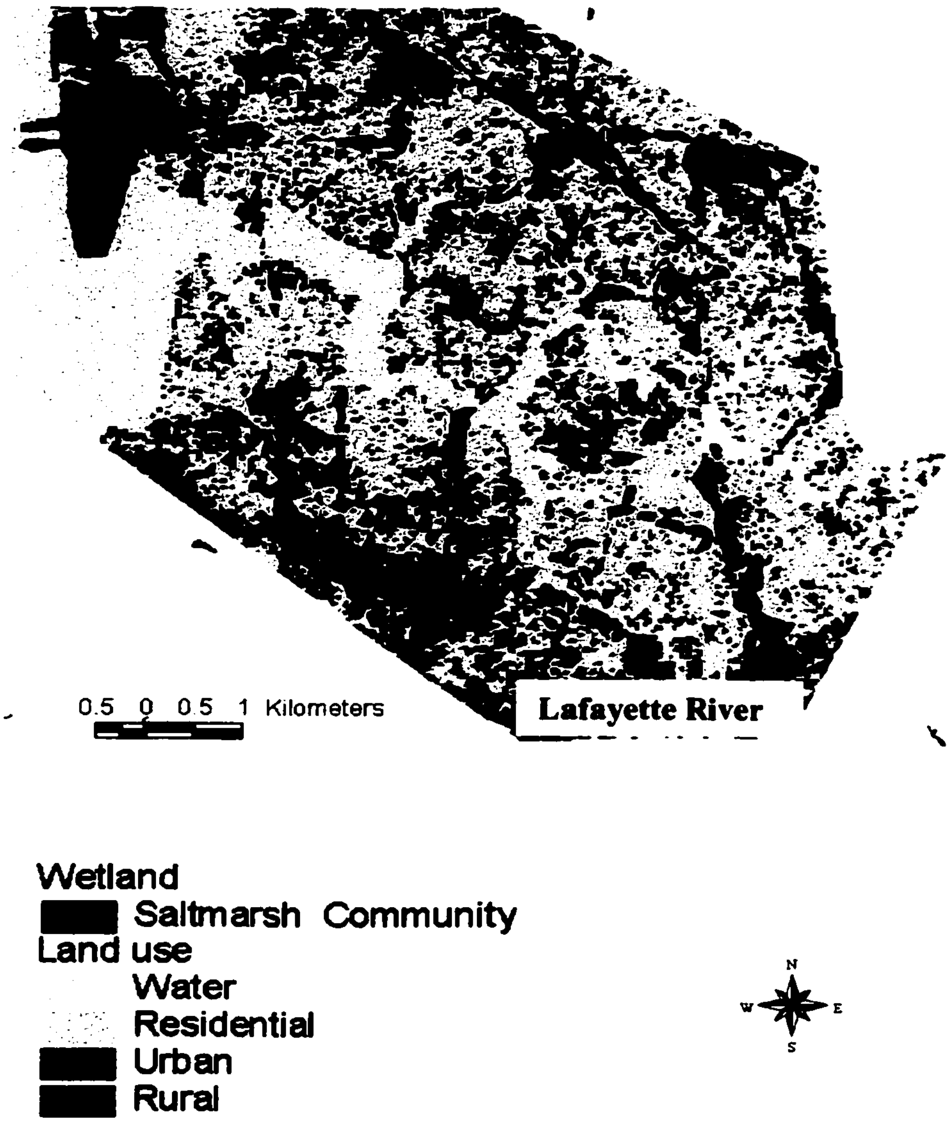

10
9
8
7
6
5
4
3
2
1
0
PAH conc (ug/g dry sed)
Residential
Rural
Urban
Land Use

Figure 3-3. Land use and wetland distribution for the Eastern (A) and Western (B) Lafayette (C) and Southern (D) Branches of the Elizabeth River.


Eastern Branch
Wetland
Saltmarsh Community
Land use
Water
Residential
Urban
Rural
0.5 0 0.5 Kilometers
N
W
E
S
B.
Western Branch
0.5 0 0.5 Kilometers
N
W
E
S

c.


0.5 0 0.5 1 Kilometers
Lafayette River
Wetland
Saltmarsh Community
Land use
Water
Residential
Urban
Rural
N
W
E
S

D.

