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Black Carbon from the Mississippi River: Quantities, Sources, and Potential Implications for the Global Carbon Cycle

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Black carbon (BC) may be a major component of riverine carbon exported to the ocean, but its flux from large rivers is unknown. Furthermore, the global distribution of BC between natural and anthropogenic sources remains uncertain. We have determined BC concentrations in suspended sediments of the Mississippi River, the 7th largest river in the world in terms of sediment and water discharge, during high flow and low flow in 1999. The 1999 annual flux of BC from the Mississippi River was 5×10^{-4} petagrams (1 Pg $= 10^{15}$ g $=$ 1 gigaton). We also applied a principal components analysis to particulate-phase high molecular weight polycyclic aromatic hydrocarbon isomer ratios in Mississippi River suspended sediments. In doing so, we determined that $\sim$27% of the BC discharged from the Mississippi River in 1999 originated from fossil fuel combustion (coal and smelter-derived combustion), implicating fluvial BC as an important source of anthropogenic BC contamination into the ocean. Using our value for BC flux and the annual estimate for BC burial in ocean sediments, we calculate that, in 1999, the Mississippi River discharged $\sim$5% of the BC buried annually in the ocean. These results have important implications, not only for the global carbon cycle but also for the fluvial discharge of particulate organic contaminants into the world's oceans.

Introduction

Escalating anthropogenic activities in coastal and estuarine environments are resulting in increased exposure to combustion byproducts such as black carbon (BC) in such nearshore environments. BC is generated from the incomplete combustion of biomass (e.g., vegetation) and fossil fuels (e.g., coal) and has been implicated in air pollution (*1*), climate studies (*2*), and coastal sediment contamination (*3*). BC may be formed from vapor-phase condensation of organic molecules (i.e., graphitic BC or soot carbon) or may be the remnants of burned materials (i.e., char) (*4*). For example, annual aerosol emissions of BC range from 5 to 6×10^{-3} Pg from vegetation fires (*5*) and 6 to 9×10^{-3} Pg from fossil fuel burning (*6*). Evidence of BC in the sedimentary record serves as an indicator of historical combustion processes, such as vegetation fires, and the increasing influence of anthropogenic processes in the global carbon cycle, such as coal and other fossil fuel combustion (*4*). In that context, BC has been found in deeper Atlantic and Pacific Ocean sediments where, in some cases, it constitutes 12−47% of the sedimentary organic carbon (OC) (*7*, *8*). Although the global cycle of BC has been studied for the last 20−30 years, the abundance and sources of large river discharge of BC to the ocean have not been accurately constrained (*9*, *10*).

Upon entering the atmosphere as aerosol particles, BC reaches rivers and streams either directly via atmospheric deposition or indirectly along with suspended solids via runoff and soil erosion (*4*). In shallow areas, sediment resuspension may also introduce sedimentary BC into the water column. Annual global BC formation has been estimated to be 0.05−0.02 Pg (*5*). Similarly, an approximate amount of 0.01 Pg of BC has been estimated to be annually discharged into coastal ocean sediments via both aeolian and fluvial inputs (*9*). The world's major rivers drain soils in large watersheds which receive the byproducts from numerous sources of combustion. Black carbon may be a major component of riverine carbon exported to the ocean (*9*), but its flux from large rivers is unknown. Furthermore, the global distribution of BC between natural and anthropogenic sources remains uncertain. Characterizing fluvial BC discharge into the oceans from large rivers is essential in quantifying (1) the importance of river−coast−ocean transition zones (i.e., coastal margins) to the global carbon cycle and (2) the escalating influence of anthropogenic stress on coastal ecosystems.

The Mississippi River is the largest river in the United States and flows 3732 km from its source at Lake Itasca in northern Minnesota to the Gulf of Mexico. It's tributaries drain $\sim$41% of the contiguous United States (*11*), and as of 1992, 27% of the United States' population resided within the area of the watershed (*12*). Thus, suspended sediment discharge from the Mississippi River into the ocean is representative of a large and extensive watershed with heterogeneous sediment sources (Figure 1a). An extensive watershed of a large river such as the Mississippi likely integrates a variety of direct and indirect particle influx processes into the water column which include anthropogenic and naturally derived BC. The Mississippi River watershed is influenced by byproducts from biomass burning (e.g., wood burning stoves, slash-and-burn agriculture) and fossil fuel combustion (e.g., automobile exhaust, coal combustion). Using the Mississippi River as an example, our objective was to quantify a large river's flux and source of BC into the ocean.

Along with BC, polycyclic aromatic hydrocarbons (PAHs) are also produced during incomplete combustion of organic matter. In this study, we apply a multivariate statistical technique to high molecular weight (HMW) PAH isomer ratios in Mississippi River suspended sediments. This allows us to infer the relative contribution of PAHs from the predominant BC-generating combustion processes in the environment (*13*).

