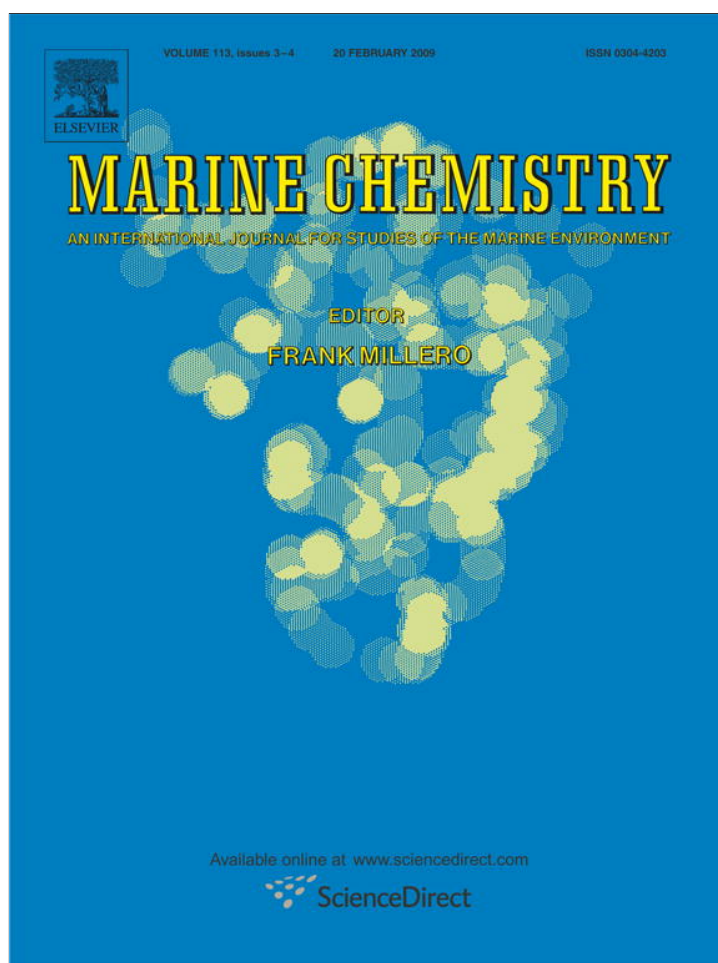


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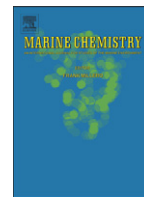
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Black carbon in marine particulate organic carbon: Inputs and cycling of highly recalcitrant organic carbon in the Gulf of Maine [☆]

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ABSTRACT

To increase our understanding of the roles of black carbon (BC), a highly sorptive and recalcitrant material, we measured BC concentrations and fluxes in marine particulate organic carbon (POC) out of the water column in the Gulf of Maine (GoM), a representative coastal area downwind of important BC sources of the Northeastern United States. Concentrations ranged from <0.1 to 16 $\mu\text{g}/\text{L}$ in the spring and late summer, typically contributing between 1 and 20% of the POC. Water-column export fluxes were near 10 $\text{g}_{\text{BC}}/\text{m}^2\text{-yr}$. These observations suggest that (a) up to 50% of the “molecularly uncharacterized” POC in this region’s seawater is combustion-derived BC, and (b) the “bioavailabilities” of hydrophobic pollutants like polycyclic aromatic hydrocarbons (PAHs) would be influenced substantially by sorption to BC. The observed BC spatial distributions imply that a large part of the BC was carried offshore by wind and that much of it is accumulated in the coastal sediments. On a global scale, these results suggest the GoM and other coastal areas with similar BC loadings accumulate significant amounts of highly recalcitrant organic carbon that remineralizes on geological time scales in the world’s oceans.

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1. Introduction

Black carbon (BC), the soot and char formed during incomplete combustion of fossil and biomass fuels, is ubiquitous (e.g., Goldberg, 1985; Masiello, 2004; Park et al., 2003; Schmidt and Noack, 2000; Suman et al., 1997). Upon its emission to the atmosphere, BC influences cloud droplet nucleation (Kaufman and Fraser, 1997) and absorbs solar radiation, thereby affecting the temperature and water content of both the atmosphere and the ground underneath (Jacobson, 2004; Kaufman and Fraser, 1997). It has been suggested that these effects have caused floods and droughts in recent years in China and India (Menon et al., 2002). In addition, BC has been characterized as carcinogenic and a cause of problems such as asthma (Dockery et al., 1993; Künzli et al., 2000). Perhaps such impacts are not surprising since we know that BC is an important carrier of organic pollutants like polycyclic aromatic hydrocarbons (PAHs) (Lohmann et al., 2005; Neff, 1979).

Seiler and Crutzen (1980) noted the potential implications of combustion processes to the global carbon cycle. BC formed during biomass and fossil fuel burning is relatively inert to biological and

chemical processes and thus may be resistant to decomposition over geological time scales (Middleburg et al., 1999). As a result, BC formed during vegetation fires and wood burning transfers materials from a fast cycling biosphere (more labile organic carbon) into a long-term geological carbon cycle (a more refractory organic carbon). A fraction of the BC emitted into the atmosphere is initially incorporated into soils (Eglinton et al., 2002; Schmidt and Noack, 2000), but erosion processes appear to transport some of this BC down rivers to the ocean (Mannino and Harvey 2004; Masiello and Druffel, 2001; Mitra et al., 2002). Other studies suggest that BC may constitute an important fraction of organic carbon in contemporary marine sediments (Gustafsson and Gschwend, 1998), where it can be preserved for thousands of years (Masiello and Druffel, 1998; Middleburg et al., 1999). BC emissions have increased over the last century and are estimated to be between 6 and 24 Tg BC/yr for fossil fuels (Hendricks et al., 2004; Penner et al., 1993; Reddy and Boucher, 2004) and 50 to 270 Tg BC/yr for biomass fuels (Kuhlbusch and Crutzen, 1995). These estimates of highly refractory OC are of the same order of magnitude as riverine transport of particulate organic carbon (POC) into the oceans (Hedges and Keil, 1995), and may represent an important sink of atmospheric CO_2 in the global carbon cycle (Kuhlbusch and Crutzen, 1995).

Presently, there is substantial uncertainty with respect to the fate of BC released to the environment. After their production, BC particles can be deposited near their source or travel in the atmosphere hundreds to thousands of kilometers reaching even the most remote ocean sites (Goldberg, 1985; Garstang et al., 1997). Since BC is found in coastal and open ocean sediments, it is reasonable to assume that BC is present within, and travels through, the oceanic water column. Previous investigators

[☆] Black carbon (BC), a highly recalcitrant material derived from incomplete combustion, contributes 1 to 20% of the particulate organic carbon (POC) in coastal seawater, explaining why (1) some POC is not recycled to CO_2 and (2) the bioavailability of many organic substances in seawater is less than expected.

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have proposed that BC cycles in the ocean as dissolved organic matter (DOM) (Masiello and Druffel, 1998), and there have been estimates of BC in ultrafiltered DOM in the Atlantic Ocean (Mannino and Harvey, 2004). However, there are no measurements of BC in marine POC. As a result, we do not know: (1) the relative importance of BC transport to the sea via rivers versus through the atmosphere; (2) the concentrations and residence times of BC in the oceanic water column; (3) the contribution of BC to the POC in seawater; and (4) whether any BC transformation mechanisms might occur within the water column.

Here we present the first measurements of BC concentrations in coastal seawater POC and export fluxes from the coastal water column. BC content in seawater was measured using the chemo-thermal oxidation method (CTO 375; Gustafsson et al., 1997a) with pre-combustion modifications to avoid charring. To support these measurements, we

also used a novel sorption-based procedure for quantifying BC suspended in water. To place our observations into context, we compared estimates of BC fluxes (1) out of the atmosphere into the seawater, (2) out of the water column, and (3) into the coastal bed sediments.

