



# A preliminary assessment of polycyclic aromatic hydrocarbon distributions in the lower Mississippi River and Gulf of Mexico

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## Abstract

Water samples were collected in the lower Mississippi River and the Gulf of Mexico in April 1999; sites in the river were sampled again in November 1999. Samples were separated into particulate ( $C_p$ ) and dissolved ( $C_w$ ) phases using 0.7  $\mu\text{m}$  glass fiber filters. Each phase was analyzed for polycyclic aromatic hydrocarbons (PAHs). Total PAH abundance in river samples was higher in November of 1999 ( $C_p$ : 1300–7000  $\text{ng gdw}^{-1}$ ;  $C_w$ : 77–430  $\text{ng l}^{-1}$ ) than in April 1999 ( $C_p$ : 1100–1700  $\text{ng gdw}^{-1}$ ;  $C_w$ : 12–25  $\text{ng l}^{-1}$ ), despite higher total suspended sediment concentrations in April. Concentration profiles of PAHs in the lower Mississippi River indicate that compositional differences in PAH particle-water distributions were a function of seasonal discharge across the year. For example, higher PAH distribution coefficients in November correspond to a greater degree of combustion-driven processes indicated by black carbon abundance analyzed in the same samples in a complementary study. Concentrations of three specific PAHs isolated in the Mississippi River and the Gulf of Mexico (anthracene, benzo[*a*]anthracene, and benzo[*g,h,i*]perylene) were fit into a mass balance model in an attempt to constrain sources of PAHs into the gulf. This portion of the study was based on a limited number of samples. However, these preliminary mass balance calculations indicated that in 1999 on an annual scale, fluvial and atmospheric contributions of PAHs to the Gulf of Mexico were relatively negligible ( $10^0$  kg) and that coastal erosion ( $10^3$  kg) may have been the most significant source of PAHs into the gulf.

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## 1. Introduction

The Mississippi River is the major commercial inland waterway in the United States and the

seventh largest river in the world in terms of water and sediment discharge (Meade, 1996). The river drains a watershed area of  $2.9 \times 10^6$   $\text{km}^2$  or 41% of the area of the contiguous United States (Meade and Parker, 1985) into the Gulf of Mexico. The abundance and composition of the Gulf of Mexico's floral and faunal resources are intimately linked to the extent of freshwater discharge into the Gulf of Mexico (Deegan et al., 1986). Hence, accurate assessment of impacts to the resources of the Gulf of Mexico depends on the role of the

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Mississippi River, the largest source of freshwater into the gulf.

One potential adverse impact to coastal ecosystems such as the Gulf of Mexico results from the influx of polycyclic aromatic hydrocarbons (PAHs). Many of these compounds, which are known and suspected carcinogens (NRC, 1983), are typically generated via anthropogenic processes such as “slash and burn” agriculture, automobile use, fossil fuel combustion, and releases from boat and ship traffic. PAHs are also produced naturally from diagenetic alteration of natural organic matter. They are subsequently introduced to coastal systems via atmospheric deposition, in situ spills, or runoff and influx from tributaries. The Gulf of Mexico is one of the few coastal ecosystems in the world where PAH influx can also occur via natural petroleum seeps (Kennicutt et al., 1988).

In a companion paper, we investigated the Mississippi River’s discharge of black carbon (BC) into the Gulf of Mexico (Mitra et al., 2002). BC is the residue remaining after incomplete combustion of organic matter or formed from vapor-phase condensation of organic molecules. BC elicits a significant role in the global carbon cycle and thus, the size and discharge of the Mississippi River necessitated a separate study on the river’s discharge of BC and its effects on the global carbon cycle. In that study, concentrations of selected particulate phase PAH isomers isolated from the water column of the Mississippi River and the Gulf of Mexico were solely used to discriminate sources of BC discharging into the gulf (Mitra et al., 2002). However, to date, few additional studies have attempted to quantify particle-water distributions of PAHs in the lower Mississippi River and the Gulf of Mexico. The size, unique nature of the gulf, and its importance in terms of natural resources caused us to make a preliminary attempt at addressing that data void.

## 2. Methods and materials

### 2.1. Field sampling

Presumably, samples taken along the lower Mississippi River such as those in our study are representative of integrated watershed-wide processes, and so in 1999, we sampled the water column of the

Mississippi River and the Gulf of Mexico during a time point in April (representative of high river flow). In November of 1999 (representative of low river flow), we re-sampled the river stations. Water column samples were collected from the river and the gulf onboard the *R/V Pelican* using a rosette array of Niskin bottles. Details pertaining to the locations and depths of study sites as well as sampling and analytical methods have been presented elsewhere (Mitra et al., 2002) and will only be briefly mentioned here. Sampling locations are depicted in Fig. 1.

Surface and bottom water samples were collected from Niskin bottles into pre-cleaned (dilute Alconox™ solution, distilled and deionized (DDI) water, 12 N HCl, and DDI water again) 20 l glass carboys and then filtered through 142 mm diameter, 0.7 μm pore size pre-combusted (450° C for 4 h) glass fiber filters (GFF) housed in a stainless-steel filter holder. Collection carboys were triple rinsed with sample water prior to the onset of collection. Approximately, 10–20 l of water were filtered for particulate phase PAH analysis. After filtration, the GFFs were stored in HPLC grade methanol in pre-combusted glass jars for subsequent PAH analysis using soxhlet extraction apparatus (see below). Filtered water samples (“dissolved” phase) were collected in additional pre-cleaned 20 l glass carboys and were preserved by placing 500 ml of GC grade hexane in the headspace. The dissolved phase is thus operationally defined as the sum of truly dissolved, colloidal, and very small particles (<0.7 μm).

An additional 1 l of unfiltered water was passed through pre-combusted and pre-tared 25 mm diameter (0.7 μm pore size) GFFs in order to determine total suspended solids (TSS) concentrations. These filters were then dried and re-weighed to determine TSS.

### 2.2. Analytical procedures

Prior to extraction, a mixture of deuterated PAH surrogate standards ( $d_{10}$ -anthracene,  $d_{12}$ -benz[*a*]anthracene,  $d_{12}$ -benzo[*a*]pyrene) was added to each sample. Filters were extracted by refluxing for 48 h in soxhlet flasks with dichloromethane (DCM). At the end of the 48 h, the filters were discarded and the extracts were combined with the methanol used initially for sample storage. Samples were gently evap-

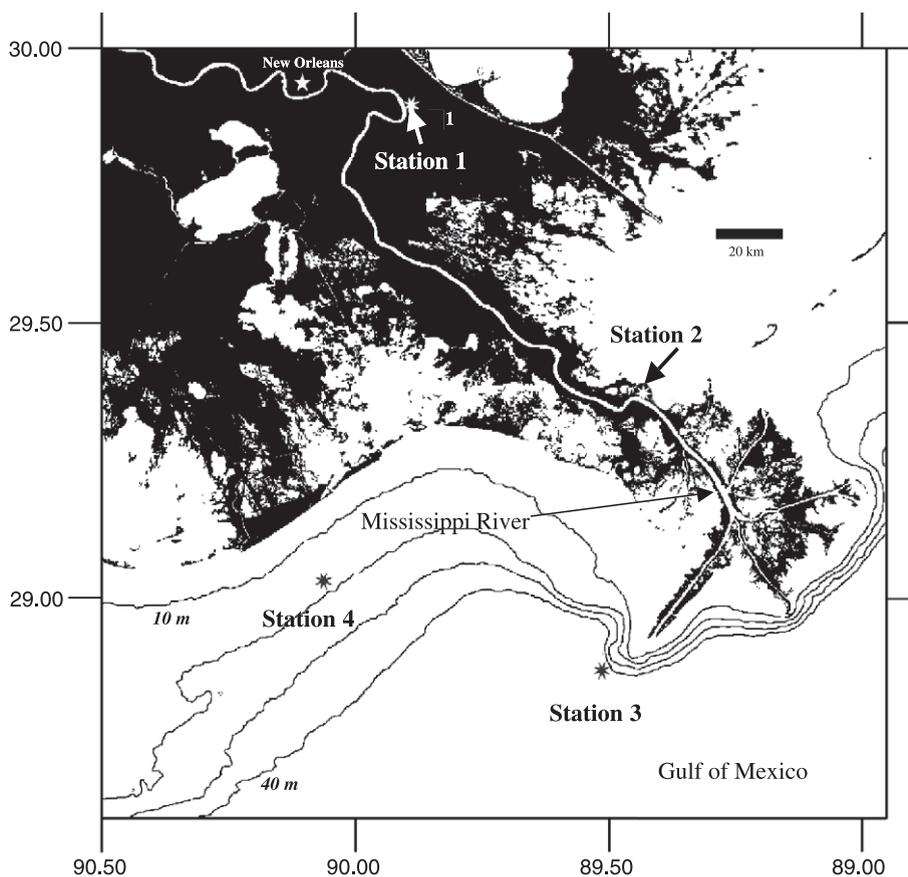


Fig. 1. Mississippi River sampling stations. Surface and bottom waters isolated from Stations 1 and 2 represent river samples in this study. Surface and bottom waters at Station 4 represent the gulf station in this study.

orated under ultra high purity (UHP)  $N_2(g)$  to approximately 100 ml at which point the extract could be back-extracted (shaken  $3 \times$  with hexane + DDI water) and solvent exchanged into hexane.