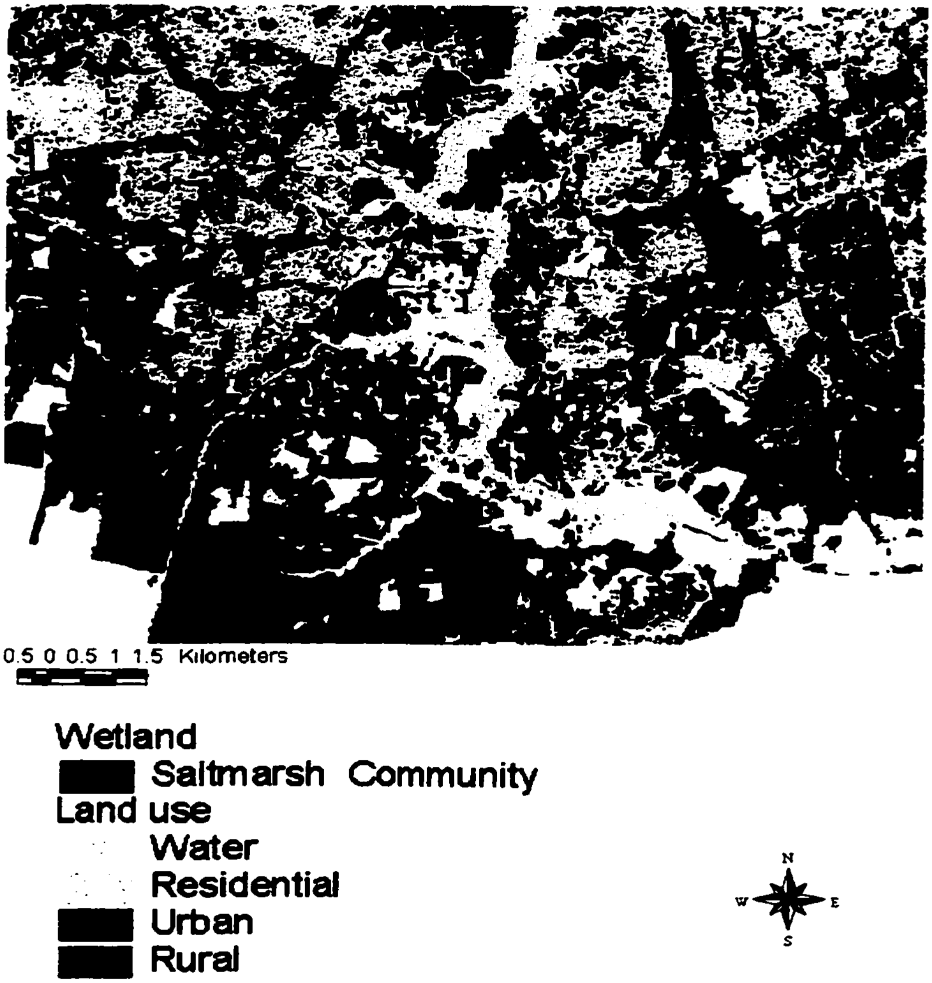

0.5 0 0.5 1 1.5 Kilometers
Wetland
Saltmarsh Community
Land use
Water
Residential
Urban
Rural
N
W
E
S

Figure 3-4. Percent wetland categorized by land use and river branch. Both land use and branch percentages add up to 100%.

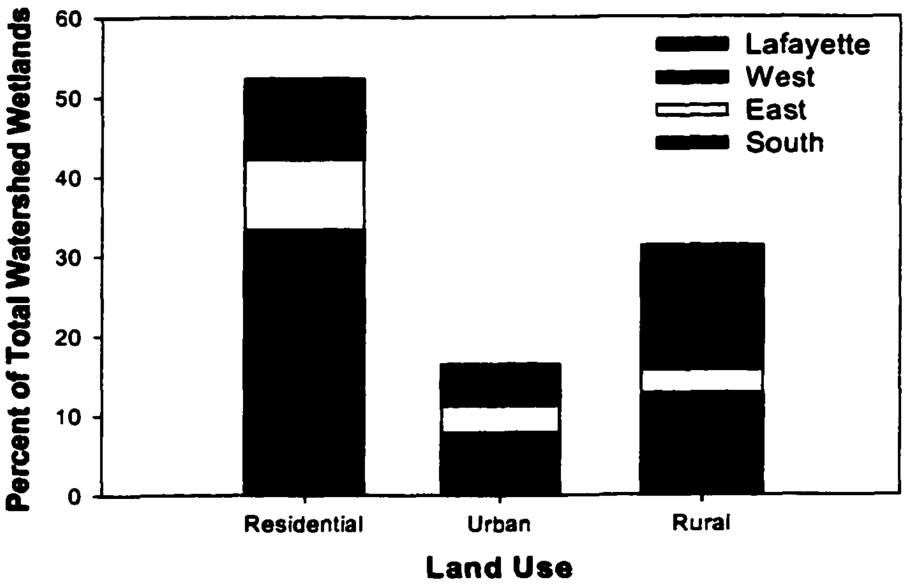

Percent of Total Watershed Wetlands
0
10
20
30
40
50
60
Lafayette
West
East
South
Residential
Urban
Rural
Land Use

Figure 3-5. Percentage total watershed PAH categorized by land use and river branch. Both land use and branch percentages add up to 100%.

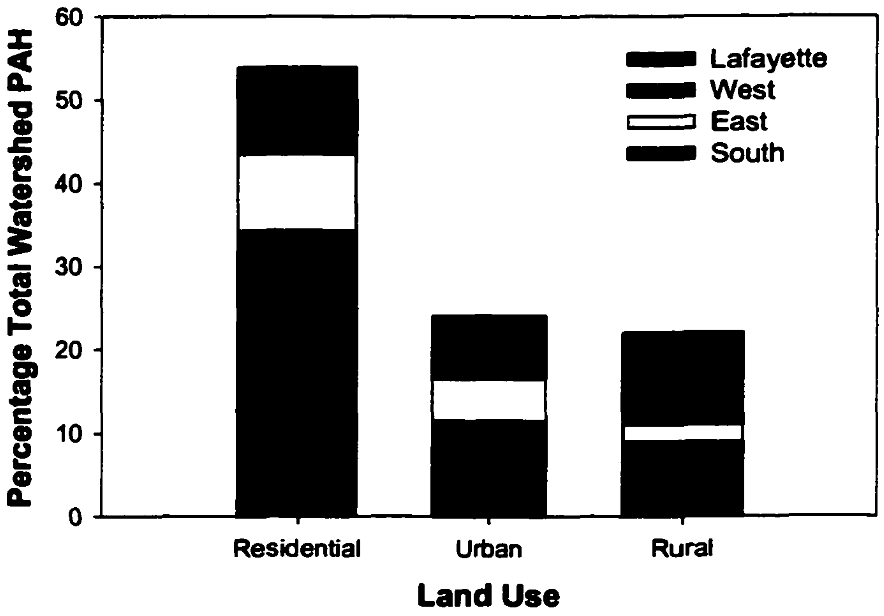

Percentage Total Watershed PAH
0
10
20
30
40
50
60
Lafayette
West
East
South
Residential
Urban
Rural
Land Use

Figure 3-6. Total weight PAH found in Elizabeth River wetland surface sediments.

