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Fossil and contemporary aerosol particulate organic carbon in the eastern United States: Implications for deposition and inputs to watersheds

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[1] Atmospheric particulate matter samples were collected from mid-Atlantic and northeastern U.S. (Virginia and New York, respectively) sites to assess the fossil versus contemporary sources contributing to aerosol organic carbon (OC) and the implications for its deposition to watersheds. Mean particulate matter total OC (TOC) deposition rates (wet + dry deposition) were calculated to be 1.6 and 2.4 mg C m⁻² d⁻¹ for the Virginia and New York sites, respectively. Wet deposition of particulate TOC was determined to be the dominant depositional mode, accounting for >65% (Virginia) and >80% (New York) of total aerosol TOC deposition. Isotopic mass balances suggest that, on average, the deposited aerosol TOC consisted of 66% (Virginia) and 68% (New York) contemporary biomass-derived material. The balance was fossil-derived material (34% and 32% for Virginia and New York, respectively), indicating significant anthropogenic fossil fuel contributions to aerosol TOC. When considered within representative northeastern U.S. watershed OC budgets, aerosol TOC depositional flux was up to 10% of net soil OC accumulation rates, and 5–70% of the OC throughfall flux for forested regions. When scaled to the entire Hudson and York River watersheds, estimated aerosol TOC depositional fluxes ranged from 6.1 to 9.7 × 10¹⁰ g C yr⁻¹ and from 8.9 to 14 × 10⁹ g C yr⁻¹, respectively, and were similar in magnitude to the mean annual river OC export for these two systems (Hudson, 7.2 × 10¹⁰ g C yr⁻¹; York, 8.4 × 10⁹ g C yr⁻¹). These findings underscore the potential importance of both natural and fossil fuel-derived aerosol OC inputs to watersheds.

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1. Introduction

[2] Globally, biogenic (e.g., natural plant emissions, biomass burning) and anthropogenic (e.g., fossil fuel combustion, biomass burning) processes are estimated to emit 8–24 Tg yr⁻¹ of black carbon (BC) [Penner *et al.*, 1993; Bond *et al.*, 2004] to the atmosphere, as well as 30–150 Tg yr⁻¹ of nonblack particulate organic carbon (OC_{NBC}) [Koch, 2001; Bond *et al.*, 2004; de Gouw *et al.*, 2008; Hallquist *et al.*, 2009]. Much of this atmospheric total particulate OC (TOC = BC + OC_{NBC}) is subsequently deposited to terrestrial and aquatic environments where it may contribute to organic matter pools and support the energetic and carbon demands of these ecosystems. Studies conducted to date on the deposition of atmospheric TOC have focused on inputs to oceanic

environments [Duce and Duursma, 1977; Zafiriou *et al.*, 1985; Duce *et al.*, 1991; Willey *et al.*, 2000; Dachs *et al.*, 2005; Jurado *et al.*, 2008]; however, atmospheric TOC delivered via wet and dry depositional processes may also be quantitatively important to terrestrial watersheds. For example, annual wet deposition of OC (particulate + dissolved) to the Hubbard Brook Experimental Forest was estimated to be 1.4 g C m⁻² yr⁻¹, or 1.14 times the value of TOC exported by streams draining the basin [Likens *et al.*, 1983], and Velinsky *et al.* [1986] estimated total (wet (particulate + dissolved) + dry) atmospheric deposition of TOC (19.0 × 10¹¹ g C y⁻¹) to the Chesapeake Bay drainage basin to be four to five times the input of riverine TOC (4.1 × 10¹¹ g C y⁻¹) to the Bay. At the global scale, Willey *et al.* [2000] estimated that 70% of the total rain-water dissolved OC (DOC) flux (430 Tg C yr⁻¹) is delivered to continents, a value similar in magnitude to the 400–800 Tg TOC yr⁻¹ exported by rivers globally [Richey, 2004].

[3] Organic aerosol budgets have estimated fossil fuel sources to account for 13–41% of aerosol TOC globally [Lioussé *et al.*, 1996; Bond *et al.*, 2004; de Gouw *et al.*, 2008; Hallquist *et al.*, 2009] and 42% of aerosol TOC in the United States [de Gouw *et al.*, 2008]. The contribution of fossil fuel combustion products to aerosol TOC is expected to be higher in regions of greater industrial development and population

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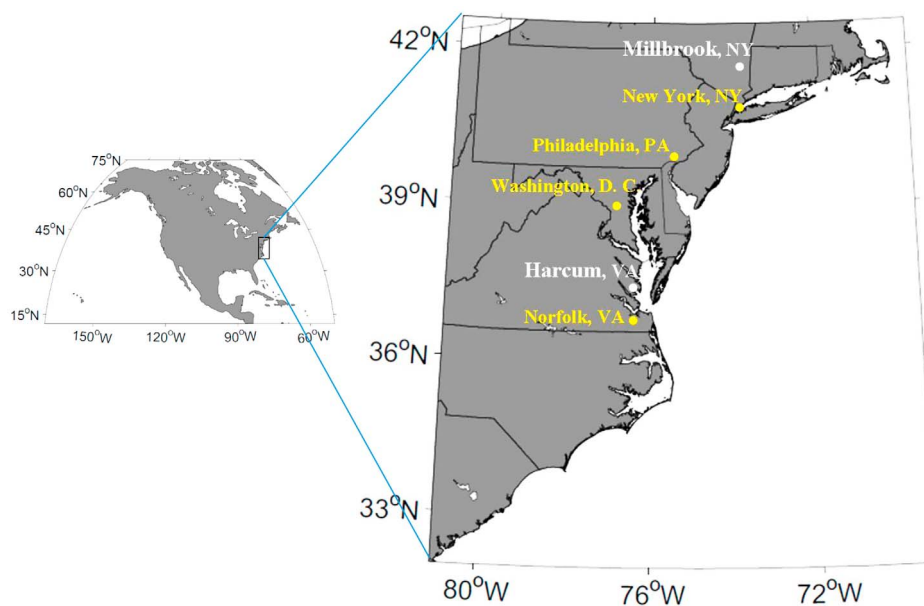


Figure 1. Map showing locations of the Millbrook, New York, and Harcum, Virginia, sites sampled during this study.

density such as the eastern United States [National Research Council, 2003; Gurney *et al.*, 2009]. Natural abundance radiocarbon (^{14}C) measurements of field-collected aerosols from the United States further reveal that fossil fuel combustion products can account for up to 80% of aerosol TOC in urban areas [e.g., Hildemann *et al.*, 1994; Klinedinst and Currie, 1999] and 14–26% of rainwater DOC [Raymond, 2005; Avery *et al.*, 2006]. While urban sites typically show higher fossil TOC contributions as compared to nearby rural or background sites [e.g., Zheng *et al.*, 2006; Schichtel *et al.*, 2008], fossil TOC has also been shown to account for up to 40% of aerosol TOC at rural sites [Tanner *et al.*, 2004; Zheng *et al.*, 2006; Ke *et al.*, 2007].

[4] Fossil fuel TOC emissions represent anthropogenic disturbances to atmospheric, watershed, and aquatic system TOC budgets and biogeochemical cycles. In addition, human alteration of terrestrial systems through deforestation, reforestation, and agriculture have also changed sources of biogenic OC to the atmosphere [Dickinson and Kennedy, 1992; Parungo *et al.*, 1994; Andreae and Merlet, 2001]. Knowledge of the quantities, sources and fates of aerosol TOC deposited to watersheds is therefore fundamental to understanding how human activities may have altered atmospheric inputs of TOC to both terrestrial and aquatic systems.

[5] The present study characterized the quantities, fossil versus contemporary contributions, and atmospheric depositional fluxes of particulate TOC to two watersheds on the Atlantic coast of the United States. The findings presented here provide new insights into the quantitative relevance of atmospheric inputs to watershed TOC budgets, and have implications for watersheds globally.

2. Methods

2.1. Study Sites

[6] Two locations in the eastern United States, the Cary Institute of Ecosystem Studies Environmental Monitoring

Station in Millbrook, New York (http://www.ecostudies.org/emp_purp.html; latitude: 41.7858, longitude: -73.7414), and the National Atmospheric Deposition Program (NADP) site (VA98) in Harcum, Virginia (<http://nadp.sws.uiuc.edu/sites/siteinfo.asp?net=NTN&id=VA98>; latitude: 37.5312, longitude: -76.4928), were chosen as representative background sites for particulate matter collection (Figure 1). Both sampling sites are located in rural environments at least 30 km from major industrial activities ensuring that air samples were not biased by proximity to fossil fuel-derived point sources. As a result, the particulate matter samples collected are assumed to represent conservative estimates of fossil fuel-derived inputs. The Millbrook site is located within the Hudson River watershed, while the Harcum site is situated adjacent to the York River watershed within the greater Chesapeake Bay watershed. Both watersheds are temperate, predominantly forested (Table S1 of the auxiliary material) regions along the Atlantic coast of the United States, a region of high population density and higher-than-average fossil fuel consumption [National Research Council, 2003; Gurney *et al.*, 2009].¹

2.2. Field Sampling

[7] Air samples were filtered at approximately $0.8\text{ m}^3\text{ min}^{-1}$ over 24 h periods during 2006–2007 using high-volume total suspended particulate (TSP) air samplers (Model GS2310, ThermoAndersen, Smyrna, Georgia). Total air volumes ranged between 850 and 1250 m^3 . At Millbrook, daily 24 h air samples were collected for five consecutive days in May, August, and December 2006, and March 2007, while Harcum air samples were collected over 24 h periods approximately twice each month between May 2006 and June 2007 (see Table S2 for sampling details).

