

Tidal Creek and Salt Marsh Sediments in South Carolina Coastal Estuaries: II. Distribution of Organic Contaminants

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Abstract. Twenty-eight tidal creeks along the South Carolina coast were sampled during the summer of 1995 to determine the levels of sediment contamination including organic chemicals (*i.e.*, polycyclic aromatic hydrocarbons [PAHs], polychlorinated biphenyls [PCBs], and DDT and its metabolites) associated with different types and varying levels of watershed development (*i.e.*, industrial/urban, suburban, forested, and salt marsh). Organic analysis utilized high-performance liquid chromatography (HPLC) with fluorescence detection and capillary gas chromatography–ion trap mass spectrometry (GC-ITMS) for PAHs, and gas chromatography with electron capture detection (GC-ECD) for pesticides and PCBs. Results indicated that creeks with industrial/urban watersheds had significantly higher concentrations of PAHs, PCBs, and DDT compared with creeks with suburban and forested (reference) watersheds. The suburban watershed class of creeks had concentrations of half the PAH analytes and the total PCBs which exceeded the concentrations found in the forested watershed class of creeks. The spatial distribution of organic contaminants was evaluated in four of these tidal creek–salt marsh systems representing urban/industrial, suburban, and forested watersheds, from the creek channel to the adjacent uplands. The distribution of organic contaminants within each representative creek was not concordant with the total organic carbon or the clay content of the sediment. The representative industrial/urban creek-marsh system, Diesel Creek, had the highest concentration of PAHs in the creek channel and the highest concentration of PCBs and DDT on the marsh surface, primarily in the upper portion of the system. The representative suburban creek-marsh system, Shem Creek, had elevated levels of both PAHs and PCBs throughout the entire system. This system also had one site with a total PAH concentration of 324,000 ppb and a total DDT concentration that was 20–100

times higher than the other sites. One of the representative forested creek-marsh systems, Rathall Creek, had low levels of the three organic contaminants except for one sampling site that had PAH concentrations a factor of 10 higher than the other sites. The other representative forested creek-marsh system, Long Creek, had low levels of PAHs and PCBs, but elevated levels of DDT were observed, particularly in the upper portion on the marsh surface. The results of this study suggest that (1) anthropogenic alteration of the land cover in the watersheds of tidal creek–salt marsh systems may increase the organic contaminant loadings in the sediment, and (2) tidal creek–salt marsh sediments, particularly in the creek channel, are repositories and potentially conduits of organic contaminants from the upland environment to the deeper estuarine areas.

Coastal regions of the southeastern United States are under ever-increasing population growth pressures. By 2010, these coastal populations are expected to increase by over 60% from their 1960 levels (Culliton *et al.* 1990). In addition, millions of tourists visit the coastal zone of the southeast each year (Miller 1993). The projected increases in population growth and tourism will be accompanied by intense development of watersheds located in coastal regions. Development of these watersheds, especially those surrounding tidal creek–salt marsh ecosystems, can potentially increase point and nonpoint source pollution loadings into these systems and the nearby estuaries. In the southeastern United States, the tidal creek–salt marsh system is the primary hydrographic link between anthropogenic activities in the upland portion of the watershed and the adjacent estuarine habitats. As such, these creeks may serve as a repository for anthropogenic contaminants derived from upland development activities.

The organic contaminants of greatest concern to tidal creeks and salt marshes are polycyclic aromatic hydrocarbons (PAHs). PAHs are a major component of lubricating oils and fuels, but are also produced during the combustion of organic matter, including fossil fuels. PAHs derived from lubricating oils and fuels are generally low molecular weight (LMW) compounds

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(\leq three rings) and are often heavily alkylated (Lee *et al.* 1981). PAHs derived from combustion of organics are generally high molecular weight (HMW) compounds (\geq four rings) with little alkylation (Lee *et al.* 1981). The LMW PAHs are degraded at a faster rate compared to the HMW PAHs (Bossert *et al.* 1984). Potential sources of PAHs to estuarine tidal creek systems include runoff from highways and parking lots, vehicle exhaust, street dust, fuel spills, recreational boating activities, and atmospheric fallout (Weinstein 1996). Historical uses of creek watersheds, such as industrial uses (*e.g.*, creosote production and power plant activities), may also contribute to contemporary patterns of PAH contamination. Pesticides are also organic contaminants of concern, particularly in tidal creeks with agricultural watersheds (Scott *et al.* 1990). Other persistent organic contaminants, including PCBs and DDT, are potentially a concern in tidal creeks and salt marshes, despite being banned from production for over 20 years.

In 1994–1995, the South Carolina Department of Natural Resources initiated the Tidal Creek Project to define the linkages between tidal creek environmental quality and human uses of their watersheds. To achieve this objective, a population of 28 tidal creek systems was studied using a comparative watershed approach. The preceding paper in this issue addresses the trace metal contamination of these systems (Sanger *et al.* 1999). The objectives of the present study were to: (1) determine if the levels of sediment organic contamination (*i.e.*, PAHs, PCBs, and DDT) in tidal creeks were associated with the degree and type of anthropogenic activity within the watershed; (2) determine the spatial distribution of organic contamination across four creek-marsh systems representative of the three major types of land use; and (3) provide baseline information on organic contaminant distributions for tidal creek and salt marsh systems that could be used as a basis for the design of assessment, monitoring, and research programs. The potential biological effects associated with these patterns of organic contamination are not addressed in this study, but will be addressed in subsequent publications.

Materials and Methods

Sampling Design

The study area and sampling design have been extensively discussed in Sanger *et al.* (1999) and will only be outlined here. This study sampled sediment organic contaminants from 28 tidal creeks located along the South Carolina coast from July to September 1995 (Figure 1). Each creek consisted of a relatively unbranched channel that drained a defined watershed and formed the first-order connection between the drainage basin and estuarine habitats. The upper boundary of each creek was defined as the point where water depth in the center of the channel was ~ 1 m deep on the average high tide. The lower boundary was defined as the point where the creek converged with another water body or the water depth in the center of the channel exceeded ~ 3 m deep on the average high tide. Creeks were stratified into 300-m reaches for sampling and the creek lengths varied from one to five reaches.

The 28 tidal creeks were classified into two populations (*i.e.*, upland and salt marsh) based on the predominant land cover of each watershed. Upland creeks were composed of 15–75% upland environments, and salt marsh creeks were entirely estuarine salt marsh. Upland creeks were classified into the following five watershed classes that represented varying degrees of anthropogenic development: (1) for-

ested or reference, (2) suburban, (3) industrial, (4) urban, and (5) agriculture. Salt marsh creeks were grouped into the following two classes: (1) unimpacted or reference, and (2) impacted (Sanger *et al.* 1999).

During this study, two sampling programs were conducted: (1) a tidal creek study (all 28 creeks), and (2) a creek-marsh transect study (four representative creeks). For the tidal creek study, a single, random sediment sample was collected at midtide elevation (intertidal) of the creek channel in both the upper- and lowermost reaches of each creek. The creek-marsh transect study examined the spatial distribution of sediment organic contaminants from the midtide level of the creek channel to the marsh-upland interface for four creek watersheds. These four creeks represented industrial (Diesel Creek), suburban (Shem Creek), and forested (Rathall Creek and Long Creek) upland watershed classes. In the upper- and lowermost reach of each creek, three randomly located transects were defined perpendicular from the creek channel to the adjacent uplands (Figure 2). A single sediment sample was collected at four fixed locations along each transect: (1) the midtide level (intertidal) of the creek channel (creek bed), (2) the creek channel edge (berm), (3) a location 50% of the distance between the creek and the upland (midmarsh), and (4) a location 5 m from the site were the vegetation shifted from *Spartina alterniflora* to *Juncus roemerianus* or an upland vascular plant (high marsh).

Sediment samples consisted of ~ 2 L of surface (top 2 cm) sediment placed in a solvent-clean stainless steel bowl using a stainless steel spoon. Sediments were homogenized, then divided into two aliquots. One aliquot was placed in a precleaned glass jar for organic contaminant analyses and the other in a plastic bag for grain size and organic carbon analyses. Collecting utensils were rinsed in acetone and site water or deionized water between sites. All samples were placed on ice until reaching the National Oceanic and Atmospheric Administration, National Ocean Service (Charleston, SC) laboratory where they were stored at -60°C until analysis.

Chemical Analysis

Sediment grain size (*i.e.*, clay, silt, sand) and total organic carbon (TOC) were determined for each sediment sample as previously described (Sanger *et al.* 1999). The methods for extraction and sample preparation for organic contaminants in sediments were similar to those of Krahn *et al.* (1988) with a few modifications, which are outlined in Sanders (1995). The PAHs were quantified by two methods: capillary gas chromatography–ion trap mass spectrometry (GC-ITMS) and high-performance liquid chromatography (HPLC) with fluorescence detection. The data presented are the average value obtained from the two methods. The instrument used for the GC-ITMS analysis was a Finnigan MAT Magnum Ion Trap Mass Spectrometer (Piscataway, NJ) equipped with a Varian 3400 gas chromatograph and Varian 8200 autosampler (Palo Alto, CA). The column was a 30 m \times 0.2 mm ID DB-5ms (J&W Scientific, Folsom, CA) with a film thickness of 0.25 μm . The carrier gas was helium at a linear velocity of 33 cm/s at 300°C . The temperatures were 280°C , 220°C , and 280°C for the injection, ion source, and transfer line, respectively. PAHs quantified using HPLC with fluorescence detection were performed using a method similar to that described by Wise *et al.* (1988) and Schantz *et al.* (1990). The instrument consisted of two HPLC pumps (Waters 6000A, Milford, MA), a 680 gradient controller (Waters Model 680), and an autosampler (Waters WISP). The column dimensions were 6 mm \times 25 cm, with a 5- μm particle size (Supelco LC-PAH, Bellefonte, PA). Fluorescence was monitored with two fluorescence detectors (Perkin-Elmer LC-240 and LS-4, Norwalk, CT) connected in series at wavelengths specific to individual PAHs. The separation between deuterated and nondeuterated PAHs was 0.44, 0.40, and 0.41 min for phenanthrene, fluoranthene, and perylene, respectively. Data collection

