# Black Carbon in Estuarine and Coastal Ocean Dissolved Organic Matter

Antonio Mannino[1,2]* & H. Rodger Harvey[1]

[1]Chesapeake Biological Laboratory, University of Maryland Center for Environmental Science,
P.O. Box 38, Solomons, MD 20688, USA

[2]To whom correspondence should be addressed. E-mail: antonio.mannino@nasa.gov

*Present Address: NASA Goddard Space Flight Center, Laboratory for Hydrospheric Processes,
Mail Stop 971.1, Greenbelt, MD 20771, USA.

Running Head: Black carbon in marine DOM

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## *Abstract*

Black carbon (BC) in ultrafiltered high-molecular-weight DOM (UDOM) was measured in surface waters of Delaware Bay, Chesapeake Bay and the adjacent Atlantic Ocean (USA) to ascertain the importance of riverine and estuarine DOM as a source of BC to the ocean. BC comprised 5-72% of UDOM-C (27±17%) and on average 8.9±6.5% of dissolved organic carbon (DOC) with higher values in the turbid 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 higher levels of BC in surface water UDOM originated from localized sources, possibly from atmospheric deposition or released from resuspended sediments. Black carbon comprised 4 to 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 $2.4 \times 10^{10}$ g BC $yr^{-1}$. The global river flux of BC through DOM to the ocean could be on the order of $5.5 \times 10^{12}$ g BC $yr^{-1}$. These results support the hypothesis that the DOC pool is the intermediate reservoir in which BC ages prior to sedimentary deposition.

## Significant Findings

Currently, there are no known published measurements of black carbon (BC) concentrations within the dissolved organic matter pool (DOM) in oceanic environments. Production of BC sequesters fossil fuel- and biomass-derived carbon into a refractory carbon pool, and BC may represent a significant carbon sink into the ocean. Analysis of high-molecular-weight DOM from two estuaries and the adjacent coastal ocean demonstrates that BC is a significant component of DOM, and suggests that river-estuary systems are important exporters of BC to the ocean through DOM. Our results show that BC comprises 4-7% of the dissolved organic carbon (DOC) at coastal ocean sites, which supports the hypothesis that the DOC pool is the intermediate reservoir in which BC ages prior to sedimentary deposition. Furthermore, our calculations suggest that BC fluxes through DOM into the ocean may exceed the inputs of dissolved lignin.

## Popular Summary

Black carbon material, by-product of fossil fuel combustion and vegetation burning, is present in the atmosphere, soils, ice, rivers, coastal ocean particles and ocean sediments. Our work presents the first published measurements of black carbon material in dissolved matter within the ocean. The contribution of black carbon to the Atlantic Ocean from Delaware Bay and Chesapeake Bay along the U.S. coast suggests that global inputs of black carbon to the ocean are likely to be significant. Black carbon in dissolved matter within the ocean represents a previously unknown carbon reservoir and sink.

## *Introduction*

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 particles in the atmosphere, ice, rivers, soils and marine sediments suggest that this material is ubiquitous (Goldberg 1985; Schmidt and Noack 2000; Masiello and Druffel 2001; Mitra et al. 2002). However, the contribution of black carbon (BC) to the ocean's DOM pool is not known.

Black carbon 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)." Mechanisms which can introduce BC to the ocean include atmospheric deposition of land-derived BC aerosols, river-estuary transported material, 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 possible.

Black carbon comprises 10-50% of sedimentary organic carbon (Gustaffson et al. 1997; Middelburg et al. 1999) and is much older (2400 to 13,900 years older) than non-black carbon material in deep ocean sediments (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 within the oceanic 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 black carbon 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, USA). We present evidence that black carbon comprises a significant fraction of marine DOM.

