Arch. Environ. Contam. Toxicol. 28, 397–405 (1995)

ARCHIVES OF
Environmental
Contamination
and Toxicology

Distribution of Polycyclic Aromatic Hydrocarbons in Oyster *(Crassostrea Virginica)* and Surface Sediment from Two Estuaries in South Carolina

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Received: 30 April 1994/Revised: 24 October 1994

Abstract. The concentration of polycyclic aromatic hydrocarbons (PAHs) was determined in oysters and sediments collected from two high salinity estuaries from the coast of South Carolina. The two estuaries were Murrells Inlet (urban), an estuary receiving urbanized drainage and run-off, and North Inlet (non-urban), receiving drainage from heavily forested terrarin and minimal anthropogenic input. A minimum of thirty (30 stations were sampled in Murrells and North Inlets, respectively. A composite oyster sample (n = 30) was analyzed for each station. For sediment, a sample from the top 3–5 cm of the sediment surface from each station was analyzed. In oyster from Murrells Inlet, total PAHs concentrations within the 75 percentile were located in the northern portion of the estuary near marinas, adjacent to residential areas of high population density, near commercial enterprises or run-off from storm drains. Total PAHs within the 25 percentile were located near the mouth of the estuary. These results showed a PAHs concentration gradient in the estuary that was highest in narrow creeks, where the urban shore interfaced with tidal creeks and lowest at the mouth of the estuary. In the case for sediment, a similar gradient was observed. In comparing the mean total PAHs of the two inlets, Murrells Inlet had significantly higher ($p < 0.01$) total PAHs concentrations than North Inlet for oyster and sediment, respectively.

In comparing PAHs concentrations among the two matrices in Murrells Inlet, these data showed that the pattern of individual PAHs in oyster and in sediment were different. Oysters tended to accumulate the lower molecular weight and the more water-soluble PAHs compared to PAHs found in sediment. As expected, differences in octanol/water partition coefficient among individual PAHs and the greater persistence of the higher molecular weight PAHs contributed to the accumulation patterns in oyster and sediment.

Polycyclic aromatic hydrocarbons (PAHs) contamination of aquatic environments results primarily from human activities (Suess 1976), although a small amount is due to natural processes (Blumer 1976). PAHs in contaminated sites are a diverse group of nonpolar, lipophilic compounds produced as a result of incomplete combustion of organic materials. Once formed, PAHs enter the near shore marine environment as a result of urban storm drain runoffs, storm water runoff from highways, effluent from industrial and sewage outfalls (Hoffman *et al.* 1984, Brown *et al.* 1985), creosote treated wharfs and pilings (Black 1982), and power boating activities (Maher and Aislabie 1992). In the marine environment, PAHs are incorporated into the sediment from particulate sedimentation and from the biota. The biota assimilate PAHs from the water column and from the sediment. Ten parent PAH compounds that are commonly found in waste crankcase oil, water runoff from highways, urban dust and nearshore marine sediment, and coastal estuaries associated with urban influence were selected for this study (Tanacredl and Cardenas 1991; Ngabe 1992; Maher and Aislabie 1992).

This paper reports on the spatial distribution of PAHs found for oyster and sediment, respectively, among two high salinity estuaries on the coast of South Carolina. Also, the pattern of individual PAH composition in oyster and sediment is presented.

Materials and Methods

Study Area

Two high salinity estuaries located on the coast of South Carolina that have no riverine input, and therefore receive little fresh water, were selected for study. The major source of fresh water in these estuaries is from rainfall and run-off. An additional selection criteria was based on the two estuaries proximity to urban activities (Figures 1, 2). Murrells Inlet (Lat. 33° 32″, Long. 79° 02″) is an urbanized area that is primarily residential and commercial (shopping centers). It has no industrial outfalls or agricultural activities (Fulton *et al.* 1993). It receives pollution in runoff from parking lots, street stormdrain, boat marinas, and atmospheric deposition. The city has approximately 18,000 permanent residents and a large seasonal tourist population utilizing motor vehicles and power boating during the summer months. North Inlet (Lat. 33° 20″, Long. 79° 10″) is heavily forested, undeveloped, and receives minimal anthropogenic input.

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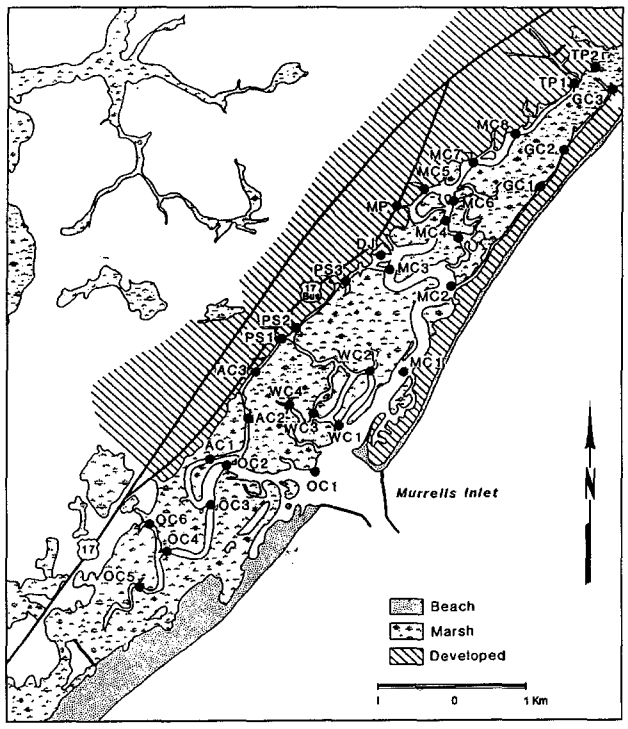

Fig. 1. Map of Murrells Inlet sampling stations (●)