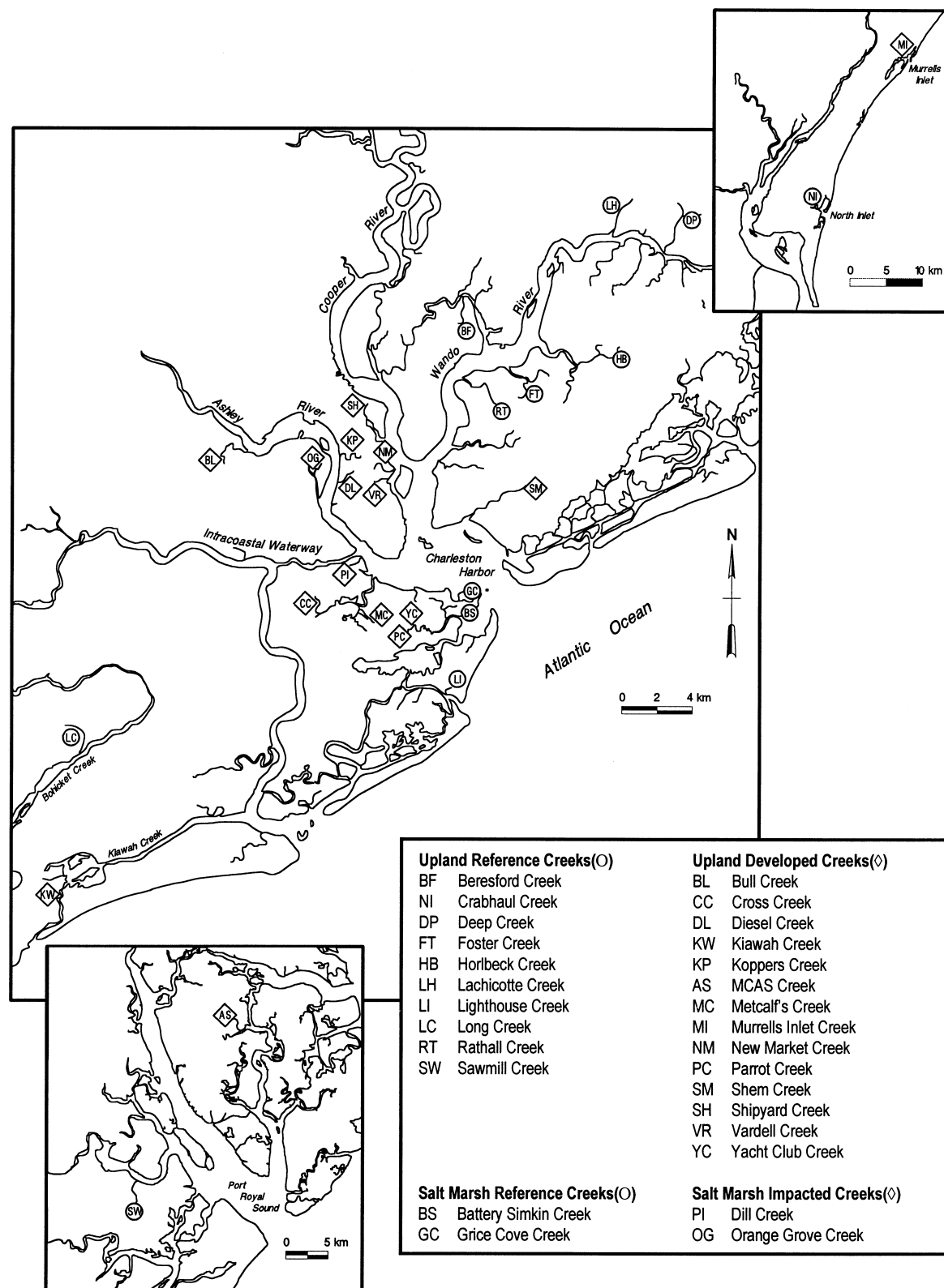


Fig. 1. Map showing location of tidal creeks sampled in South Carolina. The reference (○) and developed/impacted (◇) creeks are presented by their abbreviations. The inserts are the north (top) and south (bottom) sampling sites

was accomplished using Perkin Elmer Omega II personal computer-based software.

To determine the reliability of the PAH data, including the efficiency of extraction methods and interferences that may be introduced during

sample preparation, spiked matrix samples and blanks were analyzed using both HPLC with fluorescence detection and GC-ITMS. A total of six spiked matrix samples were analyzed using National Marine Fisheries Service (NMFS) sample 216. National Institute of Standards

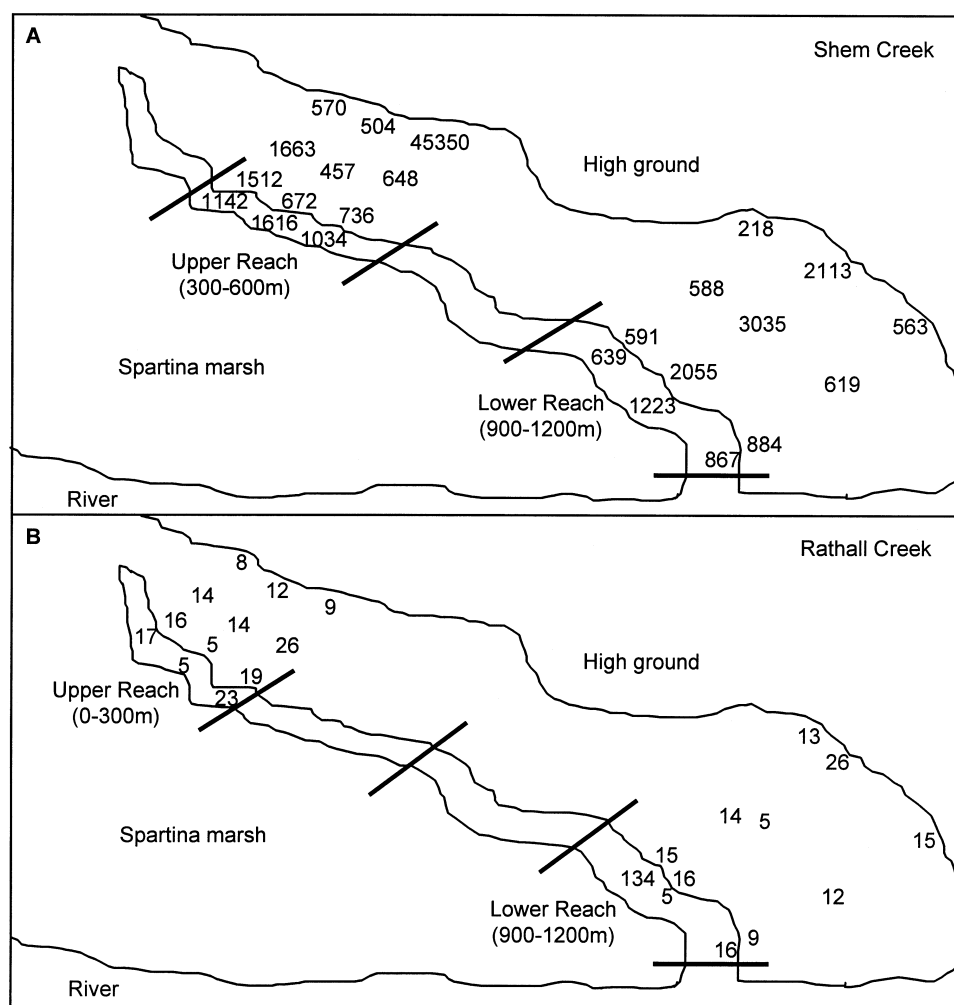


Fig. 2. The fluoranthene concentrations (ng/g dry weight) at each sampling site within Shem Creek (A) and the naphthalene concentrations (ng/g dry weight) at each sampling site within Rathall Creek (B) tidal creek–salt marsh systems

and Technology (NIST) standard reference material (SRM) 1941 (Organics in Marine Sediments) was used to evaluate the efficiency of extraction methods for removing PAHs from sediment. Overall, the average deviation from the mean NIST SRM values (both certified and noncertified) was only 1% (some observations were biased high and some low) by either HPLC or GC-ITMS.

Chlorine-containing compounds (*i.e.*, PCBs and pesticides) were analyzed using gas chromatography with electron capture detection (GC-ECD; Hewlett-Packard 5890 series II). The instrument was configured with two columns: (1) a 30 m × 0.25 mm ID (0.25 mm film thickness) DB-5 (5% phenyl; J&W Scientific, Folsom CA); and (2) a 30 m × 0.25 mm ID (0.25 mm film thickness) Rtx-50 (50% phenyl; Restek Corp., Bellefonte, PA). At the head of each column, a 5-m guard column was used to protect the analytical column. The carrier gas, helium, was held at a constant average linear velocity of 33 cm/s by pressure-programming the injector. The detector make-up gasses were an argon:methane (95%:5%) mixture. The injector and detector temperatures were 250°C and 320°C, respectively. The sample was injected (2 ml) using a splitless Grob technique (1-min split time). The sample was then split such that nearly equal portions were sent to each column. The initial oven temperature was 50°C with a 1-min hold, followed by an increase to 170°C at 4°C/min, then to 210°C at 1°C/min, and finally to 310°C at 4°C/min with a 10-min hold. The detector signal was digitized and processed using the Windows-based EZChrom software (Scientific Software Inc., San Ramon, CA).

Similar to the analysis of PAHs, organochlorine compounds were determined from both spiked sediments and a NIST SRM 1941 to obtain information on the reliability of the organochlorines and pesticides data collected. Sediments were amended with 21 PCB

congeners, 15 organochlorine pesticides, and common pesticide metabolites at three levels ranging from 1.2 ng to 5 ng total. The overall recovery (mean ± SD) of organochlorines from amended sediments was 102 ± 23% for PCBs and 89 ± 32% for organochlorine pesticides plus metabolites. The overall precision of the organochlorides and pesticides analyses was not as good as that for PAHs. Only three analytes were between the NIST upper and lower confidence limits. No systematic bias was observed in the deviation from the certified values (mean deviation = −1.6%).

