

Black Carbon in Estuarine and Coastal Ocean Dissolved Organic Matter

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One-sentence summary: Analysis of high-molecular-weight dissolved organic matter (DOM) from two estuaries in the northwest Atlantic Ocean reveals that black carbon (BC) is a significant component of previously uncharacterized DOM, suggesting that river-estuary systems are important exporters of recalcitrant dissolved organic carbon to the ocean.

Black carbon represents a refractory and chemically complex product of incomplete combustion of fossil fuels and biomass burning, including vegetation burns and forest fires. Observations of black carbon particles in the atmosphere, ice, rivers, soils and marine sediments suggest that this material is ubiquitous (1-4). However, the contribution of BC to the ocean's DOM pool is not known. We present the first evidence that black carbon comprises a significant fraction of marine DOM.

Mechanisms which 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. BC comprises 10-50% of sedimentary organic carbon (5, 6) and is much older (2400 to 13,900 years older) than non-black carbon material in deep ocean sediments (7). The radiocarbon age differences between sedimentary BC and other sedimentary organic matter represent an unresolved issue on whether the BC that ultimately resides in marine sediments ages within the oceanic DOC pool or in soils (7).

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) (8). 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.

gravitational circulation and tidal resuspension of bottom sediments (10). 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) (11). 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 $<1 \mu\text{m}$) and a coarser mode (1 to $10 \mu\text{m}$) (12). Atmospheric deposition of BC aerosols must also contribute BC to high-molecular weight DOM and suspended particles in the open ocean as well as coastal regions. For example, aerosols produced from biomass burning in southern Africa are transported at least 4000 km into the South Atlantic (13). 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 (14).

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 (7). 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 (7). Masiello and Druffel (7) 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

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 (17).” 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 (15, 18, 19). 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 even greater quantities of BC. For example, the flux of BC in suspended particles from the Mississippi River to the Gulf of Mexico was estimated at 5×10^{11} g BC yr⁻¹ (4). In our study, BC comprised a substantial portion of DOC (4-7%) in the coastal ocean adjacent to Delaware Bay and Chesapeake Bay (Table 1).

The annual flux of BC from Delaware Bay UDOM to the Atlantic Ocean was estimated at $2.37 \pm 0.27 \times 10^{10}$ 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 ± 76.0 µg l⁻¹) to estimate the flux of BC within DOM through world rivers yields a global river flux of $5.5 \pm 2.7 \times 10^{12}$ 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 ($7 \pm 3 \times 10^{12}$ g BC yr⁻¹) (20) and the global river BC particle flux (12.2×10^{12} g BC yr⁻¹) (20), implying that the total flux of BC to the ocean may exceed 24 Tg BC yr⁻¹. Because the production of BC

References and Notes

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Figure Legend

Figure 1. Distributions of black carbon (a) yields and (b) concentrations in UDOM from the Delaware Estuary and Chesapeake Bay. ● – Delaware Bay June 1996, ■ – Delaware Bay September 1996, △ – Delaware Bay March 1997, ○ – Delaware Bay May-June 1997 and ▲ – Chesapeake Bay May-June 1997 (panel b only). Inset graph displays values at salinity <1. Error bars represent 1 standard deviation for triplicate or duplicate analyses.

Table 2. Black carbon content of standard reference materials and natural organic matrices (21).

Material	TOC (% C)	BC (g BC/g dry wt)	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 1R101N			
Peat Humic Acid	51.30 ±0.26	0.00030 ±0.00038	0.058 ±0.075
IHSS 1R103H			
<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 [‡]

* mean ±1 standard deviation for triplicate or duplicate analyses. † thermal oxidation conducted after acid fuming. ‡ inorganic carbon – sample was not fumed with acid vapors.