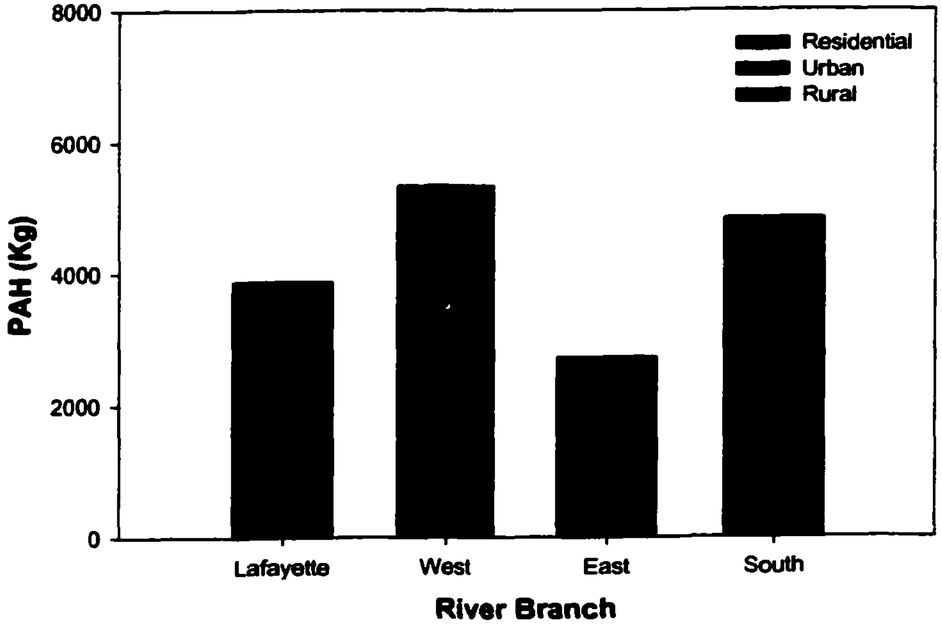

8000
6000
4000
2000
0
PAH (Kg)
Residential
Urban
Rural
Lafayette
West
East
South
River Branch

Figure 3-7 Runoff flux for urban, rural and residential land use.

Runoff Flux

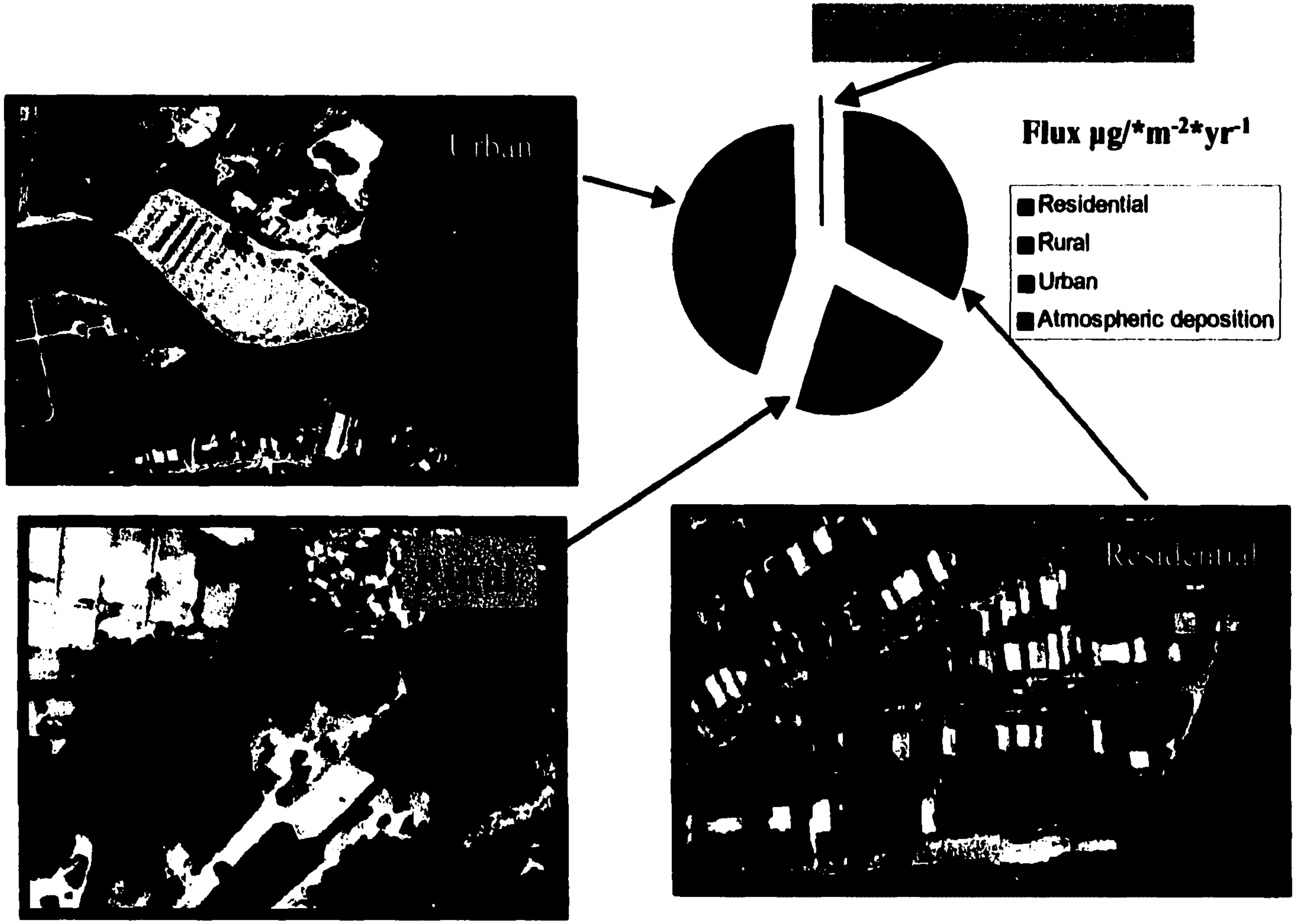

Flux µg/*m^{-2}*yr^{-1}
■ Residential
■ Rural
■ Urban
■ Atmospheric deposition
Urban
Residential

Figure 3-8. Arrows represent flux of PAHs into and out of marsh. A. Marsh with developed uplands that restrict migration. Marsh surface shrinks due to erosion resulting in decreasing PAH sediment storage. B. Marsh with undeveloped uplands capable of migrating shoreward in response to sea level rise. Migrating marshes dynamically store a static amount of PAHs.