Data Analysis

A total of 23 PAHs (acenaphthene [AceNap], acenaphthylene [AceNapy], anthracene [Anth], fluorene [Fluor], 2-methylnaphthalene [2mNap], naphthalene [Nap], phenanthrene [Phen], 1-methylnaphthalene, 1-methylphenanthrene, 2,3,5 trimethylnaphthalene, benz(a)-anthracene [B(a)A], benzo(a)pyrene [B(a)P], chrysene [Chry], dibenz(a,h)anthracene [D(ah)A], fluoranthene [Flu], pyrene [Pyr], benzo(b)fluoranthene, benzo(e)pyrene, benzo(g,h,i)perylene, benzo(k)fluoranthene, biphenyl, indeno(1,2,3-cd)pyrene, and perylene) were evaluated. The sum of these analytes was determined for the total PAH concentration; however, this paper only presents concentrations of the 13 selected PAH analytes with abbreviations provided above. These 13 PAH analytes are discussed in terms of low molecular weight (LMW) analytes (*i.e.*, AceNap, AceNapy, Anth, Fluor, 2mNap, Nap, Phen) and high molecular weight (HMW) analytes (*i.e.*, B(a)A, B(a)P, Chry, D(ah)A, Flu, Pyr). Twenty PCBs were quantified—Cl₂(8), Cl₃(18),

Cl3(28), Cl4(44), Cl4(52), Cl4(66), Cl4(77), Cl5(101), Cl5(105), Cl5(118), Cl5(126), Cl6(128), Cl6(138), Cl6(153), Cl7(170), Cl7(180), Cl7(187), Cl8(195), Cl9(206), and Cl10(209)—and summed to determine a total PCB concentration. Fifteen pesticides (aldrin, alpha-chlordane, dieldrin, HCB, heptachlor, heptachlor epoxide, lindane, mirex, trans-nonachlor, O,P-DDD, O,P-DDE, O,P-DDT, P,P-DDD, P,P-DDE, P,P-DDT) were analyzed, but only the total DDT concentration (sum of O,P-DDD, O,P-DDE, O,P-DDT, P,P-DDD, P,P-DDE, P,P-DDT) are presented here. The other pesticides were consistently below the level of detection (LOD), with the exception of chlordane and related metabolites.

Statistical analyses were performed using PC-SAS. Concentrations of organic contaminants below the LOD were set to the LOD. Utilizing the LOD concentrations in statistical analyses can bias estimates of the mean and variance (Helsel 1990; Slymen *et al.* 1994); however, less than a quarter of the PAH concentrations were set to the LOD, and most of these were from reference sites. Therefore, the reference estimates would be biased higher and this is a conservative approach. Linear regression analyses were used to determine the relationship between sediment contaminant concentrations (total PAHs, total PCBs, or total DDT) and sediment TOC or clay content. The organic contaminant concentrations were \log_{10} transformed and the clay and TOC were arcsine-square-root transformed. Three data sets were established for the regressions: (1) the creek study and creek-marsh transect study sites ($n = 144$); (2) the reference sites from the creek study and creek-marsh transect study ($n = 69$); and (3) the developed and impacted sites from the creek study and creek-marsh transect study ($n = 75$).

The tidal creek study data ($n = 54$) was analyzed using a two-way analysis of variance (ANOVA) to determine differences in organic contaminant concentrations between watershed classes and reach. Data for all watershed classes were used in these analyses; however, contrast of the least squares mean focused on comparing patterns for the upland watershed classes and the salt marsh watershed classes. The industrial and urban creeks were combined to increase the sample size for this class of creeks. Only one agricultural creek was sampled. The data for this creek have been provided, but will not be discussed. A one-way ANOVA was used to determine if the concentrations of organic contaminants differed between reaches and within watershed classes.

The creek-marsh transect study was analyzed using a two-way ANOVA model and three-way ANOVA model. The two-way ANOVAs (*i.e.*, transect position and reach) were performed to evaluate the spatial distributions of organic contaminants within the individual creek-marsh systems sampled. The three-way ANOVAs (*i.e.*, creek, transect position, and reach) were also performed to evaluate differences among creeks and to characterize the spatial distributions of organic contamination among creeks.

The nonsignificant ($\alpha = 0.10$) interaction terms were removed from both the tidal creek study two-way ANOVAs and the creek-marsh transect study two-way and three-way ANOVAs, and the analysis was reaccomplished. A significance level at $\alpha = 0.05$ was applied for all other statistical comparisons to determine significant differences. Contrasts were based on the least squares mean. The organic contaminant concentrations were \log_{10} transformed, and the percentages of clay and TOC were arcsine-square-root transformed for the ANOVAs to help satisfy the assumptions of homoscedasticity and normality.

Results

The data collected for sediment grain size (*i.e.*, clay) and TOC content in the tidal creek study and the creek-marsh transect study are presented in Sanger *et al.* (1999). The data for concentrations of organic contaminants in the tidal creek study and creek-marsh transect study are presented in Tables 1 and 2, respectively.

Neither the clay nor the TOC content of the sediment were strongly correlated with the concentrations of total PAHs, total

PCBs, or total DDT in sediments (Table 3). The highest correlation ($r^2 = 0.36$) occurred between the clay content and the total PAH concentration for the reference sites alone (*i.e.*, tidal creek study and the creek-marsh transect study); however, many of the regression models evaluating the association between the clay content and the organic contaminant concentrations were not significant. In general, the TOC and organic contaminant regression models were significant, but the correlations were weak ($r^2 \leq 0.20$). This suggested that TOC levels were not highly associated with the concentration of organic contaminants in the sediment. Therefore, concentrations of organic contaminants were not adjusted for grain size or TOC content in the analyses presented in this paper.

In the tidal creek study, the concentrations of all PAH analytes evaluated and the total PAH concentrations were significantly higher in the industrial/urban watershed class compared to that of the forested and suburban classes (Table 1, Figure 3A and 3B). In addition, Anth, Fluor, Phen, B(a)A, Chry, Flu, Pyr, and total PAH concentrations were significantly higher in the suburban watershed class compared to the forested watershed class. Although the upper reaches of the industrial/urban creeks generally had higher PAH concentrations than the lower reaches (Figure 3), these differences were not statistically significant. This lack of statistical difference was probably because of the variability in concentrations associated with sampling a population of industrial/urban creeks. Each of the industrial/urban creeks had potentially different contaminant inputs. The levels of PAHs in salt marsh impacted and unimpacted watershed classes were similar for all of the PAH analytes evaluated and the total PAH concentrations (Table 1, Figure 4A and 4B).

In the creek-marsh transect study, Diesel Creek (industrial watershed) had significantly higher concentrations for all but one of the LMW PAHs (except Phen) when compared to Shem Creek (suburban), Rathall Creek (forested), and Long Creek (forested) (Table 4, Figure 5). Concentrations of the LMW PAH analytes (except Nap) were also significantly higher in Shem Creek compared to Long Creek, but some of the analyte concentrations in Shem Creek were similar to Rathall Creek (*i.e.*, AceNapy, Nap, 2mNap). Concentrations of Phen and the HMW PAHs, except for D(ah)A, were significantly higher in Shem Creek compared to Diesel Creek and the two reference creeks. Diesel Creek also had significantly higher concentrations of the HMW PAHs compared to the two reference creeks.

Within each of the four intensively studied creek systems (*i.e.*, the creek-marsh transect study), the PAH analyte concentrations were not concordant or in agreement with the clay or the TOC content from the creek channel to the marsh-upland interface (Figure 5). PAH concentrations in Rathall Creek were generally low throughout the system, except for one of the three replicate sites on the creek bed in the lower reach (Figure 5). The levels of PAHs at this site (Rathall Creek-L-CB) were similar to the levels observed in the suburban and the industrial/urban watershed classes (Tables 1 and 2). Long Creek had low levels of PAH contamination with all of the PAH analytes (except Nap and 2mNap) close to or below the level of detection (Figure 5). In general, the PAH concentrations in Rathall and Long Creeks were similar to levels found in pristine estuaries throughout South Carolina (Fortner *et al.* 1996; Scott *et al.* 1998).

Table 1. Summary of the organic contaminant concentrations collected in the tidal creek study