Filtrates or dissolved-phase samples were transferred and extracted sequentially in 2 l separatory funnels by liquid–liquid extraction. For the dissolved phase, we extracted each 2 l aliquot of the dissolved phase with 100 ml hexane three times. The filtrate was extracted with hexane by shaking vigorously for 2 min and allowing the contents of the flask to settle. The overlying hexane layer was then removed and placed in a Rapid Vap<sup>TM</sup> flask. For a water sample of 10–20 l volume, this amounts to a total of 1.5–3 l consumption of hexane per each sample extraction. These sequential extracts for each sample were then combined in the Rapid Vap<sup>TM</sup> flask, reduced to a total

final volume of 1 ml in a Rapid Vap<sup>TM</sup> also under UHP  $N_2(g)$ .

Silica open-column chromatography was used to purify hexane extracts from each of the filter and filtrate samples (Dickhut and Gustafson, 1995). The portion of the eluent of the silica column-containing PAHs was collected and a mixed deuterated PAH internal standard ( $d_{10}$ -phenanthrene,  $d_{12}$ -chrysene,  $d_{12}$ -perylene) was added. The extract was once again evaporated gently under nitrogen, this time to a final volume of  $\sim 100 \mu\text{l}$ . Two  $\mu\text{l}$  aliquots of this final extract were injected onto a Hewlett Packard 6890 Series Gas Chromatograph–Mass Spectrometric Detector (GC–MS) in the selective ion monitoring mode with a  $30 \text{ m} \times 0.25 \text{ mm I.D.} \times 1 \mu\text{m}$  film thickness DB-5 MS capillary column (J&W Scientific). For all samples, the GC/MS conditions for analysis were as

follows: injector and detector temperatures, 300 °C; splitless injection with 1.5 cm<sup>3</sup> min<sup>-1</sup> of ultra-high purity He as the carrier gas; initial column temperature 50 °C increased to 150 °C at 25 °C min<sup>-1</sup>; increased to 230 °C at 6 °C min<sup>-1</sup>; and increased to 300 °C at 3 °C min<sup>-1</sup> and held for 3.33 min. PAHs analyzed in this manner included fluorene (fln), 2,3,5-trimethylnaphthalene (235trimeth), anthracene (anth), phenanthrene (phen), pyrene (pyr), 2-methylphenanthrene (2methph), fluoranthene (flrnth), 3,6-dimethylphenanthrene (36dimeth), benzo[*b*]fluoranthene (b[*b*]f), chrysene (chry), benzo[*a*]anthracene (b[*a*]a), benzo[*k*]fluoranthene (b[*k*]f), benzo[*e*]pyrene (b[*e*]p), benzo[*a*]pyrene (b[*a*]p), perylene (peryl), indeno[*1,2,3-cd*]pyrene (ind), dibenz[*a,h*]anthracene (dbah), and benzo[*g,h,i*]perylene (b[*g,h,i*]p). As seen above, only a selected number of alkylated PAHs were quantified in this study. Due to the incomplete number of alkyl homologs for any specific parent PAH, these compounds were not used to delineate PAH sources in this study. Recoveries of the deuterated surrogate PAHs relative to the deuterated PAH internal standards averaged across all samples were: 71 ± 13%, 80 ± 8.2%, and 85 ± 8.9% for *d*<sub>10</sub>-anth,

*d*<sub>12</sub>-b[*a*]a, and *d*<sub>12</sub>-b[*a*]p, respectively. Concentrations of PAHs were not quantified within a specific GC time window if recovery of a deuterated surrogate was below 40% within that window. Minimum detectable quantities (MDQ) were established at a 3:1 signal-to-noise ratio. The MDQ for the GC–MS setup used for the Mississippi River samples ranged from 10<sup>-2</sup> to 10<sup>-3</sup> ng for each PAH. Based on daily injections of a PAH relative response factor standard over 1 week, overall instrument precision for all PAHs injected on the GC was 2.7 ± 1.5%. Gas chromatographic response was generally linear over a range of concentrations for each PAH in a mixed PAH relative response factor (RRF) standard. Thus, a one-point calibration curve using a specific concentration of the mixed RRF standard was used on a daily basis to confirm retention times, mass spectra, and response factors for each specific PAH.

A spiked-recovery experiment was conducted immediately prior to beginning sample extractions using deuterated PAHs and DDI water. This one extraction yielded recoveries of 100% for *d*<sub>10</sub>-anth relative to *d*<sub>10</sub>-phen, 112% for *d*<sub>12</sub>-b[*a*]a relative to *d*<sub>12</sub>-chry, and 120% for *d*<sub>12</sub>-b[*a*]p relative to *d*<sub>12</sub>-peryl. The higher

Table 1  
Particulate phase PAHs in surface water (SW) and bottom water (BW)

Compound	Blanks	April River SW	April Gulf SW	April River BW	April Gulf BW	November River SW	November River BW
Fluorene	2.7 ± 3.8	NQ	NQ	NQ	NQ	NQ	NQ
2,3,5-trimethylnaphthalene	1.8 ± 2.6	NQ	NQ	NQ	NQ	NQ	NQ
Phenanthrene	25 ± 35	NQ	NQ	NQ	NQ	NQ	NQ
Anthracene	ND	0.23 ± 0.07	0.07	0.52 ± 0.15	0.03	0.51 ± 0.44	0.14 ± 0.04
2-methylphenanthrene	4.4 ± 6.2	NQ	NQ	NQ	NQ	NQ	NQ
Fluoranthene	1.9 ± 1.4	7.8	NQ	4.8 ± 0.58	NQ	NQ	NQ
Pyrene	22.0 ± 16	78.5	NQ	54	NQ	48	NQ
3,6-dimethylphenanthrene	5.0 ± 3.6	NQ	NQ	NQ	NQ	NQ	NQ
Benzo[ <i>a</i> ]anthracene	ND	2.2	0.27	2.0 ± 0.29	0.11	0.36 ± 0.05	0.49 ± 0.07
Chrysene	0.06 ± 0.09	0.89	5.44	2.4	NQ	0.71 ± 0.33	0.22 ± 0.01
Benzo[ <i>b</i> ]fluoranthene	0.40 ± 0.40	4.7 ± 1.5	ND	5.2 ± 0.44	NQ	0.98 ± 0.12	1.4 ± 0.22
Benzo[ <i>k</i> ]fluoranthene	0.14 ± 0.14	1.2 ± 0.43	ND	1.4 ± 0.12	NQ	0.35	0.40 ± 0.02
Benzo[ <i>e</i> ]pyrene	0.22 ± 0.19	2.0 ± 0.58	ND	2.1 ± 0.02	NQ	0.54	0.56 ± 0.10
Benzo[ <i>a</i> ]pyrene	0.15 ± 0.15	2.1 ± 0.84	ND	2.6 ± 0.19	NQ	0.41 ± 0.07	0.60 ± 0.08
Perylene	0.15 ± 0.15	12 ± 3.5	ND	14.8 ± 1.2	3.91	3.3 ± 0.14	5.4 ± 1.2
Indeno[ <i>1,2,3-c,d</i> ]pyrene	0.07 ± 0.10	2.0 ± 0.45	NQ	3.0 ± 0.92	0.25	0.54 ± 0.24	0.52 ± 0.07
Benzo[ <i>g,h,i</i> ]perylene	0.15 ± 0.21	2.6 ± 0.76	NQ	3.5 ± 0.66	0.58	0.71 ± 0.13	0.84 ± 0.11
Dibenz[ <i>a,h</i> ]anthracene	ND	0.67	ND	0.72 ± 0.1	ND	0.15 ± 0.02	0.18 ± 0.06

Concentrations expressed as ng l<sup>-1</sup>. River concentrations of PAHs reflect the mean and standard deviation in concentrations measured at Stations 1 and 2, while gulf samples are specifically from Station 4. The term “NQ” implies samples were not quantifiable either due to lower than 40% recoveries of deuterated standards or due to the fact that sample concentrations were less than the higher of the following two numbers: 2 × blank or the blank + one standard deviation about the blank. The term “ND” means the compound’s peak was not detectable.

percentage recovery for the latter two time windows is likely a result of the spiked recovery being conducted on a volumetric basis (greater uncertainty in solvent volume with temperature change) rather than on a mass basis. Nonetheless, there were no large losses in recoveries during the extraction process, which would have been indicated by lower percentage yields of surrogates relative to internal standards.