Experimental Section

Sample Collection. In April and November of 1999, we sampled BC and OC in total suspended solids (TSS) (particles retained on 0.7 μm pore size glass fiber filters) at several stations. In April 1999, samples were collected every 10 km along a transect originating at Station 1 in the lower Mississippi River and progressing to Station 4 in the inner shelf of the Gulf of Mexico (Figure 1b and Table 1). Water

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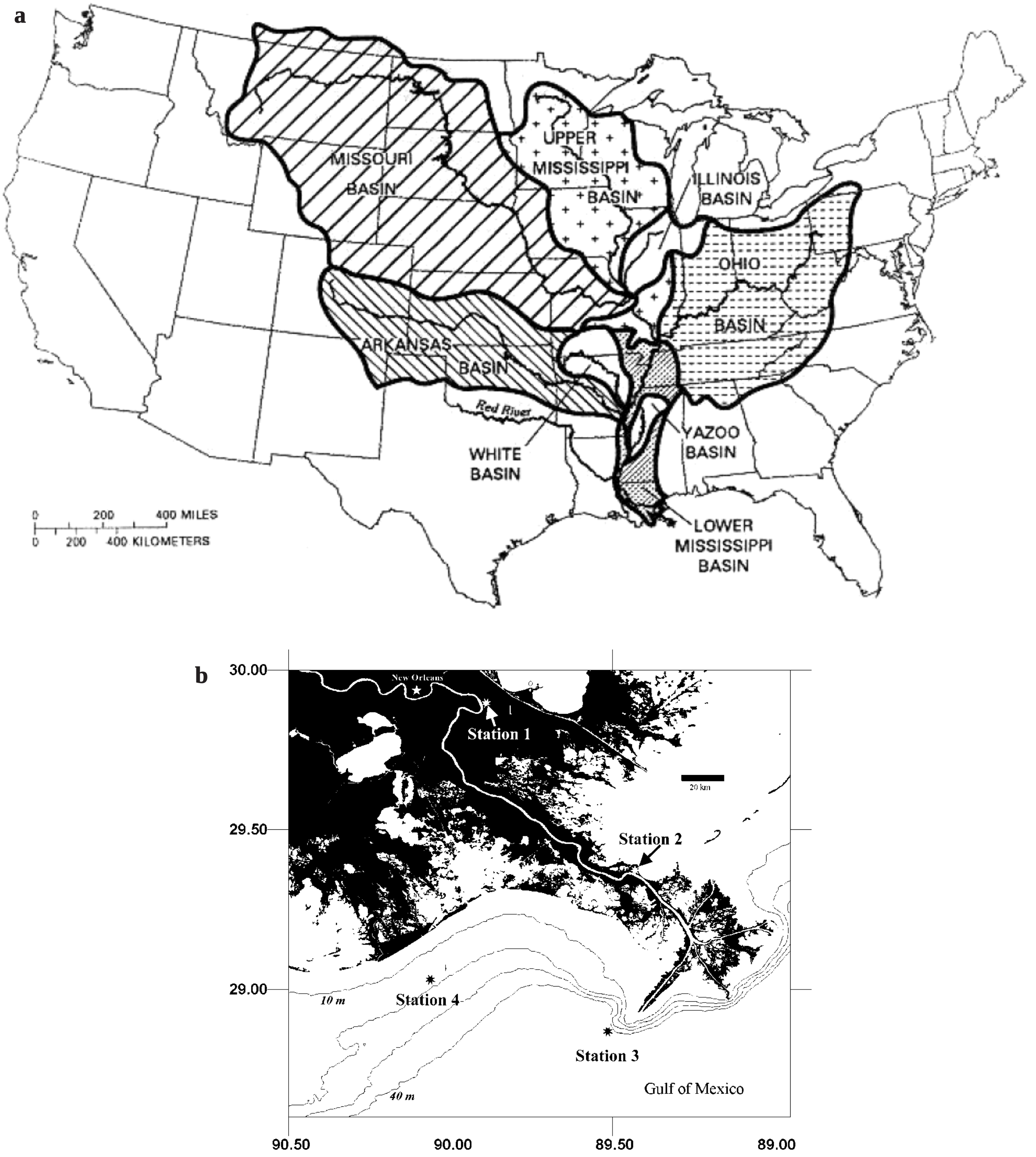

FIGURE 1. (a) Mississippi River drainage basin. (b) Site map showing geographical locations of sampling stations.

column samples were collected using the R/V Pelican using a rosette array of Nisken bottles. TSS in surface and bottom waters at two stations in the river and two stations in the gulf within the transect were also sampled for particulate-phase PAHs. The Gulf of Mexico was not sampled in November. Samples were collected during two time periods in order to obtain representative samples from high river flow (January–July) and low river flow (August–December) (Figure 2a). The months in 1999 which generally had greater than the mean annual water discharge (15 000 m^3 s^{-1}) are defined to be representative of high river flow. Conversely, we define the months with rates of discharge lower than this value to be representative of low flow. Water temperature, salinity, and sampling depth are listed in Table 1.

