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Black carbon in estuarine and coastal ocean dissolved organic matter

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Abstract

We measured black carbon (BC) in ultrafiltered, high-molecular weight dissolved organic matter (UDOM) in surface waters of Delaware Bay, Chesapeake Bay, and the adjacent Atlantic Ocean (U.S.A.) to investigate the importance of riverine and estuarine dissolved organic matter (DOM) as a source of BC to the ocean. BC was 5–72% of UDOM-C ($27 \pm 17\%$), which corresponds to $8.9 \pm 6.5\%$ of dissolved organic carbon (DOC), with higher values in the heavily urbanized midbay region of the Delaware Estuary and lower yields in the river and coastal ocean. The spatial and seasonal distributions of BC along the salinity gradient of Delaware Bay suggest that the elevated levels of BC in surface water UDOM originate from localized sources, possibly from atmospheric deposition or release from resuspended sediments. BC in UDOM made up 4–7% of the DOC in the coastal Atlantic Ocean, revealing that river–estuary systems are important exporters of colloidal BC to the ocean. The annual flux of BC from Delaware Bay UDOM to the Atlantic Ocean was estimated at 2.4×10^{10} g BC yr⁻¹, supporting the hypothesis that the DOC pool is an important contributor of BC to the ocean.

Dissolved organic matter (DOM) in the ocean constitutes one of the largest pools of organic carbon in the biosphere, yet much of its composition remains uncharacterized. In coastal waters, inputs of marine, terrestrial, and anthropogenic organic matter contribute to the complexity of DOM composition. Observations of black carbon (BC) particles in the atmosphere, ice, rivers, soils, and marine sediments suggest that this material is ubiquitous in the environment (Goldberg 1985; Schmidt and Noack 2000; Masiello and Druffel 2001; Mitra et al. 2002). The contribution of BC to the ocean's DOM pool, however, is not known.

BC represents a refractory and chemically complex product of incomplete combustion of fossil fuels and biomass, including vegetation burns and forest fires. BC is defined as a “continuum of partly charred plant material through char and charcoal to graphite and soot particles recondensed from the gas phase” (Seiler and Crutzen 1980, p. 207). Multiple mechanisms introduce BC to the ocean, including atmospheric deposition of land-derived BC aerosols, material transported by river–estuary systems, and marine diesel engine exhaust. Although most BC is deposited near the site of production, long-range transport of BC through rivers and the atmosphere is also possible (Goldberg 1985). BC accumulates in sediments, making up 10–50% of sedimentary organic carbon (Gustafsson et al. 1997; Middelburg et al. 1999) and is much older (2,400–13,900 yr older) than non-

BC material in deep ocean settings (Masiello and Druffel 1998). The radiocarbon age differences between sedimentary BC and other sedimentary organic matter present an unresolved issue on whether the BC that ultimately resides in marine sediments ages primarily within the oceanic dissolved organic carbon (DOC) pool or in soils (Masiello and Druffel 1998).

In an effort to understand the importance of riverine and estuarine DOM as a source of BC to the ocean, the BC component of ultrafiltered, high-molecular weight DOM (UDOM) was measured in surface waters of the Delaware Estuary and Chesapeake Bay (mid-Atlantic, U.S.A.). We present evidence that BC comprises a significant fraction of marine DOM, accounting for a substantial fraction of DOC that has previously remained elusive to chemical characterization.

Methods

Study sites—The Delaware Estuary is a highly urbanized coastal plain estuary, extending 215 km from the mouth of the bay to Trenton, New Jersey, the upstream limit of tidal influence (Fig. 1). Freshwater entering the estuary, with a mean annual discharge of $550 \text{ m}^3 \text{ s}^{-1}$, originates largely from the Delaware ($\sim 58\%$; $320 \text{ m}^3 \text{ s}^{-1}$) and Schuylkill ($\sim 14\%$; $78 \text{ m}^3 \text{ s}^{-1}$) rivers, with minor contributions from other individual sources (Lebo and Sharp 1993). Chesapeake Bay, also a coastal plain estuary, discharges more freshwater (mean annual discharge of $2,280 \text{ m}^3 \text{ s}^{-1}$; Schubel and Pritchard 1986) than any other river–estuary system along the U.S. Atlantic coast. The Susquehanna River, which flows into the head of Chesapeake Bay, contributes about half of the total freshwater discharge within the estuary.