To evaluate the possibility that the *R/V Pelican* may have been a significant source of contamination to our samples, field blanks consisting of DDI water were filtered during the cruise in between sample filtration. Field blanks ( $n=2$ ) consisted of 10 l of DDI water. Field blanks were filtered through the same filtration apparatus. A 10 l lab blank was extracted with the dissolved phase. All blanks were extracted upon return to the lab; PAH concentrations in all three blanks were averaged (Table 1). For this study, concentrations of each PAH in a sample were considered “not quantifiable” unless they exceeded the larger of the following two numbers: (1)  $2 \times$  mean blank concentration, or (2) mean blank concentration + one standard deviation about the mean. Quantified sample PAH concentrations are listed in Tables 1 and 2.

Operationally, we define carbon in the filtrate subsequent to filtration through GFFs as dissolved organic carbon (DOC). Concentrations of DOC were quantified with a Shimadzu TOC 5000 analyzer after acidifying with one drop of 6 N HCl per 5 ml of sample (Guo et al., 1994).

### 3. Results and discussion

#### 3.1. Total suspended solids and total PAHs

The two sampling periods in this study correspond to high and low end-members of water and sediment discharge. This is demonstrable based upon concentrations of TSS calculated for each time-period (Table 3) and annual profiles of water discharge (USGS, 1999). Surface and bottom waters in both the Mississippi River and the Gulf of Mexico yielded significantly higher TSS concentrations during April 1999, the time we define as high flow in contrast to November 1999 ( $t$ -test;  $p < 0.05$ ). Higher concentrations of TSS quantified in April correspond with relatively lower DOC and lower particulate ( $C_p$ ) and

Table 2  
Dissolved phase PAHs in surface water (SW) and bottom water (BW)

Compound	April River SW	April Gulf SW	April River BW	April Gulf BW	November River SW	November River BW
Fluorene	13.0	NQ	NQ	NQ	8.8	8.0
2,3,5-trimethylnaphthalene	4.6	NQ	4.9	NQ	6.7	350 ± 340
Phenanthrene	NQ	NQ	NQ	67	NQ	NQ
Anthracene	1.4 ± 1.1	NQ	0.28 ± 0.05	0.18	0.52 ± 0.26	0.69 ± 0.06
2-methylphenanthrene	NQ	NQ	NQ	NQ	NQ	NQ
Fluoranthene	4.16	NQ	NQ	17	4.5 ± 0.48	4.9 ± 0.69
Pyrene	NQ	NQ	NQ	NQ	51 ± 0.67	53 ± 1.5
3,6-dimethylphenanthrene	NQ	NQ	NQ	NQ	NQ	14
Benzo[a]anthracene	0.13 ± 0.00	0.05	0.48 ± 0.20	NQ	0.27 ± 0.03	0.26 ± 0.07
Chrysene	0.26 ± 0.07	NQ	0.50 ± 0.26	NQ	0.35 ± 0.06	0.30
Benzo[b]fluoranthene	NQ	NQ	1.45	NQ	NQ	NQ
Benzo[k]fluoranthene	NQ	NQ	0.39	NQ	3.20	NQ
Benzo[e]pyrene	NQ	NQ	0.70	NQ	1.04	0.60
Benzo[a]pyrene	NQ	NQ	0.67	NQ	NQ	NQ
Perylene	0.38 ± 0.02	NQ	0.55 ± 0.07	NQ	0.35	0.40
Indeno[1,2,3-c,d]pyrene	0.21	NQ	0.55	NQ	NQ	1.78
Benzo[g,h,i]perylene	0.78 ± 0.34	NQ	1.07	ND	NQ	NQ
Dibenz[a,h]anthracene	0.04	0.01	0.18	ND	NQ	NQ

Concentrations expressed as ng l<sup>-1</sup>. River concentrations of PAHs reflect the mean and standard deviation in concentrations measured at Stations 1 and 2, while gulf samples are specifically from Station 4. The term “NQ” implies samples were not quantifiable either due to lower than 40% recoveries of deuterated standards or due to the fact that sample concentrations were less than the higher of the following two numbers:  $2 \times$  blank or the blank + one standard deviation about the blank. The term “ND” means the compound’s peak was not detectable.

Table 3

Total suspended solids (TSS), dissolved organic carbon (DOC), total particulate phase PAHs ( $C_P > 0.7 \mu\text{m}$ ) expressed in nanograms per gram dry weight ( $\text{ng gdw}^{-1}$ ), total dissolved phase PAHs ( $C_W < 0.7 \mu\text{m}$ ) expressed in nanograms per liter ( $\text{ng l}^{-1}$ ), and mass-fractions particulate phase organic carbon and black carbon ( $f_{OC}$ ,  $f_{BC}$ ), respectively, isolated from the water column of the Mississippi River and Gulf of Mexico

Time	Station	Depth	TSS $\text{mg l}^{-1}$	DOC $\text{mg l}^{-1}$	$C_P$ Total ( $\text{ng gdw}^{-1}$ )	$C_W$ Total ( $\text{ng l}^{-1}$ )	$f_{OC}^a$	$f_{BC}^a$
April 1999	River	Surface	$98 \pm 19$ ( $n=26$ )	$8.9 \pm 3.7$ ( $n=12$ )	1700	25	$0.028 \pm 0.01$ ( $n=13$ )	$0.004 \pm 0.002$ ( $n=14$ )
	River	Bottom	$110 \pm 16$ ( $n=29$ )	$7.1 \pm 1.8$ ( $n=10$ )	1100	12	$0.025 \pm 0.003$ ( $n=14$ )	$0.004 \pm 0.002$ ( $n=14$ )
	Gulf	Surface	$42 \pm 33$ ( $n=10$ )	$6.7 \pm 1.1$ ( $n=4$ )	120	0.07	$0.024 \pm 0.007$ ( $n=3$ )	$0.006 \pm 0.002$ ( $n=3$ )
	Gulf	Bottom	$33 \pm 34$ ( $n=9$ )	$3.8 \pm 0.16$ ( $n=3$ )	65	85	$0.030 \pm 0.019$ ( $n=4$ )	$0.008 \pm 0.007$ ( $n=5$ )
November 1999	River	Surface	$12 \pm 3.5$ ( $n=15$ )	$7.9 \pm 0.36$ ( $n=14$ )	7000	77	$0.032 \pm 0.007$ ( $n=16$ )	0.001 ( $n=1$ )
	River	Bottom	$21 \pm 8.3$ ( $n=15$ )	$6.6 \pm 0.97$ ( $n=13$ )	1300	430	$0.025 \pm 0.007$ ( $n=13$ )	$0.001 \pm 0.000$ ( $n=2$ )

Concentrations of TSS and DOC reflect the mean and standard error of Stations 1 and 2 and all stations between Stations 1 and 2 (river) and between Stations 3 and 4 (gulf).

<sup>a</sup> Values reprinted from Mitra et al., 2002.

dissolved phase ( $C_W$ ) PAH concentrations in April (Table 3). In fact, total  $C_P$  PAH concentrations in Mississippi River surface and bottom water TSS are substantially higher in November (low flow) than in April (high flow) (Table 3). In 1999, the Mississippi River exported 90% of its total suspended sediment load ( $132 \times 10^6$  metric ton) (USGS, 1999) between the high flow months of January and August. That such high levels of suspended sediment discharge do not correspond to enriched levels of anthropogenic organic contaminants presents a conundrum in terms of fluvial discharge into coastal systems. Below, we discuss these contrasting discharge-dependant observations in particulate and dissolved phase PAH concentrations and their implications for PAH bio-availability potential.