¹Auxiliary materials are available in the HTML. doi:10.1029/2010GB003855.

Table 1. Mean Seasonal Particulate Matter TSP, OC, and BC_{soot} Concentrations for Samples Collected From Millbrook, New York, and Harcum, Virginia^a

	Spring 2006	Summer 2006	Fall 2006	Winter 2006–2007	Spring 2007	Summer 2007	Overall Mean
<i>Millbrook</i>							
Replicates	5	5	5	5	2	nc	22
TSP	20.8 (16.7–26.0)	18.4 (16.3–20.9)	16.2 (14.2–18.4)	14.4 (12.3–16.8)	50.1 (28.1–89.0)	nc	19.1 (17.1–21.2)
OC _{NBC}	4.71 (4.15–5.35)	3.43 (3.20–3.69)	1.59 (1.33–1.93)	1.63 (1.41–1.88)	11.8 (6.81–20.3)	nc	2.93 (2.52–3.41)
BC _{soot}	bd	0.123 (0.099–0.147)	0.109 (0.089–0.128)	0.180 (0.104–0.256)	bd*	nc	0.128 (0.107–0.149)
<i>Harcum</i>							
Replicates	5	5	7	5	7	2	31
TSP	34.0 (31.5–36.7)	32.1 (24.5–41.9)	22.0 (19.7–24.5)	20.4 (17.1–24.2)	26.0 (23.2–29.1)	37.9 (31.1–46.1)	26.6 (24.8–28.6)
OC _{NBC}	5.80 (5.07–6.65)	6.64 (5.16–8.55)	4.15 (3.78–4.55)	2.96 (2.62–3.35)	3.18 (2.73–3.70)	6.25 (5.38–7.23)	4.33 (3.98–4.70)
BC _{soot} ^b	0.323 (0.269–0.357)	0.322 (0.152–0.493)	0.212 (0.146–0.276)	0.228 (0.092–0.362)	0.265 (0.038–0.492)	bd*	0.244 (0.179–0.309)

^aSee text for information on how seasons were defined. Errors are expressed as 95% confidence intervals in parentheses directly below each value (lower 95% bound, upper 95% bound). Concentrations are $\mu\text{g m}^{-3}$ of air. Here “nc” denotes time period when aerosols were not collected at a given site, bd denotes below detection (see section 2 for details), and bd* denotes time periods when only one of two measurements for a given parameter was above the detection limits defined in section 2 making calculation of descriptive statistics inappropriate.

^bAt Harcum in Spring 2006 $n = 3$ for BC_{soot} reported mean values, and $n = 29$ for BC_{soot} reported mean values.

[8] Air was drawn through preashed (525°C for 3 h) and preweighed high-purity quartz microfiber filters (20.3 cm × 25.4 cm, 0.6 μm nominal pore size; Whatman type QM-A) for collection of time-integrated samples. Following collection, filters were transferred to preashed aluminum foil pouches. Filter blank samples were collected by briefly removing filters from their aluminum foil pouches in the field then placing them back in the foil pouches. Both the samples and filter blanks were stored in the dark in carefully cleaned airtight polycarbonate desiccators maintained at $\leq 10\%$ relative humidity at all times in both the field and the lab until sample analysis.

2.3. Bulk Aerosol Measurements

[9] Desiccated filters were weighed presampling and postsampling for determination of aerosol total suspended particulates (TSP). Samples and filter blanks were subsampled for TOC and soot black carbon (BC_{soot}) measurements by placing the filters on a preashed sheet of aluminum foil and removing replicate core plugs using a solvent-cleaned (hexane followed by acetone) 1.90 cm diameter stainless steel cork borer. For TOC measurements, aerosol particulate and blank filter plugs were dried overnight at 60°C, acidified with 1M HCl to remove inorganic carbonates and again dried overnight at 60°C. Triplicate acidified filter plugs were placed in 5 × 9 mm tin cups and combusted at 850°C in the presence of O₂. Concentrations of TOC were determined using a CE Elantech Flash EA 1112 elemental analyzer. Sample response areas were calibrated to a standard curve using a sulfanilamide standard. The average coefficient of variation for triplicate TOC measurements was 0.05. The mean TOC filter blank (3.31 ± 0.34 $\mu\text{g C}$ per filter plug, $n = 9$) accounted for an average of 12.4 ± 0.9% of the measured TOC and was subtracted from all sample TOC values. OC_{NBC} concentrations were calculated by subtracting BC_{soot} contributions from TOC values.

[10] BC_{soot} was quantified by combusting preacidified (1 M HCl) triplicate filter core plug subsamples (2 core plugs

for each replicate) in a muffle furnace at 375°C in the presence of high-purity air for 24 h (CTO-375 method) [Gustafsson *et al.*, 1997]. The carbon remaining on the filters after combustion was assumed to be BC_{soot} and measured using an elemental analyzer as described for aerosol particulate TOC above. Industrial forklift exhaust diesel particulate matter (National Institute of Standards and Technology SRM-2975) was used as a positive BC_{soot} standard, and its measured value agreed with published values (SRM 2975 BC_{soot} = 630 ± 9 mg gdw⁻¹, $n = 6$; this study) [Gustafsson *et al.*, 2001; Nguyen *et al.*, 2004; Elmquist *et al.*, 2006]. Filter blank BC_{soot} contributions averaged 3.76 ± 0.48 ($n = 9$) $\mu\text{g C}$ per replicate (2 filter plugs) and were subtracted from all sample values. BC_{soot} measurements below the upper 99% confidence interval (5.26 $\mu\text{g C}$) of the mean filter blank BC_{soot} contribution were considered below the method detection limit.

[11] The CTO-375 method [Gustafsson *et al.*, 1997, 2001] is thought to measure only soot and graphitic BC (BC_{soot}), the most recalcitrant components of BC, but to underestimate less refractory char BC contributions, resulting in conservatively low BC estimates [Masiello, 2004; Hammes *et al.*, 2007]. In a methodological comparison study [Hammes *et al.*, 2007], thermal-optical techniques typically used for measuring atmospheric elemental carbon (EC) were found to measure large contributions of BC in melanoidin, a negative control known to contain no BC. The thermal-optical techniques may thus be inappropriate for biogeochemical studies of BC such as the present one. The CTO-375 method is frequently used to measure BC in environments such as soils, sediments, and aquatic systems that are sinks for atmospheric BC [e.g., Schmidt *et al.*, 2001; Mitra *et al.*, 2002; Dickens *et al.*, 2004; Louchouart *et al.*, 2007], but only a few studies [e.g., Zencak *et al.*, 2007; Gustafsson *et al.*, 2009] have reported aerosol BC_{soot} concentrations using this technique. Nearly half of the samples in the present study contained levels of BC_{soot} below the detection limit, however, overall mean concentrations were similar in magnitude to values recently measured for

aerosols in south Asia [Gustafsson *et al.*, 2009] but greater than those measured in Sweden [Zencak *et al.*, 2007] (Table 1).

2.4. Isotopic Analyses

[12] For each site, a minimum of two samples from each season were selected for stable carbon ($\delta^{13}\text{C}$) and radiocarbon ($\Delta^{14}\text{C}$) isotopic analyses. TOC loadings from elemental analyzer results were used to determine the number of filter plugs required to yield $\geq 250 \mu\text{g C}$ upon combustion. Filter plugs were placed in preashed glass Petri dishes and exposed to fuming HCl for $>24 \text{ h}$ to remove carbonates then dried and oxidized by sealed tube combustion with CuO and elemental Cu metal at 850°C for 6 h in preashed 9 mm sealed quartz tubes [Sofer, 1980; Tanner *et al.*, 2004]. CO_2 produced from the oxidized samples was then purified cryogenically and isolated on a vacuum extraction line. The purified CO_2 was quantified using a calibrated Baratron absolute pressure gauge (MKS industries) and collected in 6 mm Pyrex break seal tubes. Standard organic compounds (oxalic acid II [OX-II] and acetanilide) having known isotopic compositions ($\Delta^{14}\text{C}_{\text{ox-II}} = 285\text{‰}$, $\delta^{13}\text{C}_{\text{ox-II}} = -17.8\text{‰}$, and $\Delta^{14}\text{C}_{\text{acetanilide}} = -1000\text{‰}$, $\delta^{13}\text{C}_{\text{acetanilide}} = -29.5\text{‰}$) were processed along with the samples to assess the accuracy and precision of the procedure as well as processing blanks.