Site ID	Ace Nap	Ace Napy	Anth	Fluor	2m Nap	Nap	Phen	B(a)A	B(a)P	Chry	D(ah)A	Flu	Pyr	Total PAH	Total PCB	Total DDT
Forested or Reference																
BF—U	< 3	< 1	< 2	< 1	15	22	13	20	25	13	< 1	34	31	332	7.3	1.1
BF—L	< 3	3	6	< 1	16	20	13	20	22	23	< 1	41	37	352	7.0	1.3
NI—U	< 3	< 1	< 2	< 1	6	< 5	2	< 4	< 5	< 1	< 1	< 3	< 2	69	7.6	0.6
NI—L	< 3	< 1	< 2	< 1	15	16	6	4	6	3	2	6	5	116	10.7	1.2
DP—U	< 3	< 1	< 2	< 1	6	8	7	9	9	1	< 1	12	11	127	3.9	0.6
DP—L	< 3	< 1	< 2	< 1	13	18	9	24	13	7	< 1	21	19	219	5.8	0.6
FT—U	< 3	< 1	< 2	8	18	24	12	18	19	16	< 1	33	31	323	6.8	1.1
FT—L	< 3	< 1	5	< 1	13	17	10	16	19	15	< 1	30	27	271	4.6	0.6
HB—U	< 3	< 1	4	< 1	7	9	9	19	20	14	< 1	52	49	329	6.9	2.6
HB—L	4	< 1	6	< 1	12	6	23	18	32	30	< 1	46	42	380	5.0	0.6
LH—U	< 3	< 1	< 2	< 1	15	21	11	34	15	10	5	24	22	249	4.3	0.6
LH—L	< 3	< 1	< 2	< 1	19	23	9	4	9	7	< 1	16	15	172	8.1	0.8
LI—U	< 3	2	3	1	13	15	8	5	16	12	< 1	17	15	192	4.6	0.7
LI—L	3	2	6	3	10	13	19	30	33	34	< 1	63	55	432	3.8	0.8
LC—U	< 3	< 1	< 2	2	5	11	6	5	9	7	< 1	16	16	147	6.5	29.6
LC—L	< 3	< 1	< 2	< 1	7	12	2	< 4	< 5	2	< 1	5	4	85	4.4	2.4
RT—U	4	4	3	2	12	17	12	8	13	12	< 1	19	19	229	4.3	0.8
RT—L	< 3	4	9	2	6	< 5	13	21	27	35	< 1	42	40	380	3.6	0.7
SW—U	< 3	< 1	< 2	1	6	14	3	< 4	< 5	< 1	< 1	3	2	83	4.5	1.4
SW—L	< 3	< 1	< 2	< 1	10	9	4	< 4	< 5	< 1	< 1	3	3	80	3.5	0.6
Suburban																
BL—U	5	3	9	5	13	14	41	57	83	124	< 1	188	175	1,380	8.5	2.3
BL—L	< 3	2	4	2	9	11	15	18	41	40	< 1	70	75	562	6.0	0.8
CC—U	< 3	< 1	5	5	9	11	18	32	37	36	< 1	76	65	544	7.9	1.4
CC—L	4	< 1	10	8	15	22	24	51	52	56	< 1	100	92	791	5.9	1.7
AS—U	< 3	< 1	2	2	11	10	10	14	27	38	6	52	56	586	41.8	5.3
AS—L	< 3	< 1	< 2	< 1	5	6	5	< 4	8	8	< 1	14	13	124	7.0	2.1
MC—U	13	< 1	11	14	7	9	50	32	14	23	< 1	58	49	377	4.3	0.9
MC—L	5	5	27	10	14	20	38	85	84	111	< 1	126	150	1,255	9.4	0.9
MI—U	< 3	< 1	4	< 1	15	8	15	14	26	36	< 1	51	41	379	5.7	0.8
MI—L	< 3	< 1	4	5	19	18	12	21	23	22	< 1	45	39	359	5.7	0.6
PC—U	< 3	< 1	6	2	13	13	13	9	19	21	< 1	28	26	251	3.6	0.6
PC—L	< 3	3	6	7	15	19	14	25	35	44	< 1	58	57	523	7.3	3.5
SM—U	6	3	33	7	5	6	307	585	663	649	59	1,365	1,097	7,760	11.5	6.3
SM—L	7	< 1	36	11	13	12	248	469	442	845	8	1,126	928	7,224	29.3	1.5
YC—U	5	3	13	8	10	14	20	51	47	63	< 1	102	97	763	7.4	0.9
YC—L	5	4	20	10	17	20	27	71	65	96	< 1	116	110	999	12.0	0.6
Industrial																
DL—U	88	14	482	144	99	103	527	585	431	1,187	40	1,862	1,725	10,173	16.6	2.2
DL—L	33	24	418	57	38	66	213	311	374	466	36	691	596	6,089	7.1	1.6
KP—U	78	13	76	34	61	72	102	200	164	267	21	622	561	3,341	19.6	7.1
KP—L	23	8	123	20	26	41	83	141	180	223	23	352	443	2,744	15.1	1.4
SH—U	36	19	65	45	124	104	205	243	202	340	36	533	516	4,184	74.9	40.2
SH—L	6	3	14	7	19	27	36	45	41	63	8	111	145	832	8.5	1.9
Urban																
NM—U	20	13	43	18	44	43	215	328	315	446	41	633	595	4,768	101.5	16.0
NM—L	43	152	68	26	93	115	163	389	559	420	61	576	874	6,186	45.0	6.9
VR—U	273	24	705	386	193	158	2,534	2,082	2,753	3,171	334	5,687	4,654	37,034	49.3	43.2
Agricultural																
KW—U	< 3	< 1	< 2	< 1	11	15	8	< 4	15	9	< 1	16	14	173	8.2	25.4
KW—L	< 3	< 1	3	3	6	9	6	9	10	4	< 1	13	12	157	4.6	8.4
Salt marsh unimpacted																
BS—U	< 3	< 1	< 2	2	24	28	9	< 4	12	11	< 1	14	12	207	5.1	0.9
BS—L	< 3	< 1	< 2	1	21	25	7	4	9	6	< 1	14	14	179	4.5	0.6
GC—U	< 3	< 1	7	7	11	19	13	22	23	19	< 1	51	46	371	7.1	2.3
GC—L	< 3	3	8	6	5	5	19	71	45	70	< 1	152	134	769	6.5	0.6
Salt marsh impacted																
PI—U	< 3	< 1	5	3	23	25	13	13	26	24	< 1	57	50	412	7.1	1.2
PI—L	3	2	6	3	17	21	14	15	33	37	< 1	58	57	465	5.4	0.6
OG—U	6	4	14	6	19	21	27	55	92	100	22	131	164	1,233	10.0	0.8

The first two letters of the Site ID indicate the creek (see Figure 1) and the last letter indicates the reach (U = upper and L = lower)

Concentrations are ppb (ng/g dry weight)

A < sign indicates the concentration was below the level of detection

Table 2. Summary of the organic contaminant concentrations (mean and standard error [Avg^{SE}]) collected in the creek-marsh transect study