Sampling and analyses—Size-fractionated DOM was collected at five to seven sites (1 m depth) along the salinity gradient from the Delaware River to the coastal Atlantic Ocean in June 1996, September 1996, March 1997, and May–June 1997 (Fig. 1; Table 1; Mannino and Harvey 2000;

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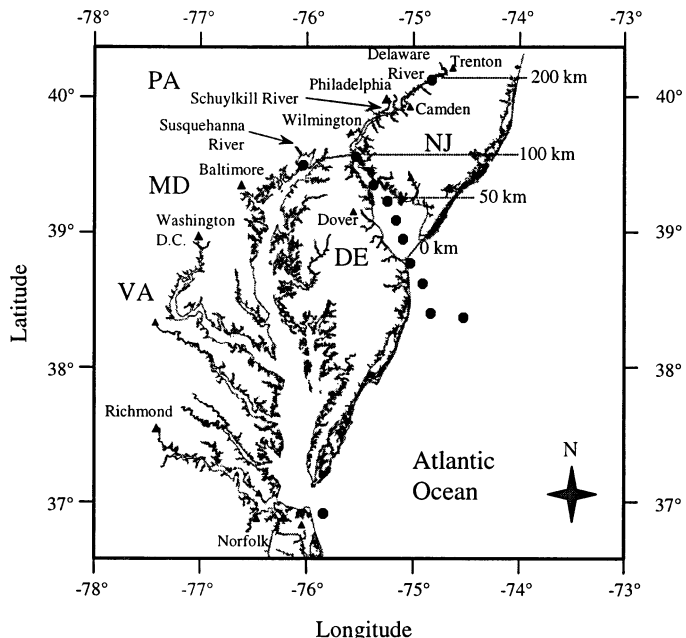


Fig. 1. Map of the Delaware Estuary and Chesapeake Bay, including station locations and designation of urban areas (triangles).

Harvey and Mannino 2001). Single samples were collected from the headwaters of Chesapeake Bay and beyond the Chesapeake Bay mouth in May–June 1997 (Table 1). DOM from filtered water ($<0.2 \mu\text{m}$) was separated into three nominal size fractions— <1 kilodalton (kDa), 1–30 kDa, and 30 kDa to $0.2 \mu\text{m}$ —by tangential-flow ultrafiltration with the use of an Amicon DC-10L unit with S10Y30 (30 kDa; regenerated cellulose membrane) and S10N1 (1 kDa; polysulfone membrane) filters following the methods of Benner et al. (1997) as previously described (Mannino and Harvey 1999; Harvey and Mannino 2001). The two high-molecular weight fractions were concentrated and desalted during ultrafiltration. High-molecular weight DOM samples were stored frozen and lyophilized to dry powders. The ultrafiltration concentration factors (CF; initial volume/concentrate volume) ranged from 37–81 for the 1–30-kDa fraction (CF = 15 for the turbidity maximum station for the June 1996 sampling) and 80–194 for the 30-kDa to $0.2\text{-}\mu\text{m}$ fraction. The retention coefficient of a 4.4-kDa fluorescently labeled dextran was $>99\%$ for the S10N1 filter (Mannino and Harvey 2000). The three DOC size fractions accounted for 83–111% of total DOC, which compares well with previous results using similar instrumentation and procedures (Guo and Santschi 1996; Benner et al. 1997). BC was measured only in the 1–30-kDa fraction (UDOM), which constitutes, on average, $35 \pm 15\%$ of DOC (Harvey and Mannino 2001). The 30-kDa to $0.2\text{-}\mu\text{m}$ fraction typically accounted for only 1–3% of DOC.

Table 1. Sampling locations, salinity, and ultrafiltered high-molecular-weight dissolved organic matter (UDOM; 1–30 kDa DOM) carbon concentrations in Delaware Bay, Chesapeake Bay (CB), and adjacent coastal ocean.