[13] Purified CO_2 from sealed tube combustions was submitted to the University of Arizona NSF Accelerator Mass Spectrometry laboratory or the National Ocean Sciences Accelerator Mass Spectrometry facility (NOSAMS) for isotopic analysis. A subsample of the CO_2 was used for $\delta^{13}\text{C}$ analyses by isotope ratio mass spectrometry (IRMS) using an Optima IRMS at NOSAMS or a dual inlet Fisons Optima IRMS at the University of Arizona. Sample $\delta^{13}\text{C}$ values are reported in standard del notation as the per mil (parts per thousand or ‰) difference from the standard reference material (Peedee Belemnite). The average measurement error for $\delta^{13}\text{C}$ analyses performed at both NOSAMS and the University of Arizona was $\pm 0.1\text{‰}$. The remainder of the CO_2 was used for radiocarbon ($\Delta^{14}\text{C}$) analysis by AMS. $\Delta^{14}\text{C}$ is a measure of the per mil difference in the $^{14}\text{C}/^{12}\text{C}$ ratios of the sample and the absolute international standard (1890 wood). $\Delta^{14}\text{C}$ measurements were corrected for isotopic fractionation using measured sample $\delta^{13}\text{C}$ values as defined by Stuiver and Polach [1977].

[14] Filter blank carbon isotopic compositions were measured by distributing 76 filter blank core plugs among 6 quartz combustion tubes, processing these as described above, and combining the CO_2 from the combustion of the blank filters for a single $\delta^{13}\text{C}$ and $\Delta^{14}\text{C}$ analysis. Filter blanks contributed $1.34 \pm 0.15 \mu\text{g C}$ per plug and measured $\delta^{13}\text{C}$ and $\Delta^{14}\text{C}$ signatures of -33.4‰ and -799‰ , respectively. All sample isotopic values were corrected for filter blank contributions as

$$X_{\text{sample}} = (X_{\text{measured}} - (f_{\text{blank}} * X_{\text{blank}}))/f_{\text{sample}} \quad (1)$$

where X_{sample} represents the corrected $\delta^{13}\text{C}$ or $\Delta^{14}\text{C}$ value for aerosol TOC, X_{measured} is the $\delta^{13}\text{C}$ or $\Delta^{14}\text{C}$ value measured for the sample including filter blank contributions, X_{blank} is the $\delta^{13}\text{C}$ or $\Delta^{14}\text{C}$ value of the filter blank material, and f_{sample} and f_{blank} are the fraction of the carbon measured for $\delta^{13}\text{C}$ or $\Delta^{14}\text{C}$ analysis attributable to the sample and filter blank material, respectively. Mean f_{blank} for all isotopic analyses

was 0.04, and the highest f_{blank} value was 0.11. Propagated errors for blank-corrected $\Delta^{14}\text{C}$ measurements averaged $\pm 9\text{‰}$ and ranged from $\pm 4\text{‰}$ to $\pm 23\text{‰}$. Blank-corrected $\delta^{13}\text{C}$ measurements averaged $\pm 0.3\text{‰}$ and ranged from $\pm 0.1\text{‰}$ to $\pm 0.6\text{‰}$. $\Delta^{14}\text{C}$ and $\delta^{13}\text{C}$ analyses of OX-II and acetanilide standards agreed with known values and did not necessitate further correction of sample values.

[15] The major sources of aerosol particulate matter in the eastern United States are assumed to be contemporary biogenic and fossil fuel-derived material, given the extensive forested and agricultural land uses (combined $>80\%$ of total land use) in the watersheds studied (see Table S1), and the United States consumption of $>20\%$ of fossil fuel worldwide [U.S. Energy Information Administration, 2009]. Therefore, a two-source isotopic model was used to estimate contributions from fossil fuel sources ($\Delta^{14}\text{C} = -1000\text{‰}$) and biogenic contemporary sources ($\Delta^{14}\text{C} = 68\text{‰}$) following the approach of several previous studies [e.g., Lewis *et al.*, 2004; Zheng *et al.*, 2006; Schichtel *et al.*, 2008] (see Text S1 for further details).

2.5. Statistical Methods and Approaches to Data Analysis

[16] Mean TSP, OC_{NBC} , $\Delta^{14}\text{C}$, and $\delta^{13}\text{C}$ values were calculated for each site and season of collection with errors reported as one standard error of the mean. The Student's *t* test was used to examine between-site differences in overall mean values of aerosol TSP, OC_{NBC} , $\Delta^{14}\text{C}$, and $\delta^{13}\text{C}$. No between-season comparisons were made for either site due to the limited number of samples analyzed for each season; however, seasonal mean values were calculated and reported for each of the above parameters as a means of describing the data set. Many BC_{soot} concentrations (25 out of 53) were below the method detection limit. Because the true BC_{soot} concentrations of these samples are unknown values between zero and the calculated detection limit, mean seasonal BC_{soot} concentrations were calculated in Minitab using the non-parametric Kaplan-Meier method, which calculates descriptive statistics for data that includes values below detection limit [Helsel, 2005]. Differences in site mean BC_{soot} concentrations were determined to be statistically significant if 95% confidence intervals (CIs) generated by Minitab did not overlap.

3. Results and Discussion

3.1. Aerosol TSP, OC_{NBC} , and BC Concentrations

[17] Overall mean atmospheric TSP and particulate OC_{NBC} concentrations were significantly higher ($p < 0.005$, Student's *t* test using log-transformed data) at Harcum, Virginia (mean TSP = $26.6 \mu\text{g m}^{-3}$, $\text{OC}_{\text{NBC}} = 4.33 \mu\text{g C m}^{-3}$; $n = 31$) relative to Millbrook, New York (mean TSP = $19.1 \mu\text{g m}^{-3}$, $\text{OC}_{\text{NBC}} = 2.93 \mu\text{g C m}^{-3}$; $n = 22$; Table 1 and Figures 2a–2d) site. These findings are similar to other studies that measured elevated aerosol TSP and OC_{NBC} concentrations for sites in the mid-Atlantic compared to the northeastern United States [Malm *et al.*, 1994, 2004; Schichtel *et al.*, 2008]. OC_{NBC} concentrations measured at rural or background sites along the Atlantic coast of North America have ranged between 1 and $10 \mu\text{g C m}^{-3}$ (Table S3). The overall and seasonal mean OC_{NBC} concentrations measured here fall within this range (Table 1 and Figures 2c and 2d), with the exception of spring

