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## Isotopic characterization of aerosol organic carbon components over the eastern United States

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[1] Carbon isotopic signatures ( $\delta^{13}\text{C}$ ,  $\Delta^{14}\text{C}$ ) of aerosol particulate matter total organic carbon (TOC) and operationally defined organic carbon (OC) components were measured in samples from two background sites in the eastern U.S. TOC and water-soluble OC (WSOC)  $\delta^{13}\text{C}$  values ( $-27$  to  $-24\%$ ) indicated predominantly terrestrial  $\text{C}_3$  plant and fossil derived sources. Total solvent extracts (TSE) and their aliphatic, aromatic, and polar OC components were depleted in  $\delta^{13}\text{C}$  ( $-30$  to  $-26\%$ ) relative to TOC and WSOC.  $\Delta^{14}\text{C}$  signatures of aerosol TOC and TSE ( $-476$  to  $+25\%$ ) suggest variable fossil contributions ( $\sim 5$ – $50\%$ ) to these components. Aliphatic OC while comprising a small portion of the TOC ( $<1\%$ ), was dominated by fossil-derived carbon ( $86 \pm 3\%$ ), indicating its potential utility as a tracer for fossil aerosol OC inputs. In contrast, aromatic OC contributions ( $<1.5\%$ ) contained approximately equal portions contemporary ( $52 \pm 8\%$ ) and fossil ( $48 \pm 8\%$ ) OC. The quantitatively significant polar OC fraction ( $6$ – $25\%$  of TOC) had fossil contributions ( $30 \pm 12\%$ ) similar to TOC ( $26 \pm 7\%$ ) and TSE ( $28 \pm 9\%$ ). Thus, much of both of the fossil and contemporary OC is deduced to be oxidized, polar material. Aerosol WSOC consistently showed low fossil content ( $<8\%$ ) relative to the TOC ( $5$ – $50\%$ ) indicating that the majority of fossil OC in aerosol particulates is insoluble. Therefore, on the basis of solubility and polarity, aerosols are predicted to partition differently once deposited to watersheds, and these chemically distinct components are predicted to contribute in quantitatively and qualitatively different ways to watershed carbon biogeochemistry and cycling.

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### 1. Introduction

[2] Carbonaceous materials are major constituents of atmospheric aerosols, frequently comprising 10–30% of aerosol particulate matter [e.g., Wolff *et al.*, 1986; Jacobson *et al.*, 2000; Tanner *et al.*, 2004; Liu *et al.*, 2005] and up to 90% of submicron aerosols [e.g., Murphy *et al.*, 2006; Zhang *et al.*, 2007] and impacting numerous environmental processes of contemporary interest including climate [e.g., Ramanathan *et al.*, 2001; Satheesh and Moorthy, 2005; Highwood and Kinnersley, 2006], biogeochemical cycling

[Likens *et al.*, 1983; Velinsky *et al.*, 1986; Jurado *et al.*, 2008; Wozniak *et al.*, 2011], visibility [Charlson, 1969; Jacobson *et al.*, 2000], human health [e.g., Davidson *et al.*, 2005; Highwood and Kinnersley, 2006; Grahame and Schlesinger, 2007], and ecosystem health [e.g., Galiulin *et al.*, 2002; Rhind, 2009]. Aerosol organic carbon (OC; see Table 1 for a comprehensive list of acronyms) and black carbon (BC) are derived from both natural (e.g., plant emissions, sea spray, dust) and anthropogenic (e.g., biomass burning, fossil fuel combustion) sources, with 13–41% of global aerosol OC [Lioussé *et al.*, 1996; Bond *et al.*, 2004; de Gouw *et al.*, 2008; Hallquist *et al.*, 2009] and as much as 42% of aerosol OC over the continental United States estimated to be derived from fossil anthropogenic sources [de Gouw *et al.*, 2008].

