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Priority Pollutant Polycyclic Aromatic Hydrocarbons in Florida Sediments

C. J. Miles,[1] J. J. Delfino[2]

[1] Food and Environmental Toxicology Laboratory, Post Office Box 116450,
University of Florida, Gainesville, FL 32611-6450, USA
[2] Department of Environmental Engineering Sciences, Post Office Box 116450,
University of Florida, Gainesville, FL 32611-6450, USA

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The USEPA has identified 16 unsubstituted polynuclear aromatic hydrocarbons (PAHs) as priority pollutants. Some of these compounds are possible or probable human carcinogens, so their distribution in the environment has been the subject of continued research (Laflamme and Hites, 1978; Menzie et al, 1992). Marine and freshwater sediments often contain organic carbon (OC) and the high affinity of non-polar organic compounds, such as PAHs, to OC results in accumulation, Agencies have been working to protect and remediate contaminated sediments that pose ecological and human health risks in aquatic ecosystems. For example, the USEPA has proposed sediment quality criteria for mixtures of PAHs in sediment (Renner, 1997).

Extensive studies of PAHs in sediments from around the world show that PAHs are ubiquitous and that PAH concentrations usually decrease with distance from urban centers (Laflamme and Hites, 1978; Windsor and Hites, 1979; Cantillo et al., 1997). The similarity of sediment PAH patterns to each other and to air particulate matter points to anthropogenic combustion of fossil fuels as a major source of PAHs and to the significance of long-range atmospheric dispersion processes (Laflamme and Hites, 1978). However, PAHs can enter aquatic ecosystems from other sources such as waste incineration, forest tires, fuel use and spills, urban runoff, agricultural runoff, domestic wastewater, and industrial wastewater.

There is concern that Florida's rapid growth is adversely affecting its aquatic ecosystems. Water and sediment samples from freshwater and estuarine sites adjacent to, nearby or downstream from potential pollutant sources throughout Florida were collected and analyzed for 82 organic priority pollutants (OPP) (Garcia et al, 1993). PAHs were the majority of OPPs quantified in these sediment samples, however, concentrations of these pollutants were not clear indicators of toxicity as determined by the Microtox bioassay (Jacobs et al., 1993). A wide variety of non-regulated organic compounds, such as alkylbenzenes, alkylphenols and terpernes was also found in these sediment samples. (Garcia et al, 1993).

Correspondence to: J. J. Delfino

The National Oceanic and Atmospheric Administration (NOAA) initiated the National Status and Trends (NS&T) Program in 1984 to assess the spatial and temporal trends in chemical contamination to the coastal marine environment. The NS&T Mussel Watch Project, started in 1986, measures metal and organic chemical concentrations in sediment and mollusk tissue (O'Conner and Beliaeff, 1995). The NS&T sampling sites represent large areas and are not knowingly near hazardous waste sites or waste discharge points. Many sites are within 20 km of population centers in excess of 100,000 people (O'Conner and Beliaeff, 1995).

In this paper, we compared the PAH data from Garcia et al. (1993) to other sediment PAH studies such as the NS&T Program. Our PAH concentrations are also compared to sediment quality guidelines and a broad assessment of Florida sediment quality is inferred.

MATERIALS AND METHODS

Nine surficial sediment samples and one field duplicate sample were collected by petite ponar dredge or with a stainless steel trowel in low water conditions at various distances (stations) from thirty-one sites throughout Florida (Garcia et al, 1993). Samples were homogenized in the field, shipped to the laboratory on ice and frozen until extracted. Sediment aliquots were extracted with acetonitrile, cleaned up on solid-phase cartridges and analyzed by gas chromatography-mass spectrometry (Garcia et al, 1993). Benzo(b)fluoranthene and benzo(k)fluoranthene were quantified as the sum of the two isomers. For toxicity unit (ΣTU; Swartz et al., 1995) calculation, the concentration of each of these isomers was assumed to be one-half the total concentration. Organic and inorganic carbon were determined using carbon dioxide coulometry (Coates and Delfino, 1993). The fraction of organic carbon in dried and sieved (#20, 840 µm openings) sediment samples was determined as the difference between the total carbon and inorganic carbon fraction analyses.

Samples were designated *impacted* by the pollutant source when they were closest to the discharge area or indistinguishable from the closest sample. In one case (site 11; Garcia et al., 1993) three stations that were distant from the main pollutant source, were considered impacted since they were affected by a different source of PAHs. All other stations were designated *background* although they were possibly impacted by other more generalized sources (e.g. atmospheric) of PAHs. Individual PAH concentrations were summarized separately and also collectively as tPAH. Therefore, tPAH is not necessarily the sum of the individual results.