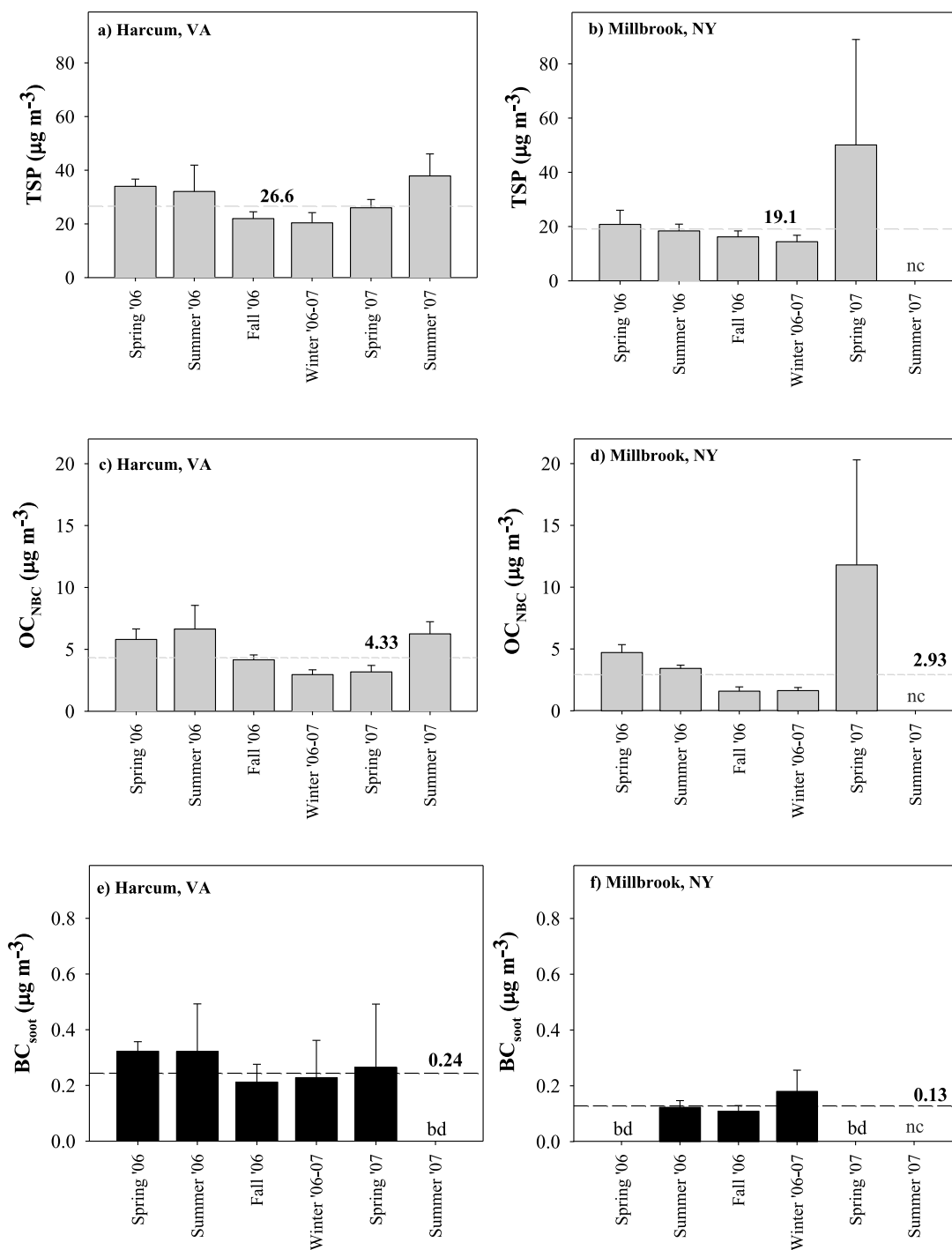


Figure 2. Particulate matter mean (a and b) TSP, (c and d) OC_{NBC}, and (e and f) BC_{soot} concentrations for air samples collected at Harcum, Virginia (Figures 2a, 2c, and 2e), and Millbrook, New York (Figures 2b, 2d and 2f), in 2006–2007. See text for details regarding how samples were differentiated by season. Vertical error bars represent upper bounds of standard errors of the mean. Overall mean values calculated for all samples at a given site (Harcum, $n = 31$; Millbrook, $n = 22$ for TSP and OC; Harcum, $n = 29$; Millbrook, $n = 22$ for BC_{soot}) are indicated in bold above dashed lines representing the value on the y axis. Here “nc” denotes time periods when aerosols were not collected at a given site, and “bd” denotes seasons in which BC_{soot} was below the detection limit of the method.

Table 2. Mean Seasonal $\Delta^{14}\text{C}$ and $\delta^{13}\text{C}$ Values for Aerosol Particulate Matter Samples From the Millbrook, New York, and Harcum, Virginia, Sites, Respectively^a

	Spring 2006	Summer 2006	Fall 2006	Winter 2006–2007	Spring 2007	Summer 2007	Mean All Seasons
<i>Millbrook</i>							
Replicates	3	2	3	3	2		13
$\Delta^{14}\text{C}$ (‰)	-172 ± 8	-266 ± 173	-233 ± 69	-539 ± 18	-45 ± 19	nc	-266 ± 53
F_m	0.833 ± 0.008	0.739 ± 0.174	0.772 ± 0.070	0.464 ± 0.018	0.961 ± 0.019	nc	0.739 ± 0.053
Fossil OC (%)	23 ± 1	32 ± 17	28 ± 6	57 ± 2	11 ± 2	nc	32 ± 3
Contemporary OC (%)	77 ± 1	68 ± 17	72 ± 6	43 ± 2	89 ± 2	nc	68 ± 3
$\delta^{13}\text{C}$ (‰)	-25.9 ± 0.02	-25.2 ± 0.2	-24.9 ± 0.2	-25.3 ± 0.3	-24.8 ± 0.1	nc	-25.2 ± 0.1
<i>Harcum</i>							
Replicates	2	2	3	3	3	2	15
$\Delta^{14}\text{C}$ (‰)	-225 ± 72	-209 ± 114	-411 ± 2	-503 ± 118	-224 ± 58	-62 ± 105	-294 ± 48
F_m	0.780 ± 0.073	0.797 ± 0.115	0.593 ± 0.001	0.500 ± 0.119	0.781 ± 0.058	0.944 ± 0.105	0.711 ± 0.048
Fossil OC (%)	28 ± 7	26 ± 11	45 ± 0.1	54 ± 11	28 ± 5	13 ± 10	34 ± 10
Contemporary OC (%)	72 ± 7	74 ± 11	55 ± 0.1	46 ± 11	72 ± 5	87 ± 10	66 ± 10
$\delta^{13}\text{C}$ (‰)	-24.9 ± 1.2	-21.4 ± 1.9	-25.0 ± 0.4	-25.3 ± 0.3	-25.0 ± 0.2	-24.5 ± 1.0	-24.5 ± 0.4

^aErrors are expressed as \pm one standard error of the mean value of n measurements. The n values for each season are listed in the first row for each site. Time periods when aerosols were not collected at the Millbrook site are denoted by "nc." F_m , fossil OC percentage, and contemporary OC percentage were calculated from $\Delta^{14}\text{C}$ values as described in the auxiliary material (Text S1).

2007 at Millbrook, due to one sample that captured high amounts of pollen resulting in elevated aerosol TSP and OC_{NBC} concentrations relative to all other sampling times (Figures 2a–2d).

[18] BC_{soot} concentrations ranged from below the detection limit on several sampling dates to $0.876 \mu\text{g m}^{-3}$ at Harcum in spring 2007 (Table 1 and Figures 2e and 2f). Comparison of 95% confidence intervals revealed Harcum to have higher overall mean BC_{soot} concentrations compared to Millbrook (Table 1). BC_{soot} values were below the detection limit for 14 of 22 samples from Millbrook and 11 of 31 Harcum samples (Table 1).

[19] Aerosols have an estimated tropospheric residence time on the order of one week [Warneck, 2000], and for this reason the aerosol composition in a given area is a mixture of materials emitted both locally and from more distant regions within an airshed. Air mass back trajectory analyses (Figure S1) for this study reveal that Millbrook samples were often associated with air masses from more northerly latitudes in Canada east of the Great Lakes. In contrast, samples collected in Harcum typically arose from air masses traversing more densely populated and industrialized areas such as the midwestern and eastern United States, although air mass trajectories from the southeastern United States were also observed for a number of Harcum samples (Figure S1). Previous studies in the northeastern United States have noted higher concentrations of particles and pollution-associated chemical components in air masses transported from midwestern and southwestern regions (i.e., south of the Great Lakes), compared to air masses arising from north and east of the Great Lakes [Kelly et al., 1984; Pierson et al., 1989; Miller et al., 1993; Lefer and Talbot, 2001]. Atmospheric emissions in the industrialized midwestern United States south of the Great Lakes, therefore, likely contribute to the higher aerosol TSP, OC_{NBC} , and BC_{soot} concentrations measured at the Harcum, Virginia, site (Table 1 and Figure 2).

[20] In addition to fossil fuel emissions, biogenic secondary organic aerosols (SOAs) formed from volatile organic compounds (VOCs) via chemical reactions in the atmosphere [e.g., Kanakidou et al., 2005, 2008; Hallquist et al., 2009] are also likely to contribute to the elevated TSP and OC con-

centrations at the Harcum, Virginia, site. SOAs are a significant component of aerosol OC_{NBC} having been estimated to account for more than half of aerosol organic matter in the United States [de Gouw et al., 2008]. Tree species composition, foliar density, ambient temperature, and average day length in the Harcum air mass source regions (south of the Great Lakes) result in conditions favorable for greater biogenic VOC emissions relative to those for Millbrook (the northeast United States and regions of Canada) [e.g., Guenther, 1997; Palmer et al., 2003; Lathière et al., 2005]. Higher emissions of biogenic VOCs within the Harcum, Virginia, airshed are predicted to result in higher yields of SOAs relative to the Millbrook, New York, airshed and represent another likely source of the disparity in aerosol OC concentrations between the two study sites.

3.2. Carbon Isotopic ($\delta^{13}\text{C}$, $\Delta^{14}\text{C}$) Source Apportionment of Aerosol TOC

[21] The majority of TOC $\delta^{13}\text{C}$ values from both sites ranged between -26‰ and -23‰ (Table 2). Terrestrial C_3 plant and fossil fuel sources have similar $\delta^{13}\text{C}$ values [see, e.g., Fry and Sherr, 1984; Schoell, 1984; Boutton, 1991; Hoefs, 2009] suggesting that the sampled TOC is primarily derived from these two sources. A July 2006 sample from Harcum, Virginia, was a notable exception with ^{13}C -enriched ($\delta^{13}\text{C} = -19.5\text{‰}$) TOC indicative of contributions from C_4 -photosynthesizing plants ($\delta^{13}\text{C} = \sim -15\text{‰}$ to -13‰) [Fry and Sherr, 1984; Boutton, 1991; Hoefs, 2009] or marine autotrophic production ($\delta^{13}\text{C} = \sim -21\text{‰}$ to -18‰) [e.g., Fry and Sherr, 1984; Boutton, 1991; Hoefs, 2009]. Overall, however, there were no significant differences (Student's t test, $p > 0.05$) in mean $\delta^{13}\text{C}$ values between the two sites (Harcum, $\delta^{13}\text{C} = -24.5\text{‰}$; $n = 15$; Millbrook, $\delta^{13}\text{C} = -25.2\text{‰}$; $n = 13$; Table 2).