2. Materials and methods

2.1. Site description

We filtered suspended solids from large-volume river and coastal seawater samples acquired in the Gulf of Maine (GoM) region on two cruises taken in April and August–September of 2004. The GoM is a semi-enclosed coastal sea located off the northeast coast of the United States and southwest of Nova Scotia, Canada (Fig. 1A). It is a good

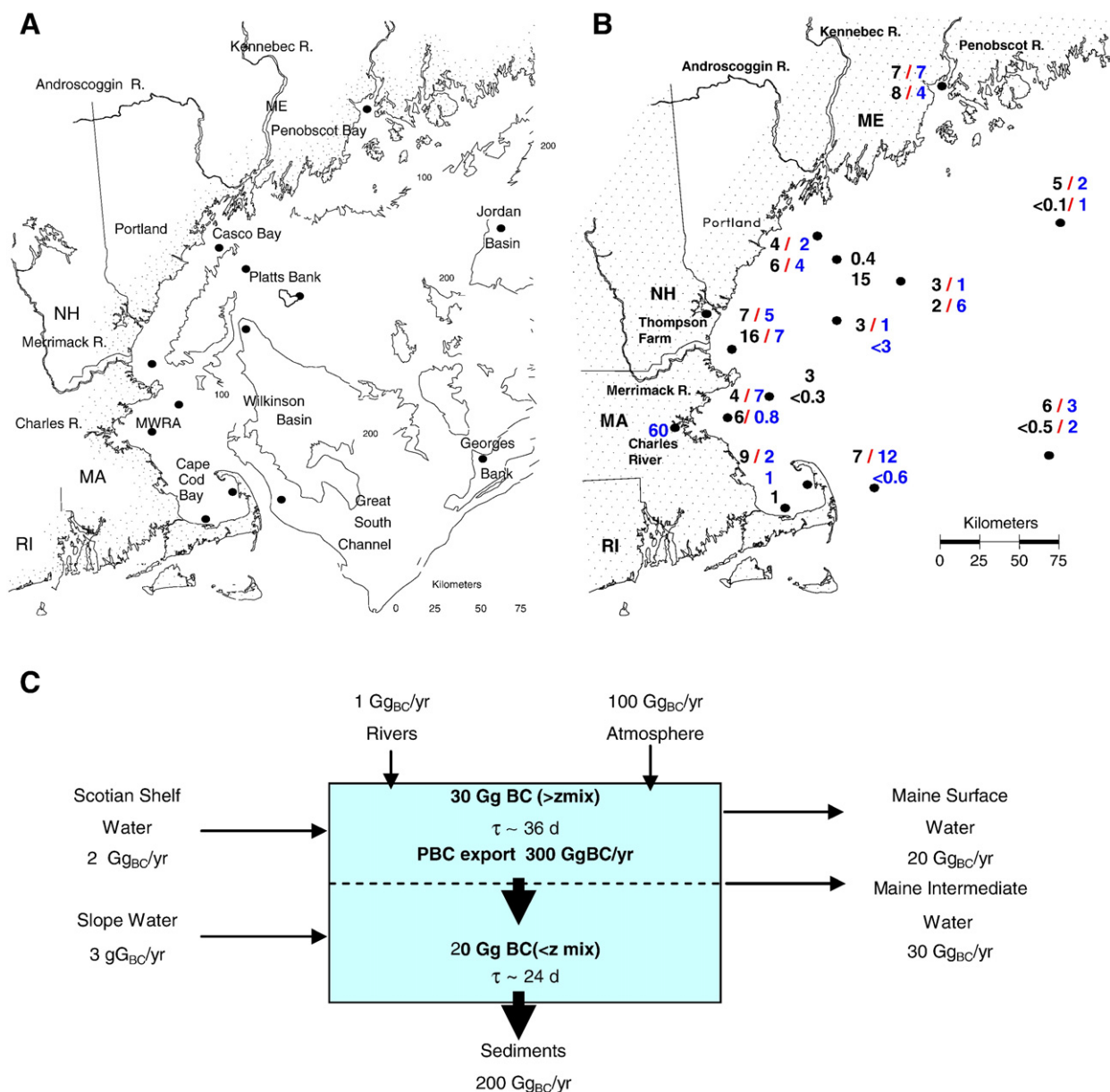


Fig. 1. A. GoM bathymetry and station locations. B. BC concentrations ($\mu\text{g/L}$) in the GoM. Upper and lower values represent mixed layer (typically ca. 10 m) and sub-mixed layer (typically ca. 60 m) samples, respectively (see Table 1). Black (left) and blue (right) data represent April and August samples, respectively. C. Mass balance model of BC in the GoM ($\text{Gg} = 10^9 \text{ g}$). Size of BC reservoir and water column flux estimates were calculated using detailed bathymetric data collected by Incze and Jakobsson (2008) from <http://pubs.usgs.gov/> and our measured BC concentrations and fluxes (Table S1); BC inputs and outputs from water currents and river flows were calculated using water volumetric flows from Townsend (1996) and BC concentrations estimated from this study (Table S2); BC atmospheric deposition was estimated using average deposition rates of 1 and $0.3 \text{ g/m}^2\text{-yr}$ (see Table 4) for the coastal ($28,000 \text{ km}^2$; regions 5 and 6 on Table S1) and central GoM ($122,000 \text{ km}^2$; regions 2, 3, 7–10 on Table S1) areas, respectively; and BC sedimentation was calculated using average BC sediment fluxes of 2 and $1 \text{ g/m}^2\text{-yr}$ (see Table 4) for the coastal ($28,000 \text{ km}^2$) and central GoM ($122,000 \text{ km}^2$) areas, respectively. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

representative of coastal areas located downwind of important industrial and urban BC sources, as well as forested areas that regularly experience natural and human-directed burns. Other important examples of such waters include the Mediterranean Sea downwind of Western Europe, the coastal Pacific downwind of China, and the coastal Pacific region downwind of Mexico City. The residence time of water in the GoM is about a year and the major inflows to this area are from the Scotian Shelf and the Northeast Channel (Townsend, 1996). Additionally, there have been intensive studies in this area in the last three decades that have provided a better understanding of the hydrography and water flow dynamics of the GoM, as well as of other carbon cycling studies (e.g. Charette et al., 2001; Dai and Benitez-Nelson, 2001; Flores-Cervantes, 2008a; Gustafsson and Gschwend, 1998).

2.2. Sample collection

Two different portions of the POC, defined by size cut-offs, were collected on each of two cruises to the GoM in 2004, one in April (*R/V Oceanus*) and the other one in August/September (*R/V Cape Hatteras*). At each sampling station, water was pumped from shallow (~10 m) or deeper depth (~60 m) using a positive-displacement, stainless-steel, gear pump (Fultz Pump Inc., Lewis Town, NJ) through stainless steel tubing that had been thoroughly washed with dichloromethane, methanol, and low-carbon water (18 mΩ, UV-treated, produced using an Aries Vaponic system, Rockland, MA). The seawater was pumped on-board directly into the ship's laboratory without ever being exposed to the atmosphere. On-board, the water was successively passed through a 142-mm diameter, stainless steel, filter holder containing a 53-μm mesh-opening pre-cleaned Nitex screen (TETKO, Depew, NY) and then through a 293-mm, stainless steel, filter holder with a 0.7-μm pre-combusted glass fiber filter (GFF) or quartz filter (Pall Gelman Sciences, Ann Arbor, MI). All filter samples were rinsed immediately after POC collection with sulfurous acid (H₂SO₃) to remove carbonates and then with low-carbon water to remove salts. Finally, filters were photographed and then transferred to aluminum foil envelopes in a laminar-flow hood and then stored frozen. Sample blanks were carried through the entire sampling procedure and consisted of "wetting" the filters with 1 L of seawater from a given site, before processing in the same manner as all the samples.

2.3. Organic carbon (OC) and black carbon (BC) measurements

We measured the BC collected on the filters and Nitex screens using the chemo-thermal oxidation (CTO-375) method (Gustafsson et al., 1997a) after slowly freezing the samples to lyse cells and therefore minimize charring artifacts. The CTO-375 method has been extensively evaluated for interferences from biogenic/diagenetic organic matter (Gustafsson et al., 1997a; Reddy et al., 2002) and is thought to be particularly suited to analysis of the soot portion of the BC spectrum. This method detects 50% or more of the carbon present in soot samples as BC, but detects almost none of the carbon present in the biomass chars (Hammes et al., 2007). The methodologies to characterize each of the two size cutoff POC fractions are described below.