Water samples were collected into precleaned (dilute Alconox solution, 3–5 rinses of distilled deionized (DDI) water, 500 mL of 12 N HCl, and 3–5 additional rinses of DDI water) 20-L glass carboys. Particles for PAH analysis were isolated by filtering through 142 mm diameter, 0.7 μm pore size precombusted (450° C for 4 h) glass fiber filters (GFF) housed in a stainless steel filter holder. Approximately 10–20 L of water was filtered for particulate-phase PAH analysis. Upon filtering, the GFFs were stored in HPLC-grade methanol in precombusted glass Mason jars for subsequent PAH analysis using Soxhlet extraction apparatus (*14*). Particles quantified for TSS, BC, and OC were quantified using precombusted (450 °C for 4h) and tared 25 mm diameter GFFs by filtering 35–40 mL of water (April 1999) and 100–

TABLE 1. Ancillary Site Information for Surface and Bottom Waters of the Mississippi River and Gulf of Mexico

station ID	collection date	river or gulf	water depth (m)	salinity (psu)	latitude (°N)	longitude (°W)
1	April 1999	river	0.46	0.29	29.54.92	89.55.16
1	April 1999	river	14	0.29	29.54.92	89.55.16
1	Nov 1999	river	0.46	0.29	29.54.92	89.55.16
1	Nov 1999	river	15	0.29	29.54.92	89.55.16
2	April 1999	river	0.46	0.29	29.15.58	89.19.46
2	April 1999	river	8.4	0.29	29.15.58	89.19.46
2	Nov 1999	river	0.43	2.7	29.15.58	89.19.46
2	Nov 1999	river	3.7	20	29.15.58	89.19.46
3	April 1999	gulf	0.46	29	28.50.41	89.29.14
3	April 1999	gulf	3.1	36	28.50.41	89.29.14
4	April 1999	gulf	0.46	28	28.57.50	89.57.98
4	April 1999	gulf	8.2	36	28.57.50	89.57.98

200 mL of water (November 1999) through each filter. Field blanks for PAHs ($n = 3$; 10 L each) and BC ($n = 12$; 100 mL each) consisted of DDI filtered through the same apparatus during the cruise.

Black Carbon Isolation. We operationally identify BC as soot and graphitic material formed in the vapor phase from combustion of biomass or fossil fuels. In this study, BC is the residual carbon remaining after vapor-phase acidification of TSS with 12 N HCl (*15*) followed by thermal oxidation at 375 °C for 24 h to remove labile carbon. A variation of this method (thermal oxidation followed by acidification) has been used to isolate biomass and fossil fuel-derived BC in water column particulates and marine sediments originating from combustion of biomass as well as fossil fuel material (*16*, *17*). We added a precautionary demineralization step (vapor-phase acidification prior to thermal oxidation) intended to expose occluded non-BC organic matter. This represents a departure from the method of Gustafsson et al. (*16*). With the exception of the thermal oxidation step, procedures identical to those published were used to isolate and quantify BC and OC on TSS. The precision of this method for isolating BC on GFFs was determined by analyzing replicate ($n = 4$) filters for NIST Standard Reference Material 1649a (SRM 1649a, urban dust) suspended in aqueous solution. OC, BC, and N were quantified on a CHNS−O analyzer (instrument detection limit = 10 ± 0.2 μg g^{-1} for carbon).

PAH Extraction. Immediately upon returning to the lab, a mixture of deuterated PAH surrogate standards was added to the filters. Filters were extracted by refluxing for 48 h in Soxhlet flasks with methylene chloride (DCM). At the end of the 48 h, filters were discarded and the DCM extracts were combined with the methanol used initially for sample storage. Samples were gently evaporated under N$_2$ (g) in Rapid-Vap flasks until the sample reached a volume suitable for back-extraction (shaken 3× with hexane + DDI water) and solvent exchanged into hexane. Extracts were then gently evaporated to a final volume of 1 mL hexane. Hexane extracts from the filters were then cleaned using silica open-column chromatography (*18*). The portion of the silica column eluent which contained PAHs was collected to which a mixed deuterated PAH internal standard was added. The extract was once again evaporated gently under nitrogen to ∼100 μL. Two microliter aliquots of these extracts were injected onto a Hewlett-Packard 6890 series gas chromatograph/mass spectrometric detector (GC/MS) in the selective ion monitoring mode with a 30 m × 0.25 mm i.d. × 1 μm film thickness DB-5MS capillary column (J&W Scientific). The GC/MS conditions for sample analysis were as follows: injector and detector temperatures, 300 °C; splitless injection with 1.5 cm^3 min^{-1} of ultrahigh purity He as the carrier gas; initial column temperature 50 °C increased to 150 °C at 25 °C min^{-1}; increased to 230 °C at 6 °C min^{-1}; and increased to 300 °C at 3 °C min^{-1} and held for 3.33 min. Concentrations of PAHs were corrected for recoveries of deuterated PAH surrogates but were only reported and used for BC source discrimination if recoveries were greater than 40% (*19*). Recoveries for the surrogates benzo[*a*]anthracene-d_{12} and benzo[*a*]pyrene-d_{12} corresponding to the same time windows as the HMW PAH isomers used in this study, were 80 ± 10% and 82 ± 10%, respectively. Instrument detection limits for our GC/MS ranged from 10^{-3} to 10^{-4} ng for each PAH. PAH data presented in this study are for selected HMW isomers and necessary for BC source discrimination. All PAH concentrations used in this study were at levels (1×) above the average of field and method blanks.