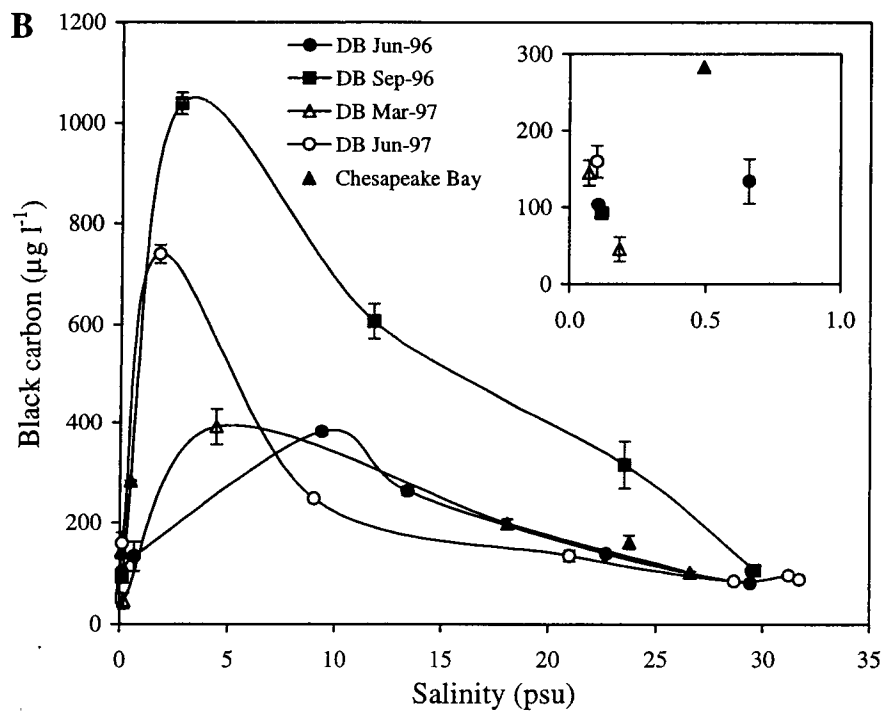
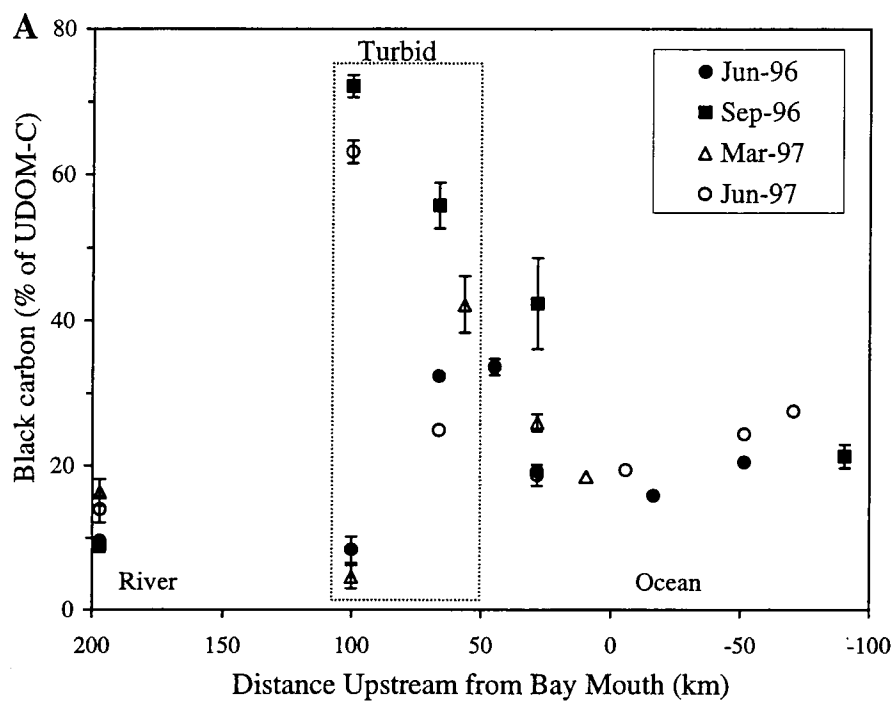


Figure 1

S2. Harvey, H. R. & Mannino, A. The chemical composition and cycling of particulate and macromolecular dissolved organic matter in temperate estuaries as revealed by molecular organic tracers. *Org. Geochem.* **32**, 527-542 (2001).

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.