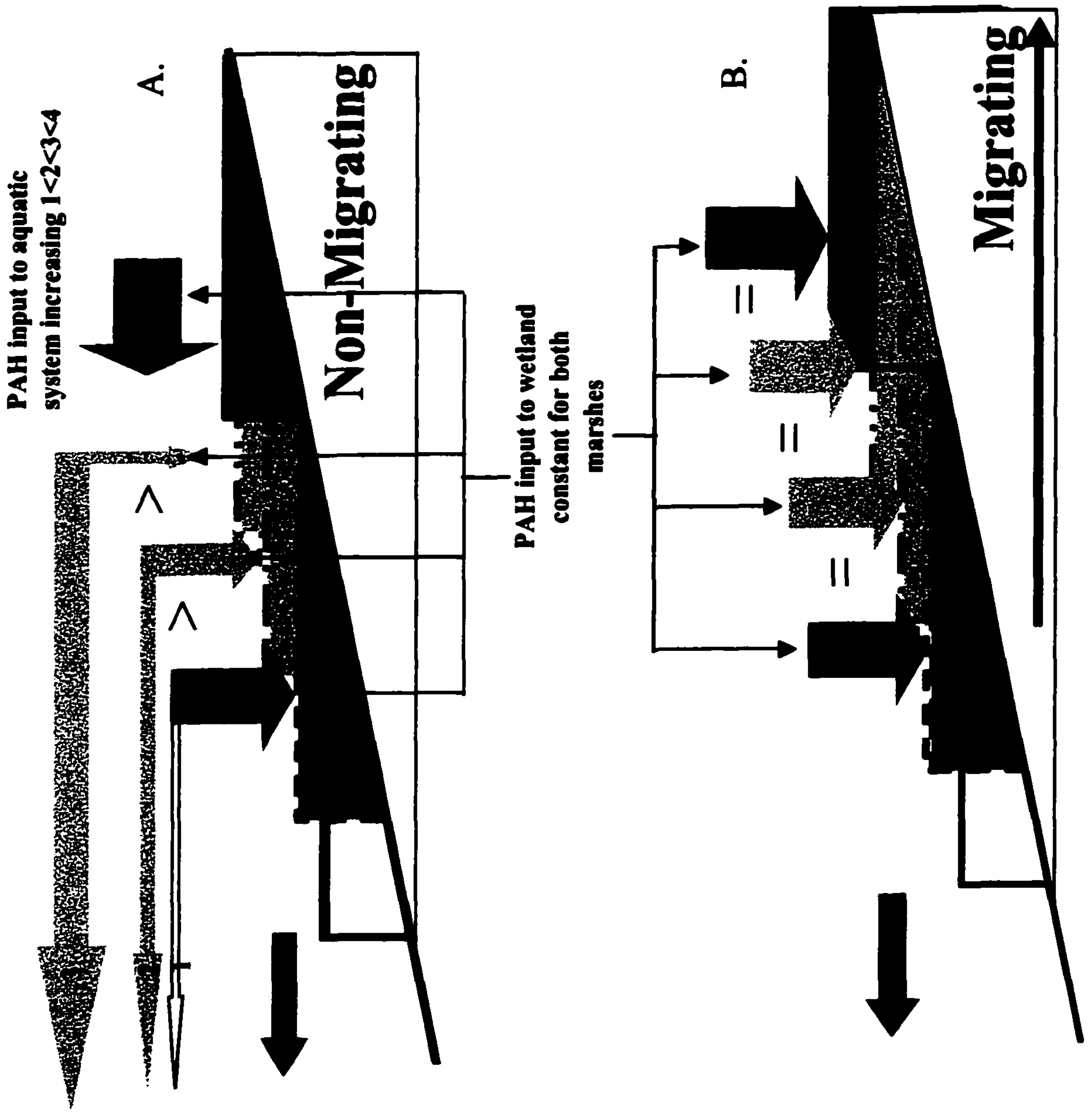
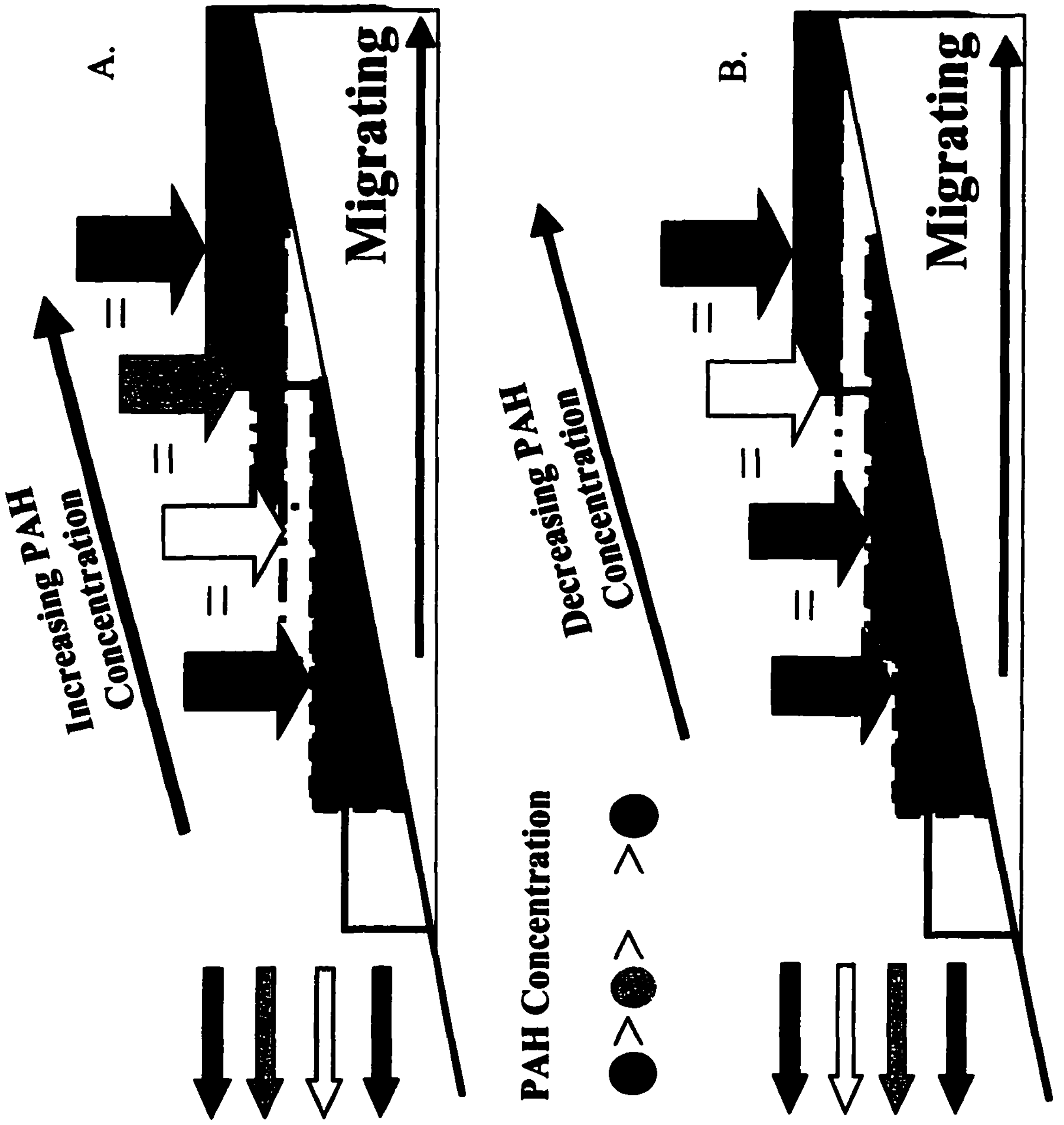