### 3.2. The role of black carbon and combustion in affecting Mississippi River PAH distributions

As noted above, we did not quantify enough alkyl PAH homologs in our samples in order to assess the relative influence of petrogenic versus pyrogenic PAHs into our study sites. However, since PAHs are formed during the same incomplete combustion processes that result in BC formation (Haynes, 1991), BC abundance in the same samples may help us make

some assessment of the role of combustion in affecting PAH distributions in these samples.

The co-production of PAHs and BC dictates that strong PAH-BC interactions may be expected in nature for PAHs which are combustion-derived (Gustafsson and Gschwend, 1997). In such cases, observed organic carbon-normalized particle-water distribution coefficients (i.e.  $(K_{OC})_{OBS}$ ) for combustion-derived PAHs are likely to be higher than predicted by linear-free energy relationships relating to a PAH molecule's octanol-water partition coefficient ( $K_{OW}$ ). Thus, in a natural system, a PAH  $(K_{OC})_{OBS}$  being substantially greater than its  $K_{OW}$  offers a preliminary indication that combustion may be playing a fundamental role in PAH fate and transport (McGroddy and Farrington, 1995). Indeed, values of PAH log  $(K_{OC})_{OBS}$  in aquatic systems often exceed their log  $(K_{OW})$  values (McGroddy and Farrington, 1995; Jonkers and Koelmans, 2002).

In this study, distributions of PAHs between particles and water and values of BC (Mitra et al., 2002) were used to establish the role of combustion in determining PAH concentrations in the Mississippi River and Gulf of Mexico in the following manner. For each sample, concentrations of particulate phase PAH were divided by dissolved phase PAH and normalized to respective values for mass fraction of

particulate organic carbon ( $f_{OC}$ ) (Table 3) for each sample to determine each PAH's  $(K_{OC})_{OBS}$ . Such a comparison indicates that in many cases, when PAH  $(K_{OC})_{OBS}$  were quantifiable, they exceeded PAH  $K_{OW}$  (Fig. 2), suggesting that in some samples, there may have been a strong association between the PAHs quantified in our study and particles such as BC co-generated during the same combustion processes. Recently, field observations of elevated sedimentary PAH  $(K_{OC})_{OBS}$  have been suggested to be a combination of adsorption of PAHs onto the condensed matrix of soot or BC, coupled with PAH partitioning into natural organic matter (Accardi-Dey and Gschwend, 2002). Thus, to further quantify the extent to which PAH distributions in our samples were dominated by PAH-BC affinity, the following equation (Accardi-Dey and Gschwend, 2002) was applied to a selected subset of the PAH data from the Mississippi River:

$$K_D = f_{OC}K_{OC} + f_{BC}K_{BC}C_W^{(n-1)} \quad (1)$$

where  $K_D$  ( $\text{ml g}^{-1}$ ) represents PAH distribution coefficient between the particulate phase relative to the total dissolved phase,  $f_{OC}$  and  $f_{BC}$  are the mass fractions of OC and BC, respectively, in TSS (Table

3),  $K_{OC}$  ( $\text{ml g}^{-1}$ ) and  $K_{BC}$  ( $\text{ml g}^{-1}$ ) are OC, and BC-normalized equilibrium PAH distribution coefficients, respectively,  $C_W$  is the total dissolved phase concentration of a PAH quantified in our study, and  $n$  is the exponent unique to a PAH-BC Freundlich sorption isotherm. We used Eq. (1) to calculate values of PAH  $K_D$  in the following manner. Literature values of  $K_{OC}$  were taken from Karickhoff et al. (1979) and applied to Eq. (1). Similarly, literature values for  $K_{BC}$  (assuming  $n=0.7$ ) for all PAHs except perylene were taken from Accardi-Dey and Gschwend, (2003) and also applied to Eq. (1).  $K_{BC}$  for perylene was provided by Lohman and Gschwend (personal communication). Substituting literature values for  $K_{OC}$  and  $K_{BC}$  and using measured concentrations of  $C_W$ ,  $f_{OC}$ , and  $f_{BC}$  (Tables 2 and 3) for surface waters of the Mississippi River (this study and Mitra et al., 2002), yields calculated (Eq. (1)) values of  $\log K_D$  (i.e.  $\log (K_D)_{CALC}$ ), as shown in Fig. 3. Values of  $\log (K_D)_{CALC}$  in these samples are estimated using literature-derived quantitative descriptors of PAH-particulate phase affinity for OC and BC for sediments isolated from a variety of environments. In contrast, values of  $\log K_D$  based on particulate and dissolved phase PAHs in this study (Tables 1 and 2) are included in Fig. 3 as  $\log (K_D)_{OBS}$ . Generally, values

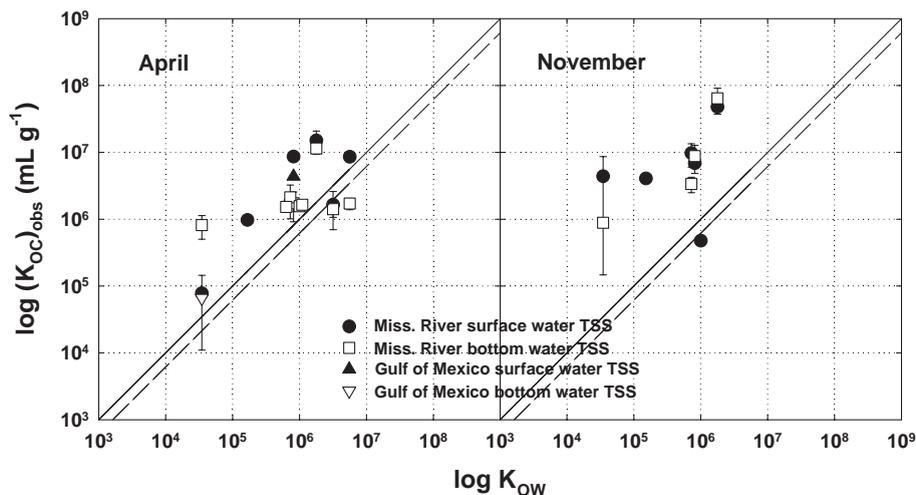


Fig. 2. Linear-free energy relationship between observed organic carbon-normalized PAH distribution coefficients  $(K_{OC})_{OBS}$  and octanol water partition coefficients  $(K_{OW})$  in Mississippi River and Gulf of Mexico during April and November 1999. Diagonal solid line depicts where  $\log (K_{OC})_{OBS} = \log K_{OW}$  and diagonal dashed line is representative of the relationship between the two variables offered by Karickhoff et al. (1979) where  $(K_{OC})_{OBS} = 1.00 \log K_{OW} - 0.21$ . Error bars represent the standard error propagated from errors in particulate and dissolved phase PAH and OC concentrations.