[22] Given the overlap in fossil fuel and contemporary C_3 biomass $\delta^{13}\text{C}$ signatures, stable carbon isotopic signatures are by themselves ineffective for distinguishing between these two apparently dominant sources to aerosol TOC. The greater dynamic range in $\Delta^{14}\text{C}$ signatures, however, can help resolve this ambiguity. TOC $\Delta^{14}\text{C}$ values ranged from -643‰ in January 2007 to 42‰ in June 2007 at Harcum (Figure 3a).

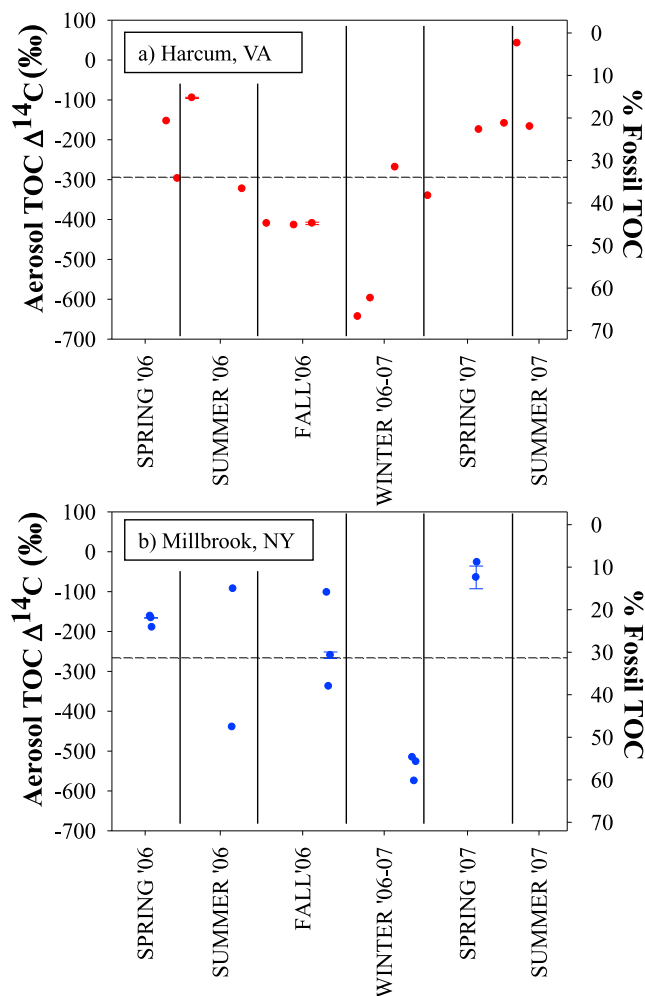


Figure 3. Particulate matter TOC $\Delta^{14}\text{C}$ (left y axis) and corresponding percent contributions from fossil TOC (right y axis) for selected air samples collected in (a) Harcum, Virginia, and (b) Millbrook, New York, in 2006–2007. Each data point represents a single 24 h sample collection. Vertical bars represent standard errors for duplicate analyses of the same sample. Horizontal dashed lines represent overall mean $\Delta^{14}\text{C}$ and percent fossil TOC values (Harcum, $n = 15$; Millbrook, $n = 13$). See text for details regarding how samples were differentiated by season. Calculation of percent fossil TOC is explained in detail in the auxiliary material (Text S1).

At Millbrook, the lowest and highest $\Delta^{14}\text{C}$ values were observed in winter (-574‰) and spring (-27‰) of 2007, respectively (Figure 3b), and reflect significant short-term variability. There was no significant difference in overall mean $\Delta^{14}\text{C}$ values between the two study sites (Student's t test; $p > 0.05$).

[23] For reasons detailed in the auxiliary material (Text S1), soil organic carbon having ages intermediate to modern contemporary biomass and fossil carbon, is assumed to be a negligible contributor to aerosol TOC on the east coast of North America, and a two-source model can therefore be used to apportion aerosol TOC into fossil fuel and contemporary sources. In general, more than 30% of particulate TOC was fossil fuel derived, but relative fossil fuel contribu-

tions varied widely at both study sites throughout the year, ranging from just over 10% in spring and summer to 50% or more during the winter months (Table 2). Despite this large range in relative contributions, fossil TOC concentrations remained relatively constant at both sites, varying by $< 2 \mu\text{g C m}^{-3}$ (Harcum, $0.79\text{--}2.09 \mu\text{g C m}^{-3}$; Millbrook, $0.49\text{--}1.65 \mu\text{g C m}^{-3}$; Figures 4a and 4b). In contrast, contemporary TOC concentrations fluctuated by up to $10 \mu\text{g C m}^{-3}$ seasonally (Harcum, $1.46\text{--}5.46 \mu\text{g C m}^{-3}$; Millbrook, $0.79\text{--}10.5 \mu\text{g C m}^{-3}$; Figures 4a and 4b). Thus, it is the amount of contemporary TOC associated with the aerosol particles that explains both the variability in overall TOC concentrations and the correspondingly high range in relative contributions from fossil fuel sources (% fossil) at the two study sites.

[24] Radiocarbon-based findings from previous studies have apportioned as much as 80% of aerosol TOC at urban sites to fossil sources [Hildemann *et al.*, 1994; Klinedinst and Currie, 1999; Lemire *et al.*, 2002; Schichtel *et al.*, 2008]. Rural and background sites typically show fossil TOC sources to be less than 30% [Bench, 2004; Zheng *et al.*, 2006;

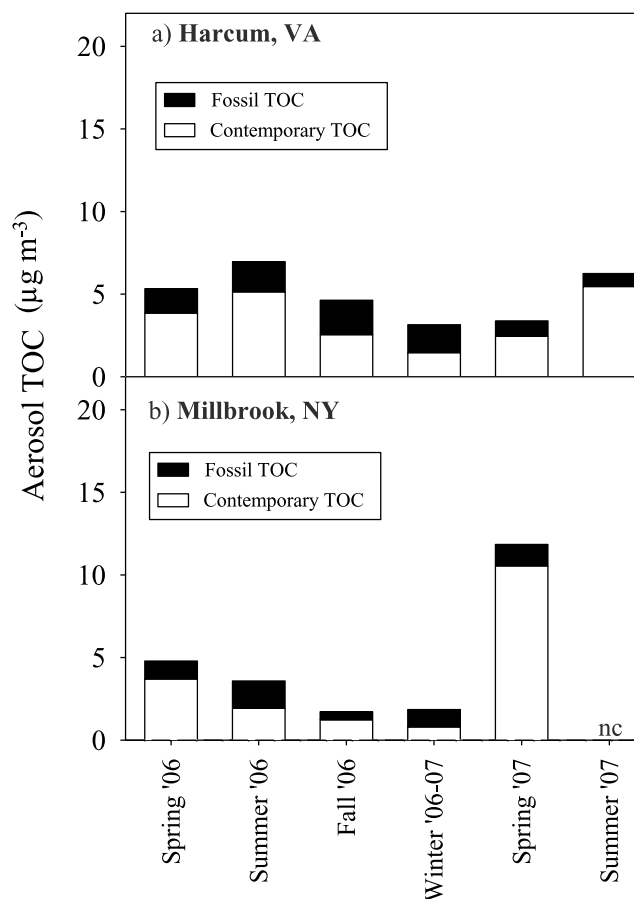


Figure 4. Mean seasonal particulate matter TOC concentrations for air samples collected at (a) Harcum, Virginia, and (b) Millbrook, New York, in 2006–2007, partitioned into fossil and contemporary TOC contributions. See text for details regarding how fossil fuel and contemporary TOC contributions and wet and dry depositions were determined. See Table S1 for how samples were differentiated by season. Here “nc” denotes time periods when aerosols were not collected at a given site.

Ke et al., 2007; Ding et al., 2008; Schichtel et al., 2008]. Nonetheless, fossil fuel-derived TOC contributions on the order of 40% are often observed for individual sampling dates at rural and background sites (Table 2 and Figures 3a and 3b) [Tanner et al., 2004; Zheng et al., 2006; Ke et al., 2007], demonstrating the ubiquity of fossil-derived aerosol sources in continental air masses and their potential importance in regional and even continent-scale biogeochemical budgets and cycles.