Date	Latitude	Longitude	Station	Distance upstream (km)	Salinity	UDOM ($\mu\text{mol C L}^{-1}$)
06Jun96	40°7.67'N	74°49.33'W	2	197	0.11	89.4
07Jun96	39°37.0'N	75°34.84'W	16	100	0.67	133.3
07Jun96	39°22.0'N	75°27.17'W	20	66.4	9.07	97.9
09Jun96	39°12.75'N	75°17.05'W	22	45	13.19	65.1
08Jun96	39°5.46'N	75°11.41'W	24	28.4	22.58	60.0
08Jun96	38°41.61'N	74°54.95'W	P3	-16.3	29.42	42.5
08Jun96	38°24.01'N	74°49.50'W	P1	-51.5	29.48	42.9
04Sep96	40°7.67'N	74°49.33'W	2	197.1	0.116	85.5
04Sep96	39°37.0'N	75°34.84'W	16	100.2	2.72	119.9
05Sep96	39°22.0'N	75°27.17'W	20	66.4	11.7	90.6
05Sep96	39°5.46'N	75°11.41'W	24	28.4	23.52	62.1
05Sep96	38°46.77'N	74°57.62'W	28	-19.3	29.6	41.7
14Mar97	40°7.67'N	74°49.33'W	2	197.1	0.070	73.8
14Mar97	39°37.0'N	75°34.84'W	16	100.2	0.181	81.9
15Mar97	39°12.62'N	75°26.87'W	21	56.6	4.44	77.2
15Mar97	39°5.46'N	75°11.41'W	24	28.4	18.10	63.9
15Mar97	38°55.0'N	75°6.4'W	26	9.4	26.60	46.3
29May97	38°48.47'N	75°4.84'W	MAB-1	-5.6	28.65	36.6
31May97	36°51.97'N	75°56.95'W	MAB-26	CB	23.76	51.2
01Jun97	38°23.44'N	74°31.03'W	MAB-42	-70.4	31.71	26.7
03Jun97	39°25.01'N	76°1.82'W	MAB-75	CB	0.492	71.1
10Jun97	39°4.685'N	75°10.63'W	24	28.4	21.03	60.2
10Jun97	38°23.97'N	74°49.44'W	P1	-51.5	31.21	33.1
11Jun97	40°7.73'N	74°49.18'W	2	197.1	0.099	94.8
11Jun97	39°37.24'N	75°34.83'W	16	100.2	1.75	97.6
12Jun97	39°21.86'N	75°26.87'W	20	66.4	9.01	82.8

Table 2. Black carbon content of standard reference materials (SRMs) and natural organic matrices.

Material*	TOC† (% C)	BC (g BC gdw ⁻¹)	BC/TOC (% C)
Diesel particulate	79.25±1.45	0.5232±0.0028	66.02±0.35
NIST SRM 1650			
Urban dust	17.96±0.04	0.0407±0.0014	22.66±0.78
NIST SRM 1649a			
Suwannee River DOM	44.81±1.16	0.0015±0.00013	0.335±0.029
IHSS IR101N			
Peat humic acid	51.30±0.26	0.00030±0.00038	0.058±0.075
IHSS IR103H			
<i>Isochrysis galbana</i>	51.75±1.01	0.0121±0.0014	2.33±0.28
<i>Skeletonema costatum</i>	21.72±0.05	0.0102±0.0016	4.68±0.75
<i>S. costatum</i> detritus	18.93±0.31	0.00155±0.000007	0.819±0.004
<i>S. costatum</i> detritus‡	18.93±0.31	0.00439±0.00038	2.32±0.20
Calcium carbonate§	11.88±0.04§	0.00024±0.00003	0.202±0.025§

* Diesel particulate and urban dust SRMs were obtained from the National Institute of Standards and Technology (NIST). Suwannee River DOM and peat humic acid are reference materials obtained from the International Humic substances Society (IHSS). *Isochrysis galbana* and *Skeletonema costatum* samples were collected from nonaxenic and axenic phytoplankton cultures, respectively. *S. costatum* is a dominant bloom-forming phytoplankton (diatom) in U.S. mid-Atlantic coastal waters. *S. costatum* detritus is residual material from an experimental bloom after >50 d of microbial degradation in darkness.

† Mean ± 1 SD for analytical error from triplicate or duplicate analyses.

‡ Thermal oxidation conducted after acid fuming.

§ Inorganic carbon, sample was not fumed with acid vapors.