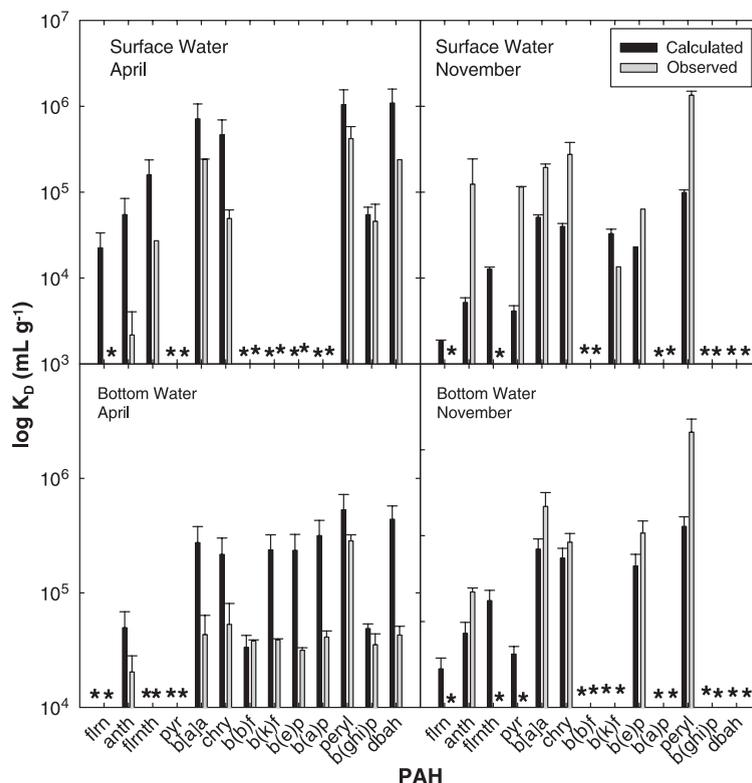


Fig. 3. Calculated and observed PAH particle-water distribution coefficients in Mississippi River surface water and bottom water total suspended solids. Calculated values of  $\log K_D$  derive from Eq. (1) (Accardi-Dey and Gschwend, 2002). Observed values of  $\log K_D$  derive from the quotient of particulate and dissolved phase PAH concentrations in this study (Tables 1 and 2). Error bars for calculated values of  $\log K_D$  are representative of standard error propagated from individual errors in  $f_{OC}$ ,  $f_{BC}$ , and  $C_w$ . In contrast, error bars in the case of  $\log (K_D)_{OBS}$  were propagated from standard errors in measurement values of  $C_p$  and  $C_w$ . The symbol “\*” implies a non-quantifiable value.

of  $\log (K_D)_{OBS}$  in November 1999 surface and bottom waters exceeded corresponding values of PAH  $\log (K_D)_{CALC}$  (Fig. 3).

Observations that periodically  $\log (K_D)_{OBS} \gg \log (K_D)_{CALC}$  (Fig. 3) requires some discussion. As noted above, Eq. (1) is derived from the sorption isotherm conceptualizing PAH absorption into OC coupled with PAH adsorption onto BC (Accardi-Dey and Gschwend, 2002). Elevated profiles of  $\log (K_{OC})_{OBS}$  versus  $\log (K_{OW})$  (Fig. 2) and  $\log (K_D)_{OBS}$  versus  $\log (K_D)_{CALC}$  (Fig. 3) in November taken together, seem to indicate that the Mississippi River at times may be enriched in particles possessing PAH affinity resembling that of activated carbon (PAH  $K_{Ac} > \text{PAH } (K_{OC})_{OBS}$ ; Walters and Luthy, 1984). In many cases, increased PAH-particle affinity in the winter months is thought to be the result of combustion-governed PAHs

derived from seasonal fossil fuel and wood use for home heating (e.g. Gustafson and Dickhut, 1997). We posit that that high non-BC absorption is not exclusively responsible for elevated PAH particle water distribution coefficients. If that were the case and PAH distributions in these samples were at equilibrium, then the observation of high PAH  $(K_D)_{OBS}$  in Nov 1999 would presumably correspond to higher overall mass-normalized particulate phase PAH concentrations in these samples relative to other geographical areas, unlike what is seen in Table 4. Below, we propose explanations for our observations.

### 3.3. Alternative explanations for PAH distributions

We must consider the possibility that our sampling efforts were not rigorous enough and that we did not

Table 4

Anthracene, benzo[*a*]anthracene, benzo[*g,h,i*]perylene in suspended particulate matter isolated with glass fiber filters ( $C_p > 0.7 \mu\text{m}$ ) in selected North American river/coastal systems

Location	Flow	anthracene	benzo[ <i>a</i> ]anthracene	benzo[ <i>g,h,i</i> ]perylene	Reference
New York-New Jersey Harbor Estuary	Low	$30 \pm 1$	$48 \pm 7.1$	$85 \pm 3.7$	(Gigliotti et al., 2002)
Susquehanna River, Maryland	High	97	260	305	(Ko and Baker, submitted for publication)
	Low	$90 \pm 49$	$270 \pm 200$	$320 \pm 210$	
Patapsco River, Maryland	High	$220 \pm 270$	$430 \pm 340$	$270 \pm 260$	(Ko and Baker, submitted for publication)
	Low	$1,120 \pm 3,300$	$1,400 \pm 2,300$	$580 \pm 560$	
York River, Virginia	Mean of 6 cruises (6/98–4/99)	$7.7 \pm 0.76$	$20.3 \pm 1.7$	$26 \pm 2.0$	(Countway et al., 2003)
Mainstem Chesapeake Bay	Mean of 6 cruises (10/90 to 8/92)	$51 \pm 4.5$	$87 \pm 13$	$230 \pm 54$	(Ko and Baker, 1995)
Lower Mississippi River	High	$4.4 \pm 1.6$	$26 \pm 2.2$	$37 \pm 11$	This Study
	Low	$40 \pm 49$	$54 \pm 7.3$	$100 \pm 16$	
Gulf of Mexico	High	$0.92 \pm 0.12$	$3.5 \pm 0.29$	7.8	This Study

Concentrations ( $\text{ng g}^{-1}$  dry weight particle) are expressed as means and standard deviations [ $x \pm \text{SD}$ ] of replicate measurements if available.

collect samples which were truly representative of typical hydrocarbon pollution in the river and gulf. For example, we may not have collected samples representative of contamination from boat traffic or diesel fuel spills. Despite this, it is still surprising (given the areal extent of the watershed of Mississippi River and the surface area of the Gulf of Mexico) that levels of PAHs are so low at the sites in our study compared to all other sites in Table 4. In 1994, measurements were made of sedimentary concentrations of PAHs in the vicinity of Sites 1 and 2 in the River as part of US EPA's Environmental Monitoring and Assessment Program-Estuaries (Maruya et al., 1997; Maruya, personal communication). Concentrations of anth, b[*a*]a, and b[*g,h,i*]p in that study were respectively,  $16 \pm 11$ ,  $42 \pm 9$ , and  $34 \pm 13 \text{ ng g}^{-1}$  dry weight of sediments, values similar to PAH concentrations determined for TSS isolated in this study. So, we feel that the concentrations of PAHs determined in this study must be somewhat representative for the Mississippi River. Moreover, the highest amounts of PAHs in the other studies noted in Table 4 correspond to sites directly adjacent to urban locations unlike our study area.

It has been suggested that dissolved and colloidal phases of carbon might bind PAHs and affect PAH partitioning (Morel and Gschwend, 1987; Burgess et al., 1996), and so we assessed how DOC levels in our samples (Table 3) might affect  $(K_{\text{OC}})_{\text{OBS}}$ . We used the following equation for PAH  $\log K_{\text{DOC}}$  in surface waters relative to  $\log K_{\text{OW}}$  ( $\log K_{\text{DOC}} = 0.97 \times \log$

$K_{\text{OW}} - 1.27$ ; Burkhard, 2000), the range of DOC in our studies (Table 3), and a three-phase model for PAH binding to DOC (Mitra and Dickhut, 1999) to calculate the effect of DOC on PAH distributions in our samples. Our calculations indicate that given the range of DOC concentrations in our samples, the apparent solubility enhancement of PAHs by DOC would only lower observed values of  $K_{\text{D}}$  by at most, a factor of 2. Thus, DOC in the Mississippi River appears to minimally influence PAH distributions in this study and hence reported values for PAH  $K_{\text{D}}$  were not adjusted for DOC levels.

There are several other factors specific to particulate and dissolved phase PAHs which may be affecting the observed distributions in these samples. Since  $(K_{\text{D}})_{\text{OBS}}$  is the ratio of PAHs in the particulate phase to the dissolved phase, any process leading to lower PAHs in the dissolved phase would result in high distribution coefficients. For example, microbial respiration and oxidation in the water column would preferentially deplete dissolved phase low molecular weight PAHs relative to high molecular weight PAHs (Capone and Bauer, 1992) resulting in a preferential elevation of  $K_{\text{D}}$  for low molecular weight PAHs. Additionally, PAH particle water distributions not being at equilibrium may render inaccurate values for  $K_{\text{D}}$ . We have not quantified any variables in our samples that allow us to unequivocally state if PAH concentrations in our samples have been affected by microbial degradation or if PAH distributions are truly at equilibrium. Also, we are unable to verify the

possibility that large inequalities in  $(K_D)_{\text{CALC}}$  versus  $(K_D)_{\text{OBS}}$  stem from literature values of  $K_{\text{BC}}$  and  $K_{\text{OC}}$  from other geographical locations not being applicable to particles in the lower Mississippi River watershed. Thus, we acknowledge that differences in  $(K_D)_{\text{CALC}}$  versus  $(K_D)_{\text{OBS}}$  between the two sampling periods in this study merit closer examination of the temporal factors affecting PAH desorption and distribution in lower Mississippi River suspended sediments.