RESULTS AND DISCUSSION

Thirty-one of the 82 OPPs were quantified in the sediment samples and PAHs were the most frequently found compounds. More than 85% of the positively identified sediment pollutants were one of the 16 priority pollutant PAHs, including naphthalene, and 66% of all the sediment samples contained at least one

PAH. This high incidence level was attributed to preferential sampling near pollutant sources and the wide range of natural and anthropogenic PAH sources.

The thirty-one sites examined represent a variety of pollution activities including those associated with high PAH emissions, such as wood preservation and manufacturing, petroleum storage and handling, and petroleum combustion (Table 1). The arbitrary division of these samples into stations impacted by and background relative to pollutant discharges, helped separate significant PAH contamination from the broad range of PAH non-point sources. In several cases, higher total PAH (tPAH; sum of individual PAH concentrations) concentrations were found adjacent to the potential pollutant sources, as one would expect from this type of sampling program (Table 1). However, there are also cases where the PAH levels at stations removed from these sources were higher than those at the stations adjacent to these sources. This could be attributed to several factors including sampling heterogeneity (Coates and Delfino, 1993) and the general urban influence at most sites.

Summary statistics for the PAHs quantified at background and impacted stations generally showed higher individual and tPAH concentrations at the impacted sites (Table 2). The number of sediment samples with quantifiable PAHs showed a similar distribution pattern for both types of stations when arranged by molecular weight (MW; Table 2). Compounds from MW 178 (phenanthrene and anthracene) through MW 252 (benzo(a)anthracene and benzo(bk)fluoranthene) were found most frequently and the median concentrations were two to three times higher than other PAHs. Other investigators have found three to five ring unsubstituted PAHs to predominate in sediments (Laflamme and Hites, 1978; Takada et al., 1990).

The median tPAH concentration found at the impacted (2.5 mg/kg) Florida stations was similar to other urban areas but below industrialized areas (Table 3). The median tPAH concentration (0.99 mg/kg) found at the background Florida stations was above background levels observed by the Mussel Watch Project (O’Conner and Beliaeff, 1995; Table 3). As discussed previously, this was likely caused by the general urban influence at our sites.

Generally, NS&T sites in Florida near urban areas had higher tPAH concentrations than remote sites. There is a good correlation between population density within 20 km of the sampling site and contaminant levels (Cantillo et al., 1997). Typically, all contaminant levels from sediments and mollusks in south Florida sites were low compared to those found nationwide. Mussel tPAH concentrations from south Florida were similar to bivalves from uncontaminated sites in central and South America (Cantillo et al., 1997). Temporal trends between time and the rank of tPAH concentration in oysters showed no significant trends in the Mussel Watch-Florida sites except for a decreasing trend (95% confidence) at Dry Bar, Apalachicola Bay. In fact, when national trends existed, they were mostly decreasing (O’Conner and Beliaeff, 1995). However, some such sequences showed tPAH concentrations that were considered high (tPAH =1.02 mg/kg for

Table 1. Sediment sampling sites, activities and maximum tPAH concentrations.