Standards and lyophilized UDOM samples were weighed into silver capsules in triplicate or duplicate and thermally oxidized within a muffle furnace at 375°C in the presence of air for 24 h to remove non-BC organic matter (Gustafsson et al. 1997). Thermally oxidized and nonthermally oxidized samples were acidified with 12 mol L⁻¹ HCl vapors for 48 h, oven dried (45–55°C), and analyzed for carbon content with a CHN elemental analyzer. Thermal oxidation of samples followed by acidification yields BC content, whereas nonthermally treated samples yield total organic carbon (TOC).

Results and discussion

Standard reference materials of BC and standard matrices composed of natural organic matter similar to DOM (but with no expected BC content) were examined to compare our BC measurements with other published BC measurements and to determine whether the thermal oxidation procedure might yield extraneous BC. Diesel particulate material (NIST SRM 1650) and urban dust (NIST SRM 1649a) contained BC levels (0.52 and 0.041 g BC gdw⁻¹ [grams dry weight], respectively; Table 2) comparable to previously published values (Gustafsson et al. 1997, 2001). Results from natural organic matter comparable in composition to DOM confirmed that little to no extraneous BC was produced during analysis. Thermal oxidation produced no extraneous BC in Suwannee River DOM (0.34% BC TOC⁻¹) or peat humic acid (0.06% BC TOC⁻¹) and virtually no BC for *Skeletonema costatum* detritus (0.82% BC TOC⁻¹; Table 2). When thermal oxidation was conducted after acid fuming, a higher amount of extraneous BC was detected in *S. costatum* detritus (2.32% BC TOC⁻¹). This suggested that acid-labile biochemicals present in diatom detritus might

lead to artifacts during thermal oxidation. To eliminate this possibility, samples and reference materials were fumed with acid vapors after thermal oxidation. A small amount of extraneous BC was measured from actively growing phytoplankton cultures of *Isochrysis galbana* (2.33% BC TOC⁻¹) and *S. costatum* (4.68% BC TOC⁻¹; Table 2). A similar level of extraneous BC (3.75% BC TOC⁻¹) was found in a culture of the diatom *Thalassiosira weissflogii* (Gustafsson et al. 2001). Thermal oxidation of calcium carbonate (0.2% BC TC⁻¹) did not produce BC artifacts. Such low levels of extraneous BC in natural organic matrices compared with the high BC yields in UDOM samples (Fig. 2A) suggest that production of BC artifacts had minimal effect on our BC measurements of UDOM. Previous work also demonstrates that thermal oxidation of diverse organic matrices produces small to insignificant amounts of extraneous BC (Gustafsson et al. 1997, 2001; Middelburg et al. 1999).

BC yields in estuarine UDOM varied substantially over space and time from 4.6% to 72% of UDOM-C (27 ± 17%, mean ± SD; Fig. 2A). BC concentrations varied with salinity and ranged from 45 to 1,038 μg BC L⁻¹ (Fig. 2B). With the exception of lower BC content at sites where salinity was <1, BC concentrations and yields in UDOM declined along the salinity gradient between the turbid region and the coastal ocean of the Delaware Estuary (Fig. 2). Least squares regression analyses revealed a significant relationship between Delaware Bay BC concentration and salinity for samples collected at sites where salinity was >1 ($r^2 = 0.84$, $P < 0.00001$, $n = 18$; Table 3). Sources of BC in the mid-estuary region introduced BC into surface water UDOM, which was then diluted downstream as bay water mixed with Atlantic Ocean water. At the Delaware River site, BC concentrations were similar (125 ± 32 μg BC L⁻¹) to values observed in the coastal ocean (93.8 ± 10.9 μg BC L⁻¹; Table