3.3. Particulate Matter TOC Deposition Fluxes

3.3.1. Annual Deposition Estimates

[25] Aerosols can be scavenged by rain, fog, or snow and wet deposited to watersheds and aquatic systems [e.g., Bidleman, 1988; Jacobson et al., 2000], or they can settle gravitationally and via impaction on terrestrial and aquatic surfaces (dry deposition) [Giorgi, 1986; Bidleman, 1988]. The relative magnitudes of wet and dry deposition are dependent in part on the magnitude, frequency, and forms of precipitation within the region of interest [Baumgardner et al., 2002; Peters et al., 2002].

[26] To calculate dry deposition fluxes (D_{dry}), aerosol TOC concentrations ([TOC]; $\mu\text{g m}^{-3}$) were multiplied by a deposition velocity (V_d , m s^{-1}) as

$$D_{\text{dry}} = [\text{TOC}] * V_d \quad (2)$$

where V_d is dependent on the depositional surface [Giorgi, 1986; Bidleman, 1988; Fowler et al., 2009], and therefore, land cover-specific V_d values were used. For forested regions, which represent 61% and 73% of land cover in the York River, Virginia, and Hudson River, New York, watersheds, respectively (Table S1), a V_d of $5.0 \times 10^{-3} \text{ m s}^{-1}$ as measured for particles (0.1–2.0 μm) in a forest canopy [Ould-Dada, 2002] was employed. For agricultural land surfaces, representing 21% and 18% of total land cover in the York and Hudson River watersheds, respectively (Table S1), a V_d of $1.5 \times 10^{-3} \text{ m s}^{-1}$ [Watterson and Nicholson, 1996; Utiyama et al., 2001] was used. Last, because the remaining urban, wetland, and aquatic land covers have less depositional surface area relative to forested environments, they were assumed to have V_d values similar to that for agricultural land cover ($1.5 \times 10^{-3} \text{ m s}^{-1}$). Overall mean [TOC] values for each site (Table 1) were used in equation (2), and upper and lower bound 95% confidence intervals for [TOC] estimates from Table 1 were used to establish a range of D_{dry} .

[27] Wet deposition (D_{wet}) of particulate TOC may be estimated using TOC concentrations ([TOC]; $\mu\text{g m}^{-3}$), a particle washout ratio (W_p ; dimensionless), and the rate of precipitation (p_o ; m yr^{-1}) as follows:

$$D_{\text{wet}} = [\text{TOC}] * W_p * p_o \quad (3)$$

where W_p is a variable parameter dependent on the nature of the aerosol particles and precipitation [Mackay et al., 1986; Dickhut and Gustafson, 1995; Bidleman, 1988; Wania et al., 1999; Lei and Wania, 2004; Jurado et al., 2005]. A constant W_p value of 2×10^5 was used to calculate rainfall D_{wet} . This value is within the range of W_p values suggested by Bidleman [1988] and has been applied in previous studies estimating D_{wet} for organic compounds [Mackay et al., 1986; Jurado et al., 2008]. Snowflakes, due to their larger size and sur-

face area, have been shown to scavenge aerosols far more efficiently than raindrops [Franz and Eisenreich, 1998; Wania et al., 1999; Lei and Wania, 2004]. Given the significant winter snowfall in New York (Table S4), snow-scavenged D_{wet} of fossil and contemporary TOC was calculated for the Millbrook site using a W_p of 60×10^5 [Wania et al., 1999]. Mean annual rain and snowfall data collected at each site (Table S4) and overall mean [TOC] values (Table 1) were used as p_o and [TOC] in equation (3), respectively. D_{wet} was calculated for three scenarios: (1) mean annual rainfall, (2) a dry year, and (3) a wet year. The dry year and wet year were defined by the lowest and highest rainfall amounts, respectively, measured at each site over the period used for the analysis (2000–2009 for Millbrook, 2005–2008 for Harcum; Table S4). Upper and lower bound 95% confidence interval [TOC] estimates from Table 1 were used to establish a range of D_{wet} for each calculation.

[28] While rainfall amounts [Hsu and Wallace, 1976] and aerosol OC concentrations [e.g., Malm et al., 2007] vary throughout the year, estimations of seasonal fluctuations in D_{total} are not justified here due to the limited TOC data available for each season. Similarly, the limited TOC data captures only a portion of the annual cycle presenting a potential source of error in our deposition estimates, however, our annual mean TOC concentration estimates are similar to previously published data along the east coast of the United States (Table S3), supporting their use for purposes of the order of magnitude comparisons below. Annual atmospheric deposition fluxes of particulate TOC were calculated using equations (2) and (3) and multiplying by appropriate time constants (Table 3). For the mean annual rainfall scenario, estimated annual D_{total} fluxes were similar at the two study sites with Millbrook receiving a slightly higher flux (1.45–1.75 $\text{g C m}^{-2} \text{ yr}^{-1}$ and 2.03–2.74 $\text{g C m}^{-2} \text{ yr}^{-1}$ for Harcum, Virginia, and Millbrook, New York, respectively; Table 3). Particulate TOC D_{dry} was similar for Harcum (0.48–0.57 $\text{g C m}^{-2} \text{ yr}^{-1}$; Table 3) and Millbrook (0.34–0.46 $\text{g C m}^{-2} \text{ yr}^{-1}$; Table 3), indicating that the greater D_{total} flux at Millbrook was due to a D_{wet} value (1.69–2.29 $\text{g C m}^{-2} \text{ yr}^{-1}$; Table 3) nearly double that of the one used at Harcum (0.98–1.18 $\text{g C m}^{-2} \text{ yr}^{-1}$; Table 3). The predominance of D_{wet} as a TOC delivery mechanism at Millbrook in particular is a result of the disproportionately efficient scavenging of aerosols by snow during winter. In a typical year, snow is a negligible fraction of precipitation at Harcum, Virginia, resulting in considerably lower mean annual D_{wet} (Table 3) than at Millbrook.

[29] D_{wet} was the dominant mode of deposition at both sites under the mean annual rainfall scenario, representing more than 65% and 80% of D_{total} at Harcum and Millbrook, respectively (Table 3). As a result of the predominance of D_{wet} , variability due to rainfall was explored by replacing the mean annual rainfall with the lowest (dry year: Millbrook, 0.80 m; Harcum, 0.98 m) and highest (wet year: Millbrook, 1.38 m; Harcum, 1.40 m) recorded annual rainfall at each site for the years considered in this analysis (Table 3). Under the dry year scenario, D_{wet} remained the dominant mode of deposition at each site (>60% and >80% of D_{total} at Harcum and Millbrook, respectively; Table 3) and decreased D_{total} by <0.25 $\text{g C m}^{-2} \text{ yr}^{-1}$ (or ~10%) at each site (Table 3). Similarly, D_{total} increased by <0.25 $\text{g C m}^{-2} \text{ yr}^{-1}$ at each site under the wet year scenario (Table 3).

Table 3. Estimated Mean Annual Wet, Dry, and Total Deposition Fluxes of Aerosol Particulate TOC at Millbrook, New York, and Harcum, Virginia, for Mean and Extreme Rainfall Conditions Using Mean TOC Concentrations of Samples Collected During 2006–2007^a

Deposition Scenarios	Dry Deposition (D_{dry})	Wet Deposition (D_{wet})	Total Deposition (D_{total})
<i>Millbrook^b</i>			
Best estimate	0.39 (0.34–0.46)	1.97 (1.69–2.29)	2.36 (2.03–2.75)
Dry year ^d	0.39 (0.34–0.46)	1.73 (1.49–2.02)	2.13 (1.83–2.48)
Wet year ^d	0.39 (0.34–0.46)	2.09 (1.80–2.44)	2.48 (2.13–2.89)
Low W_p	0.39 (0.34–0.46)	0.20 (0.17–0.23)	0.59 (0.51–0.68)
High W_p	0.39 (0.34–0.46)	19.7 (16.9–22.9)	20.1 (17.3–23.4)
Low V_d	0.039 (0.034–0.046)	1.97 (1.69–2.29)	2.01 (1.73–2.34)
High V_d	3.91 (3.36–4.55)	1.97 (1.69–2.29)	5.88 (5.06–6.84)
<i>Harcum^c</i>			
Best estimate	0.52 (0.48–0.57)	1.08 (0.98–1.18)	1.60 (1.46–1.76)
Dry year	0.52 (0.48–0.57)	0.90 (0.82–0.98)	1.42 (1.29–1.56)
Wet year	0.52 (0.48–0.57)	1.28 (1.16–1.40)	1.80 (1.64–1.98)
Low W_p	0.05 (0.05–0.06)	0.11 (0.10–0.12)	0.63 (0.58–0.69)
High W_p	0.52 (0.48–0.57)	10.8 (9.8–11.8)	11.3 (10.3–12.4)
Low V_d	0.052 (0.048–0.057)	1.08 (0.98–1.18)	1.13 (1.03–1.24)
High V_d	5.24 (4.77–5.74)	1.08 (0.98–1.18)	6.32 (5.75–6.92)

^aAll values are reported in $\text{g C m}^{-2} \text{yr}^{-1}$. See text for calculation details. Deposition ranges are listed in parentheses and were calculated using the range of mean TOC ($\text{OC}_{\text{NBC}} + \text{BC}_{\text{soot}}$) concentrations listed in Table 1.