2.3.1. OC and BC in the >53 μm POC

The Nitex screen was sonicated with 100 mL of GFF-filtered seawater (Whatman, Florham Park, NJ) for 5 to 10 min to collect the >53 μm POC in a 150-mL pre-cleaned plastic container. Following sonication, 50 mL were immediately transferred to a 60-mL pre-combusted glass vial for POC and BC analyses, while the other 50 mL were kept in the plastic container for ²³⁴Th/²³⁸U measurements. Triplicate 600 μL samples of the sonicated POC were placed in crucible-shaped Ag capsules and acidified with about 200 μL of 6% v/v H₂SO₃ (Fisher Chemicals, Fairlawn, NJ). Half of the samples were kept frozen overnight and combusted at 375 °C under air for

24 h in a F47915 Thermolyne muffle furnace. Finally, the set of the non-combusted samples was dried at 60 °C overnight, and the carbon weight percentage of both sets of samples was determined using a CHN analyzer (Vario EL, Elementar America, Inc., NJ) at a combustion temperature of 950 °C. Daily response factors were determined using acetanilide standards, and the detection limit of the analyzer was 0.6 μg of C. Response factors for all elements remained stable throughout the experiment (±0.5% for nitrogen, ±0.07% for carbon, and ±0.6% for hydrogen). Every run included two sample blanks (no sample introduced in CHN analyzer) to verify that previous combustion was complete, and blanks were subtracted from raw sample data.

2.3.2. OC and BC in the 53 μm > POC > 0.7 μm

For the smaller size fraction, POCs were determined using 1/16 of the glass fiber filter or quartz filter by drying overnight at 60 °C, followed by elemental analysis with a Vario EL CHN analyzer (Elementar Americas, Inc., NJ; see above). For BC measurements, 1/8 of the fiber glass filter or quartz filter was combusted at 375 °C under air for 24 h in the muffle furnace, followed by CHN analysis. Procedural blanks were carried throughout all OC and BC quantification procedures.

2.4. Pyrene Fluorescence Losses (PFL)

A more complete description of this method is described elsewhere (Flores-Cervantes, 2008b). In brief, the extent of pyrene sorption was used to infer the presence of BC on filter sub-samples. A small piece of the GFF/Quartz filter (about 1/300) was added to a precombusted 25 mL volumetric flask containing pyrene at about 1 μg_{pyrene}/L. Ten mM NaN₃ was used to inhibit bacterial growth. The samples were equilibrated for 30 d with continual mixing using a wrist-action shaker. Control flasks and blank flasks were used to correct for losses and matrix interference. Pyrene fluorescence was measured using a Perkin Elmer LS50B Luminescence Spectrofluorometer (Buckinghamshire, England). Fluorescence signals were quantified by synchronous ΔE scans, which were performed with ΔEnergy of −3000 cm^{−1}, an entrance slit of 5 nm, an exit slit of 5 nm, and a scan speed of 100 nm/min. The detection limit was 0.2 μg pyrene/L, and pyrene losses in control flasks (no filter added) for the duration of the experiment were <10%.

BC concentrations were inferred by introducing the sorption model proposed by Accardi-Dey and Gschwend (2002)

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

where K_d is the solid-water distribution coefficient (L/kg_{solid}), f_{OC} is the OC fraction in the sample (kg_{OC}/kg_{sediment}), K_{OC} is the OC-normalized distribution coefficient (L/kg_{OC}), f_{BC} is the BC fraction (kg_{BC}/kg_{sediment}), K_{BC} is the BC-normalized distribution coefficient ((μg/kg_{BC})/(μg/L)ⁿ), and C_w is the truly dissolved concentration (μg/L) to the (n−1) power, where n is the Freundlich exponent. In each incubation, the fraction of dissolved pyrene remaining in the water ($f_w = C_{wf}/C_{wi}$; where C_{wi} was the initial pyrene concentration at day zero and C_{wf} is the final pyrene concentration at day thirty) together with the solid-to-water ratio (r_{sw} = weight of filter with sample/volume of solution in flask (kg_{filter}/L)), allowed us to estimate K_d :

$$K_d = \frac{(1 - f_w)}{f_w r_{sw}} \quad (2)$$

Estimating BC concentrations required an iterative process in which, as a first approximation, the value of f_{OC} (f_{OC1}) was assumed to be equal to the total OC fraction measured in each sample. Using previously reported values of K_{OC} (10^{4.7}, Gawlik et al., 1997) and K_{BC} (10^{6.25}, Accardi-Dey and Gschwend, 2002), and using our fitted K_d corresponding to $C_{pyw} = 1$ μg/L (K_{d1} μg/L), so not to require the use of a

previous estimate of n (i.e., $C_w^{n-1} = 1$), we obtained a first estimate of f_{BC} (f_{BC1}):

$$f_{BC1} = \frac{[K_{d\mu\text{g/L}} - (f_{OC1}) \cdot (10^{4.7})]}{10^{6.25} \cdot C_w^{n-1}} \quad (3)$$

For the second iteration, f_{OC2} was calculated from the difference $f_{OC1} - f_{BC1}$, and the process was repeated until f_{BC} did not change, usually within three iterations.

2.5. BC vertical fluxes using $^{234}\text{Th}/^{238}\text{U}$ disequilibrium

Two fractions of ^{234}Th were collected and analyzed from water collected at different depths in pre-cleaned Niskin bottles. For dissolved/non-settling ^{234}Th , the seawater was passed through MnO_2 -impregnated adsorber cartridges to capture ^{234}Th (Buesseler et al., 1992). The impregnated cartridges were spiked with ^{230}Th and eluted with acid. For analysis of particulate/settling ^{234}Th , half of the sonicated $>53 \mu\text{m}$ POC from the Nitex screen (see above) was collected in a pre-cleaned plastic container, spiked with ^{230}Th to serve as a recovery standard, filtered through a precombusted 25-mm quartz QM-A filter (pore size $2.2 \mu\text{m}$; Whatman, Florham Park, NJ), and eluted in acid solution. Both fractions were purified using ion-exchange columns and electroplated onto stainless steel planchets following the procedure of Buesseler et al. (1992). The ^{234}Th activities were then measured using low-background beta detectors. The beta counts were repeated 4–5 times within a week to check for background interferences, to improve precision and accuracy, and to correct for the date of sample collection. The overall efficiencies for the MnO_2 cartridges (recovery, counting and beta detection) and the QM-

A filter (counting and beta detection) were estimated to be 29 and 32%, respectively. Charette et al. (2001) reported detection efficiencies between 35 and 64% for the MnO_2 cartridges, and $35 \pm 1.2\%$ for the QM-A filter geometry. Dissolved ^{238}U was calculated from salinity measurements (Chen et al., 1986) made on-board during the cruise with a calibrated 8410A Portasal™ salinometer (Guildline, Smiths Falls, Ontario, Canada).

2.6. Radiocarbon and $\delta^{13}\text{C}$ analysis

Radiocarbon analyses of OC and the CTO 375-isolated BC were done following the procedure previously reported by Reddy et al. (2002) with some slight modifications. In brief, between 24 and $240 \mu\text{g}$ of BC present in one eighth of the quartz filters, and 320 to $1600 \mu\text{g}$ of OC present in one sixteenth of the filters were HCl-fumed, dried in a desiccator, rolled up and packed into a $12 \text{ mm} \times 20 \text{ cm}$ precombusted quartz tube containing copper oxide (100 mg) and elemental silver wires. The tubes were then evacuated on a vacuum line, flame sealed, and combusted at 850°C for 5 h. The carbon dioxide produced was then isolated and purified using a series of cold traps and quantified by manometry. About 10% of the isolated carbon dioxide was analyzed for $\delta^{13}\text{C}$. The remainder was reduced to graphitic carbon and then pressed and mounted on target wheels for radiocarbon analysis by accelerator mass spectrometry at the National Ocean Sciences Accelerator Mass Spectrometry (NOSAMS) facility at Woods Hole, MA, USA (McNichol et al., 1994). Radiocarbon results were normalized to $\delta^{13}\text{C}_{\text{VPDB}} = -19$ per mil and reported relative to 95% activity of NBS Oxalic Acid I as fraction modern (f_m) and $\Delta^{14}\text{C}$ (Stuiver and Polach, 1977). Due to the large sample sizes required for $\Delta^{14}\text{C}$ measurements and the lack of excess material, our data set include only single measurements (i.e., $n = 1$).

Table 1
Gulf of Maine sampling stations site characterization.