Site ID	Ace		Nap		Anth		Fluor		2m		Nap	Phen	B(a)A	B(a)P	Chry	D(ah)A	Flu	Pyr	Total PAH	Total PCB	Total DDT	
	Nap	Ace	Nap	Ace	Anth	Fluor	Nap	Phen														
Rathall Creek (forested watershed)																						
U-CB	4 ⁰	2 ¹	4 ¹	2 ⁰	2 ⁰	13 ³	15 ⁵	13 ³	11 ²	16 ²	16 ³	2 ¹	25 ⁴	25 ⁴	25 ⁴	25 ⁴	25 ⁴	25 ⁴	25 ⁴	25 ⁴	25 ⁴	25 ⁴
U-B	4 ¹	5 ²	5 ¹	2 ⁰	2 ⁰	16 ¹	13 ⁴	16 ¹	15 ²	21 ¹	20 ¹	3 ²	38 ⁴	38 ⁴	38 ⁴	38 ⁴	38 ⁴	38 ⁴	38 ⁴	38 ⁴	38 ⁴	38 ⁴
U-MM	3 ⁰	2 ⁰	3 ⁰	1 ⁰	1 ⁰	18 ⁴	18 ⁴	13 ¹	7 ²	14 ⁵	11 ⁶	1 ⁰	27 ⁴	27 ⁴	27 ⁴	27 ⁴	27 ⁴	27 ⁴	27 ⁴	27 ⁴	27 ⁴	27 ⁴
U-HM	3 ⁰	1 ⁰	3 ⁰	1 ⁰	1 ⁰	10 ¹	10 ¹	9 ²	7 ²	12 ²	11 ³	1 ⁰	19 ⁵	19 ⁵	19 ⁵	19 ⁵	19 ⁵	19 ⁵	19 ⁵	19 ⁵	19 ⁵	19 ⁵
L-CB	12 ⁹	13 ¹⁰	47 ³⁸	11 ⁸	34 ²⁵	68 ⁵⁴	52 ⁴¹	68 ⁵⁴	153 ¹²⁶	136 ¹⁰⁵	219 ¹⁷⁹	4 ³	241 ¹⁹⁰	241 ¹⁹⁰	241 ¹⁹⁰	241 ¹⁹⁰	241 ¹⁹⁰	241 ¹⁹⁰	241 ¹⁹⁰	241 ¹⁹⁰	241 ¹⁹⁰	241 ¹⁹⁰
L-B	3 ⁰	5 ¹	15 ³	3 ¹	8 ²	13 ²	13 ²	20 ²	49 ⁷	48 ⁷	68 ⁵	2 ¹	82 ²¹	82 ²¹	82 ²¹	82 ²¹	82 ²¹	82 ²¹	82 ²¹	82 ²¹	82 ²¹	82 ²¹
L-MM	3 ⁰	3 ⁰	4 ⁰	2 ⁰	7 ²	10 ³	10 ³	14 ⁰	11 ¹	20 ⁰	19 ¹	1 ⁰	32 ²	32 ²	32 ²	32 ²	32 ²	32 ²	32 ²	32 ²	32 ²	32 ²
L-HM	3 ⁰	1 ⁰	3 ⁰	2 ⁰	12 ²	18 ⁴	18 ⁴	15 ²	7 ¹	17 ³	15 ¹	1 ⁰	28 ³	28 ³	28 ³	28 ³	28 ³	28 ³	28 ³	28 ³	28 ³	28 ³
Long Creek (forested watershed)																						
U-CB	3 ⁰	1 ⁰	2 ⁰	2 ⁰	2 ⁰	4 ⁰	9 ²	4 ⁰	4 ⁰	5 ⁰	4 ¹	1 ⁰	9 ⁰	9 ⁰	9 ⁰	9 ⁰	9 ⁰	9 ⁰	9 ⁰	9 ⁰	9 ⁰	9 ⁰
U-B	3 ⁰	1 ⁰	2 ⁰	1 ⁰	1 ⁰	3 ⁰	6 ⁰	3 ⁰	4 ⁰	5 ⁰	3 ¹	1 ⁰	7 ¹	7 ¹	7 ¹	7 ¹	7 ¹	7 ¹	7 ¹	7 ¹	7 ¹	7 ¹
U-MM	3 ⁰	1 ⁰	2 ⁰	2 ⁰	2 ⁰	6 ⁰	9 ¹	6 ⁰	5 ⁰	7 ¹	6 ¹	1 ⁰	13 ¹	13 ¹	13 ¹	13 ¹	13 ¹	13 ¹	13 ¹	13 ¹	13 ¹	13 ¹
U-HM	3 ⁰	1 ⁰	2 ⁰	2 ⁰	2 ⁰	5 ¹	9 ²	5 ¹	4 ⁰	6 ¹	6 ¹	1 ⁰	10 ¹	10 ¹	10 ¹	10 ¹	10 ¹	10 ¹	10 ¹	10 ¹	10 ¹	10 ¹
L-CB	3 ⁰	1 ⁰	2 ⁰	1 ⁰	8 ²	13 ²	13 ²	3 ¹	4 ⁰	6 ¹	4 ²	1 ⁰	7 ³	7 ³	7 ³	7 ³	7 ³	7 ³	7 ³	7 ³	7 ³	7 ³
L-B	3 ⁰	1 ⁰	2 ⁰	2 ⁰	9 ²	16 ⁵	16 ⁵	6 ¹	6 ¹	9 ¹	8 ²	1 ⁰	15 ³	15 ³	15 ³	15 ³	15 ³	15 ³	15 ³	15 ³	15 ³	15 ³
L-MM	3 ⁰	1 ⁰	2 ⁰	2 ¹	8 ⁵	25 ¹³	25 ¹³	8 ¹	7 ⁰	8 ¹	13 ⁴	1 ⁰	20 ³	20 ³	20 ³	20 ³	20 ³	20 ³	20 ³	20 ³	20 ³	20 ³
L-HM	3 ⁰	1 ⁰	2 ⁰	2 ⁰	8 ²	17 ⁶	17 ⁶	6 ³	7 ³	8 ³	7 ⁵	1 ⁰	12 ¹	12 ¹	12 ¹	12 ¹	12 ¹	12 ¹	12 ¹	12 ¹	12 ¹	12 ¹
Diesel Creek (industrial watershed)																						
U-CB	53 ²¹	26 ⁶	352 ¹⁴⁷	104 ⁴⁶	112 ⁴⁶	114 ⁴³	114 ⁴³	370 ¹¹²	516 ¹³³	458 ⁷⁰	894 ²⁷⁴	49 ¹¹	2,018 ⁹¹⁶	2,018 ⁹¹⁶	2,018 ⁹¹⁶	2,018 ⁹¹⁶	2,018 ⁹¹⁶	2,018 ⁹¹⁶	2,018 ⁹¹⁶	2,018 ⁹¹⁶	2,018 ⁹¹⁶	2,018 ⁹¹⁶
U-B	23 ⁸	81 ⁵³	139 ⁷⁷	30 ¹⁴	66 ³⁰	84 ¹⁹	219 ¹¹⁵	128 ⁴³	333 ¹⁰⁶	411 ¹⁶⁸	911 ⁴⁷⁸	59 ²⁸	349 ⁹²	349 ⁹²	349 ⁹²	349 ⁹²	349 ⁹²	349 ⁹²	349 ⁹²	349 ⁹²	349 ⁹²	349 ⁹²
U-MM	18 ²	26 ¹⁵	22 ⁵	15 ³	62 ¹⁷	66 ¹¹	128 ⁴³	106 ³³	217 ¹¹⁶	262 ¹⁴²	302 ¹⁴²	35 ¹⁶	334 ¹⁰⁴	334 ¹⁰⁴	334 ¹⁰⁴	334 ¹⁰⁴	334 ¹⁰⁴	334 ¹⁰⁴	334 ¹⁰⁴	334 ¹⁰⁴	334 ¹⁰⁴	334 ¹⁰⁴
U-HM	18 ²	15 ³	16 ¹	13 ³	60 ¹³	60 ⁶	106 ³³	111 ²⁹	111 ²⁹	118 ³⁰	163 ⁴⁶	20 ⁵	230 ⁴⁷	230 ⁴⁷	230 ⁴⁷	230 ⁴⁷	230 ⁴⁷	230 ⁴⁷	230 ⁴⁷	230 ⁴⁷	230 ⁴⁷	230 ⁴⁷
L-CB	21 ⁶	23 ¹	191 ¹¹⁴	28 ¹⁵	27 ⁶	44 ¹¹	117 ⁴⁹	398 ³⁶	268 ³⁷	314 ³²	398 ³⁶	34 ¹	456 ⁴⁸	456 ⁴⁸	456 ⁴⁸	456 ⁴⁸	456 ⁴⁸	456 ⁴⁸	456 ⁴⁸	456 ⁴⁸	456 ⁴⁸	456 ⁴⁸
L-B	11 ³	14 ⁵	62 ³⁸	12 ⁵	18 ²	31 ⁵	65 ²⁶	65 ²⁶	164 ⁶¹	167 ⁴⁰	1,086 ²⁰	21 ⁵	211 ⁸⁹	211 ⁸⁹	211 ⁸⁹	211 ⁸⁹	211 ⁸⁹	211 ⁸⁹	211 ⁸⁹	211 ⁸⁹	211 ⁸⁹	211 ⁸⁹
L-MM	4 ¹	4 ¹	35 ²³	9 ⁵	10 ¹	15 ¹	41 ¹⁸	41 ¹⁸	170 ¹¹²	242 ¹⁸⁴	562 ⁴⁵²	24 ¹⁵	120 ⁵³	120 ⁵³	120 ⁵³	120 ⁵³	120 ⁵³	120 ⁵³	120 ⁵³	120 ⁵³	120 ⁵³	120 ⁵³
L-HM	4 ¹	7 ⁴	10 ⁴	3 ¹	8 ²	11 ³	19 ⁷	19 ⁷	107 ⁷⁵	79 ⁴³	161 ¹⁰²	10 ⁵	134 ¹⁰²	134 ¹⁰²	134 ¹⁰²	134 ¹⁰²	134 ¹⁰²	134 ¹⁰²	134 ¹⁰²	134 ¹⁰²	134 ¹⁰²	134 ¹⁰²
Shem Creek (suburban watershed)																						
U-CB	6 ¹	3 ⁰	24 ³	6 ¹	6 ²	11 ⁴	21 ⁴³²	21 ⁴³²	445 ³³	503 ⁴³	844 ⁹⁰	56 ⁶	1,113 ¹⁴¹	1,113 ¹⁴¹	1,113 ¹⁴¹	1,113 ¹⁴¹	1,113 ¹⁴¹	1,113 ¹⁴¹	1,113 ¹⁴¹	1,113 ¹⁴¹	1,113 ¹⁴¹	1,113 ¹⁴¹
U-B	4 ¹	4 ¹	19 ³	7 ¹	8 ¹	12 ⁴	157 ³⁷	157 ³⁷	376 ¹¹¹	514 ³⁸	699 ²⁰⁹	55 ¹⁶	898 ²⁴⁰	898 ²⁴⁰	898 ²⁴⁰	898 ²⁴⁰	898 ²⁴⁰	898 ²⁴⁰	898 ²⁴⁰	898 ²⁴⁰	898 ²⁴⁰	898 ²⁴⁰
U-MM	5 ¹	5 ¹	12 ¹	6 ¹	7 ²	10 ⁴	97 ⁹	97 ⁹	199 ³⁹	286 ³⁶	442 ⁹³	53 ¹¹	555 ⁵⁶	555 ⁵⁶	555 ⁵⁶	555 ⁵⁶	555 ⁵⁶	555 ⁵⁶	555 ⁵⁶	555 ⁵⁶	555 ⁵⁶	555 ⁵⁶
U-HM	44 ⁴¹	10 ⁸	211 ²⁰²	66 ⁶¹	41 ²⁶	90 ⁶⁷	2,075 ^{1,999}	2,075 ^{1,999}	7,854 ^{7,731}	6,251 ^{6,059}	14,128 ^{13,842}	769 ⁷⁵⁴	15,364 ^{14,958}	15,364 ^{14,958}	15,364 ^{14,958}	15,364 ^{14,958}	15,364 ^{14,958}	15,364 ^{14,958}	15,364 ^{14,958}	15,364 ^{14,958}	15,364 ^{14,958}	15,364 ^{14,958}
L-CB	7 ⁰	8 ⁵	27 ⁶	8 ²	11 ⁴	19 ⁷	180 ³⁸	180 ³⁸	385 ⁵⁰	356 ⁵³	691 ⁸⁶	25 ⁹	881 ¹⁴⁵	881 ¹⁴⁵	881 ¹⁴⁵	881 ¹⁴⁵	881 ¹⁴⁵	881 ¹⁴⁵	881 ¹⁴⁵	881 ¹⁴⁵	881 ¹⁴⁵	881 ¹⁴⁵
L-B	5 ²	5 ²	34 ¹¹	10 ³	13 ³	19 ⁴	200 ⁷⁶	200 ⁷⁶	435 ¹⁵⁸	526 ¹⁷⁴	771 ²⁹⁵	43 ²⁸	1,041 ³⁶¹	1,041 ³⁶¹	1,041 ³⁶¹	1,041 ³⁶¹	1,041 ³⁶¹	1,041 ³⁶¹	1,041 ³⁶¹	1,041 ³⁶¹	1,041 ³⁶¹	1,041 ³⁶¹
L-MM	7 ²	2 ¹	32 ¹⁶	6 ³	8 ⁵	15 ¹⁰	213 ¹¹²	213 ¹¹²	536 ²⁹⁷	593 ³⁰⁰	978 ⁵¹⁸	74 ³³	1,274 ⁶⁹²	1,274 ⁶⁹²	1,274 ⁶⁹²	1,274 ⁶⁹²	1,274 ⁶⁹²	1,274 ⁶⁹²	1,274 ⁶⁹²	1,274 ⁶⁹²	1,274 ⁶⁹²	1,274 ⁶⁹²
L-HM	4 ¹	6 ³	23 ¹³	6 ¹	9 ³	17 ⁶	142 ⁸⁶	142 ⁸⁶	355 ¹⁸⁷	367 ¹⁹⁸	607 ³⁵³	46 ²²	844 ⁴⁷⁰	844 ⁴⁷⁰	844 ⁴⁷⁰	844 ⁴⁷⁰	844 ⁴⁷⁰	844 ⁴⁷⁰	844 ⁴⁷⁰	844 ⁴⁷⁰	844 ⁴⁷⁰	844 ⁴⁷⁰

The first letter in the Site ID indicates the reach (U = upper and L = lower) and the second letter(s) indicates the transect position (CB = creek bed, B = berm, MM = midmarsh, HM = high marsh). All concentrations are ppb (ng/g dry weight).