### 3.4. Sources of PAHs to the Gulf of Mexico

Our discussion thus far has mostly focused on PAH fate and transport in the lower Mississippi River. As noted above, our sampling efforts in April 1999 also included surface and bottom water sampling of the inner shelf at one station in the Gulf of Mexico. We realize that one station is hardly a representation of the entire gulf and therefore, the results and implications

of our calculations should be interpreted as preliminary ones.

Nonetheless, these calculations are warranted, since there are presently few quantitative studies estimating PAH influx to the gulf.

To make a comparison between the river and gulf, we selected anth, b[a]a, and b[g,h,i]p as three representative PAHs with a range of molecular weight, aqueous solubility, and hydrophobicity. An additional reason for selecting these three compounds was that they were consistently quantifiable in the majority of our samples (Tables 1 and 2). Comparisons of the amounts of particulate phase anth, b[a]a, and b[g,h,i]p in the river and gulf (Fig. 4) indicate that neither OC nor BC abundance can account for contrasting PAH levels between both sites. Either the abundance and sources of PAHs are different between the river and the gulf or other non-BC compositional variables pertaining to natural organic matter between the river and the gulf are responsible

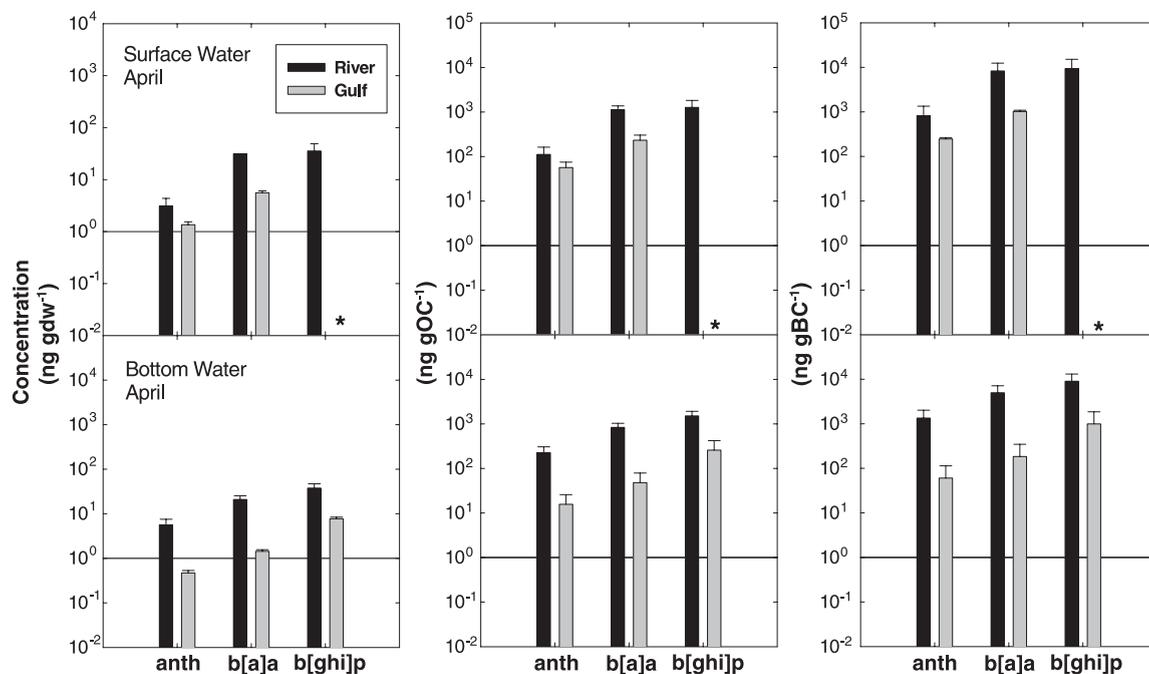


Fig. 4. A comparison of particulate phase ( $C_p > 0.7 \mu\text{m}$ ) anth, b[a]a, and b[g,h,i]p concentrations in surface and bottom waters of the Mississippi River and Gulf of Mexico in April normalized to gram dry weight particles,  $f_{\text{OC}}$ , and  $f_{\text{BC}}$ , respectively. For river samples, error bars represent the standard error propagated from errors in PAH concentration at Stations 1 and 2 and errors in TSS,  $f_{\text{OC}}$ , and  $f_{\text{BC}}$ . For gulf samples, error bars represent the standard error propagated using GC analytical precision for each respective PAH concentration and standard errors of TSS,  $f_{\text{OC}}$ , and  $f_{\text{BC}}$ . The symbol "\*" implies a non-quantifiable value.

for observed differences in PAH concentrations between each environment.

The influx of PAHs into the Gulf of Mexico may result from numerous sources. Due to its large surface area, waters of the Gulf of Mexico likely receive a significant input of PAHs directly via atmospheric deposition from remote and proximal urban sources depending on the time of year. Similarly, gas exchange via volatile flux may dominate low molecular weight PAH efflux during warmer summer months. It is also possible that in situ sources contribute significantly to PAHs in the gulf. The inner shelf of the gulf is prolific in natural petroleum seeps and stationary platforms dedicated to petroleum exploration (Kennicutt et al., 1988). Many of the platforms dedicated to petroleum exploration actively combust petroleum and may discharge by-products, which include particulate and vapor phase PAHs, into the atmosphere above the gulf. Considering the above, and the general concentrations of PAHs originating from natural petroleum seeps and their abundance in the Gulf of Mexico (NRC, 2003), and the lack of any existing budget for PAHs in the Gulf of Mexico, it is necessary to make a first order attempt at such a calculation using surface and bottom waters from our one sampling station in the gulf. In the following section, we conduct a one compartment mass balance model for anth, b[a]a, and b[g,h,i]p and quantify their mass flux in the gulf.

### 3.5. Preliminary mass-balance of PAH flux in the Gulf of Mexico

The principles of mass balance require that for a given time scale, the overall PAH flux in the gulf equates to the temporal rate of change in the sum of PAH import, export, and transformation reactions in the gulf. Our time scale of interest in performing these calculations is 1 year. The annual rate of change of tPAH input into a sediment core from the inner shelf of the gulf suggests steady-state conditions for PAH deposition into the sediment column over the course of 1 year (Santschi et al., 2001). Thus, the overall annual flux of particulate and dissolved phase PAHs into the gulf is expressed below:

$$M_{Er} + M_{Riv} + M_{Seep} + M_{Atm} = M_{Sed} + M_{Ocean} + M_{Deg} \quad (2)$$

where PAH mass influx is assumed to equate to the sum of PAH input from (1) total coastal erosion ( $M_{Er}$ ),

(2) fluvial input into the gulf ( $M_{Riv}$ ), (3) natural hydrothermal seeps from the bottom of the gulf ( $M_{Seep}$ ), and (4) atmospheric deposition (wet + dry + gas exchange) from remote urban areas surrounding the gulf ( $M_{Atm}$ ). On the other side of the equation, PAH loss out of the gulf consists of loss due to sedimentation ( $M_{Sed}$ ), advective losses from the gulf to the Atlantic Ocean ( $M_{Ocean}$ ), and any photolytic or biologically induced degradation ( $M_{Deg}$ ).

In the case of our model, we are assuming a priori that  $M_{Atm}$  is a source (rather than a sink) for anth, b[a]a, and b[g,h,i]p into the gulf. This assumption is justified based on an existing atmospheric study of PAHs in coastal Texas which indicates that the atmosphere is a net source of PAH to Galveston Bay in Texas (Park et al., 2001).

Eq. (2) may be simplified when considering several conditions. For example, we assume that sub-aqueous photolytic and other diagenetic transformations of PAHs within the gulf and the total amount of biomass-derived transformations in the gulf ( $M_{Deg}$ ) are negligible over the time course of a year relative to other terms in Eq. (2). These assumptions are justified based on the fact that the euphotic zone comprises a negligible portion of the total volume of water in the gulf, and also because of an anaerobic biodegradation rate for anth (the smallest and most degradable of the three PAHs used in the mass balance) of 200 days (Mackay et al., 1992).