Sample name ^a (depth)	Lat. +N/−S	Long. +E/−W	Approx. water depth (m)	April 2004						August/September 2004					
				Mixed layer depth (m)	Temp (°C)	Salinity (PSU)	Chl <i>a</i> (μg/L)	O ₂ (mg/L)	POC (μg/L)	Mixed layer depth (m)	Temp (°C)	Salinity (PSU)	Chl <i>a</i> (μg/L)	O ₂ (mg/L)	POC (μg/L)
MWRA (6 m)	42.37	−70.81	33	10	5.7	30.7	3.0	10.2	322	15	13.7	31.5	0.6	8.5	144
MWRA (20 m)	42.37	−70.81	33	10	3.8	32.0	6.6	10.6	248	15	8	31.8	0.3	9.6	103
NMB (20 m)	42.52	−70.45	90	21	4.6	31.3	10.1	10.5	296	−	−	−	−	−	−
NMB (50 m)	42.52	−70.45	90	21	3.5	32.8	1.2	10.7	35.6	−	−	−	−	−	−
MER (6 m)	42.81	−70.73	35	10	5.6	31.4	7.8	10.3	288	15	15	31.4	0.6	8.3	129
MER (20 m)	42.81	−70.73	35	10	3.8	32.0	2.4	10.6	258	15	9.6	31.9	0.9	9.2	93.8
CB (6 ^b /2 ^c m)	43.56	−70.05	180	24	5.2	30.8	6.3	10.4	324	10	12.4	31.7	1.0	8.7	145
CB (24 ^b /15 ^c m)	43.56	−70.05	180	24	3.1	32.1	0.5	10.8	64.3	10	10.5	31.9	0.8	9.1	190
WB 1 (6 ^b /10 ^c m)	42.99	−69.90	200	50	3.2	32.1	2.4	10.7	148	50	18.2	31.1	0.2	8	63.2
WB 1 (80 m)	42.99	−69.90	200	50	4	33.3	0.8	10.5	n.m.	50	4.7	32.7	0.1	10.3	16.7
WB 2 (8 m)	43.37	−69.89	170	50	4.1	31.8	4.7	10.6	280	−	−	−	−	−	−
WB 2 (30 m)	43.37	−69.89	170	50	2.9	32.7	1.4	10.8	71.1	−	−	−	−	−	−
EPB (6 ^b /10 ^c m)	43.11	−69.18	190	63	3.8	32.2	1.2	10.6	88.5	50	16.2	31.9	0.3	8.5	55.6
EPB (35 m)	43.11	−69.18	190	63	3.5	32.2	0.8	10.7	81.5	−	−	−	−	−	−
EPB (80 m)	43.11	−69.18	190	−	−	−	−	−	−	50	6.8	32.8	0.1	9.9	28.9
IPB (3 m)	44.42	−68.83	25	6	3.9	22.8	1.6	11.2	286	4	13.1	29.0	0.8	8.7	291
IPB (6 m)	44.42	−68.83	25	6	2.8	30.5	1.3	11	205	4	11.6	30.8	0.6	9	209
JB (8 ^b /10 ^c m)	43.41	67.41	285	50	2.8	31.9	1	10.9	127	50	18.1	32.1	0.4	7.9	72.1
JB (60 m)	43.41	67.41	285	50	2.4	32.1	0.2	11	37.0	−	−	−	−	−	−
JB (80 m)	43.41	67.41	285	−	−	−	−	−	−	50	5.1	32.8	0.1	10.2	19.9
GB (8 ^b /10 ^c m)	41.75	−68.00	195	50	5.3	32.9	7.2	10.2	155	50	18.2	32.0	0.2	7.6	52.9
GB (60 m)	41.75	−68.00	195	50	4.5	33.2	2.7	10.4	45.2	−	−	−	−	−	−
GB (80 m)	41.75	−68.00	195	−	−	−	−	−	−	50	5	32.6	0.1	10.3	51.8
GSC (8 ^b /10 ^c m)	41.83	−69.67	198	50	5.1	32.7	n.m.	10.3	149	32	17.3	31.5	0.3	7.9	188
GSC (60 m)	41.83	−69.67	198	50	3.5	33.1	n.m.	10.6	n.m.	32	4.4	32.5	0.0	7.9	23.4
CCB 1 (6 m)	41.80	−70.05	20	13	6	31.8	1.2	10.1	240	−	−	−	−	−	−
CCB 2 (6 m)	41.92	−70.17	27	13	5.2	32.2	5.4	10.3	169	15	17.4	31.3	0.3	8.0	114
CCB 2 (20 m)	41.92	−70.17	27	13	5.1	32.2	5.7	10.3	n.m.	15	7.4	32.0	0.2	9.9	114

^aMassachusetts Water Resources Authority (MWRA); North Mass Bay (NMB); Merrimack River (MER); Casco Bay (CB); Wilkinson Basin I (WB1); Wilkinson Basin II (WB2); East Platts Bank (EPB); Inner Penobscot Bay (IPB); Jordan Basin (JB); Georges Bank (GB); Great South Channel (GS); Cape Cod Bay I (CCB1); Cape Cod Bay II (CCB2); ^bsample depth in April 2004; ^csample depth in August 2004; n.m. not measured; the mixed layer depth for this study was selected as the depth up to which temperature, salinity and oxygen saturation remained relatively homogeneous.

3. Results and discussion

3.1. Seasonal patterns observed in the Gulf of Maine (GoM)

Our CTD measurements of salinity, temperature, chlorophyll *a*, and O₂ concentration indicated the expected seasonal differences between the April and August/September sampling campaigns. During the spring (April) of 2004, we observed relatively low salinities in the shallow samples at the stations close to shore, reflecting the impact of runoff. We also observed high chlorophyll *a* concentrations in the surface waters at all of our stations (high primary productivity), and small vertical and horizontal variations of temperature and O₂ throughout the GoM (high vertical mixing). In contrast, during August/September of 2004, we saw large temperature and O₂ concentration vertical gradients, small variations in salinities between the shallow and the deep samples, and low chlorophyll *a* concentrations at all of our stations. These observations are consistent with the GoM's annual cycle of: (a) large spring-time inputs of river runoff; (b) winter cooling with deep surface mixing as opposed to summer stratification; and (c) spring phytoplankton blooms in contrast to summer nutrient depletion in the surface waters limiting primary productivity (Townsend, 1996, Brown and Irish, 1993, DFO, 2004, Durbin, 1996). Our discrete water samplings were chosen to capture these spatial and temporal variations (Table 1).

3.2. BC concentrations and percentages in POC from the GoM

BC concentrations measured with the CTO-375 method in the POC fraction from GoM seawater were typically between 1 and 10 µg_{BC}/L (Fig. 1B and Table 2). Most of this BC was recovered on the GFF or quartz filters (i.e., >0.7 µm), but in many instances we could also measure BC in the >53 µm fraction (note: sample charring of this larger size fraction prevented us from using larger sample sizes to attain lower detection limits). Signal-to-noise ratios were >4:1 for

April and >3:1 for August/September. Variations between replicate subsamples of the same filter were less than 20% (*n* = 11), and we found excellent correspondence (*R*² = 0.99, *n* = 6) between samples measured by our elemental analysis and the carbon yields from closed-tube combustion used for isotopic analysis. These BC values represented 1 to 20% of the POC in these seawaters (calculated by summing the results from the Nitex screen and glass fiber filters).

We also observed 59 ± 7 µg_{BC}/L (*n* = 3) in the Charles River and 51 ± 6 µg_{BC}/L (*n* = 2) for Boston Harbor. These concentrations represented about 4% of the POC measured in these urban water samples (data not in table). These urban-area BC concentrations were much higher than observations made in the more remote Penobscot River estuary of 3 to 8 µg_{BC}/L (station "IPB").