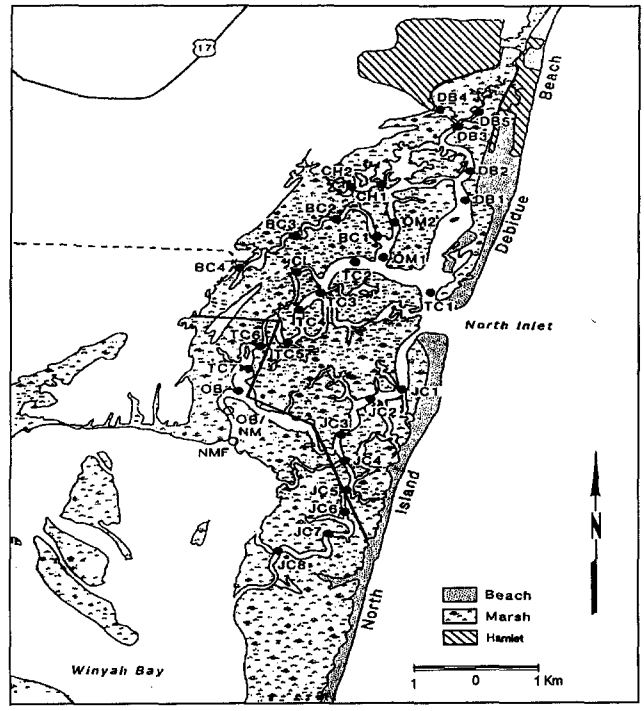

Fig. 2. Map of North Inlet sampling stations (●)

Table 1. Analysis of NBS standard reference materials (ng/g), dry weight

	NIST SRM 1974 (Mussel tissue)			NIST SRM 1941 (Marine sediment)		
	Certified	Found	%Recov.	Certified	Found	% Recov.
Phe	45 ± 11	48.8 ± 3.4	108	577 ± 59	613 ± 31	106
Ant	6.1 ± 1.7	6.0 ± 0.4	99	202 ± 42	201 ± 21	100
Flu	272 ± 47	241 ± 16	108	1220 ± 240	1233 ± 108	101
Pyr	276 ± 30	228 ± 23	83	1080 ± 200	1048 ± 137	97
B(a)A		63.9 ± 12.3		550 ± 79	721 ± 121	131
Cry		100 ± 13			847 ± 153	
B(b)F	52.3 ± 9.4	58.3 ± 10.5	111	780 ± 190	884 ± 151	113
B(k)F		59.3 ± 21.5		444 ± 49	610 ± 189	137
B(a)P	18.6 ± 3.8	16.6 ± 22.6	89	670 ± 130	636 ± 169	95
B(ghi)P	20.0 ± 2.3	26.8 ± 5.9	134	516 ± 83	763 ± 84	148

The number of SRM analyses was 12 and 13, respectively, for 1974 and 1941
The degree of uncertainty is at the 95% confidence level

Sample Collection

Oyster samples were collected in November 1990 from intertidal beds. A total of 62 sampling stations were choosen for this study. A bushel of clustered oysters was collected from each station by hand at low tide when the oysters were exposed to the air. The oysters were placed into bags and transported to the laboratory within four hours. After arriving at the laboratory, the oysters were refrigerated at 3°C. Within 24 h, the oysters were washed with tap water to remove surface mud. From the bushel of oysters, a composite sample (n = 30) of oysters were shucked from each station. The shells were opened with stainless steel knives and the tissues and shell liquor were removed, weighed, and placed in a clean beaker. The 62 composited samples averaged 159 ± 34 grams. Each composited sample was homogenized on a Omni-Mixer® at 8,000 RPM until the sample became a fluid, which took 30–45 seconds. After homogenization, 8.5 ± 0.2 g was weighed into solvent washed glass jars and stored at −80°C until analyzed. The remaining homogenate was placed in jars and archived at −80°C.

Sediment samples were collected in November 1991 for sediment. A total of 61 samples were collected from the same stations where oysters were collected from in 1990, with the exception of the MP station. At low tide when the oyster beds were exposed, approximately 200 grams of the top 3–5 cm of the sediment surface was collected with stainless spoons and stored in clean glass jars. After arriving at the laboratory, the sediment samples were stored at −80°C.

Chemical Analyses

The analytical procedure for the quantification of PAHs in oyster tissue and sediment was a modification of the methods of Krahn *et al.* (1988)

Table 2. Polycyclic hydrocarbons in oyster from Murrells Inlet, ng/g dry weight

Site	Phe	Ant	Flu	Pyr	B(a)A	Cry	B(b)F	B(k)F	B(a)P	B(ghi)P	Total
LOD>	6	3	27	33	19	16	18	14	5	10	
MP	76	30	680	407	228	261	53	161	31	41	1968
GC2	98	37	392	254	121	99	53	85	13	nd	1152
PS3	33	11	371	208	80	86	nd	65	18	nd	872
TP1	46	34	273	139	87	56	29	61	18	16	759
MC5	nd	15	218	207	59	110	36	28	20	nd	693
PS2	44	13	181	134	48	78	65	35	12	27	637
GC1	40	19	229	120	78	60	nd	62	13	12	633
DJ	67	30	275	113	34	40	21	25	7	nd	612
PS1	39	11	193	128	62	93	32	42	8	nd	608
AC3	51	14	235	118	45	52	23	42	13	14	607
MC6	43	14	157	102	43	125	56	33	6	nd	579
TP2	30	9	201	88	54	76	nd	39	8	nd	505
MC4	39	8	129	81	36	77	43	46	9	nd	468
MC8	26	12	160	86	42	68	41	32	nd	nd	467
MC7	30	13	183	98	44	74	nd	nd	nd	nd	442
WC3	40	7	105	58	25	50	24	19	nd	nd	328
MC2	37	8	87	53	23	60	26	19	nd	nd	313
MC3	26	5	103	51	22	53	30	nd	nd	nd	290
GC3	27	12	95	50	23	46	nd	21	6	nd	280
WC4	40	8	78	nd	nd	37	26	17	nd	nd	206
OC4	17	10	55	44	nd	18	nd	21	11	18	194
OC6	24	6	45	33	19	16	18	14	5	10	190
OC5	26	8	34	35	nd	39	nd	20	nd	10	172
WC2	36	6	42	39	nd	30	nd	nd	5	nd	158
AC1	29	8	56	36	nd	19	nd	nd	nd	nd	148
MC1	23	8	45	37	nd	28	nd	nd	nd	nd	141
AC2	40	9	64	nd	nd	nd	nd	15	7	nd	135
WC1	26	4	43	nd	nd	20	30	nd	nd	nd	123
OC3	33	6	41	nd	nd	30	nd	nd	nd	nd	110
OC1	31	nd	47	nd	nd	nd	30	nd	nd	nd	108
OC2	18	6	32	nd	nd	nd	nd	nd	nd	nd	56