### *Methods*

Size-fractionated DOM was collected at 5 to 7 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 (Mannino and Harvey 2000a; Harvey and Mannino 2001). Samples from the headwaters of Chesapeake Bay and beyond the Chesapeake Bay mouth were also collected in May-June 1997. DOM from filtered water (<0.2 µm) was separated into three nominal size fractions: < 1 kiloDalton (kDa), 1-30 kDa, and 30 kDa-0.2 µm, by tangential flow ultrafiltration (Mannino and Harvey 2000a). The two high-molecular-weight fractions were concentrated and desalted during ultrafiltration. BC was measured only in the 1-30 kDa fraction (UDOM), which comprised on average 35±15% of DOC (Harvey and Mannino 2001). The 30 kDa-0.2 µm fraction typically comprised only 1-3% of DOC.

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 hours to remove on-BC organic matter (Gustaffson et al. 1997). Thermally oxidized and non-thermally oxidized samples were acidified with 12 M HCl vapors for 48 hours, oven dried (45-55°C) and analyzed for carbon content using a CHN elemental analyzer.

### *Results & 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 permit comparison of 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 (g dry weight)$^{-1}$, respectively; Table 1) comparable to previously published values (Gustaffson et al. 1997; 2001; Masiello et al. 2001). Results from natural organic matter comparable in composition to DOM suggest that little to no extraneous BC was produced during analysis. Thermal oxidation produced no extraneous BC in Suwannee River DOM (0.34% BC TOC$^{-1}$), peat humic acid (0.06% BC TOC$^{-1}$) and virtually no BC for *Skeletonema costatum* detritus (0.82% BC TOC$^{-1}$; Table 1). When thermal oxidation was conducted after acid fuming, a higher amount of extraneous BC was detected in *S. costatum* detritus (2.32% BC TOC$^{-1}$). Acid-labile biochemicals present in diatom detritus may have produced the artifact material 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 1). A similar level of extraneous BC (3.75% BC TOC$^{-1}$) was found in a culture of the diatom *Thalassiosira weissflogii* (Gustaffson 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 to the high BC yields in UDOM samples (Fig. 1a) suggest that production of BC artifacts had minimal impact on our BC measurements of UDOM.

Black carbon yields in estuarine UDOM varied substantially over space and time from 4.6 to 72% of UDOM-C (27 ±17%; mean ± *sd*; Fig. 1a). BC concentrations varied with salinity and ranged from 45 to 1038 μg BC $L^{-1}$ (Fig. 1b). With the exception of lower BC content at sites where salinity <1 psu, BC concentrations and yields in UDOM declined along the salinity gradient between the turbid region and the coastal ocean of the Delaware Estuary (Fig. 1). Least squares regression analyses revealed a significant relationship between Delaware Bay black carbon and salinity for samples collected at sites where salinity >1 psu ($r^2$=0.84, $p$<0.00001, $n$=18; Web Appendix 1). 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 modestly higher (125±32 μg BC $L^{-1}$) than values observed in the coastal ocean (93.8±10.9 μg BC $L^{-1}$; Table 2). The Chesapeake Bay sites contained higher amounts of BC than observed at analogous sites along the Delaware Estuary (Fig. 1b; Table 2). BC concentration was up to three times higher (283 μg $L^{-1}$) at the freshwater site in Chesapeake Bay than observed at the Delaware River site (Table 2). The higher concentration of BC in coastal ocean waters adjacent to Chesapeake Bay compared to Delaware Bay may be due to greater freshwater discharge into Chesapeake Bay and/or urban and industrial sources of BC near the mouth of Chesapeake Bay.