PAH input to aquatic system increasing 1<2<3<4
A.
Non-Migrating
>
>
PAH input to wetland constant for both marshes
B.
=
=
=
Migrating

Figure 3-9 Arrows represent variable PAH flux into and out of the marsh. Migrating marsh modeled with increasing and decreasing PAH trends. Marshes with variable concentration are sinks (A) or sources (B) of PAHs to the aquatic system.


A.
Increasing PAH Concentration
Migrating
=
=
=
B.
Decreasing PAH Concentration
Migrating
=
=
=
PAH Concentration
● > ● > ○ > ●

Appendices

Appendix I

Residential and Rural/undeveloped Surface Sediment PAH concentration ng/g dry sediment

2-methanth	1-methanth	1-methphen	fluoranth	pyrene	b(a)a	chry	b(b)f	b(k)f	b(e)p	b(a)p	i(123cd)p	b(ghi)p	Total		
4.28	18.73	18.93	214.15	192.03	90.19	83.95	128.87	44.16	71.13	75.77	92.26	76.67	1287.84		
9.59	42.77	41.69	459.04	405.18	182.70	181.32	419.95	138.48	225.92	224.15	214.30	195.37	3113.57		
7.17	23.11	24.97	251.08	225.97	116.52	124.57	226.64	76.59	122.91	135.09	158.60	121.18	1828.03		
5.50	25.09	23.66	255.79	230.28	108.93	119.80	183.62	68.45	105.23	113.01	115.92	107.89	1662.51		
12.08	36.19	30.21	791.87	621.73	304.39	283.78	481.59	149.37	218.44	324.06	304.12	278.99	4094.84		
18.32	88.69	101.21	724.07	666.64	332.85	337.36	666.27	238.17	356.33	388.41	380.39	312.06	5171.55		
13.84	77.87	61.92	603.67	565.61	284.17	291.58	544.29	179.92	289.89	302.06	290.04	266.67	4197.59		
74.50	132.82	114.71	1374.30	1302.94	671.62	583.09	1064.27	339.97	599.67	692.00	826.19	629.62	9703.08		
40.04	112.23	118.14	1199.04	1092.98	463.58	421.10	1445.86	457.79	759.71	561.86	825.54	539.49	9052.32		
48.90	81.94	66.19	1103.61	919.37	430.31	317.07	1190.22	340.10	633.68	539.78	668.36	555.62	7673.66		
30.55	71.60	53.92	956.15	824.23	314.74	248.14	981.05	277.27	563.54	445.08	545.07	441.02	6391.76		
83.53	161.02	131.47	1847.83	1679.99	1034.72	848.31	1475.82	502.36	783.53	1062.30	933.93	806.14	12737.74		
40.11	97.73	80.59	1310.48	1152.12	614.82	524.88	1004.16	322.83	505.30	649.56	657.35	485.80	8237.19		
37.39	142.57	127.18	874.47	803.79	395.45	354.99	809.23	251.55	443.97	450.88	544.00	481.16	6520.75		
24.56	57.99	56.11	720.72	671.39	360.69	327.04	592.30	197.32	322.84	400.85	477.30	352.43	5083.56		
3.77	18.11	21.74	223.33	176.42	69.26	81.46	205.96	63.09	114.15	89.65	85.97	79.53	1400.20		
2.93	17.04	17.20	209.11	156.65	57.81	59.19	183.72	55.38	106.03	72.18	82.55	69.21	1196.88		
5.88	18.29	19.74	247.89	205.35	77.50	66.11	229.70	68.02	130.95	83.83	91.78	83.66	1466.76		
9.57	9.50	10.54	231.44	214.07	128.43	172.48	330.03	107.89	176.44	149.63	150.24	127.61	1901.48		
12.19	15.51	16.57	389.85	355.81	242.17	347.80	752.63	248.48	394.96	329.78	394.38	303.64	3956.58		
9.24	25.02	31.18	590.74	484.38	178.59	249.57	526.28	167.77	264.00	213.26	249.36	179.84	3547.92		
9.49	12.81	10.52	245.50	213.93	133.77	209.63	331.77	96.79	150.73	153.15	234.84	163.31	2055.74		
5.11	14.56	13.37	215.79	188.79	69.17	61.59	164.13	50.84	92.80	74.34	66.50	62.94	1193.74		
49.85	63.34	38.95	788.82	950.36	1004.32	986.97	1616.22	534.86	716.51	823.79	836.67	548.85	9409.27		
21.00	57.57	71.34	852.41	768.82	390.38	357.07	923.38	322.93	473.40	449.61	480.51	384.99	6094.85		
13.42	36.26	38.15	747.67	759.07	316.38	298.70	667.92	226.74	334.74	333.87	305.98	239.78	4663.23		
16.06	75.07	77.20	738.94	682.50	334.39	346.03	684.45	233.50	385.04	388.48	422.14	388.40	5439.11		
12.10	77.10	67.66	683.21	629.60	283.92	302.65	590.96	200.30	330.50	326.48	342.56	279.90	4693.97		
28.42	86.95	73.52	733.85	684.66	358.25	299.80	651.74	200.83	366.71	400.07	598.63	415.73	5604.18		

fluor = fluorene, 1-methfluor = 1-methylfluorene, phen = phenanthrene, 2-methphen = 2-methylphenanthrene, anth = anthracene, 1-methanth = 1-methylanthracene, fluoranth = fluoranthene, b(a)a = benzo(a)anthracene, chry = chrysene, b(b)f = benzo(b)fluoranthene, b(k)f = benzo(k)fluoranthene, b(e)p = benzo(e)pyrene, b(a)p = benzo(a)pyrene, I(1,2,3,c,d)p = indeno(1,2,3,c,d)pyrene, b(ghi)p = benzo(ghi)perylene