Using PAH Isomer Ratios to Discriminate Sources of BC. Greater than 50% of the PAHs in the following isomer pairs are associated with aerosol particles in the atmosphere: benz[*a*]anthracene/chrysene (b[*a*]a/chry), benzo[*b*]fluoranthene/benzo[*k*]fluoranthene (b[*b*]f/b[*k*]f), and benzo[*a*]pyrene/benzo[*a*]pyrene (b[*a*]p/b[*e*]p) (*13*). Distinct PAH isomer signatures for combustion sources exist for b[*a*]a/chry, b[*b*]f/b[*k*]f, and b[*a*]p/b[*e*]p (*13*). Thermodynamic partitioning and kinetic mass transfer coefficients of these PAH isomer pairs are similar and PAH isomer pairs are diluted to the same extent upon advective mixing with natural particulate matter. Furthermore, HMW PAHs have a high affinity for aromatic carbonaceous materials (i.e., BC) produced during the combustion process (*20*). Thus, isomer ratios of b[*a*]a/chry, b[*b*]f/b[*k*]f, and b[*a*]p/b[*e*]p are useful indicators of sources of combustion-derived aerosols such as BC cogenerated during the combustion process. In this context, PAH isomer ratio analyses on TSS may also be used to infer the relative contribution of fossil fuel-derived BC (depleted in ^{14}C) to that originating from biomass combustion (contemporary ^{14}C) in the oceans.

PAH isomer ratios in samples were adjusted for photodegradation to constrain changes that may have occurred during atmospheric transport. Using eq 1 (*13*) and assuming an aerosol residence time of 5 days in the atmosphere (*21*) with 12 h of sunlight per day (60 h), PAH isomer ratios in TSS were adjusted using the following equation:

$$(\text{isomer ratio})_{\text{photoadjusted}} = (\text{isomer ratio})_{\text{TSS}} \exp[(\lambda_n - \lambda_d) \times 60\ \text{h}] \quad (1)$$

where λ_n and λ_d are the average photodegradation rate constants of the PAH on gray atmospheric particles (*22*) in the numerator and denominator of the same isomer ratio pair, respectively. The isomer ratio of b[*b*]f/b[*k*]f does not appear to be affected by photodegradation (*23*) and was not adjusted via eq 1. Principal components analysis (PCA) was conducted on the photoadjusted isomer ratios for samples isolated from the Mississippi River and the Gulf of Mexico and compared to isomer ratios for combustion sources. PCA was performed using Statistical Analysis Systems software.

Results and Discussion

Mississippi River. In 1999, the Mississippi River exported 90% of its total suspended sediment load (132 × 10^6 metric tons) between the high flow months of January and August (Figure 2b) (*24*). This number is similar to the 29 year mean (135 × 10^6 metric tons) for suspended sediment discharge from the Mississippi River calculated between the years of 1963 and 1991 (*12*). It follows that the majority of particle reactive contaminants associated with fluvial TSS are also discharged from the Mississippi River during high flow and that discharge of such particle reactive contaminants from January to July of 1999 (high flow) is representative of the Mississippi River's average annual flux.