Table 3. Regression analysis results between the organic contaminant concentrations and the clay content or the total organic carbon (TOC) content

	Clay						TOC					
	Reference		Developed		Ref/Dev		Reference		Developed		Ref/Dev	
	r ²	p value	r ²	p value	r ²	p value	r ²	p value	r ²	p value	r ²	p value
Total PAH	0.36	0.0001	0.03	0.1696	0.09	0.0002	0.15	0.0010	0.20	0.0001	0.17	0.0001
Total PCB	0.02	0.2538	0.00	0.6697	0.02	0.0996	0.02	0.2706	0.06	0.0326	0.08	0.0008
Total DDT	0.17	0.0004	0.01	0.4759	0.06	0.0046	0.07	0.0235	0.07	0.0262	0.00	0.7098

The bold values indicate the regression was not significant at $\alpha = 0.05$

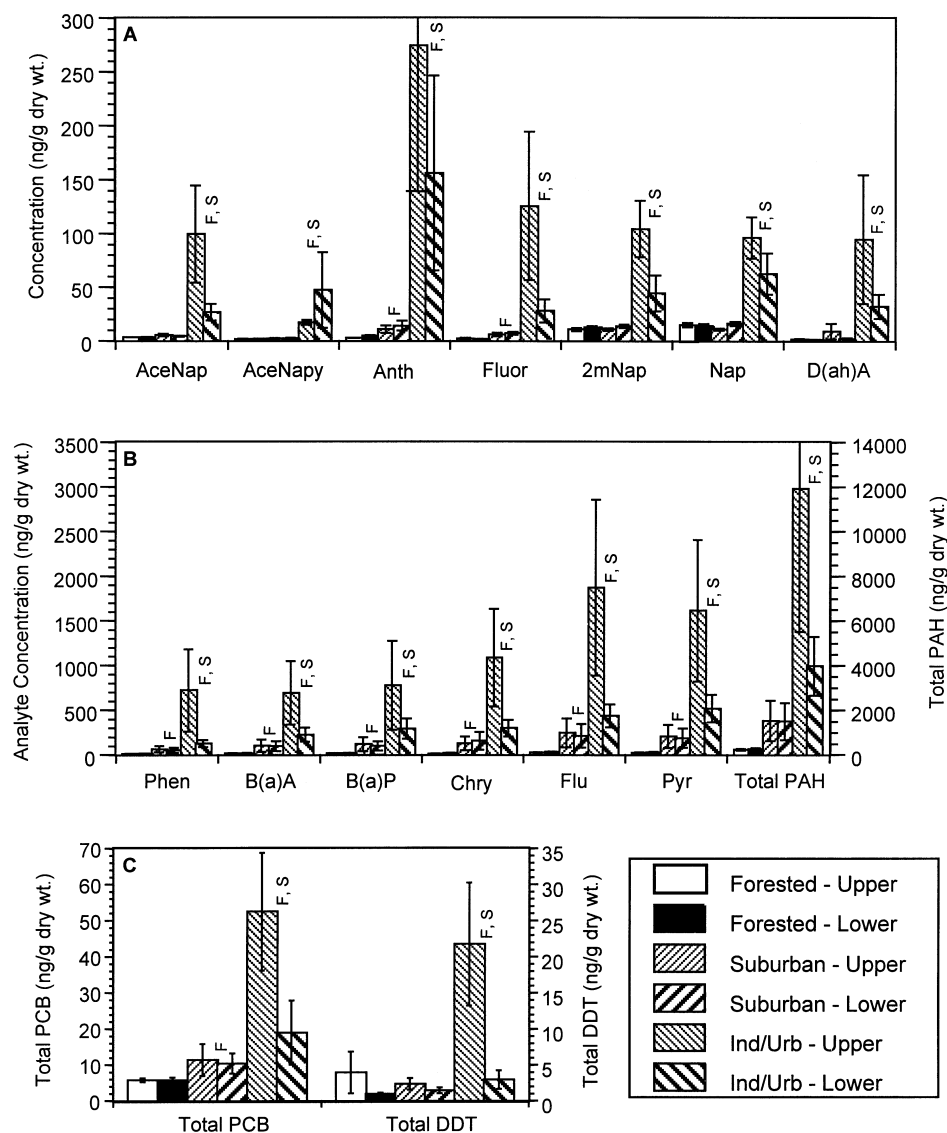


Fig. 3. The mean and standard error of the organic contaminant concentrations (ng/g dry weight) for the forested, suburban, and industrial/urban (ind/urb) watershed types by reach for PAHs (A and B) and persistent organochlorines (C). F or S indicate the watershed class (combined upper and lower reach effect) was significantly higher than the forested or suburban classes, respectively

In contrast to the relatively homogenous spatial distributions of PAHs in the two reference creeks, Diesel Creek had distinct spatial distributions (Table 2, Figure 5). PAH concentrations in the upper reach were significantly higher than the lower reach; however, spatial distributions from the creek channel to the marsh-upland interface were similar in both reaches. With the exception of AceNapy and Chry, PAH concentrations decreased from the creek bed to the high marsh. PAH concentrations in the creek bed were always significantly higher than the concentrations in the high marsh (Figure 5).

The representative suburban creek-marsh system, Shem Creek, had one site on the high marsh with a total PAH concentration of 324,000 ppb, which was 20–100 times higher than the PAH concentrations measured at all of the other Shem Creek sites (Table 2). Concentrations from this single site influenced both the LMW and HMW PAH analyte patterns from the creek channel to the marsh-upland interface in the upper reach (Figure 5). In general, the concentrations of LMW analytes were similar in both reaches of Shem Creek and along the transect from the creek channel to the marsh-upland

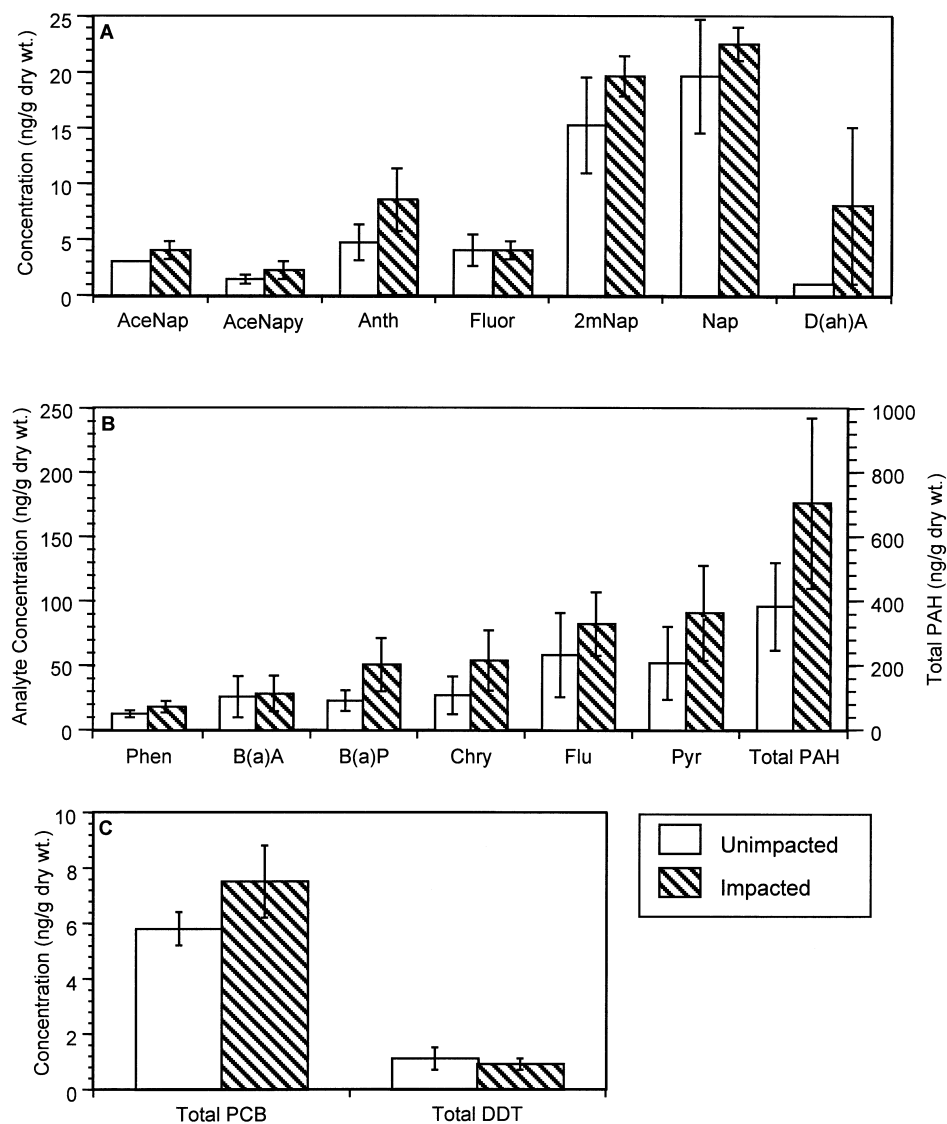


Fig. 4. The mean and standard error of the organic contaminant concentrations (ng/g dry weight) for the salt marsh unimpacted and impacted watershed types for PAHs (A and B) and persistent organochlorines (C). Note: There were no significant differences between the impacted and unimpacted classes of creeks

interface. In contrast, concentrations of HMW analytes had different patterns in the upper and lower reaches. In the upper reach, concentrations decreased from the creek channel to the marsh-upland interface, whereas in the lower reach, concentrations were highest on the midmarsh.

In the tidal creek study, sediment PCB concentrations were significantly higher in the industrial/urban watershed class compared to the suburban or forested classes (Figure 3C). In addition, PCB concentrations were significantly higher for the suburban watershed class than the forested class. Sediment PCB concentrations were similar between the impacted and unimpacted salt marsh watershed classes (Figure 4C). PCB concentrations were not different between the upper and lower reaches of creeks for both the upland and salt marsh watershed groups.

The spatial distributions (*i.e.*, the creek-marsh transect study) of PCB concentrations were not concordant with the clay or the TOC distributions in the sediment (Figure 5). The two developed watershed creeks, Diesel and Shem, had significantly higher concentrations of PCBs than the two reference creeks, Rathall and Long. Low levels of PCBs were homogenously

distributed across Rathall and Long Creeks (Figure 5E). Diesel Creek had the highest PCB concentrations on the midmarsh in the upper reach, but these concentrations were not significantly higher than the other transect positions (Figure 5E). The variability in PCB concentrations across the Diesel Creek system was high. Sanger *et al.* (1999) reported similar patterns of variability for the trace metal concentrations in this system. In Shem Creek, the only elevated PCB concentrations occurred on the creek bed in the lower reach (Figure 5E).