Site No.	FL county	Primary pollution activities	Impacted stations (s) max tPAH (mg/kg)	Background stations (s) max tPAH (mg/kg)
1	Hillsborough	steel manufacturing	16.2 (4)	1.5 (6)
2	Hillsborough	agricultural chemical production	2.2 (7)	0.4 (2)
3	Hillsborough	chemical manufacturing	1.3 (4)	0.2 (1)
4	Hillsborough	waste oil disposal	18.3 (1)	2.2 (6)
5	Escambia	wood preservation	85.1 (1)	3.2 (7)
6	Escambia	wood chemical production	2.5 (1)	3.5 (5)
7	Escambia	paper mill	BQL* (0)	0.1 (1)
8	Escambia	oil and hazardous waste recycling	0.2 (1)	0.2 (2)
9	Palm Beach	pesticide mixing and loading	0.3 (1)	0.9 (2)
10	Palm Beach	pesticide mixing and loading	3.2 (5)	BQL (0)
11	Dade	steel manufacturing	11.2 (3)	0.8 (1)
12	Monroe	diesel and jet fuel storage	42.3 (5)	0.4 (2)
13	Duval	wood preservation	75.5 (9)	0.1 (1)
14	Duval	hazardous waste disposal	173 (4)	8.8 (4)
15	Duval	hazardous waste disposal and industrial wastewater treatment	0.4 (2)	1.3 (4)
16	Duval	wood preservation	1086 (5)	6 (5)
17	Putnam	paper mill	10.5 (3)	7.5 (5)
18	Sarasota	electronic manufacturing	BQL (0)	0.7 (3)
19	Charlotte	landfill	0.1 (1)	BQL (0)
20	Lee	landfill	BQL (0)	1.1 (2)
21	Lee	pesticide mixing and loading	4.1 (5)	47.8 (4)
22	Lee	municipal sewage treatment	14 (1)	0.4 (1)
23	Pinellas	electronic manufacturing	1.1 (2)	14.8 (7)
24	Pinellas	airport	0.4 (1)	2.4 (4)
25	Pinellas	electronic manufacturing	3.7 (4)	9.5 (3)
26	Pinellas	asphalt manufacturing incineration and coal/gas conversion plant	2.9 (5)	21.4 (4)
27	Polk	pesticide mixing and loading	BQL (0)	0.2 (4)
28	Columbia	wood product manufacturing	BQL (0)	BQL (0)
29	Martin	pesticide storage	0.4 (2)	2.7 (1)
30	Orange	industrial chemical distribution	41.6 (2)	113 (8)
31	Gulf	landfill	BQL (0)	2.8 (1)

BQL = below quantification level. Number of sites with measurable tPAH shown in parentheses.

Table 2. Summary statistics of PAH compounds in order of molecular weight in background and impacted FL stations (mg/kg).

Compound	Background				Impacted			
	mean	median	range	n	mean	median	range	n
Naphthalene				0	33	1.1	0.26-226	7
Acenaphthylene	0.08	0.08	0.08	1	0.54	0.31	0.08-3.0	15
Acenaphthene	0.16	0.14	0.12-0.22	5	23	0.44	0.08-262	13
Fluorene	0.25	0.20	0.08-0.62	6	11	0.37	0.07-128	14
Phenanthrene	0.74	0.16	0.05-13.5	60	6.2	0.34	0.05-228	56
Anthracene	0.32	0.13	0.05-3.4	26	1.5	0.62	0.04-11	38
Fluoranthene	1.4	0.38	0.05-22	87	4.2	0.67	0.06-85	66
Pyrene	1.1	0.34	0.04-22	94	3.6	0.56	0.05-78	73
Chrysene	0.77	0.28	0.04-9.8	43	1.7	0.68	0.04-13	48
Benzo(a) anthracene	0.71	0.23	0.04-8.6	55	1.5	0.62	0.04-11	51
Benzo(a)pyrene	1.3	0.50	0.24-6.6	32	1.4	0.77	0.18-9.5	42
Benzo(b,k) fluoranthene	1.1	0.33	0.10-4.5	23	1.6	1.0	0.11-7.6	38
Indeno(1,2,3-c,d)pyrene	6.7	4.5	0.76-17.8	10	5.1	5.1	0.72-9.5	2
Benzo(ghi) perylene	4.2	2.9	1.1-7.5	7	7.6	7.6	4.5-10.6	2
Dibenzo(a,h) anthracene	1.2	1.2	1.2	1	0.59	0.49	0.36-1.0	7
Total PAHs	5.3	0.99	0.04-113	98	26	2.5	0.05-1086	77

24 PAHs). Watson Bayou in St. Andrews Bay (Panama City, FL) and Joes Bayou, Choctawhatchee Bay (Destin, FL) were two Florida sites that had high tPAH concentrations in oysters from 1990-1993 (O' Conner and Beliaeff, 1995).

The importance of sediments in determining fate and effects of a wide variety of contaminants has become apparent in recent years (DiToro et al., 1991; Renner, 1997). Sediments often accumulate metal and organic compounds which can affect aquatic organisms. Establishing sediment quality criteria is necessary to assess, regulate and ultimately protect human health and aquatic ecosystems.

Several approaches have been used to derive sediment quality assessment guidelines. Most of these approaches derive criteria for individual PAHs. However, PAHs rarely occur alone and generally co-vary along pollution gradients (Swartz et al., 1995). The USEPA has proposed sediment quality criteria for mixtures of PAHs. Swartz et al. (1995) developed a ΣPAH model to predict the

Table 3. Range of tPAH (mg/kg DW) from the literature.