Appendix II

Commercial and Industrial Surface Sediment PAH concentration ng/g dry sed

	fluor	1-methfluo	phen	anth	2-methphe	2-methant	1-methant	1-methphe	fluoranth	pyrene	b(a)a	chry	b(b)f	b(k)f	b(e)p
odu1	28.84	20.22	301.68	34.59	84.05	11.97	38.65	34.29	892.45	748.95	307.44	313.99	888.01	258.83	467.75
odu2-1	28.79	17.59	301.16	31.62	73.02	9.28	37.98	39.74	1366.35	1100.18	369.60	428.97	969.68	308.81	504.59
odu3-1	23.86	14.24	255.23	41.11	76.56	13.34	42.39	43.51	986.56	868.89	333.38	378.02	750.06	240.64	401.96
odu4-1	16.87	8.31	218.00	43.40	56.20	20.26	34.57	27.14	863.14	742.91	367.86	306.56	523.74	133.02	285.19
mcj3	28.56	16.16	377.37	73.61	103.71	22.69	67.00	65.29	1476.30	1237.29	584.93	568.06	1407.54	448.78	752.51
mcj4	27.03	13.52	197.18	34.72	57.78	10.80	46.25	35.52	635.11	508.28	251.81	248.97	654.93	201.72	361.45
mcj5	40.22	22.82	341.53	58.65	106.03	18.08	67.40	81.22	1269.05	1097.39	423.66	494.49	947.14	304.53	553.30
mcj7	11.65	5.35	94.25	16.38	23.96	4.41	15.77	16.57	319.22	275.87	116.87	125.42	243.82	79.74	139.59
vzp1	55.29	33.49	447.43	99.65	146.58	33.49	91.51	81.32	1568.11	1382.17	719.44	677.38	1050.37	377.21	572.73
vzp4	58.35	25.82	532.84	113.95	148.82	41.81	90.55	759.51	1773.52	1485.53	756.39	659.85	873.02	311.91	476.95
vzp5	52.69	34.30	449.54	88.40	143.71	25.60	81.17	76.85	1326.26	1214.06	607.56	573.92	1037.68	346.18	597.02
vzp6	56.12	38.58	437.08	87.90	136.44	26.75	71.62	74.38	1536.87	1380.72	578.33	520.36	1056.79	355.11	571.37
pce1	96.53	40.06	500.20	194.66	132.92	55.65	96.69	76.99	2387.77	1967.19	736.29	709.34	2295.49	661.12	1223.36
pce3	112.62	47.88	598.80	258.27	154.30	75.83	104.29	77.20	2327.52	1889.26	803.53	1029.73	3510.92	1017.87	1813.51
pce4	110.13	43.46	500.72	248.19	387.91	347.11	246.84	790.51	1519.79	1612.29	667.96	595.23	2448.51	709.09	1329.84
pce5	84.57	32.89	370.30	228.70	115.35	70.55	81.01	59.82	1467.67	1249.85	529.97	432.32	1930.59	520.30	1045.53
sc3	75.25	34.65	358.54	203.91	112.11	59.76	89.32	69.56	1454.62	1236.72	578.98	638.74	1880.38	622.64	1057.76
sc6	97.15	40.98	406.35	200.77	129.61	60.65	104.81	81.94	1458.84	1229.33	602.51	648.47	2108.98	711.66	1140.59
nc1	85.39	30.88	444.11	146.13	91.71	52.39	80.88	71.29	1178.09	995.41	543.31	672.84	874.19	291.41	508.23
nc3	29.92	13.09	192.76	97.10	64.09	40.50	43.17	52.12	653.95	645.94	347.69	483.86	560.94	193.46	332.25
nc5	48.64	44.63	406.05	240.13	122.22	94.37	91.06	79.41	1543.25	1480.69	878.06	1132.49	1047.04	367.40	577.32
nc6	47.13	24.75	713.72	196.05	264.24	113.13	191.58	155.72	3551.51	3508.19	2069.82	1581.08	2564.03	734.19	1537.63
mc3	25.32	78.54	151.90	38.72	37.65	9.49	37.14	31.03	621.65	487.24	251.51	271.67	623.45	196.12	339.30
mc4	20.59	37.72	254.78	59.03	42.26	11.15	22.10	24.13	737.39	585.10	295.11	320.58	644.70	211.74	343.99
mc5	19.56	35.89	101.89	17.51	19.22	3.26	11.64	16.39	356.41	267.62	97.32	118.70	286.35	93.22	155.37
mc8	26.99	22.21	156.34	32.16	64.73	10.36	36.65	37.04	455.76	396.51	166.89	159.21	369.42	115.06	197.51
sbc1	57.59	28.83	269.76	73.58	87.49	20.83	54.60	47.96	800.94	698.00	293.11	244.12	407.54	124.48	223.60
sbc2	73.52	45.46	385.37	104.77	160.08	33.40	94.59	92.07	857.61	757.59	344.31	307.16	590.78	184.15	331.47
sbc3	56.91	30.30	338.89	76.87	116.48	22.62	87.61	61.86	772.89	689.40	359.30	310.85	619.63	190.90	338.98
sbc4	47.64	22.73	251.43	48.46	79.25	13.47	48.85	49.89	541.12	473.17	228.22	208.57	423.23	137.09	233.49

fluor = fluorene, 1-methfluor = 1-methylfluorene, phen = phenanthrene, 2-methphen = 2-methylphenanthrene, anth = anthracene, 1-methanth = 1-methylanthracene, fluoranth = fluoranthene, b(a)a = benzo(a)anthracene, chry = chrysene, b(b)f = benzo(b)fluoranthene, b(k)f = benzo(k)fluoranthene, b(e)p = benzo(e)pyrene, b(a)p = benzo(a)pyrene, I(1,2,3,c,d)p = indeno(1,2,3,c,d)pyrene, b(ghi)p = benzo(ghi)perylene