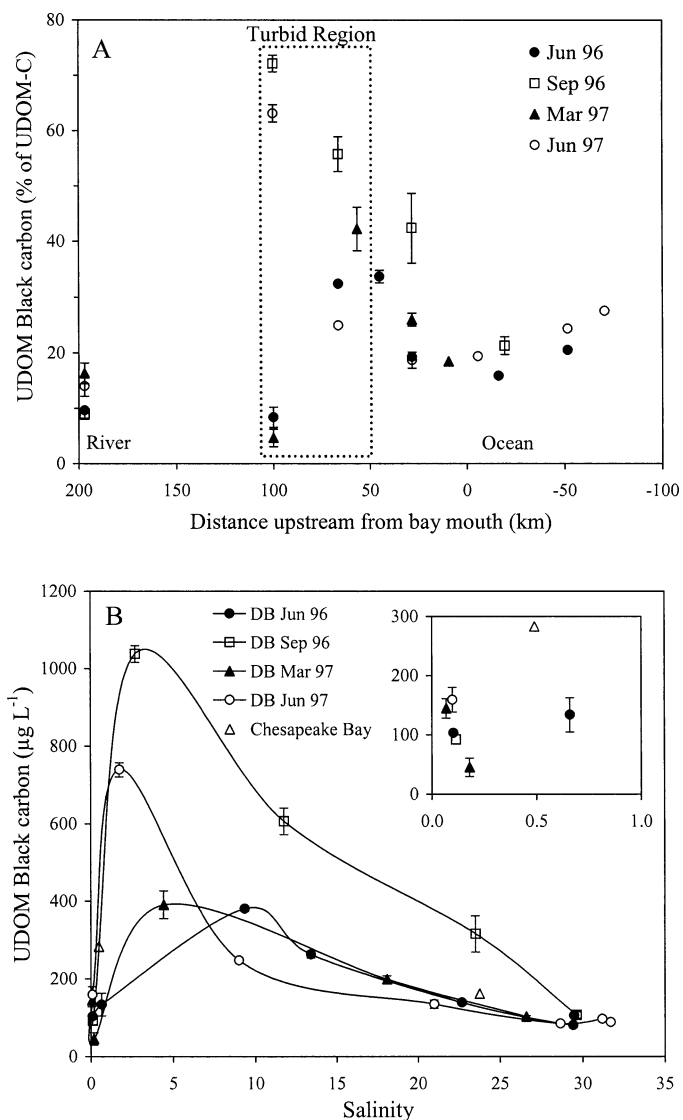


Fig. 2. Distributions of (A) black carbon yields in Delaware Bay UDOM and (B) black carbon concentrations in UDOM from the Delaware Estuary (DB) and Chesapeake Bay. Inset graph in panel B displays values at salinities <1 . Error bars represent 1 standard deviation from analytical error.

4). The lower variability for BC measurements in Chesapeake Bay samples was a result of reduced spatial and temporal coverage. The Chesapeake Bay sites contained higher amounts of BC than observed at analogous sites along the Delaware Estuary (Fig. 2B; Table 4). BC concentration was up to three times higher ($283 \mu\text{g L}^{-1}$) at the freshwater site in Chesapeake Bay than observed at the Delaware River site (Table 4). The higher concentration of BC in coastal ocean waters adjacent to the Chesapeake Bay compared with the Delaware Bay could be a consequence of greater freshwater discharge into Chesapeake Bay; industrial, military, shipping, and urban sources of BC present near the mouth of Chesapeake Bay (Norfolk and adjoining metropolitan region); or a combination of sources (Figs. 1, 2).

The distribution of BC in Delaware Bay suggests that in addition to riverborne BC, localized sources through atmospheric deposition or desorption from resuspended sediments might also introduce BC to estuarine waters. The highest and most variable BC concentrations and yields were found in the turbid region of Delaware Bay (110–50 km upstream from the bay mouth; Fig. 2A; Table 4), a region immediately downstream of Philadelphia with substantial shipping, industrial, and urban activity (Albert 1988). The high-turbidity region of Delaware Bay is particle-rich ($30\text{--}120 \text{ mg L}^{-1}$; Harvey and Mannino 2001) and formed through a combination of flocculation induced by gravitational circulation and tidal resuspension of bottom sediments (Biggs et al. 1983). The highest amounts of BC in UDOM (BC_{UDOM}) occurred during periods of low discharge of the Delaware River (two to three times lower in September 1996 and May–June 1997; USGS 2003). Higher river discharge in June 1996 and March 1997 likely diluted and transported the localized inputs of BC near the 100-km site further downstream (Fig. 2).