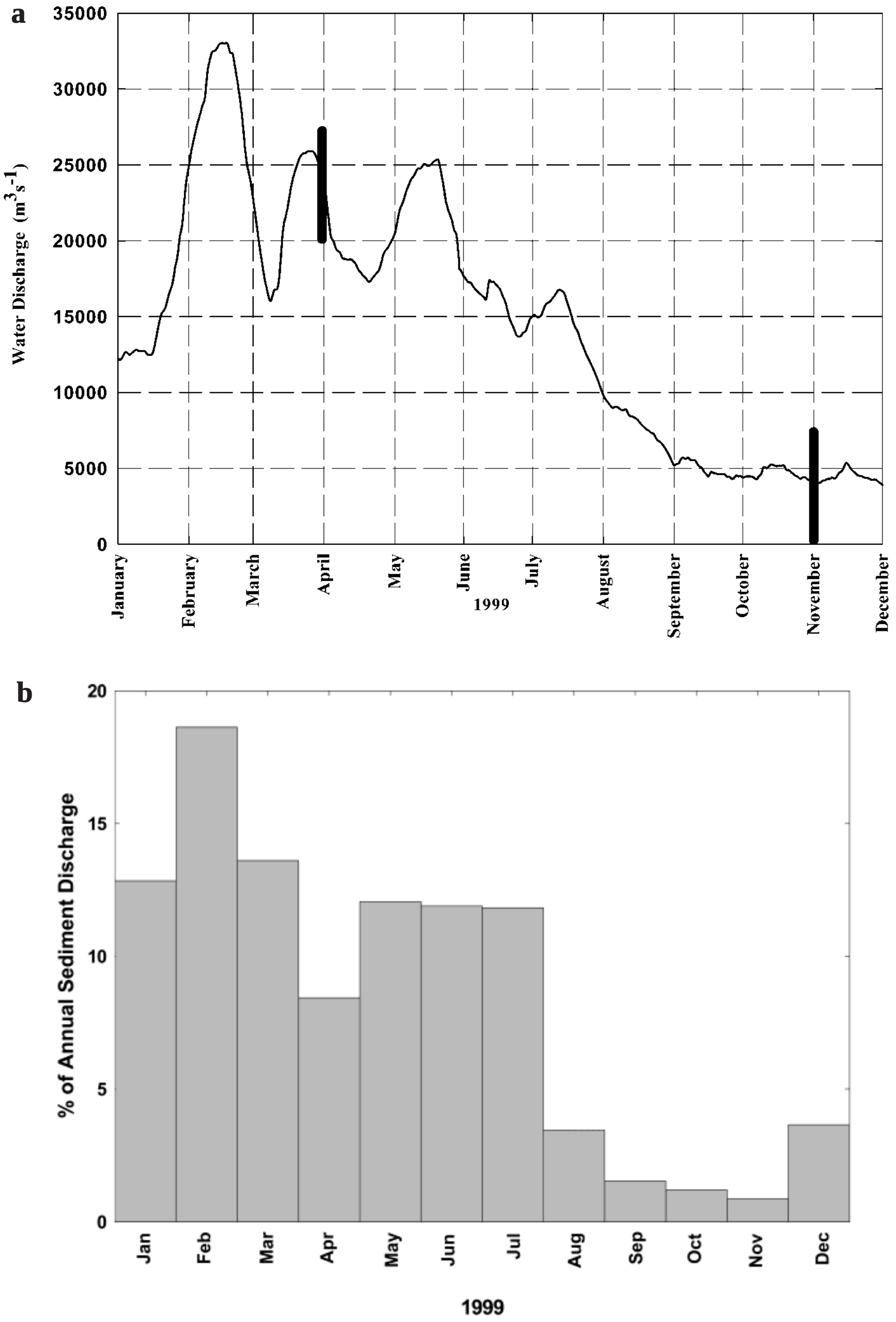

FIGURE 2. (a) Water discharge at Tarbert Landing, MS. Vertical bars represent sampling times with April 1999 representative of high flow and November 1999 representative of low flow (*24*). (b) Percentage of annual sediment discharge versus month (*24*).

The Mississippi River's annual discharge of BC into the Gulf of Mexico was 4.8 ± 2.2 × 10^{-4} Pg for 1999 [mean ± standard error]. This number is calculated with the following equation:

$$F = \sum_{I=1,12;J=1,2} [(\mathrm{C})_I \times (\mathrm{BC})_J] \qquad (2)$$

in which F is the 1999 annual flux of BC from the Mississippi River, C is the concentration of suspended sediment discharged from the Mississippi River each month (I) in 1999, and BC is the average Mississippi River BC concentration isolated in April 1999 extrapolated across high flow ($J = 1$) and the average Mississippi River BC concentration isolated in November 1999 extrapolated across low flow ($J = 2$). The 1999 annual flux of BC assumes average concentrations of 4.0 ± 1.8 mg g^{-1} and 0.66 ± 0.27 mg g^{-1} for BC, extrapolated across high flow (January–July) and low flow (August–December), respectively. These values are the arithmetic mean of all BC concentrations between Stations 1 and 2 during April and November of 1999, respectively (Table 2). Stations 3 and 4 were omitted from these calculations, as they were nonriver stations. The majority of the propagated standard error in this estimate for the Mississippi River's BC flux derives from the relatively high standard error in the estimate for the river's monthly suspended sediment discharge.