Appendix III

Elizabeth River Surface Sediment total organic carbon (TOC) (g C/g sed)

Sites	Carbon		Sites	Carbon		Sites	Carbon		Sites	Carbon
cc1-1	9.25		dclp1-1	16.40		mc8-1	11.00		mcj5-1	13.48
cc1-2	9.85		dlpp1-2	15.94		mc8-2	10.50		mcj5-2	14.20
cc2-1	10.94		dclp3_1	13.65		mc4-1	9.61		mcj7-1	5.80
cc2-2	10.57		dclp3_2	13.91		nc1-1	13.20		mcj7-2	5.31
cc3-1	12.96		dclp4-1	14.37		nc3-1	10.47		vzp1-1	6.34
cc3-2	12.44		dclp4-2	13.92		nc4-1	6.28		vzp1-2	6.41
cc6-1	10.27		dclp5-1	11.98		nc6-1	13.69		vzp2-1	6.09
cc6-2	10.76		dclp5-2	11.57		nc5-1	10.32		vzp3-1	8.08
cb2-1	17.14		gb1-1	18.02		sbc1-1	12.33		vzp4-1	6.35
cb2-2	17.93		gb1-2	19.28		sbc2-1	12.39		vzp5-1	6.92
cb3-1	15.10		gb2-1	17.81		sbc3-1	15.68		vzp6-1	7.32
cb3-2	12.07		gb2-2	18.37		sbc4-1	12.27			
cb5-1	12.24		gb4-1	14.32		sbc5-1	16.22			
cb5-2	10.35		gb5-1	12.86		odu1-1	3.02			
cb1-1	13.82		gb6-1	21.71		odu1-2	2.91			
cb1-2	14.06		pce1-1	8.27		odu2-1	4.14			
cb4-1	13.26		pce3-1	7.20		odu2-2	2.97			
cb4-2	16.83		pce4-1	7.98		odu3-1	4.34			
gill1-1	13.13		pce5-1	8.73		odu3-2	3.53			
gill1-2	13.32		gblp1-1	25.00		odu4-1	5.00			
gill2-1	11.97		gblp2-1	25.22		odu4-2	3.95			
gill2-2	11.99		gblp3-1	25.70		lp2-1	13.48			
gil5-1	14.03		gblp4-1	24.64		lp2-2	14.31			
gill5-2	14.12		sc3-1	7.82		lp4-1	12.22			
gill6-1	15.22		sc3-2	8.06		lp4-2	11.98			
gill6-2	14.17		sc6-1	10.05		lp6-1	15.71			
lvr2-1	11.29		sc6-2	9.89		lp6-2	16.12			
lvr3-1	9.52		mc5-1	13.38		mcj3-1	10.11			
lvr4-1	8.82		mc5-2	13.62		mcj3-2	10.54			
lvr5-1	11.51		mc3-1	10.95		mcj4-1	9.20			
lvr6-1	11.45		mc3-2	7.35		mcj4-2	9.30			

Appendix IV

^{210}Pb uncorrected activity and cumulative Mass

cb		gill		gb		sc		sbc		
UNCORRECTE	cumm mass	UNCORRECTED	cumm mass	UNCORRECTED	cumm mass	UNCORRECTED	cumm mass	UNCORRECTED	cumm mass	
ACTIVITY	(g/(cm2*yr))	ACTIVITY	(g/(cm2*yr))	ACTIVITY	(g/(cm2*yr))	ACTIVITY	(g/(cm2*yr))	ACTIVITY	(g/(cm2*yr))	
12.63	0.37	10.49	0.45	8.63	0.36	7.39	0.38	1.66	2.06	
12.75	0.87	10.89	0.99	7.28	3.11	5.93	1.30	1.30	11.24	
11.56	2.14	9.30	2.34	3.54	6.40	3.92	7.00	1.23	13.51	
5.17	6.02	7.35	3.60	0.83	11.14	2.26	13.12	1.13	20.97	
3.83	8.84	4.10	6.49	1.57	20.75	1.38	17.62	1.14	25.16	
0.99	18.65	2.88	12.45	1.28	28.07	0.23	29.44	1.11	27.77	
1.96	22.92	2.17	16.39	1.39	31.00	0.55	42.75	1.10	34.37	
3.58	25.45	2.01	18.63	1.17	36.96	0.66	49.61	1.13	38.39	
1.94	29.01	1.67	28.41	1.25	44.31	1.63	72.12			
1.60	33.61	1.29	33.30			1.63	75.07			
1.86	38.92	1.15	37.68			1.17	80.80			
1.72	44.01	1.03	42.09			0.97	98.43			
1.76	49.64	1.15	58.84			1.03	106.57			
1.48	55.01									
1.01	60.98									
0.92	79.20									
1.18	95.57									
vzp		lvr		mcj		nc		dclp		
UNCORRECTE	cumm mass	UNCORRECTED	cumm mass	UNCORRECTED	cumm mass	UNCORRECTED	cumm mass	UNCORRECTED	cumm mass	
ACTIVITY	(g/(cm2*yr))	ACTIVITY	(g/(cm2*yr))	ACTIVITY	(g/(cm2*yr))	ACTIVITY	(g/(cm2*yr))	ACTIVITY	(g/(cm2*yr))	
9.71	0.37	10.83	0.37	4.97	1.51	5.46	0.75	7.98	0.32	
8.46	1.46	10.43	1.47	4.64	4.65	5.43	1.88	6.49	1.49	
6.47	3.21	9.60	3.96	2.76	10.75	3.78	3.57	1.46	6.59	
4.44	6.12	2.26	6.04	3.35	15.76	2.39	5.88	0.95	16.61	
2.73	9.20	1.80	8.59	2.14	24.02	1.27	8.21	0.84	20.46	
1.85	15.70	1.40	10.19	1.10	30.56	0.94	11.81	0.73	22.04	
1.39	20.41	1.28	12.78	0.31	45.18	0.92	17.23	0.63	40.53	
1.50	23.91	1.02	15.20	0.45	65.21	0.90	31.84	0.61	41.79	
0.80	25.94	1.02	21.03	0.33	84.18	0.94	40.71	0.31	50.84	
0.63	32.46	1.11	25.94	0.26	110.34			0.33	58.92	
1.03	42.86	1.31	31.28	0.35	150.83			0.34	72.92	
1.08	45.07							0.31	83.54	
0.79	47.78							0.26	106.13	