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 the estuary. The highest and most variable BC concentrations and yields were found in the turbid region of Delaware Bay (110 to 50 km upstream from the bay mouth; Fig. 1a; Table 2), a region immediately downstream of Philadelphia with substantial industrial and urban activity (Albert 1988). The turbid region is 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 occurred during periods of lower discharge of the Delaware River (2 to 3 times lower in September 1996 and May-June 1997) (USGS 2003). Higher river discharge in June 1996 and March 1997 probably diluted and transported the localized inputs of BC near the 100 km site to areas further downstream (Fig. 1). The BC found in UDOM was likely derived from deposition of ultra-fine soot aerosols and/or material that shed or desorbed from suspended particles. Aerosols derived from urban-industrial pollution and biomass burning each contain a sub-micron size mode (<0.1 to <1 μm) and a coarser mode (1 to 10 μm) (Dubovik et al. 2002). Atmospheric deposition of BC aerosols must contribute BC to high-molecular weight DOM and suspended particles in the open ocean as well as coastal regions. BC was recently discovered within aerosol dust deposited on an ocean buoy located about 600 km off the coast of Africa in the northeast Atlantic (Eglinton et al. 2002).

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 (2400 to 13,900 years older): 1) either BC ages within soils prior to erosion and transport to the ocean, or 2) that BC ages within the ocean's DOC pool prior to final deposition into deep ocean sediments (Masiello and Druffel 1998). Masiello and Druffel (1998) estimated that BC should comprise 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 that we found supports the hypothesis that the oceanic DOC pool represents the reservoir in which BC ages prior to final deposition.

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 (Gustaffson et al. 2001; Schmidt et al. 2001; Gelinas et al. 2001). Our measurements of BC within DOM constitute only a portion of the BC continuum and thus are conservative estimates of the total BC content within coastal DOM. Suspended particles in coastal and open ocean regions may contribute additional quantities of BC. For example, the flux of BC in suspended particles from the Mississippi River to the Gulf of Mexico was estimated at $5\times10^{11}$ g BC $yr^{-1}$ (Mitra et al. 2002). In our study, BC comprised a substantial portion of DOC (4-7%) in the coastal ocean adjacent to Delaware Bay and Chesapeake Bay (Table 2).

The annual flux of BC from Delaware Bay UDOM to the Atlantic Ocean was estimated at $2.37 \pm 0.27\times10^{10}$ g BC $yr^{-1}$ (Table 3), illustrating the potential contributions of estuarine BC to the ocean. Extrapolating BC concentrations in UDOM from the Delaware River and headwaters of Chesapeake Bay ($156.4 \pm 76.0$ μg $L^{-1}$) to estimate the flux of BC within DOM through world rivers yields a global river flux of $5.5 \pm 2.7\times10^{12}$ g BC $yr^{-1}$. Comparisons of BC and lignin (biopolymer of vascular plants) fluxes to the ocean suggest that the flux of black carbon to the ocean through DOM may be greater than the flux of lignin (Table 3). The global river flux estimate of BC from DOM is the same order of magnitude as estimates of atmospheric deposition of BC aerosols to the ocean ($7 \pm 3\times10^{12}$ g BC $yr^{-1}$) and the global river BC particle flux ($12.2\times10^{12}$ g BC $yr^{-1}$) (Suman et al. 1997), implying that the total flux of BC to the ocean may exceed 24 Tg BC $yr^{-1}$. Because the production of BC sequesters carbon into a refractory pool, BC may represent an important sink for carbon into the ocean. The ubiquity of black carbon and its abundance in coastal ocean particles (Mitra et al. 2002) and DOM suggest that BC represents an important component of the ocean's carbon cycle.

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Table 1. Black carbon content of standard reference materials and natural organic matrices. Diesel particulate and urban dust are standard reference materials (SRM) 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). *Isochryis galbana* and *Skeletonema costatum* samples were collected from non-axenic 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 days of microbial degradation in darkness.