and Schantz (1990). Briefly stated, the samples were removed from storage and allowed to thaw at room temperature. For oyster, the pre-weighed 8.5 g of the oyster homogenate were placed into a glass mortar and mixed with 100 g of ashed (700°C) anhydrous sodium sulfate. Any clumps that formed were broken-up with a glass pestle to form a dry powder. For sediment, all visible debris such as shells, sticks, etc. was removed from the thawed sample and mixed by stirring with a stainless spatula. From the mixed sediment, 8.5 g was weighed and treated with anhydrous sodium sulfate. The sulfated samples were placed into glass Soxhlet thimbles, three method internal standards (d-phenanthrene, d-fluoranthene, and d-perylene) were added to each sample and Soxhlet extracted for 18 h with methylene chloride. After extraction, each extract was concentrated to 500 uL on an automatic concentrator (TurboVap®). Initial clean-up began by injecting 400 uL of the extract into a semiautomated high performance liquid chromatographic (HPLC) system equipped with autosample injector (Gilson Model 231), a fraction collector (Gilson model 201), a Water's 501 pump, a Linear UV-106 monitor and 2 Phenomonex Phenogel size exclusion columns connected in series (22.5 × 250mm, 100 A). High molecular weight compounds such as lipids were removed from the extract in the first 14 min fraction of the chromatogram. The fraction of interest was collected between 1 min before the retention time of dibromooctafluorobiphenyl (DBOFBP) and 2 min after perylene. The mobile phase was methylene chloride at 9.0 mL/min (see Krahn *et al.* 1988 for further details). The methylene chloride in the collected fraction was replaced with hexane and the volume reduced to 500 μL. The hexane extract was transferred onto a pre-hexane rinsed cyanopropyl solid phase extraction (SPE) column and eluted with 12 mL of hexane. The hexane was replaced with acetonitrile and the extract reduced to 500 μL. For sediment samples, activated copper was added prior to the SPE step to remove sulfur. After the final clean-up, the PAHs residue was separated by high performance liquid chromatography (HPLC) and the individual PAHs were measured by wavelength programmed fluorescence detection at pre-selected wavelengths chosen for maximum sensitivity and selectivity (Wise *et al.* 1988; Schantz *et al.* 1990). An NIST-certified PAH standard solution and three deuterated PAH (Supelco Co. Inc.) internal standards were used to calibrate the HPLC and the detectors. Sample peaks were identified by retention times and fluorescence specific wavelength. Calibration response factors relative to internal standards were determined by analyzing certified aromatic hydrocarbon standards. For quantification of PAH, the HPLC system consisted of two Water's 6000A pumps, a 680 gradient controller, autosampler (WISP), an LC-PAH column (4.6 mm × 25cm) from Supelco, a Fiaton TC-50 column heater con troller, a CH-30 column heater, and two Perkin Elmer's fluorescence detectors, an LC-240 and LS-4 connected in series. The gradient program consisted of a linear ramp from 60% methanol in water to 100% methanol in 30 min at 1.0 mL/min. Using these chromatographic parameters, peak resolutions between perdeuterated and its associated nondeuterated PAHs were 0.44, 0.40, and 0.41, respectively for phenanthrene, fluoranthene, and perylene. The data were collected on a Perkin Elmer's workstation, using Omega II chromatographic software.

Two distinct sets of PAHs limits of detection (LOD) were used for oyster and sediment, respectively (Tables 1,2,3,4). The oyster LOD (1990) was higher than that for sediment (1991). The higher LOD for oyster is due to sporadic method blank values and the high moisture content found in oyster. The moisture content for oyster and sediment samples was 89.3 ± 1.6 and 48.3 ± 14.0 percent, respectively. The limit of detection was defined as the mean blank values + 3 standard