Appendix V

^{137}Cs measurements for Elizabeth River wetland sediment cores

SAMPLE	MID -	WET	DRY	SAMPLE	NET PEAK	COUNTING	TOTAL	
ID	POINT	WEIGHT	WEIGHT	WEIGHT	AREA	ERROR	ACTIVITY	ERROR
							(dpm/g)	(dpm/g)
cb								
3.00	0.37	87.88	27.12	60.76	48	10	0.21	0.02
5.00	2.77	90.12	29.78	60.34	74	14	0.22	0.02
8.00	4.75	89.24	27.67	61.57	404	24	1.52	0.04
11.00	6.71	90.11	29.97	60.14	305	22	0.89	0.03
13.00	8.11	90.21	30.23	59.98	60	12	0.17	0.02
17.00	13.42	138.31	101.76	36.55	0	0	0.00	0.00
20.00	22.92	112.22	64.46	47.76	0		0.00	0.00
27.00	30.09	96.51	38.78	57.73	0		0.00	0.00
36.00	41.30	101.64	45.68	55.96	0		0.00	0.00
gcc								
2.00	0.99	89.89	32.38	57.51	81	13	0.16	0.01
4.00	2.34	88.18	28.86	59.32	132	16	0.38	0.02
8.00	5.14	89.00	28.66	60.34	212	24	0.54	0.03
10.00	6.49	88.06	28.54	59.52	371	24	1.07	0.03
12.00	7.83	87.80	28.55	59.25	86	12	0.19	0.01
14.00	9.25	89.49	30.20	59.29	34	11	0.12	0.02
18.00	12.45	92.50	32.78	59.72	0	0	0.00	0.00
26.00	20.77	95.94	40.41	55.53	0	0	0.00	0.00
59.00	60.00	103.13	49.19	53.94	0	0	0.00	0.00
lvr								
4.00	2.11	90.02	29.21	60.81	48	12	0.14	0.02
9.00	7.28	110.33	63.57	46.76	1625	45	2.23	0.08
11.00	12.47	123.28	84.59	38.69	1902	48	2.24	0.12
12.00	15.22	128.12	94.91	33.21	794	32	1.25	0.14
14.00	21.78	132.50	100.26	32.24	121	15	0.37	0.14
24.00	52.70	141.46	115.63	25.83	37	10	0.05	0.06
29.00	69.60	142.16	117.01	25.15	10	6	0.01	0.02
32.00	81.10	135.92	119.20	16.72	0	0	0.00	0.00
34.00	88.47	143.29	124.07	19.22	0	0	0.00	0.00
39.00	107.80	151.00	127.92	23.08	0	0	0.00	0.00
43.00	119.57	129.27	89.17	40.10	0	0	0.00	0.00
gb								
2.00	0.92	92.96	31.41	61.55	59	14	0.12	0.01
4.00	2.36	90.01	36.74	53.27	40	11	0.09	0.02
6.00	3.87	91.14	32.12	59.02	87	14	0.25	0.02
8.00	5.56	94.38	32.64	61.74	99	18	0.20	0.02
10.00	7.25	91.35	31.80	59.55	41	11	0.13	0.02
12.00	9.38	93.14	35.47	57.67	0	0	0.00	0.00
14.00	13.84	123.81	78.73	45.08	0	0	0.00	0.00
20.00	25.16	103.40	46.00	57.40	0	0	0.00	0.00
35.00	45.97	102.67	46.75	55.92	0	0	0.00	0.00

Appendix VI

^{137}Cs measurements for Elizabeth River wetland sediment cores

SAMPLE ID	MID - POINT	WET WEIGHT	DRY WEIGHT	SAMPLE WEIGHT	NET PEAK AREA	COUNTING ERROR	TOTAL ACTIVITY (dpm/g)	ERROR (dpm/g)
vzp								
4	3.79	98.16	45.75	52.41	193	25	0.319	0.036
7	7.82	100.38	47.86	52.52	277	22	0.432	0.031
11	14.32	111.11	64.95	46.16	323	17	0.316	0.023
17	24.31	110.76	62.96	47.8	71	17	0.072	0.023
20	29.74	111.68	65.1	46.58	35	10	0.034	0.014
23	37.28	116.08	71.7	44.38	0	0	0.000	0.000
25	42.44	125.25	89.28	35.97	0	0	0.000	0.000
37	78.71	123.33	84.01	39.32	0	0	0.000	0.000
41	86.67	125.45	87.81	37.64	0	0	0.000	0.000
mcj								
1	0.65	92.22	34.35	57.87	35	12	0.065	0.013
3	2.61	90.07	30.38	59.69	55	13	0.115	0.014
6	5.64	92.56	34.5	58.06	38	12	0.147	0.028
8	8.00	98.58	43.7	54.88	126	19	0.183	0.022
10	10.75	97.59	40.52	57.07	83	13	0.408	0.045
12	13.36	95.33	39.28	56.05	116	14	0.187	0.016
16	17.94	96.61	38.33	58.28	5	5	0.008	0.005
22	25.38	103.53	50.61	52.92	0	0	0.000	0.000
28	39.97	139.98	114.25	25.73	0	0	0.000	0.000
ncc								
1	0.31	88.22	25.3	62.92	31	11	0.078	0.011
3	1.31	87.46	26.63	60.83	42	12	0.100	0.013
5	2.49	86.39	25.84	60.55	54	13	0.182	0.019
8	4.15	88.87	24.26	64.61	125	18	0.721	0.039
10	5.32	85.37	25.14	60.23	61	13	0.211	0.019
12	6.50	84.78	26.84	57.94	0	0	0.000	0.000
14	7.64	87.96	25.8	62.16	0	21	0.000	0.021
20	11.27	88.93	25.21	63.72	0	23	0.000	0.023
33	17.76	91.33	29.27	62.06	0	26	0.000	0.027
68	51.79	93.87	33.54	60.33	0	33	0.000	0.035

VITA

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