| Material | TOC (% C) | BC (g BC (g dry wt)$^{-1}$) | BC/TOC (% C) |
|---|---|---|---|
| Diesel Particulate<br>NIST SRM 1650 | 79.25 ±1.45[*] | 0.5232 ±0.0028 | 66.02 ±0.35 |
| Urban Dust<br>NIST SRM 1649a | 17.96 ±0.04 | 0.0407 ±0.0014 | 22.66 ±0.78 |
| Suwannee River DOM<br>IHSS 1R101N | 44.81 ±1.16 | 0.0015 ±0.00013 | 0.335 ±0.029 |
| Peat Humic Acid<br>IHSS 1R103H | 51.30 ±0.26 | 0.00030 ±0.00038 | 0.058 ±0.075 |
| *Isochrysis galbana* | 51.75 ±1.01 | 0.0121 ±0.0014 | 2.33 ±0.28 |
| *Skeletonema costatum* | 21.72 ±0.05 | 0.0102 ±0.0016 | 4.68 ±0.75 |
| *S. costatum* detritus | 18.93 ±0.31 | 0.00155 ±0.000007 | 0.819 ±0.004 |
| *S. costatum* 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[‡] |

* mean ±1 standard deviation for analytical error from triplicate or duplicate analyses

† thermal oxidation conducted after acid fuming

‡ inorganic carbon – sample was not fumed with acid vapors

Table 2. Black Carbon content in UDOM across salinity regions in the Delaware Estuary and Chesapeake Bay.

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

* mean ±1 standard deviation for samples collected on multiple cruises

† mean ±1 standard deviation

Table 3. Fluxes of black carbon and lignin phenols through DOM from Delaware Bay and global rivers to the ocean. Delaware Bay fluxes are based on a surface volume outflow of 8000 $m^3 s^{-1}$ at the bay mouth (Garvine 1991) and an average coastal ocean UDOM black carbon concentration of 93.8 $\mu g L^{-1}$. Estimates of global river fluxes are based on a global river discharge of 35,300 $km^3 yr^{-1}$ (Cauwet 2002) and average BC concentration in UDOM from the Delaware River and headwaters of Chesapeake Bay (156.4 $\mu g L^{-1}$). The global river flux of lignin is based on the average DOM lignin phenol concentration of 21.6 $\mu g L^{-1}$ from the Amazon and Mississippi rivers (Opsahl and Benner 1997).

| DOM material | Delaware Bay flux ($g yr^{-1}$) | Global river flux ($g yr^{-1}$) |
|---|---|---|
| Black carbon | $2.4 \times 10^{10}$ | $5.5 \times 10^{12}$ |
| Lignin | $2.3 \times 10^{8}$* | $0.76 \times 10^{12}$ |

* Mannino and Harvey 2000b.