Potential sources of BC emissions to Delaware Bay and Chesapeake Bay include diesel-powered ships, trucks and other vehicles, automobiles without catalytic gasoline engines, coal- and oil-fired power plants, aircraft, oil refinery activities, remnants of worn tires, other urban and industrial sources, forest fires, and domestic wood burning for home heating, which is prevalent in the northeast United States (Goldberg 1985). The highest concentrations of BC in Delaware Bay were observed in the proximity of major shipping ports (Philadelphia and vicinity), urban regions (greater metropolitan areas of Philadelphia and Wilmington), heavily industrialized areas (oil refining, petrochemical plants, and power plants; Albert 1988), and major highways (Interstate 95, which crosses Chesapeake Bay near the mouth of the

Table 3. Least squares regression analyses of black carbon in Delaware Estuary UDOM (BC_{UDOM}) versus salinity for stations where salinity >1 ($n = 18$).

	BC_{UDOM} ($\mu\text{g L}^{-1}$)	$\text{BC}_{\text{UDOM}}/\text{UDOM-C}$ (% C)	$\text{BC}_{\text{UDOM}}/\text{DOC}$ (% C)
Data transformation	$[\log_{10}(Y)]^{0.5}$	$(Y)^{0.5}$	$(Y)^{0.1}$
Slope \pm SE	-0.0101 ± 0.0011	-0.098 ± 0.021	-0.00591 ± 0.00086
Intercept \pm SE	1.708 ± 0.023	7.39 ± 0.449	1.357 ± 0.019
r^2	0.839	0.558	0.729
P	<0.00001	<0.0005	<0.00001

Table 4. Black carbon content in UDOM across salinity gradients in the Delaware Estuary and Chesapeake Bay.

Sampling region	Salinity	BC _{UDOM} ($\mu\text{g L}^{-1}$)	BC _{UDOM} /UDOM-C (% C)	BC _{UDOM} /DOC (% C)
Delaware River	0.097 \pm 0.020*	125 \pm 32*	12.2 \pm 3.5*	5.4 \pm 1.9*
Delaware turbid region	5.0 \pm 4.5*	448 \pm 331*	38 \pm 25*	14.0 \pm 9.2*
Delaware lower estuary	20.9 \pm 4.6*	192 \pm 83*	26.4 \pm 9.8*	8.0 \pm 2.5*
Coastal ocean	30.02 \pm 1.17*	93.80 \pm 10.87*	21.49 \pm 4.05*	5.52 \pm 1.03*
Chesapeake Bay headwaters	0.492	282.92 \pm 1.49†	33.16 \pm 0.18†	12.74 \pm 0.067†
Chesapeake Bay coastal ocean	23.76	161.8 \pm 13.5†	26.3 \pm 2.2†	7.06 \pm 0.59†

* Mean \pm 1 SD for samples collected on multiple cruises.

† Mean \pm 1 SD (analytical error).

Susquehanna River and continues northward near the shores of the Delaware River, and the Delaware Memorial Bridge, which connects Delaware to New Jersey 100 km upstream from the bay mouth; Fig. 1). The Delaware Bay Port complex is the largest freshwater port in the world, and Philadelphia is one of the largest cities in the United States (Albert 1988). We hypothesize that shipping activity and urban-industrial inputs are the most plausible sources for the elevated levels of BC in the midbay region. Aerosols derived from urban-industrial pollution and biomass burning each contain a submicron-size mode (<0.1 to $<1 \mu\text{m}$) and a coarser mode (1 – $10 \mu\text{m}$; Dubovik et al. 2002). Hence, atmospheric deposition of BC aerosols contributes BC to high-molecular weight DOM and suspended particles in the open ocean as well as coastal regions. The recent discovery of BC within aerosol dust deposited on an ocean buoy about 600 km off the western coast of Africa suggests that substantial transport distances are possible (Eglinton et al. 2002).

Bulk measurements of BC alone provide limited potential for interpreting whether BC is derived from fossil fuel combustion or biomass burning. Radiocarbon ($\Delta^{14}\text{C}$) measurements of BC material can be helpful in defining sources. Fossil fuel-derived BC would have a radiocarbon age of about 50,000 yr ($\Delta^{14}\text{C} \approx 1,000\text{‰}$), whereas BC produced from biomass burning would be expected to have a relatively modern ^{14}C age ($\Delta^{14}\text{C} \geq 0\text{‰}$) or equivalent to the age of the source material. Masiello and Druffel (2001) found eroded old soils contributed aged biomass-derived BC ($\Delta^{14}\text{C}$ of -357‰ to -781‰) to the Santa Clara River. Mitra et al. (2002) estimated that 27% of the BC in suspended particles exported from the Mississippi River to the Gulf of Mexico was derived from fossil fuel combustion. Such findings illustrate that both biomass- and fossil fuel-derived BC can contribute old BC material to the ocean, whereas only biomass-derived BC introduces modern BC to the ocean.