[3] Fossil sources of aerosol OC include primary emissions from the combustion of fossil fuels (e.g., coal, gas, and petroleum [Rogge *et al.*, 1993a, 1993b, 1997]) and secondary organic aerosols (SOA) formed from reactions of volatile organic compound (VOCs) byproducts from fossil fuel combustion with atmospheric oxidants such as  $\text{NO}_x$  or  $\text{O}_3$  [e.g., Forstner *et al.*, 1997; Odum *et al.*, 1997; Jang and Kamens, 2001; Kanakidou *et al.*, 2005]. Contemporary sources of aerosol OC include SOAs formed from reactions between

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**Table 1.** Alphabetical List and Definitions of Acronyms Used in the Paper<sup>a</sup>

Acronym	Definition
ANOVA	Analysis of Variance
BC	Black Carbon
CI	International Atomic Energy Agency "C1" Carrara marble standard
DCM	Dichloromethane
EC	Elemental Carbon
MeOH	Methanol
OC	Organic Carbon
PAH	Polycyclic Aromatic Hydrocarbon
PM <sub>1,1.2,5,10</sub>	Particulate Matter <1.1 μm (or 2.5 or 10)
SOA	Secondary Organic Aerosol
TOC	Total Organic Carbon (= OC + BC – inorganic carbonates)
TSE	Total Solvent Extract
TSP	Total Suspended Particulates
VOC	Volatile Organic Compound
WIOC	Water Insoluble Organic Carbon (= TOC – WSOC)
WSOC	Water Soluble Organic Carbon

<sup>a</sup>All acronyms are also defined in the text.

VOCs emitted from terrestrial and marine plants (e.g., monoterpene compounds, isoprene) and atmospheric oxidants (e.g., O<sub>3</sub>, NO<sub>x</sub>, etc. [Kanakidou et al., 2005; Kroll et al., 2007; Surratt et al., 2008; O'Dowd and de Leeuw, 2007]), as well as primary aerosols emitted naturally from plant biomass [e.g., Rogge et al., 1993c], sea spray [O'Dowd and de Leeuw, 2007], or via biomass burning [e.g., Rogge et al., 1998; Bond et al., 2004; Hallquist et al., 2009]. On local scales, natural radiocarbon (<sup>14</sup>C) analyses of ambient aerosol particulate OC (using total suspended particulate (TSP) and PM<sub>2.5</sub> samplers) have shown highly variable fossil contributions ranging from 0 to 50% at different locations and times of year in the United States [Lemire et al., 2002; Bench and Herckes, 2004; Schichtel et al., 2008; Wozniak et al., 2011], but the post-depositional impact of these fossil contributions to terrestrial and aquatic biogeochemical processes and budgets is largely unexplored.

[4] Recent studies of aerosol total suspended particulates (TSP) have demonstrated that combined wet and dry deposition of aerosol OC from combined fossil and contemporary origins to watersheds of the east coast of the United States is similar in magnitude to the total OC export from these watersheds via rivers [Wozniak et al., 2011]. Approximately one third of the OC at the sampling sites from this study were attributed to fossil fuel sources, underscoring the anthropogenic footprint in atmospheric-terrestrial-aquatic OC biogeochemical cycles [Wozniak et al., 2011]. Further work in these same systems has demonstrated that the aerosol water soluble OC (WSOC) consistently showed greater relative contributions from contemporary OC sources than did the total OC (TOC) and water insoluble OC (WIOC) [Wozniak et al., 2012], a finding also observed at selected European sites for aerosol PM<sub>10</sub> [Szidat et al., 2004]. As water solubility is dependent on the molecular characteristics of component organic compounds, these findings may also be indicative that fossil fuel and contemporary sourced aerosol OC forms have different molecular characteristics, and presumably, different fates within aquatic and terrestrial systems.