The Mississippi River's 1999 annual flux of BC noted in the previous discussion (~5.0 × 10^{-4} Pg year^{-1}) is the first estimate of a large river's discharge of BC into coastal waters. This number is approximate for two reasons: first, concentrations of suspended sediment collected from USGS Open File Reports are based on particulate material isolated on

TABLE 2. BC, OC, C/N, and BC/OC (mean ± standard error) in Mississippi River and Gulf of Mexico TSS

	BC (mg g^{-1})	OC (mg g^{-1})	C/N (mol/mol)	BC/OC
		April 1999		
river surface water	3.8 ± 1.9	28 ± 6.2	14 ± 4.5	0.16 ± 0.03
(Stations 1 and 2)	$n = 14$	$n = 13$	$n = 14$	$n = 13$
river bottom water	4.2 ± 1.6	25 ± 2.5	13 ± 2.5	0.17 ± 0.03
(Stations 1 and 2)	$n = 14$	$n = 14$	$n = 14$	$n = 13$
shelf surface water	5.5 ± 2.1	24 ± 7.0	8.3 ± 0.96	0.25 ± 0.05
(Stations 3 and 4)	$n = 3$	n = 3	$n = 3$	n = 3
shelf bottom water	7.8 ± 6.8	30 ± 19	23 ± 7.2	0.28 ± 0.05
(Stations 3 and 4)	$n = 5$	n = 4	$n = 4$	$n = 4$
		Nov 1999		
river surface water	0.466	32 ± 6.8	8.01 ± 1.1	0.019
(Stations 1 and 2)	$n = 1$	$n = 16$	$n = 12$	$n = 1$
river bottom water	0.76 ± 0.28	25 ± 7.2	10 ± 2.9	0.04 ± 0.01
(Stations 1 and 2)	$n = 2$	$n = 13$	$n = 11$	$n = 2$

0.45 μm pore size filters while our definition of particulate material is based on a 0.7 μm pore diameter cutoff; and second, under some circumstances, this BC extraction method can char non-BC organic matter, resulting in overestimates of BC concentration (see BC verification section) (*25*). However, in the case of our Mississippi River samples, we believe this latter effect to be minor. If we assume that all riverine BC is transported to ocean sediments without any transformation or burial, then the Mississippi River's annual flux of 5.0×10^{-4} Pg year^{-1} contributes ∼5% of the 0.01 Pg of BC buried annually in oceanic and coastal sediments (*9*). Taken together, the world's 10 major rivers transport approximately 40% of the freshwater and particulate materials entering the ocean (*26*). Thus, even with the limitations noted previously, large river discharge is expected to contribute extensively to the global BC budget.

Presently, the only existing measurement of fluvial BC discharge is 5.4×10^{-5} Pg year^{-1} for the Santa Clara River (*27*), a small mountainous river located on the west coast of the United States. Much of the BC flux from the Santa Clara is suggested to originate from erosion of old soils rather than influx from fossil fuel-derived carbon (*27*). Taken together as a class of rivers, small mountainous rivers yield a substantial amount of carbon to the world's oceans (*28*). Thus, as a class of rivers, the world's small mountainous rivers may contribute extensively to the global riverine discharge of non fossil fuel-derived BC. However, as an individual river, the Mississippi's annual discharge of BC is a significant quantity.

In April 1999, TSS in the Gulf of Mexico samples had significantly higher BC/OC ratios, 0.27 ± 0.03, as compared to riverine TSS values, 0.16 ± 0.02 (*t*-test; $p < 0.05$) (Table 2). Higher BC/OC ratios in TSS isolated from the Gulf of Mexico relative to the river (despite similar OC in TSS isolated from the river and the gulf) suggests the presence of an enriched (nonriver-derived) distinct source of BC directly influencing the water column of the inner shelf of the Gulf of Mexico or possibly charring of non-BC organic matter. Another potential explanation for these observations is that long-range aeolian transport from the continental United States to the Gulf of Mexico is selective for smaller particles enriched in soot (*4*).

Sources of Mississippi River BC. BC is extremely heterogeneous with respect to its size, age, and chemical composition (*29*). Typically, the ^{14}C age of BC is used to infer its source (*30*, *31*). Biomass burning produces BC with a modern ^{14}C age, while fossil fuel combustion produces ^{14}C-depleted BC. As BC in coastal environments originates from a mixture of biomass and fossil fuel combustion processes and is transported across various distances, applying ^{14}C mixing models to coastal environments may not always produce significant results. The complications associated with radiocarbon dating of heterogeneous BC are reduced when using source-specific markers of natural organic matter combustion, such as PAHs.

TABLE 3. Polycyclic Aromatic Hydrocarbon Isomer Ratios in Combustion Sources and Mississippi River and Gulf of Mexico Total Suspended Solids

combustion sources	PAH isomer ratios[a]		
	b[*a*]a/chry	b[*b*]f/b[*k*]f	b[*a*]p/b[*e*]p
automobiles	0.53 (0.06)	1.26 (0.27)	0.88 (0.13)
coal/coke	1.11 (0.06)	3.7 (0.17)	1.48 (0.03)
smelters	0.6 (0.06)	2.69 (0.2)	0.81 (0.04)
wood	0.79 (0.13)	0.92 (0.16)	1.52 (0.19)

time	station	water sample location	PAH isomer ratios		
			b[*a*]a/chry	b[*b*]f/b[*k*]f	b[*a*]p/b[*e*]p
April 1999	1	surface	NQ	4.1	0.72
	1	bottom	0.96	3.6	0.93
	2	surface	3.0	3.8	0.93
	2	bottom	1.2	3.6	1.1
	4	surface	0.06	NQ	NQ
	4	bottom	1.7	2.1	0.65
Nov 1999	1	surface	0.49	3.1	0.73
	1	bottom	2.4	3.2	0.92
	2	surface	1.0	3.8	0.70
	2	bottom	3.0	4.0	0.85

[a] Isomer ratios in combustion sources are reprinted from ref *13* with permission. Copyright (2000) American Chemical Society.