Radiocarbon dating of recalcitrant BC found in deep ocean sediments has demonstrated an age disparity between sedimentary BC and other fractions of sedimentary organic matter (Masiello and Druffel 1998). Two hypotheses have been proposed to explain the older radiocarbon dates for sedimentary BC (2,400–13,900 yr older). Either (1) BC ages within soils prior to mobilization and transport to the ocean or (2) BC ages within the ocean's DOC pool before its final deposition in deep ocean sediments (Masiello and Druffel 1998). Masiello and Druffel (1998) estimated that BC should constitute 4–22% of the deep ocean DOC pool to account

for the BC content in sediments. The presence and magnitude of BC within the DOC pool observed here supports the hypothesis that the oceanic DOC pool represents an important reservoir that ultimately contributes to sedimentary BC. Our results are insufficient to assess whether BC ages primarily in soils or within the DOC pool.

Thermal oxidation yields primarily the soot component of BC and is less effective for quantifying char-type BC, which is more thermally labile than soot or graphite BC (Gelinias et al. 2001; Gustafsson et al. 2001; Schmidt et al. 2001). Consequently, measurements of BC within UDOM presented here constitute only a portion of the BC continuum and should be considered a conservative estimate of the total BC content within coastal UDOM. Nevertheless, BC in UDOM comprised a substantial portion of DOC (4–7%) in the coastal ocean adjacent to Delaware Bay and Chesapeake Bay (Table 4). Suspended particles in coastal and open ocean regions contribute additional quantities of BC. For example, the flux of BC in suspended particles from the Mississippi River to the Gulf of Mexico has been estimated at 5×10^{11} g BC yr^{-1} (Mitra et al. 2002).

We estimate an annual flux of BC from Delaware Bay UDOM to the Atlantic Ocean at $2.37 \pm 0.27 \times 10^{10}$ g BC yr^{-1} (on the basis of a surface volume outflow of $8,000 \text{ m}^3 \text{ s}^{-1}$ at the bay mouth [Garvine 1991] and an average coastal ocean BC_{UDOM} concentration of $93.8 \mu\text{g BC L}^{-1}$), illustrating the potential contributions of estuarine BC to the ocean. Although this estimate does not include BC measurements from throughout the year (particularly from late autumn and winter), concentrations of BC_{UDOM} near the bay mouth and coastal ocean are consistent during our sample collections (from late winter–early spring, twice in late spring–early summer, and late summer–early autumn; Fig. 2; Table 1). Contributions during winter from home heating sources such as wood-burning stoves, fireplaces, and oil-fired furnaces could augment the estimated flux from Delaware Bay. If the global river flux of BC from DOM is on the same order of magnitude as estimates of atmospheric deposition of BC aerosols to the ocean ($7 \pm 3 \times 10^{12}$ g BC yr^{-1}) or the global river BC particle flux (12.2×10^{12} g BC yr^{-1}) (Suman et al. 1997), then the total flux of BC to the ocean could exceed 20 – 34×10^{12} g BC yr^{-1} . Because the production of BC sequesters carbon into a refractory pool, BC represents an important sink for carbon into the ocean. The ubiquity of BC and its abundance in coastal ocean particles (Mitra et al. 2002) and DOM suggest that BC comprises an important component of the ocean's carbon cycle.

Future considerations

Much work remains to elucidate the source inputs and fates of BC in the ocean. Measures of BC fluxes from the atmosphere and land to rivers, estuaries, and ocean for both particulate and colloidal BC are essential to better constrain the inputs of BC to the ocean. Understanding the role of BC in the ocean's carbon cycle requires that we examine the mechanisms and rates of BC removal, as well as the transfer of BC from dissolved to sedimentary pools. Radiocarbon and other techniques should be used to distinguish the sources of BC within ocean DOM and suspended particles. Detailed structural and isotopic characterization of BC from multiple environments will be required to fully understand the sources and fates of BC in the ocean.

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