To support the accuracy of these results, we used pyrene fluorescence loss observations (Flores-Cervantes, 2008b) as a second approach to measure BC in Jordan Basin seawater. Since BC has a strong affinity for PAHs like pyrene (Accardi-Dey and Gschwend, 2002; Gustafsson and Gschwend, 1997), we inferred BC concentrations by observing diminished pyrene fluorescence when filter subsamples were added to pyrene solutions. Using the Jordan Basin (JB) surface samples and a range of initial pyrene concentrations (from 0.3 to 4 ppb, *n* = 6), we observed a nonlinear sorption isotherm (Flores-Cervantes, 2008b). Previous researchers have recognized that PAHs exhibit nonlinear isotherms for sorption onto BC (Accardi-Dey and Gschwend, 2002; Bucheli and Gustafsson, 2000; Lohmann et al., 2005). Hence, the isotherm was consistent with the presence of a BC adsorbent in the filtered solids, in addition to natural organic matter acting as an adsorbent (i.e., $K_d = f_{oc}K_{oc} + f_{BC}K_{BC}C_w^{n-1}$) (Gustafsson et al., 1997a; Accardi-Dey and Gschwend, 2002). Moreover, the absolute value of the observed *K_d* was much greater than expected using the *f_{oc}K_{oc}* adsorbent model (Karickhoff, 1981; Chiou et al., 1979). Using the isotherm and assuming a log *K_{BC}* of 6.25 (Accardi-Dey and Gschwend, 2002), BC collected on the filter at this particular site was estimated to be present at 4.2 ± 1.4 µg_{BC}/L, as compared to the 4.5 ± 1.8 µg_{BC}/L

Table 2
Concentrations of BC in POC >53 µm (Nitex) and 53 µm > POC > 0.7 µm (GFF/quartz filter).

Station (depth)	April 2004					August/September 2004					SUM		SUM		Average	±
	VF ^a	GFF	±	NITEX	±	VF ^a	QUARTZ	±	NITEX	±	April	±	August	±		
	(L)	C (µg/L)		C (µg/L)		(L)	C (µg/L)		C (µg/L)							
MWRA (6 m)	85	4.0	0.4	0.18	0.08	110	7.1	0.4	0.27	0.09	4.2	0.4	7.3	0.5	5.8	0.6
MWRA (20 m)	110	6.5	2.8	<0.07	–	116	0.80	0.26	<3.5	–	6.5	2.8	0.8	0.3	3.6	2.8
NMB (6 m)	179	3.0	1.7	<0.05	–	–	–	–	–	–	3.0	1.7	–	–	3.0	1.7
NMB (50 m)	117	<0.3	–	<0.05	–	–	–	–	–	–	<0.3	–	–	–	<0.3	–
MER (6 m)	144	3.9	2.4	2.8	0.3	501	5.4	0.1	<0.24	–	6.6	2.4	5.4	0.1	6.0	2.4
MER (20 m)	43	16	7.1	<0.6	–	170	7.3	0.2	<0.01	–	16	7.1	7.3	0.2	12	7.1
CB (6 ^b /2 ^c m)	251	3.5	1.2	0.30	0.09	197	1.8	1.1	0.19	0.03	3.8	1.3	2.0	1.1	2.9	1.7
CB (24 ^b /15 ^c m)	206	3.6	1.5	2.2	0.1	438	3.8	0.5	<1.6	–	5.8	1.5	3.8	0.5	4.8	1.6
WB 1 (6 ^b /10 ^c m)	205	3.3	1.5	<0.4	–	815	0.81	0.04	0.03	0.01	3.3	1.5	0.8	0.0	2.1	1.5
WB 1 (80 m)	–	–	–	–	–	198	<0.4	–	<2.2	–	–	–	<2.6	–	<2.6	–
WB 2 (8 m)	68	0.4	1.6	<0.2	–	–	–	–	–	–	0.4	1.6	–	–	0.4	1.6
WB 2 (30 m)	68	15	4.5	<1	–	–	–	–	–	–	15	4.5	–	–	15	4.5
EPB (6 ^b /10 ^c m)	270	2.8	1.2	0.07	0.01	676	1.5	0.1	0.04	0.01	2.8	1.2	1.5	0.1	2.2	1.2
EPB (35 m)	205	2.1	1.5	<0.4	–	–	–	–	–	–	2.1	1.5	–	–	2.1	1.5
EPB (80 m)	–	–	–	–	–	257	5.6	0.1	<0.9	–	–	–	5.6	0.1	5.6	0.1
IPB (3 m)	101	6.1	3.0	0.79	0.2	340	6.9	0.1	0.43	0.05	6.9	3.0	7.3	0.1	7.1	3.0
IPB (6 m)	128	8.4	2.4	<1	–	221	3.4	0.1	<0.01	–	8.4	2.4	3.4	0.1	5.9	2.4
JB (8 ^b /10 ^c m)	182	4.5	1.8	0.41	0.12	817	1.6	0.0	0.06	0.01	4.9	1.8	1.6	0.0	3.2	1.8
JB (60 m)	181	0.1	1.7	<0.5	–	–	–	–	–	–	0.1	1.7	–	–	0.1	1.7
JB (80 m)	–	–	–	<0.01	–	396	1.3	0.1	<0.01	–	–	–	1.3	0.1	1.3	0.1
GB (8 ^b /10 ^c m)	344	5.6	0.9	<0.2	–	379	2.8	0.1	<2.0	–	5.6	0.9	2.8	0.1	4.2	0.9
GB (60 m)	9	<0.3	–	<0.2	–	–	–	–	–	–	<0.5	–	–	–	<0.5	–
GB (80 m)	–	–	–	–	–	185	2.1	0.2	<0.11	–	–	–	2.1	0.2	2.1	0.2
GSC (8 ^b /10 ^c m)	342	6.6	0.9	<0.2	–	200	12	0.2	<0.44	–	6.6	0.9	11.6	0.2	9.1	0.9
GSC (60 m)	–	–	–	–	–	144	<0.6	–	<0.01	–	–	–	<0.6	–	<0.6	–
CCB 1 (6 m)	120	1.1	3.2	0.08	–	–	–	–	–	–	1.1	3.2	–	–	1.1	3.2
CCB 2 (6 m)	122	8.7	2.5	<0.35	–	425	2.2	0.1	<0.01	–	8.7	2.5	2.2	0.1	5.4	2.5
CCB 2 (20 m)	–	–	–	–	–	194	0.54	0.16	0.3	0.06	–	–	0.86	0.17	–	–

^aVF = Volume of water filtered; ^bsample depth in April 2004; ^csample depth in August 2004. Note 1: <x if signal-to-noise ratio is less than 3:1. Note 2: Absolute uncertainty calculated using error propagation (including sampling and analytical error).

seen by the CTO-375 procedure (Table 2). The strong correspondence of these diverse BC analytical approaches indicated that the CTO-375 method gave an accurate measure of soot-derived BC for our samples. We note that the PFL method is thought to respond to both soot and char BC fractions (Flores-Cervantes, 2008b). Therefore, correspondence between the two methods suggested that the BC in seawater from the Jordan Basin included for the most part soot-like BC.

3.3. Spatial and temporal variation of BC concentrations

The highest BC concentrations (i.e., >5 µg_{BC}/L) were generally found at nearshore stations (Fig. 1). During April, our surface concentration data showed a best-fit-exponential “decay” of 0.022 ± 0.007 km⁻¹ within a distance of 70 km from shore (Fig. 2A), but concentrations did not fall off at distances further away from shore (data not shown in Fig. 2A). During August/September, the overall falloff with distance from shore was much lower than in April (0.002 ± 0.001 km⁻¹; data not shown). The April decrease rate for BC in GoM surface waters was similar to the 0.031 ± 0.001 km⁻¹ decline previously reported within 100 km from Boston for sediment concentrations of closely related compounds, PAHs, in the same coastal area (Windsor and Hites, 1979; Fig. 2B). Similarly, Gustafsson

et al. (1997b) found pyrene export fluxes from the surface ocean decreased nearshore with a decay constant of 0.1 km⁻¹ and further from shore at 0.0019 km⁻¹. PAHs are also produced during the incomplete combustion of fossil and biomass fuel, and their specific ratios are commonly interpreted as reflecting pyrogenic inputs to the environment (e.g., Lima et al., 2003; Youngblood and Blumer, 1975, Gschwend and Hites, 1981). Assuming that transport processes do not separate the PAHs from the soot on which they initially occurred, the observed fall off with distance from their source might be expected to be similar for such pyrogenic PAH and BC products. This BC decline with distance also suggests that the isolated BC was continentally derived, as opposed to a methodological artifact.