## Figure Legend

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

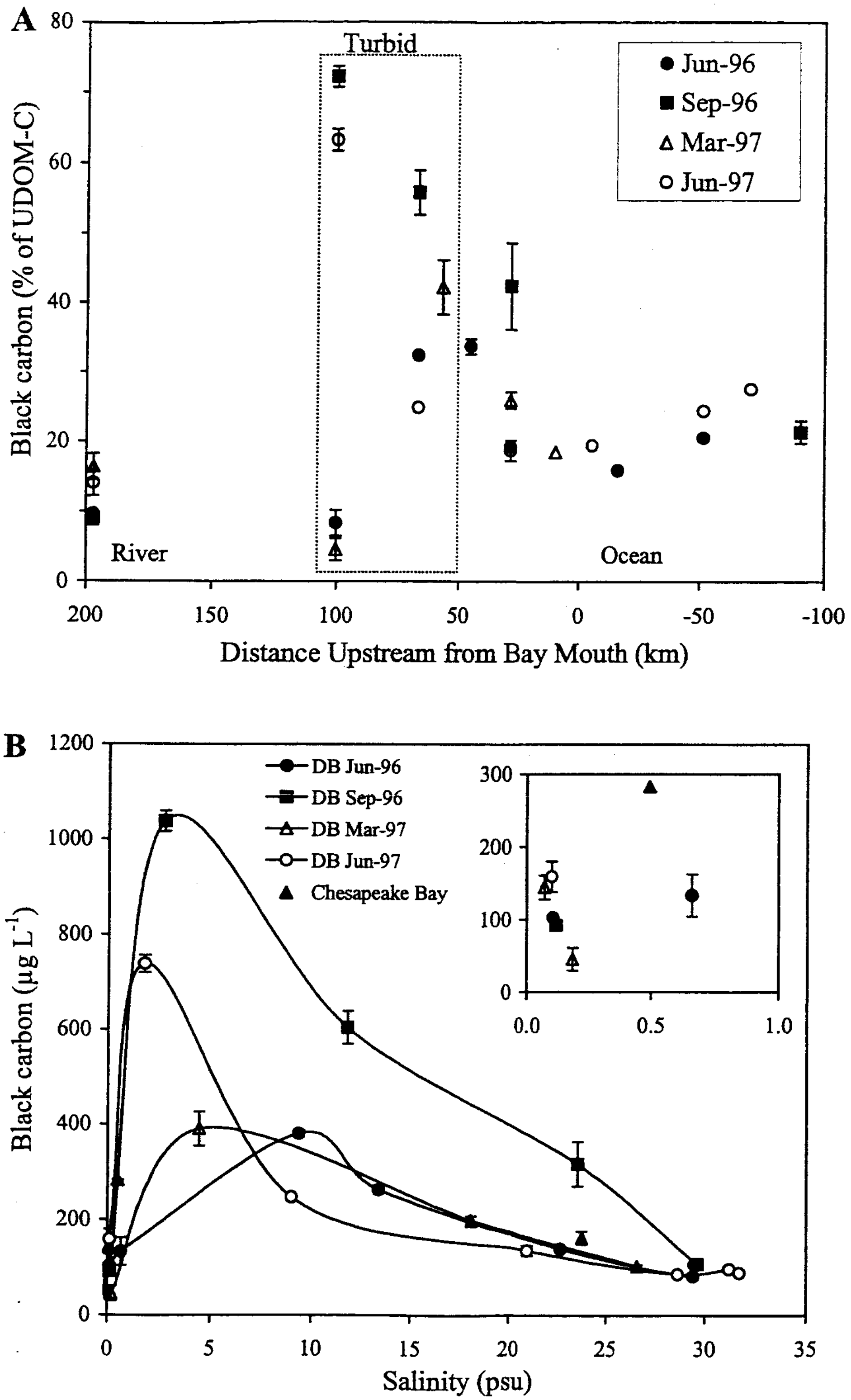

Figure 1: Mannino & Harvey

## Web Appendix 1

Table A1. Least-squares regression analyses of Delaware Estuary black carbon versus salinity >1 psu.

| | BC ($\mu$g $L^{-1}$) | BC/UDOM-C (% C) | BC/DOC (% C) |
|---|---|---|---|
| Data Transformation | $[\text{Log}_{10}(Y)]^{0.5}$ | $(Y)^{0.5}$ | $(Y)^{0.1}$ |
| Slope ±SE* | -0.0101 ±0.0011 | -0.098 ±0.021 | -0.00591 ±0.00086 |
| Intercept ±SE | 1.708 ±0.023 | 7.389 ±0.449 | 1.357 ±0.019 |
| $r^2$ | 0.839 | 0.558 | 0.729 |
| $p$ | <0.00001 | <0.0005 | <0.00001 |

* standard error

## Significant Findings

Currently, there are no known published measurements of black carbon (BC) concentrations within the dissolved organic matter pool (DOM) in oceanic environments. Production of BC sequesters fossil fuel- and biomass-derived carbon into a refractory carbon pool, and BC may represent a significant carbon sink into the ocean. Analysis of high-molecular-weight DOM from two estuaries and the adjacent coastal ocean demonstrates that BC is a significant component of DOM, and suggests that river-estuary systems are important exporters of BC to the ocean through DOM. Our results show that BC comprises 4-7% of the dissolved organic carbon (DOC) at coastal ocean sites, which supports the hypothesis that the DOC pool is the intermediate reservoir in which BC ages prior to sedimentary deposition. Furthermore, our calculations suggest that BC fluxes through DOM into the ocean may exceed the inputs of dissolved lignin.

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