[5] The roles of aerosol carbonaceous materials in environmental and biogeochemical processes are dependent on the quantities, sources (i.e., natural versus anthropogenic), and molecular-level characteristics of OC and BC within the deposited aerosols. For example, BC and the aromatic components of OC are highly light absorbing and are therefore considered important climate warming agents [Andreae and Gelencser, 2006]. From a biogeochemical standpoint, the microbial and photochemical fates of aerosol OC have also been found to vary between different sources [Slater et al., 2005; Wakeham et al., 2006] as well as between different molecular components. Aromatic components have been found to be more photoreactive [Kujawinski et al., 2004; Stubbins et al., 2010] and concomitantly resistant to microbial degradation [Baldock and Smernik, 2002; Kim et al., 2006] relative to aliphatic components. Analytical approaches for assessing the chemical and isotopic composition of aerosols and aerosol components, including stable carbon and radiocarbon isotopic signatures ( $\delta^{13}\text{C}$  and  $\Delta^{14}\text{C}$ , respectively), offer an opportunity to link the sources of aerosol OC to their defining molecular characteristics, and these characteristics can in turn be linked to environmental effects. For example,  $\Delta^{14}\text{C}$  values of aerosol OC can range from entirely fossil fuel derived ( $\sim -1,000\text{‰}$ ) to fully derived from contemporary sources (e.g., newly produced biomass;  $\sim 55\text{‰}$  [Hsueh et al., 2007]). The very large dynamic range in  $\Delta^{14}\text{C}$  ( $> \sim 1,000\text{‰}$ ) and the difference between potential end-member  $\Delta^{14}\text{C}$  values minimize any potential fractionation effects due to combustion or photochemistry and are thus extremely useful for determining the relative contributions of fossil and contemporary sources to aerosol OC. Natural radiocarbon analyses have been used to characterize fossil fuel inputs to total OC [e.g., Hildemann et al., 1994; Lemire et al., 2002; Bench and Herckes, 2004; Schichtel et al., 2008; Wozniak et al., 2011], WSOC [e.g., Wozniak et al., 2008; Kirillova et al., 2010; Wozniak et al., 2012], WIOC [e.g., Szidat et al., 2004], elemental carbon (EC) [e.g., Gustafsson et al., 2009; Heal et al., 2011], and several individual compounds [e.g., Matsumoto et al., 2001; Eglinton et al., 2002; Kumata et al., 2006]. However,  $\Delta^{14}\text{C}$  alone is unable to distinguish between different types of fossil materials or contemporary vegetation.

[6] The major contemporary and fossil sources to aerosol OM show typical ranges of  $\delta^{13}\text{C}$  values that can aid in source apportionment.  $\delta^{13}\text{C}$  signatures for C<sub>4</sub> terrestrial vegetation (e.g., corn, salt marsh plants;  $\delta^{13}\text{C} \sim -14$  to  $-12\text{‰}$ ) and marine ( $\delta^{13}\text{C} \sim -22$  to  $-18\text{‰}$ ) OC sources are distinct from one another and enriched in <sup>13</sup>C relative to C<sub>3</sub> terrestrial vegetation and fossil fuel OC ( $\delta^{13}\text{C} \sim -30$  to  $-23\text{‰}$  for both) [e.g., Fry and Sherr, 1984; Schoell, 1984; Boutton, 1991; Lajtha and Marshall, 1994]. Interpretation of  $\delta^{13}\text{C}$  signatures in aerosol OC is, however, not always straightforward because C<sub>3</sub> terrestrial vegetation and fossil fuel signatures overlap and combustion and photochemical processes cause isotopic fractionations. OC from biomass combustion shows  $\delta^{13}\text{C}$  values that are both lighter and heavier than the original biomass depending on the type of combustion (e.g., smoldering versus flaming) and specific fuel source [Ballentine et al., 1996; Turekian et al., 1998; Currie et al., 1999; Czapiewski et al., 2002]. Studies have also shown atmospheric photochemical processes to

selectively enrich  $^{13}\text{C}$  in aerosol OC, leaving more positive  $\delta^{13}\text{C}$  values in the remaining aerosol OC [Pavuluri and Kawamura, 2012]. This photochemical effect can result in materials of  $\text{C}_3$  or fossil fuel origin that appear (incorrectly) to be influenced by marine or  $\text{C}_4$  terrestrial (i.e.,  $^{13}\text{C}$ -enriched) sources. For these reasons,  $\delta^{13}\text{C}$  values of aerosol OC should be interpreted with caution and in the context of other measurements such as air mass trajectories or molecular biomarkers. Thus, the  $\delta^{13}\text{C}$  and  $\Delta^{14}\text{C}$  techniques have unique advantages and limitations, however, when used in combination they are robust geochemical tools for general source apportionment of aerosol OC.