No general BC concentration differences were observed between April and August/September or as a function of water depth. This differs from OC concentrations for the GoM which generally decrease with depth and are higher during the months of March and April than September and August (Charette et al., 2001; Table 1). As a result, we generally found that BC contributed increasing percentages of the POC with depth (and into sediments). These BC observations are not surprising since (1) BC is likely more recalcitrant than OC, therefore, surviving remineralization in the water column, and (2) atmospheric BC concentrations in this area have been seen to be similar during the winter (due to increased fuel used for heating) and summer (due to air conditioning use and forest fires prevalent at this time of the year) (Gryparis et al., 2006; <http://airmap.unh.edu/>). However, it is important to note that our method of choice, CTO-375, would not be able to recognize spatial and temporal differences in charcoal-like BC concentrations.

3.4. ²³⁴Th/²³⁸U disequilibria and BC water column export fluxes

Using the BC concentrations and our contemporaneous measures of disequilibrium between the particle-reactive ²³⁴Th and its highly water-soluble radiogenic source, ²³⁸U, in the same seawaters (Table 3), we solved for the particle-associated export of BC out of the water column at some of our sampling stations. Buesseler et al. (1992) proposed that POC fluxes could be estimated empirically by measuring the ratio of POC-to-²³⁴Th on settling particles (>53 µm). By this same approach, we estimated BC export fluxes (*f*_{BC}) out of the mixed surface layer (*z*_{mix}) by measuring the BC-to-²³⁴Th ratio on POC >53 µm in the water column at a given depth:

$$F_{BC} = \frac{BC_{/53}}{^{234}Th_{/53}} \int_{z_1}^{z_2} F_{Th} \cdot dz, \quad (4)$$

where *z*₁ and *z*₂ are the depth intervals over which *F*_{Th} is estimated. *F*_{Th} is the ²³⁴Th particulate export flux and can be derived from the total ²³⁴Th activity balance (particulate and dissolved):

$$\frac{\partial A_{Th}}{\partial t} = A_U \lambda_{Th} - A_{Th} \lambda_{Th} - F_{Th} + K \nabla^2 A_{Th} + U \nabla A_{Th} \quad (5)$$

where the first term represents the radiogenic production of ²³⁴Th with *A*_U the ²³⁸U activity and λ_{Th} is the ²³⁴Th decay constant (0.0288 d⁻¹); the second term is the loss of total ²³⁴Th by radioactive decay and *A*_{Th} is the total ²³⁴Th activity; and the last two terms represent the contributions from mixing (where *K* is the eddy diffusion coefficient vector) and advection (where *U* is the velocity vector). Previous studies have reported that in pelagic, continental shelf, and many coastal regimes, there are only modest differences between fluxes estimated using one dimensional (1-D) and three dimensional (3-D) models (i.e., <factor of 2 except during storm-driven resuspensions at near-shore locations; Gustafsson et al., 1998; Charette et al., 2001). The weather was relatively calm during April 2004 and even calmer throughout our August/September sampling campaign.

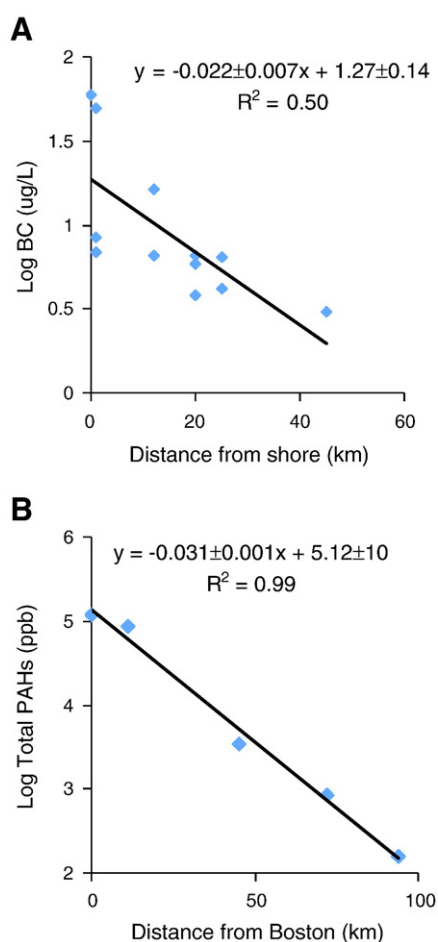


Fig. 2. Log BC and PAH concentrations versus distance. Comparison of (A) BC surface (<20 m) concentrations in locations within a distance of 70 km from shore and (B) observations by Windsor and Hites (1979) of logarithmic decrease of total PAHs concentrations with distance. The data set in (A) includes samples collected on board of *R/V Oceanus* during April 2004 (MWRA (6 and 20 m), NMB (6 m), MER (6 and 20 m), CB (6 and 15 m), IPB (6 and 3 m), and GSC (8 m)), and Charles River (59 ± 7 µg/L; *n* = 3) and Boston Harbor (51 ± 6 µg/L; *n* = 2) samples collected from shore during May–June 2004).

Table 3
²³⁴Th and ²³⁸U radionuclide activities in the GoM.

Station	²³⁸ U (dpm/L)				Total ²³⁴ Th (dpm/L)				Nitex ²³⁴ Th (mdpm ^c /L)			²³⁴ Th/ ²³⁸ U %			
	April	May ^a	Aug/Sept	Sept ^{a,b}	April	May ^a	Aug/Sept	Sept	April	Aug/Sept	Sept	April	May ^a	Aug/Sept	Sept
CCB1	2.12 ± 0.02		2.11 ± 0.02		0.83 ± 0.02		1.04 ± 0.02		2.4 ± 0.1	1.1 ± 0.1		39		50	
CCB2	2.14 ± 0.02		n.m.		0.49 ± 0.02		n.m.		3.7 ± 0.2	n.m.		23			
MWRA	2.05 ± 0.02	1.92 ± 0.02	2.09 ± 0.02	2.20 ± 0.02 ^a	0.37 ± 0.02	0.50 ± 0.03	1.39 ± 0.01	0.12 ± 0.02 ^a	13 ± 1	1.7 ± 0.1	n.m.	18	26	66	5 ^a
NMB	2.09 ± 0.02		n.m.		0.91 ± 0.03		n.m.		33 ± 2	n.m.		43			
MER	2.07 ± 0.02		2.09 ± 0.02		1.47 ± 0.06		0.79 ± 0.01		35 ± 2	1.7 ± 0.1		71		38	
WB1	2.14 ± 0.02		2.08 ± 0.02	2.24 ^b	1.93 ± 0.10		0.89 ± 0.01	1.03 ^b	21 ± 1	0.71 ± 0.04	6.4 ^b	90		43	46 ^b
WB2	2.11 ± 0.02		n.m.	2.30 ^b	1.87 ± 0.10		n.m.	0.95 ^b	200 ± 10	n.m.	25.2 ^b	89			41 ^b
OCB	2.07 ± 0.02	2.04 ± 0.02	2.08 ± 0.02	2.24 ± 0.02 ^a	0.66 ± 0.04	0.78 ± 0.04	0.84 ± 0.01	0.22 ± 0.04 ^a	2.6 ± 0.1	1.3 ± 0.1	n.m.	32	38	40	10 ^a
IPB	1.86 ± 0.02		1.97 ± 0.02		0.16 ± 0.01		0.03 ± 0.00		7.4 ± 0.4	1.0 ± 0.1		9		1	
EPB	2.14 ± 0.02	2.20 ± 0.02	2.13 ± 0.02	n.m.	1.91 ± 0.11	1.81 ± 0.05	1.00 ± 0.01	n.m.	18 ± 1	0.89 ± 0.04	n.m.	90	82	47	
JB	2.12 ± 0.02		2.14 ± 0.02	2.30 ^b	2.05 ± 0.12		1.99 ± 0.02	1.14 ^b	46 ± 2	1.5 ± 0.1	1.3 ^b	97		93	49 ^b
GB	2.19 ± 0.02		2.13 ± 0.02	2.29 ^b	1.62 ± 0.06		1.87 ± 0.02	0.72 ^b	12 ± 1	3.5 ± 0.2	8 ^b	74		88	32 ^b
GSC	2.17 ± 0.02		2.11 ± 0.02		1.85 ± 0.08		1.17 ± 0.01		42 ± 2	2.9 ± 0.1		85		55	

^aGustafsson et al. (1997b); ^bCharette et al. (2001); n.m. not measured; ^cmdpm = 10⁻³ dpm.