Site	Reference	Median	Mean	Range
Rural soil	Menzie et al., 1992	0.07		0.01-1.0
Benthic Survey, 84-91*	NOAA, 1997	0.07	1.6	0.002-55
NOAA NS&T	Menzie et al., 1992	0.1		0.002-13.2
Global background	Laflamme and Hites, 1978	0.11	0.31	0.005-1.8
Mussel Watch, 86-91*	NOAA, 1997	0.17	1.2	0.002-31.3
Background stations	This study	0.99	5.3	0.04-113
Urban soil	Menzie et al., 1992	1.1		0.06-5.8
Contaminated sites	Menzie et al., 1992	1.4		0.003-232
Penobscot, ME	Johnson et al., 1985	1.7	2.6	0.29-8.8
Impacted stations	This study	2.5	26	0.05-1086
Global impacted	Laflamme and Hites, 1978	3.4	24	0.8-87
Newark Bay, NJ	Huntley et al., (1995)	14	44	0.22-400

* only FL sites data retrieved from the Web site (www-orca.nos.noaa.gov) and tPAH calculated for 16 OPP PAHs.

toxicity of PAH mixtures in field-collected sediments using three kinds of data; percent mortality of marine and estuarine amphipods based on toxicity tests, the sediment concentration of 13 individual PAHs, and the total organic carbon (OC) content of the sediment. Using the equilibrium partitioning approach, the interstitial water concentration (PAHiw) of the individual PAHs was determined from the PAH content and fraction of OC in the sediment and the organic carbon-water partition coefficient. The 10-d LC50 of each compound in interstitial water (10-d LC50iw) was predicted by a quantitative structure-activity relationship regression of 10-d LC50iw (from spiked sediment tests) compared to the octanol-water partition coefficient. Toxic unit concentrations of the individual compounds (TUi) were predicted as PAHiw/10-d LC50iw and the total number of toxic units of the 13 PAHs (ΣTU) was calculated assuming additivity. Swartz et al. (1995) found good agreement between predicted and observed toxicity in field-collected sediment samples from PAH-contaminated sites.

This model assumes that all carbon in sediment adsorbs contaminants equally. However, Gustafsson and co-workers (1997) showed that anthropogenic soot is a dilute but strongly sorbing medium for PAHs. Their results support the hypothesis that pyrogenic PAHs may be less available for biological uptake than petroleum PAHs. The strong influence of PAH association with soot should be considered in establishing sediment quality criteria.

Application of the ΣPAH model to our data showed that 34% of the impacted stations and 11% of the background stations exceeded the threshold of acute toxicity (Table 4). These values are similar to the percent exceedance of the effects range-low (ERL) for total PAHs determined by Long et al (1995). The agreement between these two approaches is remarkable since the ERL is not normalized to OC and does not account for unusually high concentrations of individual PAHs. Swartz et al., (1995) calculated a ΣTU using ERL guideline values for the individual PAHs and used estimates for missing PAHs and found close agreement with the threshold of acute toxicity value. Application of the ΣPAH model to our data set showed that 5% of the impacted stations and 1% of the background stations exceeded the level of certain acute toxicity (Table 4). These values are similar to the percent exceedance of the effects range-median (ERM) for total PAHs determined by Long et al (1995).

Determination of ΣTU values for the available National Status and Trends sediment data showed only 1% of the 101 Florida Benthic Survey samples (NOAA, 1997) were above the threshold of acute toxicity while none were above the level of certain acute toxicity. Similarly, only 2% of the 166 Florida Mussel Watch samples (NOAA, 1997) were above the threshold of acute toxicity and while none were above the level of certain acute toxicity.

Table 4. Percentage of FL stations that exceed sediment guidelines.

	Percentage of stations with greater ΣTU		
Sediment guideline	Impacted stations	Background stations	All stations
Effects range-low; total PAHs	39	16	26
ΣPAH threshold of acute toxicity	34	11	21
Effects range-median; total PAHs	8	3	5
ΣPAH level of certain acute toxicity	5	1	3

A 5% exceedance of the level of certain toxicity and 34% exceedance of the threshold of acute toxicity in sediments impacted by suspected pollution sources is notable since many of the sites examined were not expected to be significant sources of PAH contamination (i.e. pesticide mixing and loading and electronic manufacture). An 11% exceedance of the threshold of acute toxicity in background sediments raises concern that PAH contamination from non-point sources may be significant. However, the 11% exceedance for these sites compared to the 1-2% of NS&T sites indicates bias towards an anthropogenic influence. Continued monitoring will help determine the extent of ecological impact of PAHs to aquatic ecosystems.

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