In the tidal creek study, total DDT concentrations were significantly higher in the industrial/urban watershed class compared to the suburban and forested classes (Figure 3C). The suburban and forested watershed classes had similar total DDT concentrations. Across all watershed types in the two-way ANOVA, total DDT concentrations were significantly higher in the upper reaches of creeks compared to the lower reaches. In addition, a one-way ANOVA found DDT concentrations in the upper reach to be significantly higher than the lower reach of the industrial/urban watershed class. Total DDT concentrations were not significantly different between unimpacted and impacted salt marsh watershed classes (Figure 4C).

Table 4. Significant differences from the three-way ANOVA least squares mean analyses comparing the creek-marsh systems

	Shem vs. Rathall	Diesel vs. Rathall	Shem vs. Long	Diesel vs. Long	Diesel vs. Shem
AceNap	>	>	>	>	>
AceNapy	=	>	>	>	>
Anth	>	>	>	>	>
Fluor	>	>	>	>	>
2mNap	=	>	>	>	>
Nap	=	>	=	>	>
Phen	>	>	>	>	<
B(a)A	>	>	>	>	<
B(a)P	>	>	>	>	<
Chry	>	>	>	>	<
D(ah)A	>	>	>	>	=
Flu	>	>	>	>	<
Pyr	>	>	>	>	<
Total PAHs	>	>	>	>	<
Total PCBs	>	>	>	>	=
Total DDT	>	>	<	<	=

Rathall Creek = reference; Long Creek = reference; Diesel Creek = industrial/urban; Shem Creek = suburban

An = indicates there were no significant differences, > indicates the first creek listed was significantly greater than the second creek, and a < indicates the first creek listed was significantly less than the second creek

The spatial distributions of total DDT concentrations within each intensively studied creek-marsh system were also not concordant with the clay or the TOC distributions (Figure 5). Long Creek (forested) had significantly higher concentrations of total DDT compared to Diesel, Shem, or Rathall Creeks (Table 4, Figure 5E). Sediment DDT concentrations for the two developed creeks were similar, but both were significantly higher than the levels in Rathall Creek. Total DDT concentrations in Rathall Creek were low across the entire system (Figure 5E). In contrast, Long Creek tended to have higher total DDT concentrations on the marsh surface of the upper reach (*i.e.*, midmarsh and high marsh) compared to the lower reach, but these differences were not significant (Figure 5E). The total DDT concentrations in Diesel Creek mirrored total PCB distributions, with the highest levels found at one of the midmarsh, upper reach sampling sites (Figure 5E). Shem Creek had low levels of DDT throughout the system, except for the one site on the high marsh of the upper reach that had extremely high PAH concentrations.

Within-system variability in organic contamination within the tidal creek-salt marsh system was different among the organic contaminant groups evaluated and among watershed types. In general, the variability in contaminants within the representative individual systems was often greater than or equivalent to the variability among creeks composing a watershed class. This primarily was the result of a few localized sites having extremely high concentrations of some organic contaminants (*i.e.*, "hot spots"). For example, variability in Shem Creek (suburban) was similar to the variability among suburban watersheds for the LMW PAHs and the total PCBs. But the variances for the HMW PAHs and total DDT within Shem Creek were similar to the variances observed for the industrial/urban class of creeks. This increase in the variability was driven by the high PAH and DDT concentrations observed at one site

(Figure 2A). Similar to Shem Creek, Rathall Creek had one site with unusually high PAH concentrations. This site increased the variance in the PAHs within the Rathall Creek system (Figure 2B). In contrast, Diesel and Long Creeks generally had within system variance that was similar to the variance observed among systems in the industrial/urban and forested watershed classes, respectively.

Discussion

The patterns of organic contamination (*i.e.*, PAHs, PCBs, and DDT) in this study were similar to the trace metal findings presented in Sanger *et al.* (1999). Levels of PAHs were significantly higher in the industrial and urban watershed class of creeks compared to the suburban and forested classes. The increased levels of PAHs in these industrial and urban creeks were due to both uncombusted fossil fuels (*i.e.*, LMW PAHs) and combusted fossil fuels (*i.e.*, HMW PAHs). This suggests the PAH contamination was from multiple sources, potentially both historic and contemporary. In addition to PAH contamination, the industrial/urban class of creeks sampled had significantly higher concentrations of DDT and PCBs compared to the suburban and forested classes of creeks. The upper reaches of the industrial/urban class of creeks functioned as repositories of DDT and PCBs. This indicates that DDT and PCBs are tightly bound to organics in marsh sediments and may serve as focal points of pollution for considerable periods of time given their long half-lives and resistance to microbial degradation.

Historic sources of PAHs into these systems include a creosote wood-treatment facility, power plants, and many other industrial activities. Present sources of PAHs include port-related activities, ship rebuilding, trucking companies, fuel storage and distribution centers, atmospheric deposition, and runoff from roads, highways, and parking lots. All of the industrial and urban creeks are located in the neck of the Charleston peninsula, where industrial development has existed for over a 100 years. PCBs and DDT are contaminants of antiquity due to their ban in the United States in the 1970s. PCBs were commonly used in cooling agents and insulators in capacitors, transformers, gaskets, caulking compounds, paints, and oils (Hutzinger *et al.* 1974; Kennish 1992). DDT was considered the "miracle" insecticide in the 1940s and was used extensively to control agricultural and human pests (Leary *et al.* 1946) until its ban in the 1970s.

The intensively sampled representative industrial/urban creek-marsh system, Diesel Creek, had distinct spatial patterns of PAH and organochlorine contamination. PAH concentrations decreased from the upper to the lower reaches and from the creek channel to the high marsh. These spatial patterns suggest that the PAHs were entering the headwaters of Diesel Creek from the adjacent uplands. Potential upland sources of PAHs include runoff from the major interstate highway leading into downtown Charleston, several truck storage facilities, and a fuel storage and distribution center. In addition to the repository action of the creek channel sediments, the channel of Diesel Creek appears to be a conduit for PAHs from the upland portion of the watershed to the Ashley River and Charleston Harbor Estuary. In contrast, the spatial distributions of organochlorine contaminants in Diesel Creek (*i.e.*, total PCBs, total DDT) were relatively homogeneous from the creek channel to the high marsh. However, the organochlorine concentrations at one

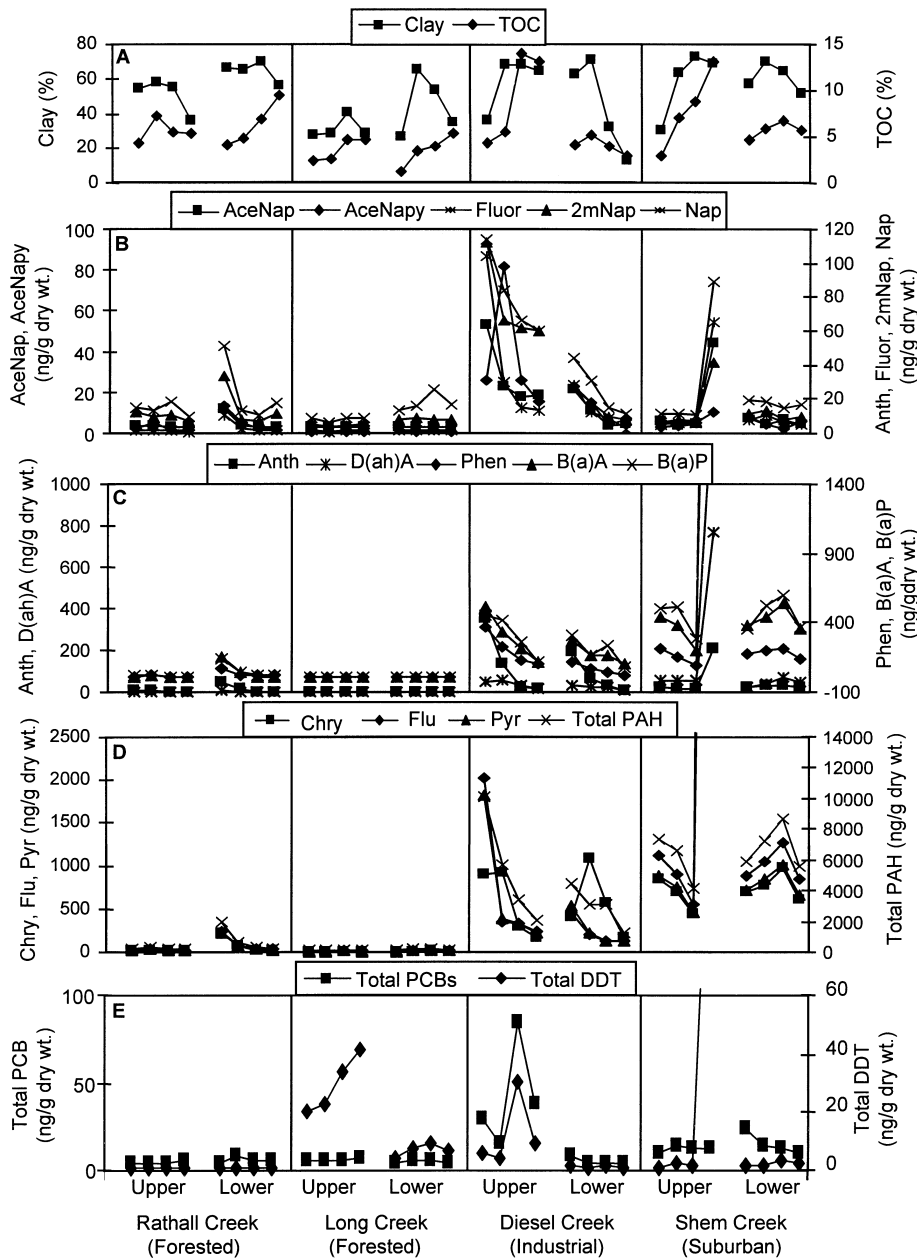


Fig. 5. Sediment characteristics (A), polycyclic aromatic hydrocarbons (B, C, and D), and organochlorine (E) distributions from the creek channel to the marsh-upland interface within each creek and reach. The four concentrations (ng/g dry weight) for each group represent the average for the creek bed, berm, midmarsh, and high marsh, proceeding from left to right. The reader is referred to Table 2 for the concentrations on the high marsh of Shem Creek, which are above the figure scale

upper reach, midmarsh site were 3 to 60 times higher than the concentrations at the other Diesel Creek sampling sites. This site appears to have been a historical, undocumented disposal area for fly ash from an old power plant and other types of industrial wastes. Some of the trace metal concentrations were also elevated at this site (Sanger *et al.* 1999).