Table 3. Polycyclic hydrocarbons in oyster from North Inlet, ng/g dry weight

Site	Phe	Ant	Flu	Pyr	B(a)A	Cry	B(b)F	B(k)F	B(a)P	B(ghi)P	Total
LOD>	6	3	27	33	19	16	18	14	5	10	
TC7	41	12	48	52	nd	nd	nd	19	nd	nd	172
JC7	35	9	nd	56	nd	25	nd	20	7	16	168
JC8	22	13	62	nd	nd	32	nd	21	nd	nd	150
JC3	23	13	56	50	nd	nd	nd	nd	nd	nd	142
TC6	21	10	43	nd	nd	19	nd	11	nd	nd	104
CH2	30	10	45	nd	nd	17	nd	nd	nd	nd	102
OM1	13	8	36	28	nd	nd	nd	nd	5	nd	90
OB	27	12	nd	48	nd	nd	nd	nd	nd	nd	87
DB5	47	4	30	nd	nd	nd	nd	nd	nd	nd	81
TC3	21	9	45	nd	nd	nd	nd	nd	6	nd	81
CH1	63	4	nd	nd	nd	nd	nd	13	nd	nd	80
DB4	16	4	32	nd	nd	nd	27	nd	nd	nd	79
TC5	44	nd	nd	nd	nd	nd	nd	26	nd	nd	70
JC6	28	nd	nd	nd	nd	nd	40	nd	nd	nd	68
JC2	nd	nd	nd	50	nd	nd	nd	15	nd	nd	65
DB3	38	nd	nd	nd	nd	nd	nd	16	7	nd	61
OB	31	6	nd	nd	nd	nd	nd	13	6	nd	56
JC5	16	5	25	nd	nd	nd	nd	nd	5	nd	51
OM2	nd	3	nd	nd	nd	35	nd	nd	10	nd	48
DB1	25	nd	nd	nd	nd	nd	nd	15	5	nd	45
CL	26	nd	nd	nd	nd	nd	nd	19	nd	nd	45
TC4	26	nd	nd	nd	nd	nd	nd	18	nd	nd	44
BC2	24	nd	nd	nd	nd	nd	nd	16	nd	nd	40
BC3	22	nd	nd	nd	nd	nd	nd	17	nd	nd	39
JC1	nd	3	nd	nd	nd	nd	nd	nd	26	nd	29
DB2	23	nd	nd	nd	nd	nd	nd	nd	nd	nd	23
TC2	22	nd	nd	nd	nd	nd	nd	nd	nd	nd	22
BC1	14	3	nd	nd	nd	nd	nd	nd	4	nd	21
TC1	20	nd	nd	nd	nd	nd	nd	nd	nd	nd	20
JC4	nd	4	nd	nd	nd	nd	nd	nd	11	nd	15

deviations based on a 8.5 g of wet sample. The wet weight limit of detection was extrapolated to dry weight limit of detection.

For lipid analysis, a second aliquot of oyster tissue was Soxhlet extracted with methylene chloride. Percent lipid was measured on the wet weight of each sample. Organic carbon content in sediment was measured on a Perkin Elmer 2400 CHN Elemental Analyzer as described by Kuehl *et al.* (1993). Oyster and sediment PAH concentration data were converted to ng/g dry weight based on the dry matter content.

A National Institute of Standards and Technology (NIST) SRM-1974 (mussel tissue) or SRM-1941 (sediment; Table 1), a spiked field sample, and a method blank were included with each set of thirteen (13) samples. Control charts of SRMs and percent recoveries of spiked field samples were created and used to ensure the integrity of the analytical method. Sample extraction, extract clean-up, and HPLC analyses were performed under subdued light source of yellow fluorescent tubes to minimize possible photo-oxidation. All glassware were sonicated with soap and water, rinsed with hot tap water, air dried, and solvent-rinsed with methylene chloride prior to use. All solvents were of pesticide grade.

Statistical tests were performed with PC-SAS and Excel statistical software. A one-way analysis of variance (ANOVA) was used to determine significant differences among means. Additionally, Pearson's coefficient of determination (r^2) was used to determine relationships among individual PAHs. To derive numeric values for analytical results of samples below the limit of detection in Tables 7 and 8, a random number between zero and one was multiplied by the detection limit value for a given compound to assign values to each not detected sample. The random number was drawn from a uniform distribution. The PAHs names and identificaton (I.D.) are listed: {PAH I.D. = Phe - phenanthrene; Ant - anthracene; Flu-fluoranthene; Pyr - pyrene; B(a)A - benz{a}anthracene; Cry-chrysene; B(b)F - benzo{b}fluoranthene; B{k}F-benzo{k}fluoranthene; B(a)P - benzo{a}pyrene; B(ghi)P-benzo{ghi}perylene.

Results

PAHs in Oyster

The concentrations of the 10 individual PAHs and total PAH in oyster are shown in Tables 2 and 3. In Murrells Inlet, the total concentration of the 10 PAHs ranged from 1968 ng/g at MP to 56 ng/g at OC2 with a mean of 450 ± 388 ng/g. Stations within the 75th percentile included MP>GC2>PS3>TP1>MC5>PS2>GC1>DJ. These stations with high PAH concentrations were located in the northern portion of the inlet and towards marinas and high residential and commercial population density. In the 25th percentile were stations OC2<OC1<OC3<WC1<AC2<MC1<AC1<WC2 which were located on the southern portion of the inlet and away from areas of high population density. In general, stations in the middle and near the mouth of Murrells Inlet had concentrations between these two extremes. Fluoranthene was the most abundant PAH in Murrells Inlet; it was found at 100% of the stations and contributed 34% to the total PAH concentration measured in Murrells Inlet oysters.

At North Inlet, total PAH concentrations ranged from 172 ng/g at TC7 to 15 ng/g at JC4 with a mean of 70 ± 43 ng/g.