The quantification of PAH export from the Gulf of Mexico into the Atlantic Ocean ( $M_{Ocean}$ ) relies on accurate estimations for flushing time and residence time for the entire water column of the Gulf of Mexico. Such parameters are difficult to quantify for a water body as large as the gulf that has a well-established thermocline. Estimates of particle and hydraulic residence time, which do exist, are extremely variable. An average of two estimates for residence times (5 and 500 years; Guo et al., 1995; Powell, personal communication, respectively) enables us to consider the time scale for flushing out water (and PAHs) from the gulf to be  $\sim 10^2$  years. Presumably, these estimates for residence time are lower limits since they are based on calculations made above the thermocline. Thus, in relation to the time scale of interest for our study (i.e.  $10^0$  years), we assume that  $M_{Ocean}$  is also a negligible quantity (Eq. (2)). Using anth, b[a]a, and b[g,h,i]p as three representative PAHs ranging in molecular

weight, aqueous solubility, and hydrophobicity, we proceed below to quantify the remaining parameters in Eq. (2).

### 3.5.1. PAH influx to the Gulf of Mexico

As noted above, the total input of PAHs into the Gulf of Mexico is equal to  $M_{\text{Atm}}$ ,  $M_{\text{Seep}}$ ,  $M_{\text{Riv}}$ , and  $M_{\text{Er}}$ . Lack of existing data on the seep contribution of PAHs into the gulf results in  $M_{\text{Seep}}$  being considered as an unknown in Eq. (2). We can conduct preliminary assessments for the other influx terms in the following manner.

Atmospheric loading of semivolatile chemicals such as PAHs to water bodies can be estimated by summing dry deposition ( $F_{\text{Dry}}$ ), wet deposition ( $F_{\text{Wet}}$ ), and gas exchange fluxes ( $F_{\text{Vol}}$ ) (Dickhut and Gustafson, 1995). The atmospheric loading of PAHs into the Gulf of Mexico was made by extrapolation of available estimates for each term above derived from Galveston Bay, a regional water body exerting potential influence to the gulf (Park et al., 2001). The atmospheric inputs based on the airshed influencing Galveston Bay presumably represents atmospheric loading from nearby Texas City and should be considered representative of some of the highest air pollution in the country (between Baton Rouge, LA and Corpus Christi, TX). So, our estimates for atmospheric loading should be considered an upper limit compared to other regions around the periphery of the Gulf of Mexico. According to Park et al. (2001), total PAH  $F_{\text{Dry}}$  and  $F_{\text{Wet}}$  for Galveston Bay in 1995–1996 were 99  $\mu\text{g}$  and 135  $\mu\text{g}$   $\text{m}^{-2}$   $\text{year}^{-1}$ , respectively. Annual estimates of PAH dry deposition are related to the product of the particulate phase PAH concentration ( $C_{\text{P}}$ ) and each PAH's dry deposition velocity. Similarly, annual estimates of PAH wet deposition are the product of volume-weighted PAHs in rain (i.e.  $C_{\text{P}}$  and  $C_{\text{W}}$ ) and monthly rainfall volume ( $\text{m}^3$   $\text{month}^{-1}$ ). The concentration of anth, b[a]a, and b[g,h,i]p in atmospheric aerosols above Galveston Bay were 1.3%, 2.6%, and 5.9% of the total aerosol PAH concentration reported in Park et al. (2001). These values for fractional contribution of each molecule to total aerosol PAH were then multiplied by the total  $F_{\text{Dry}}$  to yield  $1,301 \pm 1,183$ ,  $2,602 \pm 3,667$ , and  $5,913 \pm 6,978$   $\text{ng}$   $\text{m}^{-2}$   $\text{year}^{-1}$  for anth, b[a]a, and b[g,h,i]p  $F_{\text{Dry}}$  fluxes, respectively. Similarly, 0.43%, 1.1%, and 2.4% of the total PAHs in rain (dissolved + particulate) collected in Galveston

Bay (Park et al., 2001) were made up of anth, b[a]a, and b[g,h,i]p, respectively. Thus, 579, 1,429, and 3,298  $\text{ng}$   $\text{m}^{-2}$   $\text{year}^{-1}$  were estimated as the respective  $F_{\text{Wet}}$  flux of anth, b[a]a, and b[g,h,i]p via wet deposition. Gas exchange fluxes for PAHs were calculated from the equation below:

$$F_{\text{Vol}} = k_{\text{OL}} \left[ C_{\text{W}} - \frac{C_{\text{V}}}{H'} \right] \quad (3)$$

where  $C_{\text{W}}$  is the dissolved phase PAH concentration in the water body in question,  $C_{\text{V}}$  is the atmospheric gas phase concentration,  $H'$  is the dimensionless Henry's Law Constant, and  $k_{\text{OL}}$  is the overall mass transfer coefficient for each PAH which is a function of wind speed and molecular diffusivity in air and water. For purposes of this study, values of  $k_{\text{OL}}$  and  $C_{\text{V}}$  for anth, b[a]a, and b[g,h,i]p are from Galveston Bay (Park, personal communication) and were used in conjunction with our measured values of  $C_{\text{W}}$ . Values for  $H'$  were calculated from the equations provided in Bamford et al. (1999). In this manner,  $F_{\text{Vol}}$  was calculated to be:  $-12,375$ ,  $505$ , and  $1879$   $\text{ng}$   $\text{m}^{-2}$   $\text{year}^{-1}$ , for anth, b[a]a, and b[g,h,i]p, respectively. Note the negative sign in front of  $F_{\text{Vol}}$  for anth, signifying that the net flux of anth is out of the gulf. In applying these fluxes to the Gulf of Mexico, we assume that the source of PAHs to Galveston Bay in 1995–1996 are representative of average annual PAH fluxes to the Gulf of Mexico. Taking the product of the fluxes above and the surface area of the gulf ( $1.5 \times 10^6$   $\text{km}^2$ ; Solis and Powell, 1999) yields values for atmospheric loading ( $M_{\text{Atm}}$ ) of anth, b[a]a, and b[g,h,i]p, as listed in Table 5.

The annual fluvial contribution of anth, b[a]a, and b[g,h,i]p into the Gulf of Mexico was calculated with the following equation:

$$M_{\text{Riv}} = \sum_{I=1,12; J=1,2} [(Q)_I (C_{\text{P}} + C_{\text{W}})_J] \delta_{\text{Riv}} \quad (4)$$

in which  $M_{\text{Riv}}$  is the mass (kg) of each selected PAH entering the gulf from all fluvial sources in 1999,  $Q_I$  is the monthly water discharge from the Mississippi River in 1999 (USGS, 1999), and  $\delta_{\text{Riv}}$  is a multiplication factor to adjust the fraction of fluvial discharge provided by the Mississippi River relative to total fluvial input into the gulf. The Mississippi River and Atchafalaya River complex provides  $\sim 55\%$  of total fresh water and sediment discharge into the Gulf of

Table 5  
Preliminary estimates of annual flux for selected PAHs in the Gulf of Mexico

Compound		anth	b[a]a	b[g,h,i]p
<i>Influx</i>				
Coastal Erosion	$M_{\text{ER}}$	$(2.3 \pm 2.7) \times 10^3$	$(4.1 \pm 4.2) \times 10^3$	$(1.3 \pm 1.4) \times 10^3$
Atmospheric	$M_{\text{Atm}}$	$-16 \pm 14$	$6.8 \pm 9.6$	$17 \pm 19$
	$(M_{\text{Atm}})_{\text{Dry}}$	$2.0 \pm 1.8$	$3.9 \pm 5.5$	$8.9 \pm 10$
	$(M_{\text{Atm}})_{\text{Wet}}$	0.9	2.1	4.9
	$(M_{\text{Atm}})_{\text{Vol}}$	-19	0.76	2.8
Fluvial	$M_{\text{Riv}}$	$1.3 \pm 0.54$	$2.2 \pm 0.35$	$3.5 \pm 0.54$
<i>Efflux</i>				
Sedimentation	$M_{\text{Sed}}$	$(2.5 \pm 1.1) \times 10^2$	$(9.5 \pm 4.2) \times 10^2$	$(3.4 \pm 1.1) 10^3$

All quantities are expressed as kilograms (kg). See text for calculations. Total error associated with each parameter is propagated from the error associated with each individual term in Eqs. (3)–(6).