[7] The present study builds on previous studies of aerosol particulate matter isotopic characteristics at the same two rural sites in the eastern United States by measuring the radiocarbon content of solvent extracts of aerosol OC across a gradient of compound polarity. Aerosol OC was partitioned into its operationally defined WSOC, aliphatic, aromatic, and polar OC components and analyzed for  $\Delta^{14}\text{C}$  and  $\delta^{13}\text{C}$  to evaluate the sources of OC to the various components. Recent work has established the incredible diversity of aerosol OC compounds [Wozniak et al., 2008; Nizkodorov et al., 2011], and characterizing the sources of individual compounds is thus insufficient. Analyzing the isotopic composition of these intermediately sized OC subfractions will provide important source information for compound groups of unique attributes and environmental importance. The findings presented here provide a more complete assessment of the distribution of fossil and contemporary OC among the various components comprising aerosol OC, providing novel, insights into the potential biogeochemical impacts and fates of fossil anthropogenic and contemporary aerosol OC.

## 2. Methods

### 2.1. Sampling

[8] Six aerosol particulate matter samples ( $>4,000\text{ m}^3$ ,  $\sim 1.7\text{ m}^3\text{ min}^{-1}$ ) were collected from two sites in the eastern U.S. at three different times during 2007 using high-volume total suspended particulate air samplers (Model GS2310, ThermoAndersen, Smyrna, GA). The sites were located at the Cary Institute of Ecosystem Studies Environmental Monitoring Station in Millbrook, NY (41.7858 N, 73.7414 W; [http://www.caryinstitute.org/emp\\_overview.html](http://www.caryinstitute.org/emp_overview.html)) and the National Atmospheric Deposition Program site (VA98) in Harcum, VA (37.5312 N, 76.4928 W; <http://nadp.sws.uiuc.edu/sites/siteinfo.asp?net=NTN&id=VA98>). Both sampling sites are located at least 30 km from major industrial activities ensuring that air samples were not biased by proximity to fossil fuel-derived point sources (see Wozniak et al. [2011] for a complete description). A companion study [Wozniak et al., 2011] conducted at these sites over the same study period measured OC concentrations (Millbrook:  $2.93\ \mu\text{g OC m}^{-3}$ ; Harcum:  $4.33\ \mu\text{g OC m}^{-3}$ ) characteristic of rural background northeast and mid-Atlantic U.S. sites in general [Malm et al., 2004; Schichtel et al., 2008]. Samples were collected over 2–3 day periods in March, May, and August and February, April, and August 2007 at the Millbrook and Harcum sites, respectively. These sampling periods cover

a range of ambient temperatures detailed in the auxiliary material (Table S1 in the auxiliary material).<sup>1</sup>

[9] Air was drawn through pre-ashed (3 h,  $525^\circ\text{C}$ ) and pre-weighed high-purity quartz microfibre filters ( $20.3\text{ cm} \times 25.4\text{ cm}$ , nominal pore size  $0.6\ \mu\text{m}$ ; Whatman type QM-A) for collection of time-integrated particulate matter samples. Following collection, filters were transferred to pre-ashed aluminum foil pouches and stored in the dark in carefully cleaned air-tight polycarbonate desiccators ( $\leq 10\%$  relative humidity) until analysis. Filter blanks were assessed by transporting filters prepared in the same way to the field, briefly removing them from their individual aluminum foil pouches and returning them back to the pouches for storage in desiccators with the samples.