Table 4. Polycyclic aromatic hydrocarbons in sediment from Murrells Inlet, ng/g dry weight

Site	Phe	Ant	Flu	Pyr	B{a}F	Cry	B{b}F	B{k}F	B{a}P	B{ghi}P	Total
LOD>	2.0	0.2	3.5	0.8	0.5	1.0	1.0	1.5	0.4	0.4	
TP2	166.5	40.4	329.2	411.9	328.9	210.9	201.2	336.6	306.3	245.9	2578
GC3	82.2	126.3	150.5	202.8	211.8	242.1	205.5	320.8	238.4	279.6	2060
DJ	54.0	28.9	129.8	186.2	146.3	140.2	146.9	244.6	168.0	169.7	1415
MC8	29.6	13.5	100.4	141.4	111.1	118.9	121.1	194.9	129.3	149.3	1109
MC6	37.9	14.0	83.4	107.2	98.1	90.9	89.4	155.4	120.5	147.1	944
MC4	23.6	7.3	66.2	90.0	101.1	76.6	136.9	149.2	87.1	22.9	761
TP1	17.8	10.2	60.0	79.9	68.0	67.3	70.2	127.5	85.3	122.1	708
GC1	34.1	7.6	45.6	60.9	46.5	57.3	47.1	88.6	60.3	75.1	523
AC1	23.1	25.3	65.5	45.7	64.5	54.2	63.4	102.1	44.8	7.8	496
MC5	15.7	10.4	52.3	66.5	54.1	47.5	44.2	76.5	51.7	65.7	485
MC2	20.9	5.6	42.3	54.1	50.5	43.1	41.7	77.7	63.2	70.5	470
MC7	15.4	6.8	39.6	50.1	42.1	31.7	36.1	67.0	42.8	53.3	385
GC2	19.8	5.7	38.2	39.3	37.1	37.9	36.0	62.5	41.1	48.1	365
OC5	21.1	4.9	48.4	37.4	34.4	30.0	42.1	86.1	31.1	6.7	342
PS3	12.3	6.0	29.0	38.9	32.0	34.1	36.6	59.6	38.6	54.8	342
OC6	23.3	4.8	46.3	35.7	37.0	28.3	35.6	73.2	29.6	6.2	320
WC3	12.1	7.5	39.9	32.3	32.8	29.1	43.1	57.4	29.4	7.4	291
MC3	13.6	2.7	40.1	51.8	25.4	26.8	28.1	42.7	27.4	32.3	291
AC2	13.8	7.0	32.6	31.2	31.7	31.1	35.9	67.9	26.0	6.3	284
OC4	11.9	3.0	28.3	23.2	25.0	22.2	31.8	65.3	24.1	5.7	240
PS2	8.9	4.0	22.2	27.6	22.1	21.6	23.8	40.8	23.9	31.1	226
PS1	10.8	1.5	17.5	23.4	17.0	18.2	17.6	35.1	19.3	25.6	186
WC4	8.4	2.8	20.4	26.9	20.4	16.9	17.8	30.1	19.8	16.6	180
AC3	8.1	1.8	15.5	11.2	13.2	11.5	22.6	57.0	17.0	5.4	163
OC3	7.6	1.6	17.3	14.4	15.0	14.6	18.8	42.2	14.8	4.6	151
WC2	6.4	nd	9.8	9.6	7.6	10.5	13.1	8.7	6.5	11.3	84
MC1	2.1	0.2	3.7	3.8	4.5	2.3	7.4	10.2	6.7	25.0	66
WC1	2.9	0.4	5.8	7.4	4.9	4.2	3.8	8.7	3.6	4.0	46
OC2	3.9	0.5	nd	1.4	2.1	5.3	1.0	1.9	0.4	2.0	19
OC1	2.1	0.3	nd	0.8	1.1	2.9	1.8	3.8	1.2	0.4	14

Stations in the 75th percentile were TC7>JC7>JC8>JC3>TC6>CH2>OM1>OB. Many of these stations were located in small tidal creeks in the southern portion of the inlet. Two of the four stations in the 10th percentile were located at the mouth and larger creeks in the center of the inlet. Of the 10 PAHs tested, phenanthrene, which was found at 86 % of the stations, was the most abundant PAH in North Inlet oysters. This could be due to the high water solubility of phenanthrene with respect to the other PAHs. If phenanthrene were excluded from the calculations, then stations TC2< TC1 located at the mouth of North Inlet had the lowest total PAH concentrations. Interestuarine comparison indicated that Murrells Inlet oyster had significantly higher ($p < 0.01$) total PAH concentration than North Inlet tissue.

The oyster lipid concentrations were randomly distributed throughout Murrells and North Inlets, respectively. The average lipid contents were 0.62 ± 0.13 and 0.61 ± 0.08 percent, respectively, for Murrells and North Inlets. No statistically significant differences were observed for lipid concentration in oysters among the two inlets.

PAHs in Sediment

The concentrations of the 10 individual PAHs and total PAH measured on a dry weight basis in sediment are shown in Tables 4 and 5. In Murrells Inlet, total PAH concentrations range from 2,578 ng/g at TP2 to 14 ng/g at OC1, with a mean of 518 ± 590 ng/g. Stations in the 75th percentile included TP2>GC3>DJ>MC8>MC6>MC4>TP1>GC1. These stations were located on the northern end of the estuary near marinas, adjacent to residential areas of high population density, near commercial enterprises, or from storm drain outfalls. These stations were located in shallow creeks, where the urban shore interfaced with tidal creeks. Stations OC1<OC2<WC1<MC1<WC2<OC3<AC3, located at the mouth of the inlet, dominated the 25th percentile. In general, total PAH concentrations tended to be highest at stations located at or near the urban shore interface and lowest at stations near the mouth of Murrells Inlet.

In the case of North Inlet, total PAH concentrations ranged from 308 ng/g at OM1 to 9 ng/g at TC4, with a mean of 104 ± 55 ng/g. Stations in the 75th percentile were BC4>OM1>BC3>DB3>OM2>CH2>DB2>TC7. Station BC4, located at the base of a creosote-treated wooden bridge, had a total PAH concentration of 5,847 ng/g. Concurrently, no oysters were found at BC4 due to fresh water runoff. This value was not included in the statistical calculations because it was determined to be an outlier that represented a point source of contamination. Stations in the 25th percentile were TC4<DB4<JC2<JC4<JC8<JC1<JC3<TC5. In comparing the mean PAH levels of the two inlets, Murrells Inlet had a significantly higher ($p < 0.01$) total PAH concentration than North Inlet.