PCA is a statistical technique that linearly transforms a set of original multiple experimental variables into a substantially smaller set of principal components (PC) (*32*). We apply PCA to two photoadjusted and one nonadjusted HMW PAH isomer ratios isolated from Stations 1−4 and compare them to the same three HMW PAH isomer ratios found in common sources of combustion (Table 3). The scores for PC 1 and 2 together accounted for 95% of the variance of the data set. In other words, PC 1 and 2 offer an accurate and "compressed" two-dimensional representation of the three sets of PAH isomer ratios. The PCA indicates that many of TSS samples representative of the Mississippi River proper cluster about coal combustion and smelter-derived combustion (Figure 3). The PCA also indicates that the majority of samples isolated from the Mississippi River (during high flow) and the Gulf of Mexico are each distinct in their sources of PAHs and presumably BC.

The distance in PC loadings between PAH isomer ratios in specific combustion sources and specific sampling stations which fall outside the cluster around coal combustion and smelter-derived combustion can be explained to some extent by seasonal differences in hydrodynamic mixing of the river

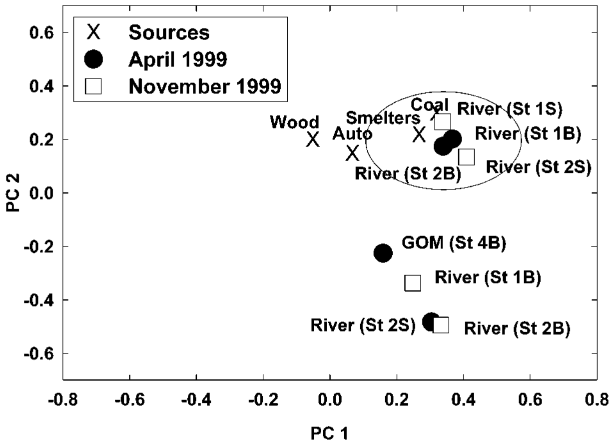

FIGURE 3. Results from principal components analysis comparing PAH isomer ratios for high molecular weight PAHs derived from various sources of combustion and those isolated on Mississippi River and Gulf of Mexico TSS in April 1999 and November 1999. Either an "S" for surface water TSS or "B" for bottom water TSS follows each Mississippi River or Gulf of Mexico station number for bottom water TSS. Circle represents cluster of principal components about coal and smelter-derived combustion.

and the gulf. For example, during November 1999 (low flow), saltwater intrusion from the Gulf of Mexico was evident in bottom waters at Station 2 where salinity was 20 (Table 1). Similarly, salinity in water at Station 4 displays a predominantly marine signature of 36. Levels of PAH isomer pairs in Station 1S and 4S samples were below method detection limits and, therefore, were omitted from the PCA.

A question that arises from our PCA and BC flux calculations is how much of the Mississippi River's BC flux to the coastal ocean is fossil fuel-derived. Such an estimate would be valuable, as this is the first study to constrain anthropogenic versus natural sources of fluvial BC in the environment using combustion-specific markers. Estimating such a quantity is not immediately obvious from visual inspection of Figure 3 because the graphical depiction of the results of a PCA should not be interpreted as a mixing model. However, it appears that the PC for April 1999 river bottom waters and for November 1999 river surface waters cluster about the PCs for fossil fuel combustion sources (Figure 3). From this, if we assume that the majority of the BC from these four stations (April 1999, Stations 1B, 2B; November 1999, Stations 1S, 2S; Figure 3) is predominantly fossil fuel-derived, approximately 27% of the total of the average BC concentrations (Table 2) are derived from coal and smelter-derived combustion. We have not tested the veracity of our aforesaid assumption; therefore, this quantity should be interpreted as an upper-limit.

BC and more specifically soot carbon are known to form from coal combustion and as a byproduct of smelting operations (*17*), as smelters also combust tar and coal. Our analyses indicate that coal-fueled combustion processes in the watershed influence BC in the Mississippi River significantly. Our analyses do not offer any estimate of direct inputs of coal into the river or the Gulf of Mexico from the surrounding watershed. Considering the spatial extent of coal combustion in the Mississippi River watershed (*33*) and the high volume of water and suspended sediment (i.e., surface soil runoff) discharge in 1999, our values for BC and explanation of its provenance are quite plausible.