[10] Non-denuded high volume aerosol samplers such as those used in this study are known to adsorb gas-phase OC onto quartz filters [McDow and Huntzicker, 1990; Turpin et al., 2000; Subramanian et al., 2004; Watson et al., 2009]. The relative magnitude of the positive artifact has been shown to decrease at increased sampling durations [Turpin et al., 2000; Subramanian et al., 2004] and face velocities [McDow and Huntzicker, 1990; Turpin et al., 2000] such as those used in the current study ( $\sim 40\text{--}70\text{ h}$  sampling duration,  $\sim 60\text{--}80\text{ cm s}^{-1}$  face velocities). The TOC positive artifact was not measured for the samples in this study; however, samples collected near the Harcum site using the same sampling apparatus at shorter sampling durations ( $\sim 24\text{ h}$ ) and lower face velocities ( $\sim 30\text{--}45\text{ cm s}^{-1}$ ) showed a TOC positive artifact of 10–16% (Table S2). Given that the positive artifact decreases with sample duration and face velocity, the operationally defined particulate matter samples collected in this study are expected to contain levels of adsorbed gas-phase OC  $\leq \sim 10\text{--}16\%$  of TOC.

### 2.2. Laboratory Analyses

#### 2.2.1. TOC and WSOC Preparation

[11] Between one and four filter core plugs ( $2.84\text{ cm}^2$ ) were subsampled from each quartz filter using a solvent (hexane followed by acetone) cleaned stainless steel cork borer, combined, and processed for isotopic analyses of TOC as previously described (Figure 1) [Wozniak et al., 2011]. The combined TOC samples ranged in size from 323 to 553  $\mu\text{g C}$ .

[12] For aerosol-derived WSOC measurements, between 3 and 12 filter core plugs were water-extracted by immersion in 20 ml of low-OC (Milli-Q Gradient A10, Millipore,  $<5\ \mu\text{M OC}$ ) water, and WSOC was allowed to desorb from aerosol particles for a minimum of 8 h (Figure 1). The water containing the WSOC was then filtered through a  $0.45\ \mu\text{m}$  polytetrafluoroethylene filter (Gelman) to remove aerosol particulate matter from the filter. The WSOC filtrate was transferred to pre-ashed 12 mm quartz tubes, and the water was evaporated at  $55^\circ\text{C}$  under a stream of ultrahigh purity  $\text{N}_2$ , leaving the dried, operationally defined WSOC in the quartz tube. The WSOC was then oxidized to  $\text{CO}_2$  as described elsewhere for aerosol TOC [Wozniak et al., 2011] and analyzed for  $\delta^{13}\text{C}$  and  $\Delta^{14}\text{C}$ . Per-sample WSOC amounts ranged between 197 and 589  $\mu\text{g C}$ .

<sup>1</sup>Auxiliary materials are available in the HTML. doi:10.1029/2011JD017153.

Table 2. Isotopic Signatures and Carbon Contents of Large-Volume Aerosol Samples Collected for Detailed Isotopic Analyses<sup>a</sup>