Table 5. Polycyclic aromatic hydrocarbons in sediment from North Inlet, ng/g dry weight

Site	Phe	Ant	Flu	Pyr	B{a}F	Cry	B{b}F	B{k}F	B{a}P	B{ghi}P	Total
LOD>	2.0	0.2	3.5	0.8	0.5	1.0	1.0	1.5	0.4	0.4	
BC4	143.6	81.5	1188.6	1077.8	630.4	1597.7	391.6	274.9	259.3	201.9	5847
OM1	21.4	5.4	35.8	41.6	46.7	29.1	23.9	46.4	33.6	24.1	308
BC3	11.3	1.7	14.7	19.0	18.2	32.5	18.6	32.1	21.1	15.6	185
DB3	7.3	1.9	16.9	20.1	17.8	18.7	18.5	31.1	21.1	16.6	170
OM2	8.9	12.5	14.4	16.2	13.9	12.1	14.6	26.2	15.2	16.5	151
CH2	8.5	1.6	14.3	18.5	11.0	11.3	14.0	26.3	17.0	15.6	138
DB2	10.8	2.1	14.6	17.4	12.3	12.1	13.1	24.4	13.6	13.1	134
TC7	9.5	1.0	14.1	20.0	10.7	13.0	11.0	21.3	14.9	14.3	130
OB	8.6	1.1	10.9	18.1	9.3	24.7	10.1	20.4	12.9	12.6	129
DB1	7.4	0.8	9.8	12.7	9.1	14.6	13.6	23.4	14.0	13.5	119
TC3	4.4	0.7	8.0	11.8	16.5	10.7	11.9	22.1	16.4	12.9	116
BC2	7.9	1.0	10.7	13.0	8.9	14.6	12.0	20.7	10.9	12.1	112
CH1	5.1	0.7	8.1	10.5	13.9	11.5	11.9	19.6	12.1	11.5	105
JC6	9.6	0.7	8.3	11.0	9.4	18.2	9.9	15.1	8.5	11.2	102
JC5	8.5	1.3	9.9	11.3	8.3	11.1	11.2	19.6	9.6	9.8	101
NMF	9.6	1.1	11.4	12.3	5.9	19.8	10.2	12.0	5.7	10.3	98
TC2	5.5	1.2	8.3	7.1	6.4	16.9	12.9	19.3	7.5	11.8	97
TC1	5.1	1.8	9.2	7.6	7.6	8.5	12.8	20.3	10.0	12.7	96
DB5	8.1	1.3	8.3	10.2	7.5	9.7	11.1	17.4	10.7	9.4	94
TC6	4.7	0.6	9.2	12.8	10.0	10.1	8.9	15.9	9.9	9.2	91
JC7	nd	0.7	7.8	7.7	5.2	15.0	9.9	14.8	6.7	16.1	84
CL	4.8	0.6	8.2	10.0	6.3	6.7	8.9	15.4	9.1	9.0	79
BC1	4.6	0.6	8.5	11.3	7.2	4.9	7.2	11.8	7.5	9.2	73
TC5	4.7	0.8	7.6	9.9	9.7	7.1	6.0	10.6	5.7	6.0	68
JC3	4.0	0.5	7.3	10.8	9.5	7.8	5.4	10.9	5.6	5.5	67
JC1	3.7	0.6	6.0	7.1	5.2	9.8	5.9	10.7	7.7	8.1	65
JC8	3.8	0.4	5.2	7.4	4.4	19.2	5.2	8.3	5.1	5.5	64
JC4	5.2	0.7	5.7	6.6	4.1	5.7	5.4	8.4	4.6	6.2	53
JC2	3.5	0.4	4.8	5.7	3.1	3.4	3.7	7.3	4.3	4.2	40
DB4	2.6	0.9	4.9	4.7	2.9	3.5	2.9	5.3	3.0	3.4	34
TC4	nd	nd	nd	1.4	0.6	1.4	1.3	2.1	0.7	1.3	9

Organic Carbon Concentration in Sediment

The concentrations of organic carbon in sediment are shown in Table 6. In Murrells Inlet organic carbon ranged from 5.67 percent at DJ to 0.10 percent at MC1. Within the 75th percentile were stations DJ>TP2>OC1>GC3>AC1>MC4>AC2>MC8. In the 25th percentile were stations MC1<WC1<OC4<WC3<MC3<MC2<GC1<PS2. In general, organic carbon concentrations were sporadically distributed throughout the estuary.

In North Inlet, Schwing *et al.* (1980), observed a nodal point as a result of tidal influence from two distinct hydrographically systems, mainly the Atlantic Ocean and Winyah Bay. They also observed differences in vegetation on each side of the node. North of the nodal point, tidal input is from the Atlantic Ocean, which supplies a constant high salinity of 30–34 ppt. The dominant vegetation north of the node was *Spartina alterniflora,* a cord grass that thrives in a more salinate environment. South of the nodal point is brackish water, salinity of 5 ppt, due to the tidal influence from Winyah Bay. Winyah Bay has a greater range of salinity due to periodic large freshwater input from the Pee Dee, Black, and Waccamaw rivers. A mixture of vegetation, including *Juncus roemerianus* and *Spartina cynosuroides,* was observed south of the node. No single plant species dominates.