In contrast to the industrial and urban class of creeks, the suburban class only had three LMW PAH analytes and four HMW PAH analytes with concentrations significantly higher than those of the forested watershed class of creeks. These elevated levels of PAHs in the suburban creeks may have resulted from runoff of roads and parking lots, boating activities, and creosote-treated docks. In addition to the elevated levels of PAHs, the levels of PCBs were significantly higher in the suburban class of creeks compared to forested class of creeks. Although the commercial production of PCBs were

banned in 1977, the level of historic contamination was significant enough to impact creeks with no industrial development. This probably occurred because of the use of PCBs in paints, varnishes, hydraulic oils, and caulking compounds (Hutzinger *et al.* 1974). Levels of DDT were similar between the suburban and forested classes. The lack of differences between these classes of creeks is driven by the high concentrations of DDT in one of the forested creeks. Both PCBs and DDT have long half-lives and it is apparent that they still pose a threat to estuarine communities despite their ban over 25 years ago.

The representative suburban creek-marsh system, Shem Creek, had the highest population density (15.7 individuals per ha) and percent impervious surface (34.5%) of the creeks comprising the suburban watershed class. A commercial fishing fleet (>50 vessels) is docked ~3 km downstream of the lower reach defined in this study. PAH contamination, particularly the

HMW PAHs, was prevalent throughout the Shem Creek system sampled. This suggests PAHs are entering the system from the watershed (*e.g.*, commercial and residential land uses) and from the anthropogenic activities downstream (*e.g.*, commercial fishing fleet and high recreational boating). The predominance of the HMW PAH analytes throughout the Shem Creek system indicates two likely sources: (1) the PAHs entering this system are primarily combusted, and/or (2) historical fuel spills occurred in this system and the LMW PAH analytes have degraded leaving a higher proportion of the HMW PAH analytes. In addition, one site in the upper reach, high marsh had extremely high PAH and DDT concentrations. One possible explanation for these high isolated concentrations is that a mixture of DDT and fuel oil may have been released at this location accidentally or to control pests years ago. DDT was historically mixed with oil such as fuel oil to control mosquitoes and other pests (Leary *et al.* 1946) and to treat wood products used in shrimping operations (personal observation). Similar to the suburban watershed class of creeks, levels of PCBs in the sediments of Shem Creek were elevated compared to the levels in reference creek-marsh systems. The source of PCBs into this system may be related to the use of PCB-containing paints, varnishes, caulking compounds, and hydraulic oils (Hutzinger *et al.* 1974) by the commercial fishing fleet, recreational boaters, and home owners.

Limited and patchy organic contamination was also found in the reference creek-marsh systems. For example, one of the lower reach, creek channel sample sites in Rathall Creek had elevated levels of PAHs. The patchy PAH contamination indicates a very localized source. One possible explanation is a small fuel spill or exhaust from recreational and commercial boat usage of tidal creeks for fishing and crabbing. Hoss and Engle (1996) reported that PAH discharges from outboard engines accounted for 20% of total PAH loadings in coastal regions of North Carolina. In contrast to Rathall Creek, Long Creek was found to have historical contamination with DDT and associated metabolites. Previous to its present-day forested land cover, the Long Creek watershed was extensively used for agriculture. In addition, the upper 300–600 m of Long Creek was an impounded freshwater lake until 1974 when the dike was destroyed during a storm. DDT was commonly used prior to its ban in the 1970s to control agricultural pests and mosquitoes (Leary *et al.* 1946). Collectively, these findings suggest that both present and past land uses need to be considered when interpreting organic contaminant data.

A number of authors (*e.g.*, Boehm and Farrington 1984; Barrick and Prahl 1987) have reported strong associations between the level of enrichment by organic contaminants with the TOC content of the sediment. However in this study, correlations between the TOC content and the organic contaminants measured generally accounted for only a small portion of the variance. Other studies have also found no or weak relationships between the organic contamination and sediment properties (Wade *et al.* 1994; Kucklick *et al.* 1997). They generally attributed the absence of a relationship to spatial gradients from identifiable sources. Our data support this explanation in that we clearly observed decreasing concentrations from potential sources regardless of sediment properties. In addition, atmospheric deposition of PAHs, PCBs, and DDT may complicate the interpretation of contaminant spatial distributions.

This study linked organic contamination in intertidal creek–salt marsh habitats with varying levels of anthropogenic activity in the watershed. A similar study (Vernberg *et al.* 1992; Sanders 1995) conducted ~120 km north of Charleston examined subtidal sediment PAH concentrations from a small, suburbanized estuary (Murrells Inlet) and a small, pristine estuary (North Inlet). They also linked watershed development and the degree of PAH contamination, but at the scale of an estuary. The industrial and urban sites examined in our study had mean concentrations of individual PAH analytes that were substantially higher than the maximum concentrations reported by Sanders (1995). Concentrations of the PAH analytes from the suburban sites of the present study were similar to the upper 20% of the suburbanized sites sampled by Sanders (1995). In addition, the mean level of PAH contamination from the forested sites in the current study were generally similar to the lower 33% of the suburbanized estuarine sites and the upper 20% of the reference estuarine sites sampled by Sanders (1995). This finding suggests that our reference sites in the Charleston Harbor region had a greater degree of contamination than the pristine North Inlet. These findings suggest that the selection of reference areas may strongly influence study findings. For example, if a pristine environment (*e.g.*, the North Inlet Estuary) had been used as the only reference site, it is likely that differences between suburban development and forested areas would have been accentuated.

Sediment concentrations of PAHs in the industrial/urban creeks in this study were generally higher than that for other subtidal southeastern U.S. coastal regions (Hyland *et al.* 1998). In addition, the suburban watershed class of creeks had sediment concentrations of total PAHs that were elevated above those concentrations found in other subtidal southeastern U.S. coastal regions (Hyland *et al.* 1998). By contrast, the forested watershed class of creeks had sediment concentrations of PAHs that were lower than the PAH concentrations found in subtidal southeastern U.S. coastal regions (Hyland *et al.* 1998). PAH concentrations in the industrial/urban sites would be classified as “high” (mean of National Status and Trends sites plus 1 standard deviation) for the coastal United States with one site classified as “5Xhigh” (NOAA 1991). The PCB concentrations found in the industrial/urban class of creeks were substantially higher than the concentrations found in subtidal southeastern U.S. coastal regions, but the suburban class of creeks was only slightly higher (Hyland *et al.* 1998). Contrary to PAH and PCB concentrations, DDT concentrations observed in the sediment from the industrial and urban class of creeks were similar to subtidal southeastern U.S. regions, and the suburban and forested classes were lower compared to these other regions. Only a few sites from this study had PCB or DDT concentrations which would be classified as high for the coastal United States (NOAA 1991).

One of the major objectives of the Tidal Creek Project was to develop recommendations for monitoring the status and trends of these important ecological systems. We recommend measuring both the LMW and HMW PAHs as these data often assist in identifying potential sources. The results from this and other studies suggest that DDT and PCBs are still a problem in South Carolina that warrant continued monitoring even though the use of both compounds has been banned for over 20 years. This is particularly important given the fact that the major types of organic contaminants observed in finfish (Mathews 1994) and

shellfish are still PCBs and DDT. In addition, both PCBs and DDT are considered potent endocrine-disrupting chemicals, which may interact in a greater than additive toxicity potential in affecting neuroendocrine function (Sota *et al.* 1995). Based on our results, the levels of pesticide contamination (other than DDT) in these shallow tidal creeks and salt marshes suggest that pesticides are not a major problem. However, the impacts of pesticides on tidal creek–salt marsh systems in agricultural watersheds was not the focus of this study. In agricultural watersheds, we recommend that a suite of contemporary-use pesticides be quantified since it is currently unknown whether these tidal creek–salt marsh systems serve as repositories and/or conduits for pesticides to the adjacent estuary. Selection of these pesticides should be based on agricultural and urban pesticide usage within a given region. This type of knowledge is critical because these systems are known to serve as nursery habitats for many estuarine and marine species.

Similar to the trace metal monitoring recommendations, we recommend sampling the creek channel in both the upper and lower reaches (Sanger *et al.* 1999). The creek channel is the area where organisms are concentrated for a large portion of their “average” day and the physical-chemical conditions that increase the bioavailability of contaminants (*e.g.*, low dissolved oxygen, salinity, and pH fluctuations) are more likely to occur in the creek habitats than on the salt marsh platform. Both the upper and lower reaches are important sampling endpoints for evaluating associations with land and the estuary. If only one sample can be taken, then we recommend that the upper reach be sampled because it has the closer association with land-based activities.

From this study, it is evident that the alteration of the surrounding land cover in watershed may impact the levels of organic contamination in tidal creek and salt marsh habitats. These environments, particularly the creek channel, are acting as repositories and potential conduits of organic contaminants from the upland environment to the main body of the estuary. If the contaminant levels observed in this study are found to cause biological effects, this would be especially disconcerting since these habitats also serve as nurseries and feeding grounds for fish and crustaceans (*e.g.*, Hackney *et al.* 1976; Weinstein 1979; Wenner 1992; Wenner and Beatty 1993). These larvae and juveniles are the most toxicologically sensitive life history stages (Scott *et al.* 1992). In addition, the potential for human contaminant exposure from these contaminated creeks and salt marshes is an important consideration that needs to be further investigated.

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