Aerosol OC Component	Parameter	Millbrook			Harcum			Mean	Feb 19–21	April 10–12	Aug 6–8	Mean	Overall Mean
		March 7–10	May 14–16	Aug 10–12	March 7–10	May 14–16	Aug 10–12						
TOC	$\delta^{13}\text{C}$ (‰)	-25.3	-25.8	-24.7	-25.3	-26.2	-26.5	-24.4	-25.7	-25.5			
	$\Delta^{14}\text{C}$ (‰)	-448	-39	25	-154	-252	-388	-165	-268	-211			
WSOC	$f_{\text{TOC}}$	0.134	0.228	0.281	0.214	0.179	0.169	0.154	0.167	0.191			
	$\delta^{13}\text{C}$ (‰)	nd <sup>b</sup>	-25.1	-24.4	-24.7	-26.1	-24.8	-25.2	-25.4	-25.1			
WIOC <sup>d</sup>	$\Delta^{14}\text{C}$ (‰)	nd	-17	6	-6	26	11	22	20	10			
	$f_{\text{WSOC}}$	nd	0.22	0.47	0.34	0.29	0.16	0.26	0.24	0.28			
TSE <sup>e</sup>	$\delta^{13}\text{C}$ (‰)	nd	-26.0	-25.1	-25.6	-26.7	-26.8	-24.2	-25.9	-25.8			
	$\Delta^{14}\text{C}$ (‰)	nd	-45	42	-1	-367	-461	-231	-353	-212			
Aliphatic	$f_{\text{WIOC}}$	nd	0.78	0.53	0.66	0.71	0.84	0.74	0.76	0.72			
	$\delta^{13}\text{C}$ (‰)	-27.0	nd	-26.2	-26.6	nd	-27.3	-28.2	-27.6	-27.2			
Aromatic	$\Delta^{14}\text{C}$ (‰)	-476	nd	-90	-283	nd	-430	-119	-190	-227			
	$f_{\text{TSE}}$	0.67	nd	0.90	0.79	nd	0.43	0.74	0.59	0.69			
Polar	$\delta^{13}\text{C}$ (‰)	-28.6	-27.7	nd <sup>f</sup>	-28.2	nd	-27.3	-28.9	-28.1	-28.1			
	$\Delta^{14}\text{C}$ (‰)	-794	-820	-961	-858	nd	-834	-858	-846	-853			
Polar	$f_{\text{aliphatic}}$	0.007	0.001	0.003	0.0039	nd	0.007	0.002	0.004	0.004			
	$\delta^{14}\text{C}$ (‰)	-27.8	-29.6	-28.3	-28.6	-28.3	-28.4	-27.8	-28.2	-28.4			
Polar	$f_{\text{aromatic}}$	0.015	0.009	0.004	0.009	0.009	0.007	0.003	0.007	0.006			
	$\delta^{13}\text{C}$ (‰)	-27.8	-26.1	-28.0	-27.3	-28.6	nd	-26.2	-27.4	-27.3			
Polar	$\Delta^{14}\text{C}$ (‰)	-750	24	-93	-273	-168	nd	-240	-204	-245			
	$f_{\text{polar}}$	0.24	0.039	0.25	0.18	0.063	nd	0.066	0.065	0.13			

<sup>a</sup>All reported  $\delta^{13}\text{C}$  and  $\Delta^{14}\text{C}$  values were corrected for blank contributions following procedures outlined in the text.

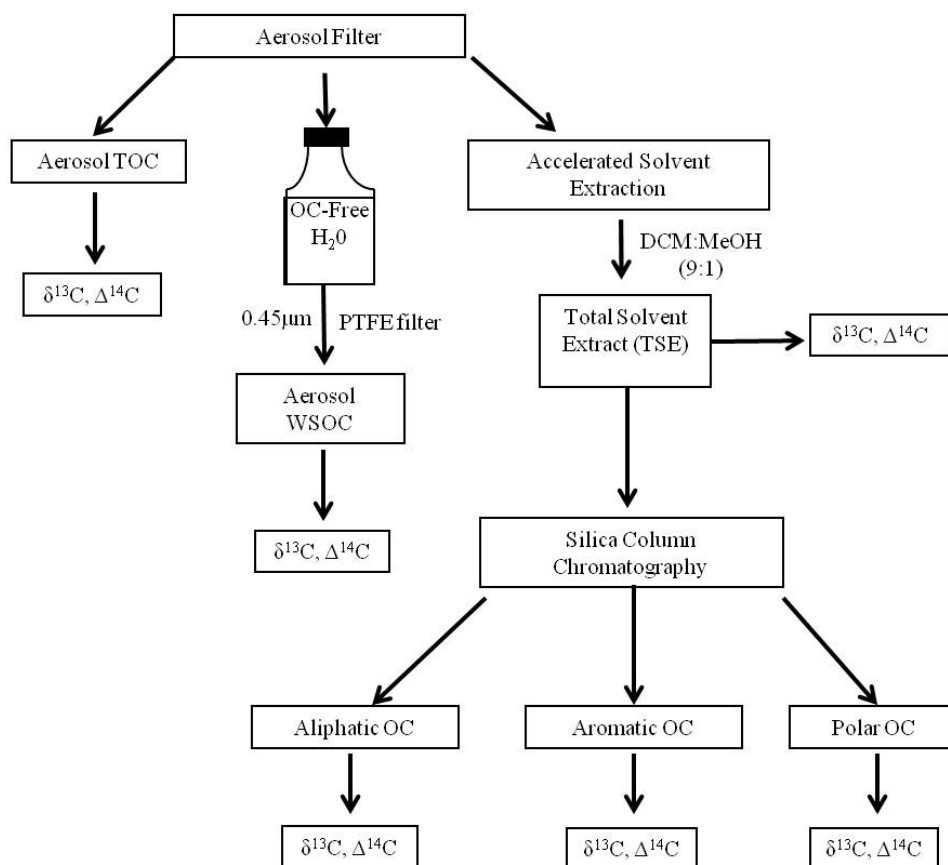
<sup>b</sup>nd<sup>f</sup> denotes samples for which values were not determined.