For organic carbon in North Inlet, a definite difference in concentration north and south of the node was observed. Stations in the 83rd percentile were JC7>OB>JC6>NMF>JC5>TC7. These stations represent 75% of the stations south of the nodal point, which represents tidal influence from Winyah Bay. Stations in the 20th percentile were DB4<JC2<BC1<TC2<TC1<JC1. These stations were located north of the tidal nodal which represents tidal influence from the Atlantic Ocean. In general, organic carbon concentrations were highest in the southern portion of the estuary and were distributed sporadically throughout the northern portion of the estuary. In North Inlet, the organic carbon concentration ranged from 4.88% at JC7 to 0.26% at DB4. In comparing the mean carbon concentration among the two inlets, North Inlet sediments (2.55 ± 1.16%) had a significantly higher carbon concentration than sediments from Murrells Inlet (1.50 ± 1.45%).

When the total PAHs concentrations (dry weight) in Murrells Inlet were compared to organic carbon concentrations and total PAHs concentration (organic carbon weight) based on organic carbon concentrations in sediments, r^2 values of 0.48 and 0.06 respectively, were observed. Similar comparison of r^2 values for North Inlet data were 0.30 and 0.03, respectively.

Comparison of Oyster PAHs vs Sediment PAHs in Murrels Inlet

For purposes of comparison, coefficient of determination (r^2) measured among the 10 individual PAHs found in Murrells

Table 6. Organic carbon in sediment from Murrells Inlet and North Inlet. Percentage is based on dry weight of sediment

Murrells Inlet	% Carbon	North Inlet	% Carbon
DJ	5.67	JC7	4.88
TP2	4.62	OB	4.82
OC5	4.21	JC6	4.82
GC3	3.40	NMF	4.74
AC1	2.98	JC5	3.55
MC4	2.70	TC7	3.27
AC2	2.66	DB2	3.05
MC8	2.46	BC2	2.97
OC2	2.10	CH1	2.87
TP1	1.52	TC5	2.85
AC3	1.30	JC8	2.80
MC6	1.00	DB5	2.73
WC2	0.95	DB1	2.62
PS3	0.87	BC3	2.56
WC4	0.86	DB3	2.55
PS1	0.81	CH2	2.43
OC3	0.79	JC3	2.27
MC5	0.76	OM1	2.23
OC6	0.68	TC3	2.11
OC1	0.66	JC4	2.11
MC7	0.61	CL	2.09
GC2	0.58	TC4	2.06
PS2	0.57	TC6	2.02
GC1	0.56	BC4	1.76
MC2	0.49	JC1	1.74
MC3	0.37	TC1	1.41
WC3	0.36	TC2	1.31
OC4	0.31	BC1	0.99
WC1	0.19	JC2	0.87
MC1	0.10	DB4	0.26
		OM2	0.00

Inlet oyster and sediment are shown in Tables 7 and 8. Some disparity in the r^2 data between the two matrices was observed. For example, r^2 among individual analytes in oyster ranged from a low of 0.09 for B{ghi}P/Phe to a high of 0.93 for Pyr/Flu and B{k}F/B(a)A. Of the 45 r^2 values, only 31% of the values were >0.70. The higher values existed between members of the four-ring PAHs. For example, Flu and Pyr (r^2 = 0.93); Flu and B{a}A (r^2 = 0.92); and Pyr and B{a}A (r^2 = 0.92). Other pairs, e.g., B{k}F and B{a}A; B{k}F, and Flu, were also high, with r^2 values of 0.93 and 0.86, respectively. B(ghi)P had the lowest value with the other PAHs for the oyster data. For the sediment data, r^2 values ranged from 0.37 (Flu/Ant) to 0.98 (Flu/Pyr) and had 78% of the values > 0.70. The higher values were among the four- and five-ring PAHs. Anthracene (Ant) had the lowest value with the other PAHs for the sediment data. Phenanthrene (Phe) and B{ghi}P values with other PAHs were between these two extremes. In comparing the mean r^2 values between matrices, sediment had a significantly higher ($p < 0.01$) r^2 value than oyster.

Further, comparison of individual PAHs on a weight percent of total PAHs showed a difference in accumulation patterns for oyster and sediment (Figure 3). Figure 3 shows that the lower molecular weight PAHs, such as phenanthrene, pyrene and flouranthene had higher concentrations in respect to these PAHs found in sediment. Also, when the oyster data were converted from dry weight basis to lipid basis and plotted, the PAHs accumulation pattern was similar to the dry weight-based pattern.

Discussion

In comparing the r^2 values for individual PAHs in oyster vs sediment, respectively, a disparity in values was observed. This disparity in r^2 values among the two matrices indicates that the accumulation of individual PAHs is different for oyster (physiological) and sediment (physiochemical). The compositional differences among individual PAHs in oyster and sediment suggest that oyster selectively accumulate the lower molecular weight PAHs which include the more water soluble PAHs compared to PAHs found in sediment. Similarly, Wade *et al.* (1988) reported accumulation patterns in oyster and sediment in Gulf Coast oyster consistent with the patterns shown in this report (Fig. 3). Also, in sedimentation studies, Lee *et al.* (1978) observed accumulation patterns of individual PAHs comparable to those reported for sediments here. As expected, differences in octanol/water partition coefficient among individual PAHs as shown in Table 9 (Mackay 1992) and the greater persistence of the high molecular weight PAHs contributed to the individual PAHs patterns in oyster and sediment. Further, the moderate r^2 values (0.48, 0.30) for total PAH (dry weight) versus organic carbon concentration in sediment, the weak r^2 value (0.06, 0.03) for PAH (dry weight), versus PAH (organic carbon weight); and the higher organic carbon content found in North Inlet sediment indicated that the source of individual PAHs rather than the organic carbon concentration in the sediment was the dominant factor determining PAH burden in these sediments.

When comparing the estuary sediments, North Inlet had a higher concentration of organic carbon. One explanation for the higher organic carbon concentration in North Inlet is the input of organic matter from the adjacent forested terrain and from Winyah Bay. Similarly, Kortelainen (1993) reported in a study of lakes in Finland that organic carbon in lake water was influenced by drainage from boggy and forested terrain, and a negative relationship between organic carbon and pH was reported. Also, Fulton *et al.* (1993) reported significantly lower pH at North Inlet (7.59) than at Murrells Inlet (7.87).