^bMillbrook rainfall data are for the most recent available 10 year period (2000–2009).

^cHarcum rainfall data are for the period 2005–2008, the only data on record.

^dThe dry and wet years represent lowest (Millbrook, 80 cm; Harcum, 98 cm) and highest (Millbrook, 138 cm; Harcum, 140 cm) annual rainfall amounts at each site over the years included in the analysis.

[30] Harcum annual D_{wet} ($0.98\text{--}1.18 \text{ g C m}^{-2} \text{yr}^{-1}$), D_{dry} ($0.48\text{--}0.57 \text{ g C m}^{-2} \text{yr}^{-1}$), and D_{total} ($1.45\text{--}1.75 \text{ g C m}^{-2} \text{yr}^{-1}$) values from this study were lower than those calculated by *Velinsky et al.* [1986] for four sites within the lower Chesapeake Bay watershed in 1981 (mean $D_{\text{wet}} = 5.70 \text{ g C m}^{-2} \text{yr}^{-1}$, mean $D_{\text{dry}} = 5.60 \text{ g C m}^{-2} \text{yr}^{-1}$, mean $D_{\text{total}} = 11.3 \text{ g C m}^{-2} \text{yr}^{-1}$). The lower deposition fluxes calculated for Harcum in 2006–2007 are consistent with other studies which demonstrated declines in the emissions of both inorganic [*Husain et al.*, 2004] and carbonaceous [*Husain et al.*, 2008] particulate matter in the northeastern United States between the 1970s and early 2000s, likely resulting from passage of amendments to the U.S. Clean Air Act in 1990 [e.g., *Streets et al.*, 2006] aimed at curbing levels of ozone, carbon monoxide, and particulate matter in U.S. cities. *Husain et al.* [2004, 2008] attributed these declines specifically to decreases in coal combustion and improvements in diesel combustion efficiency. However, a decline in aerosol TOC deposition was not observed for our northeastern site relative to other published reports. In 1976–77, *Likens et al.* [1983] measured annual D_{wet} to be $1.4\text{--}2.4 \text{ g C m}^{-2} \text{yr}^{-1}$ at two sites in the northeastern United States near Millbrook, New York. The estimated mean annual D_{wet} in the present study ($1.69\text{--}2.29 \text{ g C m}^{-2} \text{yr}^{-1}$) falls within this range. It is therefore unclear whether the lower deposition estimates calculated in the present study for the Harcum site represent differences in methodologies, natural temporal variability, or true long-term decreases in aerosol TOC.

[31] The choices of W_p and V_d are also acknowledged to affect deposition estimates. W_p values calculated for individual compounds, for example, have been shown to vary over several orders of magnitude, with the majority of values ranging between 10^4 and 10^6 [*Jurado et al.*, 2005, and references therein]. V_d values ranging over orders of magnitude from 10^{-4} to 10^{-2} m s^{-1} [*Fowler et al.*, 2009] have similarly been observed. The W_p and V_d values used in our best estimate deposition calculations are justifiable for the

reasons described above. However, to demonstrate the effects due to the choices of W_p and V_d deposition estimates were also made for cases in which W_p and V_d values were increased and decreased by an order of magnitude (Table 3). Because of the greater contribution of D_{wet} compared to D_{dry} ($D_{\text{wet}} > 65\%$ and $> 80\%$ for Harcum and Millbrook, respectively) on D_{total} , D_{total} was more sensitive to the order of magnitude changes in W_p than V_d (Table 3). When V_d is altered by ± 10 -fold, D_{total} ranged from 1.13 to $6.32 \text{ g C m}^{-2} \text{yr}^{-1}$ at Harcum and from 2.01 to $5.88 \text{ g C m}^{-2} \text{yr}^{-1}$ at Millbrook (Table 3), remaining within the range of values previously measured [*Likens et al.*, 1983; *Velinsky et al.*, 1986]. Altering W_p by ± 10 -fold produced D_{total} values of $0.63\text{--}11.3 \text{ g C m}^{-2} \text{yr}^{-1}$ and $0.59\text{--}20.1 \text{ g C m}^{-2} \text{yr}^{-1}$ at Harcum and Millbrook, respectively (Table 3), such that the low estimates of D_{total} are more than threefold lower than previously measured values [*Likens et al.*, 1983; *Velinsky et al.*, 1986]. Thus, it is unlikely that significantly lower values of W_p are appropriate for modeling wet deposition scavenging of aerosol TOC, and the values used in the present study may be conservative. For simplicity, the remainder of the discussion will refer to our best estimate deposition calculations only unless otherwise specified.

3.3.2. Watershed Implications

[32] *Raymond* [2005] noted the potential significance of atmospherically derived fossil TOC inputs to watershed C budgets by comparing an estimated rainwater flux of $0.5 \text{ g fossil DOC m}^{-2} \text{yr}^{-1}$ to terrestrial systems in the northeastern United States to an estimated watershed flux of $0.22 \text{ g fossil C m}^{-2}$ exported to northeast rivers annually [*Raymond et al.*, 2004]. Fossil contributions to D_{wet} can be estimated by multiplying D_{wet} estimates by the overall mean values for the % fossil OC listed in Table 1. The estimated fossil TOC deposition due to scavenging of aerosols alone ($0.54\text{--}0.73 \text{ g C m}^{-2} \text{yr}^{-1}$; Table 3) at the Millbrook site in the present study was similar to that estimated by *Raymond* [2005] for both aerosol and gas phase scavenged TOC. Thus, if gas phase

Table 4. Representative Watershed OC Fluxes as Measured in Studies of Forested Areas in North Carolina, Virginia, Massachusetts, and New Hampshire and Scaled to the York and Hudson River Watershed Areas

	Literature Range (kg C ha ⁻¹ yr ⁻¹)	York River Watershed (g C yr ⁻¹)	Hudson River Watershed (g C yr ⁻¹)
Throughfall ^a	47–240	3.2×10^{10} – 1.7×10^{11}	1.6 – 8.0×10^{11}
Litterfall ^b	2110–7440	1.5 – 5.1×10^{12}	7.1×10^{12} – 2.5×10^{13}
Net biomass accumulation ^c	1000–8050	6.9×10^{11} – 5.6×10^{12}	3.3×10^{12} – 2.7×10^{13}
Soil OC accumulation ^d	200–370	1.4 – 2.5×10^{11}	6.7×10^{11} – 1.2×10^{12}
Aerosol particulate matter TOC deposition ^e	—	1.1×10^{10} (8.9×10^9 – 1.4×10^{10})	7.9×10^{10} (6.1 – 9.7×10^{10})

^aThe throughfall flux measures the C flux in rainwater that drips down through the tree canopy. Literature values are derived from *Gosz et al.* [1976], *McDowell and Likens* [1988], *Christophersen et al.* [1994], and *Schlesinger and Lichter* [2001].

^bThe litterfall flux measures the C flux from plant matter that has fallen to the soil. Literature values are derived from *Gosz et al.* [1976], *Christophersen et al.* [1994], *Nadelhoffer and Raich* [1992], and references therein, and *Schlesinger and Lichter* [2001].

^cThe net biomass accumulation flux is a measure of C accumulation in biomass. Literature values are derived from *Christophersen et al.* [1994], *Nadelhoffer and Raich* [1992], and references therein, and *Barford et al.* [2001].

^dThe soil OC accumulation flux is a measure of the increase in the soil OC pool. Literature values are derived from *Christophersen et al.* [1994], *Barford et al.* [2001], and *Schlesinger and Lichter* [2001].

^eNumbers in parentheses represent the range of values for aerosol particulate matter TOC deposition from the present study. These numbers represent the lower and upper bound estimates for the extreme dry and wet year cases described in Table 2, respectively.

contributions to D_{wet} were included, our fossil TOC D_{wet} estimates would be even larger than those of *Raymond* [2005]. Moreover, inclusion of aerosol D_{dry} increases the atmospheric fossil TOC inputs even more (0.11 – 0.15 g C m⁻² yr⁻¹ and 0.16 – 0.20 g C m⁻² yr⁻¹ for Millbrook and Harcum, respectively) and further emphasizes the potential importance of atmospheric fossil TOC sources to watershed carbon budgets (Table 3).