BC Verification. There are presently no universally accepted BC standards; thus, accuracy cannot be reported for any BC methods. Our BC extraction procedure, slightly modified to that of Gustafsson's procedure (*16*), was verified for precision using SRM 1649a. BC isolated on GFFs yielded BC/OC values of 0.11 ± 0.03, which correlated reasonably with BC quantified in SRM 1649a isolated via dichromate/sulfuric acid oxidation, 0.10 ± 0.01 (*30*) and the 375 °C thermal oxidation procedure conducted in another laboratory, 0.08 (*34*). Moreover, BC/OC ratios in our samples (2−28%; Table 2) were within the range of BC/OC ratios (3−38%) isolated using the 375 °C thermal oxidation procedure for several sedimentary samples (*35*).

BC concentrations can be overestimated if labile non-BC organic matter is incompletely removed or if incomplete demineralization of the particle matrix results in occlusion of non-BC organic matter (*25*). Such labile non-BC can participate in condensation reactions during thermal oxidation, yielding a false-positive for BC (*25*). Other researchers have addressed this topic in detail (*8, 29, 30, 34*) and references contained therein); thus, we have purposefully omitted such a detailed discussion in the context of this study.

We believe that charring minimally affects our Mississippi River BC measurements. During combustion, organic matter pyrolysis rates assert considerable control on the formation of BC (*36*). For example, condensation reactions leading to BC formation are favored during rapid temperature gradients (*37*). To minimize potential artifacts from charring, the oven used for BC isolation in our samples was heated at a moderate rate of 2.5 °C min^{-1}. Furthermore, charring appears to occur more readily as a function of the labile nature of organic matter (*25*). Trends in C/N ratios (an indicator of reactivity of bulk organic matter) do not correlate with trends in BC concentrations (Table 2) in TSS isolated from the river during April 1999, as would be expected if labile organic matter was charring. Significant differences do exist in C/N ratios of TSS isolated from the river during November of 1999 in contrast to samples from April 1999. The C/N ratios isolated in TSS during high flow (ca. 13−14) (Table 2) and biomarkers of terrigenous organic matter isolated from Mississippi River sediments at the same stations for another study (*38*) suggest a predominantly terrigenous organic matter source in the river stations during high flow. Furthermore, these C/N ratios are consistent with C/N ratios found for Mississippi River suspended particles derived from soils (*39*). Therefore, using C/N ratios as a first-order indicator for charring-potential, we believe that our high flow BC measurements are minimally charred.

We have not compared our BC extraction procedure directly to another technique incorporating a more robust demineralization procedure. However, a recent study comparing the BC isolation technique of Gustafsson et al. (*16*) to a BC isolation technique incorporating additional chemical oxidation steps illustrated a 12% difference between the two techniques in BC/OC ratios for Madiera River suspended particulate matter (*25*). In contrast, techniques used on all other natural sedimentary and soil organic matter in that study yielded considerably larger differences between the two techniques. One interpretation of their data is that non-BC organic matter in fluvial TSS may not be as susceptible to charring as in sediments or soils. These results taken with our C/N data suggest that, in the case of Mississippi River TSS during high flow, the method used here does not lead to charring of non-BC labile carbon.

Implications for the Global Carbon Cycle. Recent investigations have been unable to unequivocally constrain the source of "old" ^{14}C in some oceanic particulate organic carbon (POC) and dissolved organic carbon (DOC) samples (*40, 41*). Aged terrestrial OC depleted in ^{14}C and entering the oceans via fluvial discharge has been suggested to be one potential contributor to old oceanic carbon (*41*). Globally, the Mississippi River ranks 7th largest in terms of water and sediment discharge into the ocean (*42*). If the watershed of the Mississippi River were representative of other large rivers in terms of fossil fuel combustion, BC entering the ocean from global fluvial discharge would be depleted in ^{14}C.

We can estimate the role of the Mississippi River's flux and sources of BC on the ocean carbon cycle in the following manner. Assuming an average BC residence time of 1000 years (*27*) and a total carbon reservoir size of 45 Pg for the world's surface ocean (5 Pg POC, 40 Pg DOC) (*43*), BC discharged from the Mississippi River alone (5×10^{-4} Pg) contributes to 1% of the total OC in the surface waters of the world's oceans. Because the chemical and physical role of particulate BC in the environment is strongly influenced by its interactions in aqueous phase (*44*), specific oxidation conditions could occur in the water column, promoting dissolution of particulate BC to dissolved BC. In such a case, fossil fuel-derived fluvial BC originating from coal- and smelter-derived combustion may also affect the ^{14}C age of bulk DOC, confounding interpretation of its sources and residence time in the environment. Thus, the world's major rivers taken together may indeed provide a heretofore-underestimated amount of anthropogenically derived BC and other combustion-derived pollutants to the oceans and influence the global carbon cycle.

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