Therefore, for this study, it was assumed that a 1-D, steady state model could be used, so Eq. (5) was simplified to:

$$F_{Th} = A_U \lambda_{Th} - A_{Th} \lambda_{Th} \quad (6)$$

Substituting Eq. (6) into Eq. (4) and using our contemporaneous ²³⁴Th and ²³⁸U data (Table 3), the calculated BC export fluxes fell within a range of <0.3 and 36 g_{BC}/m²·yr with larger fluxes closer to shore and during the August/September sampling campaign (Table 4). Concentrations of particulate ²³⁴Th were highest during April and similar to what others have reported for this area (Charette et al., 2001; Gustafsson et al., 1997c). ²³⁴Th-to-²³⁸U ratios increased with increasing distance from particle-rich coastal areas. Smaller ²³⁴Th-to-²³⁸U ratios closer to shore and in August/September suggested larger exports of particulate matter out of the surface ocean, while higher concentrations of particulate ²³⁴Th in April indicate the larger amounts of suspended particles in the water column. These observations agree well with the larger BC export fluxes observed

close to shore (urban, semi-urban, and close to shore areas) and during the month of August/September (Table 4), the higher concentrations of BC collected on the Nitex screens during the month of April (Table 2), and the GoM's annual cycle described above (Section 3.1). During the spring in this area, rivers discharge large amounts of suspended particles that flocculate and settle as they enter slower flowing, salty coastal waters. The exceptionally low ²³⁴Th-to-²³⁸U ratio observed at IPB indicated the importance of particle deposition in this estuary. During the late summer, reduced nutrient availability (as a consequence of the stratification of the water column) causes decreased primary productivity (as reflected by about 10× lower chlorophyll *a* and 2× lower POC values in August/September versus April, Table 1), thereby limiting delivery of organic matter to depth. Zooplankton grazing and fecal pellet production might have further contributed to the high POC fluxes observed in August/September (Durbin, 1996). In both of these cases, settling particles will remove highly “sorbing/coagulating” chemicals/materials such as ²³⁴Th and BC.

Table 4
 Comparison of estimated BC fluxes (g_{BC}/m² yr) at different distances from shore and urban sites.

Near urban sites	Non-urban/near-shore sites		Continental shelf regimes ^s		Open ocean ^s			
<i>Atmospheric deposition</i>								
Thompson Farm, NH ^{a,c}	0.13	Acadia National Park, ME ^{b,1}	0.21	Gulf of Maine ^{a,m}	0.001	Pacific open ocean ^{a,n} 0.002–0.01		
Halifax, NS ^{a,d}	0.41	Brockport, NY (rural) ^{a,f}	0.28	Pacific coast ^{a,n}	0.04–0.08			
Sable Island, NS ^{a,e}	0.09	Quabbin State Park, MA ^{a,f}	0.19	Northern Sweden ^{b,o}	0.02			
Kenmore, MA (urban) ^{a,f}	0.56			Southern Sweden ^{b,o}	0.06			
Queens, NY ^{a,g}	0.1–3.0			North Atlantic ^{b,p}	0.30			
Greater Boston, MA ^{a,h}	0.02–1.7							
<i>Water column export (Gulf of Maine)</i>								
MWRA, MA ⁱ	April 2.9 ± 1.3	Aug/Sept 20 ± 7	Inner Penobscot Bay ⁱ Off Merrimack River ⁱ Cape Cod Bay ⁱ Casco Bay ⁱ	April 26 ± 6 6.0 ± 0.5 6.9 ± 0.9 31 ± 9	Aug/Sept 36 ± 5 – – 21 ± 4	Jordan Basin ⁱ Wilkinson Basin ⁱ East Platts Bank ⁱ	April 1.2 ± 0.4	Aug/Sept 11 ± 2 16 ± 6 20 ± 5
<i>Sediment fluxes</i>								
Fort Point Channel, MA ^j	23	Mouth of Providence River, RI ^l	14	Santa Barbara Basin, CA ^q	0.4	N., S. Pacific Ocean ^r 0.0001–0.001		
Spectacle Island, MA ^j	4.7	Palos Verdes Shelf, CA ^j	7–10	Saanich Inlet, BC ^q	0.7			
Portland Harbor, ME ^j	6.5	New England Harbors ^j	5–23	W. Med. Sea ⁿ	1			
MWRA, MA ^k	1.1	Gulf of Maine Inner Penobscot Bay ^k Cape Cod Bay I Cape Cod Bay II ^l Casco Bay ^k	1.7 1.9 ^j , 0.9 ^k 1.0 0.9	Gulf of Maine Wilkinson Basin Jordan Basin ^k	1.2 ^j , 0.8 ^k 1.7			

^aUnder-cloud scavenging fluxes estimated from atmospheric concentrations according to Seinfeld and Pandis (1998), scavenging coefficients from Daggupaty et al. (2006), a mean annual average precipitation of 1200 mm (NOAA, 2002), and a dry deposition rate of 0.1 cm/s was assumed; ^bmeasured atmospheric flux; ^cairmap.nhu.edu; ^dChylek et al. (1999); ^eCooke et al. (2002); ^fPedersen (2002); ^gVenkatachari et al. (2006); ^hGryparis et al. (2006); ⁱthis study. Calculated using ²³⁴Th/²³⁸U disequilibrium data and BC/²³⁴Th ratios in the POC > 53 mm (Nitex); ^jGustafsson et al. (1998); ^kFlores-Cervantes (2008a). Calculated using ²¹⁰Pb-based sedimentation rates and BC sediment concentrations; ^lCachier et al. (1990); ^mLiousse et al. (1996); ⁿSuman et al. (1997); ^oOgren et al. (1984); ^pVan Dingenen et al. (1995); ^qGriffin and Goldberg (1995); ^rSmith et al. (1973); ^satmospheric deposition in remote areas may be underestimated by a factor of four (Liousse et al., 1993).

To check our estimated water-column export fluxes for geochemical consistency, we contrasted them with estimates of atmospheric BC deposition and sediment BC burial for this region and similar regions (Table 4). Although there are difficulties in comparing BC data measured via different methods (see Hammes et al., 2007), our calculated water column BC export fluxes were of the same order of magnitude ($g_{BC}/m^2\cdot yr$) as the estimated atmospheric BC deposition and reported BC sedimentation. Some of the observed variability could be due to the use of very different BC quantification methods. The concentration of aerosol BC used to check for geochemical consistency was measured using a combination of thermal and optical techniques (e.g., Birch and Cary, 1996; Hansen et al., 1983), while sedimentary and water column BC results were measured using chemical or chemo-thermal oxidation methods (e.g., Wolbach and Anders, 1989; Gustafsson et al., 1997a). Recent method intercomparison studies (Currie et al., 2002; Hammes et al., 2007) show that thermal-optical techniques and chemo-thermal oxidation methods yield BC data that differ by up to a factor of 10 depending on the nature of the samples and the BC. Furthermore, Lioussé et al. (1993) pointed out that variations in the specific attenuation cross-section (σ) used for measurements of BC in optical analyzers in remote areas can lead to the underestimation of about four times the measured BC concentration. Differences in our GoM observations could also be due to the substantially different time-scales integrated in each environmental compartment. Atmospheric concentrations and fluxes may vary on timescales of days as phenomena like wind direction and precipitation vary; in contrast, the water column export results reflect processes occurring over many months and burial observations reflect fluxes averaged over many-year time periods. For the purpose of data comparison, we extrapolated our seasonal results to an annual basis. However, our data indicate that large seasonal surface-water export fluxes were present during our sampling events, indicating that our values, calculated on an annual basis, may be somewhat uncertain. Finally, spatial variations may play some role; for example, deposition into some of the basins may reflect sediment focusing. Despite all these difficulties, it is clear that the diverse data sets exhibit substantial consistency with BC fluxes in the order of $g_{BC}/m^2/year$ for this region.