[33] Aerosol measurements from rural background areas may be extrapolated to provide conservative regional estimates of atmospheric deposition of TOC to watersheds. The atmospheric deposition fluxes of fossil and contemporary TOC from Harcum and Millbrook are assumed to be representative of deposition to the York River, Virginia, and Hudson River, New York, watersheds, respectively. Comprehensive watershed carbon budgets for these systems are not available so data for several important watershed OC fluxes measured at forested sites in North Carolina, Virginia, Massachusetts, and New Hampshire were compiled to represent the range of values present in east coast forests. These fluxes were scaled to the areas of the Hudson (~33,500 km²) and York (~6900 km²) river watersheds for comparison to the aerosol TOC fluxes calculated in this study (Table 4). For both the York and Hudson River watersheds, atmospheric deposition of particulate TOC (Hudson $D_{\text{total}} = 6.1$ – 9.7×10^{10} g C yr⁻¹, York $D_{\text{total}} = 8.9$ – 14×10^9 g C yr⁻¹; Table 4) is two orders of magnitude lower than both biomass litterfall (7.1 – 25×10^{12} g C yr⁻¹ and 1.5 – 5.1×10^{12} g C yr⁻¹ for the Hudson and York, respectively; Table 4) and net biomass accumulation (3.3 – 27×10^{12} g C yr⁻¹ and 6.9 – 56×10^{11} g C yr⁻¹ for the Hudson and York, respectively; Table 4). However, aerosol TOC fluxes are ~5–70% the size of estimated OC throughfall fluxes (1.6 – 8.0×10^{11} g C yr⁻¹ for the Hudson watershed and 3.2 – 17×10^{10} g C yr⁻¹ for the York watershed; Table 4), and an order of magnitude smaller than soil OC accumulation (6.7 – 12×10^{11} g C yr⁻¹ for the Hudson watershed and 1.4 – 2.5×10^{11} g C yr⁻¹ for the York watershed; Table 4).

[34] The postdepositional reactivity of aerosol TOC in soils is unknown, therefore, it is not possible to compare the net accumulation of aerosol TOC in surface environments (e.g., plant surfaces, soils, etc.) to soil OC accumulation. However, if aerosol TOC is demonstrated to be both immobile

and refractory, it may account for as much as 10% of York and Hudson River watershed soil OC accumulation annually. In contrast, if aerosol TOC or its components are mobile following deposition, it may be transported through watersheds to aquatic systems. The annual flux of aerosol particulate TOC (D_{total}) to the entire Hudson River watershed (6.1 – 9.7×10^{10} g C yr⁻¹; Figure 5) is approximately equivalent to TOC export from the Hudson River (7.2×10^{10} g C yr⁻¹; Figure 5). In the York River watershed, annual TOC D_{total} (8.9 – 14×10^9 g C yr⁻¹; Figure 5) is larger than the riverine TOC flux (8.4×10^9 g C yr⁻¹; Figure 5) exported from the York River. On this basis it is evident that aerosol particulate TOC deposition is a potentially important flux in watersheds and their associated riverine systems. In fact, fossil TOC alone contributed 3.0 – 4.8×10^9 g C yr⁻¹ and 2.0 – 3.1×10^{10}

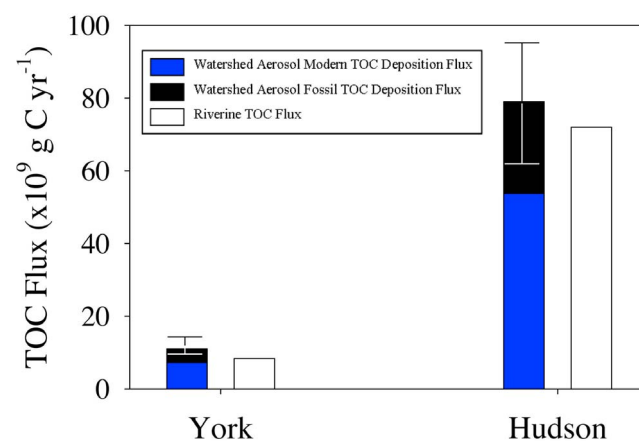


Figure 5. Mean annual particulate matter TOC deposition fluxes to the York (watershed area is 6,900 km²) River and Hudson (watershed area is 33,500 km²) River watersheds in Virginia and New York, respectively, partitioned into modern and fossil-derived portions of total deposition plotted along with riverine TOC fluxes from the York and Hudson rivers. Error bars represent the range of values for particulate TOC deposition. These numbers represent the lower and upper bound estimates for the extreme dry and wet year cases described in Table 2, respectively.

g C yr⁻¹ to the aerosol deposition fluxes of TOC to the York and Hudson River watersheds, respectively. These values represent considerable portions of the river TOC export fluxes (~36–57% for the York, ~28–43% for the Hudson; Figure 5), demonstrating that anthropogenic fossil TOC inputs can be a significant input to these systems.

[35] While it is unlikely that all aerosol TOC is transported completely through watersheds it is noteworthy that the majority of aerosol particles are extremely small in size (<10 μm [Warneck, 2000]) and may therefore be transported considerable distances in suspended form in surface and groundwaters. Additional studies on aerosols collected in this study found that an average of 20% of the TOC was water soluble (<0.7 μm) and desorbed within minutes [Wozniak, 2009]. If 100% of water-soluble TOC associated with aerosol particulate matter, or 1.2–1.9 × 10¹⁰ g C yr⁻¹ and 1.8–2.8 × 10⁹ g C yr⁻¹ for the Hudson and York River watersheds, respectively, and 0% of water-insoluble TOC is assumed to be transported along with surface and groundwaters through watersheds to rivers, aerosols are estimated to contribute ~17–26% and ~21–33% of the TOC exported annually by the Hudson and York rivers, respectively. Aerosol particulate matter TOC inputs to rivers may be even higher here and in other watershed-river systems across the globe because some component of water-insoluble TOC is likely to reach river systems and water-soluble TOC is often a much larger component of TOC (up to 75%) [e.g., Zappoli et al., 1999; Yang et al., 2004] than that reported in the present study. Therefore, inputs of aerosol particulate OC to rivers may in general be correspondingly higher.

4. Summary and Conclusions

[36] Findings from the current study demonstrate the potential importance of aerosol particulate TOC deposition from both fossil and contemporary sources to watershed carbon budgets. Total (wet + dry) area-normalized particulate TOC atmospheric deposition estimates were similar for the two eastern U.S. sites studied. When compared to representative OC fluxes for east coast U.S. forested watersheds, atmospheric deposition of particulate TOC is two orders of magnitude smaller than OC litterfall and biomass accumulation fluxes but is ~5–70% the size of OC throughfall and an order of magnitude smaller than soil OC accumulation. Scaled to the area of the adjacent watershed (i.e., for the Millbrook site, the Hudson River watershed; for the Harcum site, the York River watershed), aerosol TOC depositional fluxes (York River watershed, 8.9–14 × 10⁹ g C yr⁻¹; Hudson River watershed, 6.1–9.7 × 10¹⁰ g C yr⁻¹) are of a magnitude similar to or greater than the OC export for the corresponding rivers (York River, 8.4 × 10⁹ g C yr⁻¹; Hudson River, 7.2 × 10¹⁰ g C yr⁻¹).

[37] Radiocarbon measurements provide a simple and direct estimate of fossil fuel-derived contributions to aerosol TOC, and the data presented here suggest that a minimum of 34% (Harcum, Virginia) and 32% (Millbrook, New York) of aerosol particulate matter TOC deposition fluxes can be attributed to anthropogenic fossil fuel emissions. However, for a number of reasons, these estimates of fossil-derived aerosol particulate TOC inputs do not fully capture the impacts that humans may have on the atmospheric delivery of TOC to watersheds. First, fossil fuel combustion also emits

inorganic species (e.g., NO_x, SO₂) [e.g., Bates et al., 1992; Graf et al., 1997; Paerl et al., 2002; Holland et al., 2005] that are important in oxidation reactions forming SOA compounds from both fossil and contemporary biogenic volatile organic compounds [e.g., Jang and Kamens, 2001; Alfarra et al., 2006; Surratt et al., 2008]. Any increases in contemporary SOA compounds mediated by combustion-derived inorganic species are not accounted for in radiocarbon measurements of aerosol TOC. Biofuel combustion is another contemporary anthropogenic source of aerosol OC and is currently estimated at approximately 85% and 50% of United States and global fossil fuel emissions, respectively [Park et al., 2003]. Furthermore, anthropogenic biomass burning is employed to deforest large areas of land in many parts of the world so that it can be used for agriculture [Crutzen and Andreae, 1990; van der Werf et al., 2006] and represents an aerosol OC source approximately twice that of fossil fuel combustion worldwide [Hallquist et al., 2009].

[38] In addition to these postindustrial anthropogenic sources of aerosol OC, humans have likely reduced aerosol OC inputs by other means (e.g., conversion of land to agriculture and urban areas, wildfire suppression). Without a full accounting of the additions and reductions of aerosol OC inputs to the atmosphere, the quantitative impact of postindustrial anthropogenic activities on aerosol OC cycling is unclear. Our estimate that approximately one-third of eastern United States aerosol TOC is fossil fuel derived, however, demonstrates the quantitatively important influence of humans on aerosol TOC delivery to watersheds worldwide. The fate of this aerosol OC within watersheds and aquatic systems therefore deserves further study.

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