Even though oyster and sediment were sampled 12 months apart, these data indicate that the distribution of PAHs in the two estuaries was highly influenced by urban activities on coastal uplands and estuarine waters. Also, the distribution of individual PAHs was different for oysters and sediments at Murrels Inlet. Although oysters bioaccumulate PAHs from the marine environment, their ability to metabolize PAHs is limited (Bender *et al.* 1988). Therefore, caution should be exercised when extrapolating oyster PAHs data to other species.

No attempt was made to distinguish between natural and anthropogenic inputs of PAHs. The PAHs levels in North Inlet would be indicative of natural input (*i.e.*, forested terrain and water shed runoff) and atmospheric deposition of PAHs for the Southeastern United States (Ngabe 1992). However, the higher PAH concentrations found at the urban sites in Murrells Inlet indicated anthropogenic sources. Thus, these findings are important to the management of coastal areas. As more and more coastal areas are being developed, special attention should be focused on ways to reduce anthropogenic input of PAHs into estuaries.

Table 7. Coefficient of determination (r^2) for PAHs found in oyster at Murrells Inlet

	Phe	Ant	Flu	Pyr	B(a)A	Cry	B(b)F	B(k)F	B(a)P	B(ghi)P
Phe	1.00									
Ant	0.54	1.00								
Flu	0.45	0.60	1.00							
Pyr	0.34	0.54	0.93	1.00						
B(a)A	0.40	0.55	0.92	0.92	1.00					
Cry	0.22	0.29	0.73	0.79	0.80	1.00				
B(b)F	0.21	0.13	0.18	0.25	0.22	0.35	1.00			
B(k)F	0.43	0.49	0.86	0.82	0.93	0.71	0.20	1.00		
B(a)P	0.17	0.45	0.73	0.79	0.72	0.54	0.13	0.74	1.00	
B(ghi)P	0.09	0.15	0.29	0.30	0.38	0.30	0.14	0.41	0.41	1.00

Table 8. Coefficient of determination (r^2) for PAHs found in sediment at Murrells Inlet

	Phe	Ant	Flu	Pyr	B(a)A	Cry	B(b)F	B(k)F	B(a)P	B(ghi)P
Phe	1									
Ant	0.40	1								
Flu	0.96	0.37	1							
Pyr	0.94	0.38	0.98	1						
B(a)A	0.92	0.50	0.96	0.98	1					
Cry	0.76	0.72	0.79	0.83	0.90	1				
B(b)F	0.71	0.59	0.77	0.81	0.90	0.94	1			
B(k)F	0.77	0.59	0.83	0.86	0.92	0.96	0.96	1		
B(a)P	0.86	0.56	0.90	0.94	0.98	0.96	0.89	0.96	1	
B(ghi)P	0.66	0.61	0.69	0.76	0.79	0.90	0.77	0.83	0.88	1

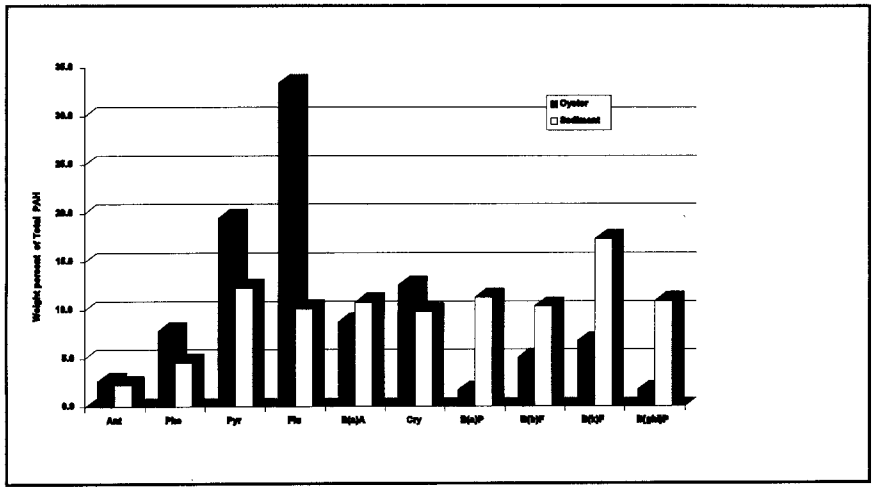

Fig. 3. Individual PAH distribution pattern for oyster and sediment from Murrells Inlet

Table 9. Statistics of octanol/water partition coefficient for PAHs. Data summarized from Mackay *et al.* (1992)

Compound	Mean log K0w	Median log K0w	Median solubility	No. of aromatic rings	Molecular weight
Anthracene	4.47	4.45	7.10E−02	3	178.2
Phenanthrene	4.47	4.46	1.21E+00	3	178.2
Pyrene	5.06	5.03	1.34E−01	4	202.3
Fluoranthene	5.20	5.22	2.43E−01	4	202.3
Benzo{a}anthracene	5.80	5.66	1.10E−02	4	228.3
Chrysene	5.81	5.79	2.00E−03	4	228.3
Benzo{a}pyrene	6.19	6.06	3.80E−03	5	252.3
Benzo{b}flouranthene	6.29	6.42	7.75E−03	5	252.3
Benzo{k}fluoranthene	6.59	6.50	8.05E−04	5	252.3
Benzo{ghi}perylene	7.06	7.10	2.60E−04	6	276.3

Acknowledgments. The author thanks Erich D. Strozier, Jeffrey Seel and Wendell L. Richardson for their assistance in sample analysis; and Wendell Richardson for assistance in statistical analysis of the data.

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