Mexico and the Atchafalya River's discharge is approximately 30% of that of the Mississippi River's (Solis and Powell, 1999). Thus,  $\delta_{\text{Riv}}$  is equal to 2.1. The terms  $C_{\text{P}}$  and  $C_{\text{W}}$  are the Mississippi River's average particulate and dissolved phase concentration of anth, b[a]a, or b[g,h,i]p, isolated in April 1999 extrapolated across high flow ( $J=1$ ; January to July) and the average concentration isolated in November 1999 extrapolated across low flow ( $J=2$ ; August to November). In Eq. (4),  $C_{\text{P}}$  and  $C_{\text{W}}$  are expressed in units of  $\text{ng l}^{-1}$ . The 1999 annual  $C_{\text{P}}$  flux is based on average high Eq. (2) flow concentrations of  $0.38 \pm 0.08$ ,  $2.1 \pm 0.15$ , and  $3.1 \pm 0.50 \text{ ng l}^{-1}$  and average low flow concentrations of  $0.33 \pm 0.22$ ,  $0.43 \pm 0.04$ , and  $0.78 \pm 0.09 \text{ ng l}^{-1}$  respectively, for anth, b[a]a, and b[g,h,i]p in the Mississippi River. Similarly, values for  $C_{\text{W}}$  are based on average high flow concentrations of  $0.84 \pm 0.55$ ,  $0.31 \pm 0.10$ , and  $0.93 \pm 0.17 \text{ ng l}^{-1}$  for anth, b[a]a, and b[g,h,i]p and average low flow concentrations of  $0.61 \pm 0.13$  and  $0.27 \pm 0.04 \text{ ng l}^{-1}$  for anth and b[a]a, respectively. Concentrations of b[g,h,i]p were not quantifiable in the river during low flow. Assuming that the composition of all of the fluvial-derived particulate and dissolved phase anth, b[a]a, and b[g,h,i]p entering the gulf from other freshwater sources are similar to that of the Mississippi River, the total influx into the gulf from fluvial sources in 1999 ( $M_{\text{Riv}}$ ) (Eq. (4)), is listed in Table 5.

An upper limit end member for erosion-derived input of PAHs into the gulf was calculated using the following equation:

$$M_{\text{Er}} = A_{\text{Er}} \text{RSL} C_{\text{P}} \rho_{\text{dry}} \delta_{\text{Er}} \quad (5)$$

from the product of  $A_{\text{Er}}$ , an estimate for marsh loss from the Louisiana coast ( $75 \text{ km}^2 \text{ year}^{-1}$ ; USGS 1995), RSL, an average relative sea level rise for the Louisiana coast of  $1 \text{ cm year}^{-1}$  (LCWPPR, 2003),  $C_{\text{P}}$ , particulate phase PAHs measured in Pass Fourchon (in  $\text{ng g}^{-1}$  units), a coastal harbor located in the southern Louisiana which drains into the gulf (Mitra et al., 2001),  $\rho_{\text{dry}}$  an average dry sediment density of  $1.0 \text{ g cm}^3$ , and  $\delta_{\text{Er}}$  which is a length multiplication factor to scale the length of the Louisiana coastline to the coastline bordering the Gulf of Mexico. We approximate  $\delta_{\text{Er}}$  to be 8.0. Average  $C_{\text{P}}$  values for anth, b[a]a, and b[g,h,i]p at Pass Fourchon in 1999 were calculated to be:  $380 \pm 460$ ,  $685 \pm 700$ , and  $208 \pm 237 \text{ ng g}^{-1}$ , respectively (Mitra et al., 2001). Corresponding values of  $M_{\text{Er}}$  for anth, b[a]a, and b[g,h,i]p are listed in Table 5. These values should be considered an upper limit for erosion based on that fact that the northern Gulf of Mexico's coastline (the basis for these erosional calculations) is undergoing a greater degree of erosion relative to the remainder of the gulf.

### 3.5.2. PAH efflux from the Gulf of Mexico

Losses of particulate phase PAHs in the Gulf of Mexico due to sedimentation were calculated based on our measurements which indicated that particulate phase anth, b[a]a, and b[g,h,i]p concentrations in surface and bottom waters at one station in the gulf (i.e.  $C_{\text{P}}$ ) were, respectively,  $1.3 \pm 0.38$ ,  $4.9 \pm 1.6$ , and  $18 \text{ ng g}^{-1}$ . For purposes of our model, we assumed that these concentrations were representative annual PAH concentrations for the entire Gulf of Mexico. It is necessary to make this extrapolation since there are no

existing measurements of individual PAHs in the water column of the gulf. Losses of PAHs due to sedimentation in the entire Gulf of Mexico were calculated using:

$$M_{\text{Sed}} = C_p \delta_A S (\text{Area})_{\text{gulf}} \quad (6)$$

Typically, sediments delivered to coastal margins undergo several cycles of transport and deposition. For example, Corbett et al. (submitted for publication) have noted that sediments from the Mississippi River are initially transported less than 30 km from the river mouth. Much of this same sediment is then exported out across the continental shelf and dispersed throughout the Gulf of Mexico over time at lower overall mass accumulation rates ( $S = 1.3 \text{ g cm}^{-2} \text{ year}^{-1}$ ; Corbett et al., submitted for publication). To scale Mississippi River-derived sediments from an area immediately adjacent to the main fluvial discharge zone to its eventual dispersal throughout the entire Gulf of Mexico, we introduced an area extrapolation factor,  $\delta_A$ . The value for  $\delta_A$  is based on the following calculations. The entire area of the Gulf of Mexico was spatially divided into quadrants. The area of the quadrants in the study site identified by Corbett et al. (submitted for publication), for which they determined a nearshore sediment deposition rate, was divided by the total quadrant area covered by the entire Gulf of Mexico. The term  $\delta_A$  is the ratio of these two spatial areas ( $\delta_A = 0.01$ ). Using the PAH concentrations and approximate sediment accumulation rate noted above and a value of  $1.5 \times 10^6 \text{ km}^2$  for spatial area of sediment delivery to the gulf ( $\text{Area}_{\text{gulf}}$  (Solis and Powell, 1999), overall annual particulate phase PAH loss due to sediment deposition (i.e.  $M_{\text{Sed}}$ ) was calculated for anth, b[a]a, and b[g,h,i]p (Table 5).

### 3.5.3. Net PAH flux in the Gulf of Mexico

We can combine the calculations made thus far and provide a preliminary estimate for a net PAH mass balance in the Gulf of Mexico. The results in Table 5 listing the riverine and atmospheric contribution of PAHs into the gulf (order of magnitude:  $10^0$ ) suggests that these fluxes are several orders of magnitude lower than PAH flux from coastal erosion and sedimentation in the gulf (order of magnitude  $M_{\text{Sed}}$ :  $10^2$ – $10^3$ ). This leads us to conclude two important facts with respect to PAH loading into the Gulf of Mexico (Eq. (2)).

First, atmospheric and fluvial sources of PAHs into the Gulf of Mexico (based on anth, b[a]a, and b[g,h,i]p) are relatively so low that they may be considered negligible and second, the influx of PAHs to the gulf from coastal erosion contributes the majority of PAHs into the Gulf of Mexico, as represented by anth, b[a]a, and b[g,h,i]p.

## 4. Conclusions

Several conclusions ensue from these measurements of PAH distributions in the particulate and dissolved phases of the lower Mississippi River and one site in the Gulf of Mexico. First, as represented by our two flow-regime end member-driven sampling time periods, it appears that PAH distributions in the lower Mississippi River varied seasonally in 1999 and may have originated predominantly from combustion-derived processes, at least during November. This conclusion may be of interest to resource managers focusing on PAH bioavailability in the lower Mississippi River. Next, despite a combustion-derived source of PAHs into the Mississippi River, the overall amount of PAHs introduced into the Gulf of Mexico from atmospheric and fluvial sources is negligible compared to the “standing stock” of PAHs in the gulf.

Our mass balance calculations indicate that PAH influx from coastal erosion into the Gulf of Mexico may be the dominant source to the gulf. These latter conclusions, stemming from our mass balance calculations based on a single sampling station in the Gulf of Mexico, should be interpreted with caution and should most definitely be considered to be preliminary. Nonetheless, these mass balance calculations indicate that more representative and temporally intensive sampling efforts adjacent to seeps, offshore in the water column, and in the atmosphere above the Gulf of Mexico are in order.

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