3.5. Radiocarbon measurements of BC and OC

Radiocarbon (^{14}C) measurements of the BC in selected samples were used to test for POC charring artifacts (i.e., if POC and BC showed the same ^{14}C) and to assess whether fossil fuel combustion was the dominant source of BC in the GoM seawater (i.e., if BC was ^{14}C depleted). In no case did the ^{14}C signature of the BC match the ^{14}C of the same sample's POC, implying that the data did not reflect charring of POC. Rather the ^{14}C signature of the BC always indicated fossil fuel contributions, although these ranged widely from only about 15 to as much as 90% (Fig. 3). The highest fossil fuel-contribution to the BC was

observed for the sample closest to Boston near the Massachusetts Water Resources Authority sewage discharge site, indicating the importance of fossil fuel-combustion for soot inputs in this area. The samples with lower fossil fuel-derived BC content were distant from urban centers (Georges Bank, Inner Penobscot Bay, and Wilkinson Basin). Therefore, if charring of the collected POC was not present, the relatively modern ^{14}C content of these BC samples indicated they contained substantial quantities of soots from biomass burning.

The importance of biomass burning appears reasonable for this region. Energy use data from the Energy Information Administration (<http://www.eia.doe.gov/>), combined with a technology based emission factor approach (Bond et al., 2004), suggests that within New England 30% of the soot BC ($<1\ \mu m$) is produced from biofuel or biomass combustion, while 70% comes from petroleum, coal, and natural gas combustion (Flores-Cervantes, 2008a). Moreover, in the summer of 2004, large plumes of smoke deriving from intense boreal forest fires were observed in the GoM during August of 2004 (e.g. Val Martin et al., 2006; Quinn et al., 2006). Long distance transport selects for smaller, soot-like BC particles formed during biomass/biofuel combustion (Garstang et al., 1997). Therefore, our August/September cruise samples (Fig. 3) may have been especially affected by distant forest fires.

Stable carbon isotope ($\delta^{13}C$) data were also collected for some of our samples (Table S3). In three of the five cases, the $\delta^{13}C$ data were not particularly revealing. But unusually ^{13}C -depleted values were seen for the BC in two of the five cases (-45% near the MWRA outfall and -48% in the deeper water from the Wilkinson Basin), and in both instances the $\Delta^{14}C$ strongly indicated the predominance of a fossil carbon source. We do not believe that measurement uncertainty (Table S3) or inaccuracy (e.g., fractionation during combustion processes; e.g., Czimeczka et al., 2002; Krull et al., 2003; Turekian et al., 1998) caused these isotopic source signatures (Table S3). However, the most common ^{13}C -depleted fossil fuel components (e.g., methane) do not contribute a large fraction of the energy emission in New England (ca. one thousandth of the regional total; Flores-Cervantes, 2008a). Hence, these carbon isotope signatures of the BC in these two samples remain unexplained.

3.6. BC mass balance in the GoM

To characterize the fate of BC emanating from the Northeast United States coastline, we calculated the various BC sources and sinks into and out of the GoM on an annual average basis (Fig. 1C). We believe this approach is appropriate since (a) atmospheric BC concentrations (airmap.nh.edu) and rainfall data (NOAA, 2002; Keim and Rock, 2001), show no distinct pattern in the New England area, and (b) information about annual variations in OC fluxes out of the water column into the sediments in the GoM (Charette et al., 2001), show that most of the OC export occurs during Spring and late Fall, while little or no OC export occurs in the summer and the winter. Therefore, we consider that our weighted annual BC flux-out-of-the-water-column-average based on our two sampling campaigns can be considered appropriate.

Atmospheric deposition (mainly wet) was the main BC input into the GoM. In contrast to previous reports in areas where erosive flooding events are important (Masiello and Druffel, 2001), rivers only contribute minor BC inputs to this coastal system, despite having elevated BC concentrations in slow-flowing urban systems like the Charles River (Table S2). The observed discrepancy between these two studies could simply be due to differences in river types between the two regions, but could also be due to methodological differences if charcoal-like BC was a major component of the isolated material in the Santa Clara River (Masiello and Druffel, 2001). The chief output of BC from the GoM was sedimentation, although there was significant water-borne transport offshore (i.e., Maine Surface Water and Maine Intermediate Water have higher concentrations than Scotian Shelf Water and Slope Water). Based on the BC reservoir size in our mass balance, and the estimated flux out of the surface water (i.e., $\tau = BC\text{ reservoir size}/BC\text{ export}$), the residence

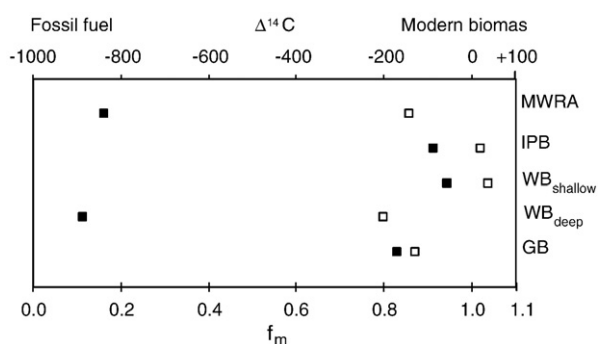


Fig. 3. $\Delta^{14}C$ and fraction modern (f_m) of BC and OC in the GoM. Open squares represent OC, and solid symbols represent BC. End members used for the calculations of fraction modern (f_m) were $\Delta^{14}C = -1000\%$ for fossil fuel combustion, and $\Delta^{14}C = 100\%$ for biomass combustion. April 2004 samples: Georges Bank shallow (GB); August 2004 samples: Inner Penobscot Bay shallow (IPB), Massachusetts Water Resources Authority shallow (MWRA) and Wilkinson Basin shallow (WB_{shallow}) and deep (WB_{deep}).

time of BC in the water column was about two months. This residence time is consistent with our observed changes in BC concentrations between April and August/September.

An imbalance in our inputs and outputs in the GoM mass balance suggests that either we are underestimating our BC sources, that we are not accounting for an important source, or that we might be overestimating the amount of BC due to methodological artifacts (such as charring of the POC). It is possible that atmospheric concentrations of BC in the central Gulf were higher than we estimated based on data from land measurements obtained with methods that differ from ours (Table 4). Non-local or intermittent pollution plumes may also be important sources to this area, as well as the transit of ships across the GoM. However, ocean-based measurements for this area are not readily available.

Using the estimated surface-ocean export fluxes from this study, the GoM sediments capture about 80% of the BC in that body of seawater. Extrapolating this view of BC cycling to a global scale suggests that annual BC deposition rates (1–10 g/m²·yr) into coastal areas (3.15 × 10⁶ km²; Sverdrup et al., 1946) between 16 and 275 Tg BC/yr can account for most of the estimated annually produced BC (4–270 Tg BC/yr; Hendricks et al., 2004; Kuhlbusch and Crutzen, 1995; Penner et al., 1993; Reddy and Boucher, 2004).

4. Summary

These BC data allowed an improved understanding of the impacts of BC suspended in coastal seawater. First, BC contributed, on average, 6% of the POC carbon suspended in the GoM, implying that about half of the chemically unidentifiable POC (Eglinton and Repeta, 2004) may simply be these combustion-derived particles. The recognized presence of this recalcitrant BC carbon may well explain why some POC is not recycled to CO₂ during its transport to depth and even within the sediment beds below. Hwang and Druffel (2003) previously reported that an important fraction of the unidentifiable POC in the Northeast Pacific could correspond to a lipid-like material found in the marine environment. However, they also pointed out that additional old and terrestrial sources were needed to explain the previously reported ¹³C NMR spectra (Hedges et al., 2001) and stable and radioisotope characteristics of the unidentifiable POC. Finally, the contributions of the fossil fuel-derived BC to POC can explain some of the ¹⁴C-depleted nature of the uncharacterized material previously reported in POC and sedimentary OC (Masiello and Druffel, 1998; Eglinton and Repeta, 2004); in contrast to the hypothesis that century- and millennia-scale transport processes are contributing weathered organic matter off the continents. This result suggests that efforts to control BC in the atmosphere over the Northeast USA must be concerned with biomass burning activities as well as fossil fuel uses.

Additionally, the BC concentrations imply these particles would substantially affect the speciation of high molecular weight pollutants like PAHs and polychlorinated dibenzodioxins (PCDD) in GoM seawater (Lohmann et al., 2005; Accardi-Dey and Gschwend, 2002). BC-sorption of these toxic substances limits their degradation as well as their toxic effects.

Recognizing the importance of BC in environments beyond the atmosphere strongly suggests that environmental scientists, engineers, and policy makers need to assess the presence and impacts of combustion processes in all environmental compartments (soils, lakes, oceans, coastal sediments).

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.marchem.2009.01.012.

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