<sup>c</sup>Values represent the fraction of TOC accounted for by the parameter of interest ( $f_{\text{WSOC}}$ ,  $f_{\text{WIOC}}$ ,  $f_{\text{TSE}}$ ,  $f_{\text{aliphatic}}$ ,  $f_{\text{aromatic}}$ ,  $f_{\text{polar}}$ ).

<sup>d</sup>WIOC (water-insoluble organic carbon) values were calculated by mass balance using values for TOC and WSOC ( $\text{WIOC} = \text{TOC} - \text{WSOC}$ ):  $X_{\text{WIOC}} = \frac{(X_{\text{TOC}} - X_{\text{WSOC}}) \cdot f_{\text{WIOC}}}{f_{\text{WIOC}}}$ , where X represents either  $\delta^{13}\text{C}$  or  $\Delta^{14}\text{C}$  for the component of interest (TOC, WSOC, WIOC).

<sup>e</sup>TSE = Total Solvent Extract.

<sup>f</sup>Sample was too small for measurement of both  $\delta^{13}\text{C}$  and  $\Delta^{14}\text{C}$ . A value of -25.0‰ was assumed for  $\Delta^{14}\text{C}$  fractionation corrections.



**Figure 1.** Methodological flow diagram for total organic carbon (TOC), water-soluble organic carbon (WSOC), and solvent-extractable aerosol particulate OC components and subfractions used for isotopic characterization as part of the present study. See section 2 for additional details.

### 2.2.2. Solvent Extraction and Aliphatic, Aromatic, and Polar OC Subfraction Preparation

[13] After core plugs were removed from the quartz filters for TOC and WSOC isotopic analyses, the remainder of the filter was extracted in an accelerated solvent extraction system (1,000 psi, 100°C) using dichloromethane and methanol (DCM:MeOH; 9:1 v/v) (Figure 1). A portion of the DCM:MeOH extract was then transferred to a pre-ashed 9 mm quartz tube, the solvent was evaporated at room temperature (~23°C) under a stream of ultrahigh purity N<sub>2</sub>, and the remaining OC residue was analyzed for  $\delta^{13}\text{C}$  and  $\Delta^{14}\text{C}$  of the TSE as described elsewhere [Wozniak *et al.*, 2011]. The remainder of the solvent extract was separated into operationally defined aliphatic, aromatic, and polar compound groups using silica column chromatography (Fisher Scientific 100–200 mesh Silica Gel). The aliphatic OC eluted first in hexane, followed by aromatic OC eluting in a 1:1 mixture of hexane/DCM, and finally polar OC eluting in a 1:1 mixture of DCM/MeOH. This extraction protocol has been used in numerous studies to isolate characteristic aliphatic (e.g., *n*-alkanes), aromatic (e.g., polycyclic aromatic hydrocarbons (PAHs), and polar (e.g., fatty acids, alkanols) OC components of natural organic matter [Volkman *et al.*, 1981; Aceves and Grimalt, 1993; Ostrom *et al.*, 1998; Mazquiarán and Cantón Ortiz de Pinedo, 2007]. The solvent-extracted components

were then dried under a stream of ultrahigh purity N<sub>2</sub> in pre-ashed 9 mm quartz tubes and subsequently combusted to carbon dioxide and converted to graphite prior to  $\delta^{13}\text{C}$  and  $\Delta^{14}\text{C}$  analyses as described elsewhere [Wozniak *et al.*, 2011].

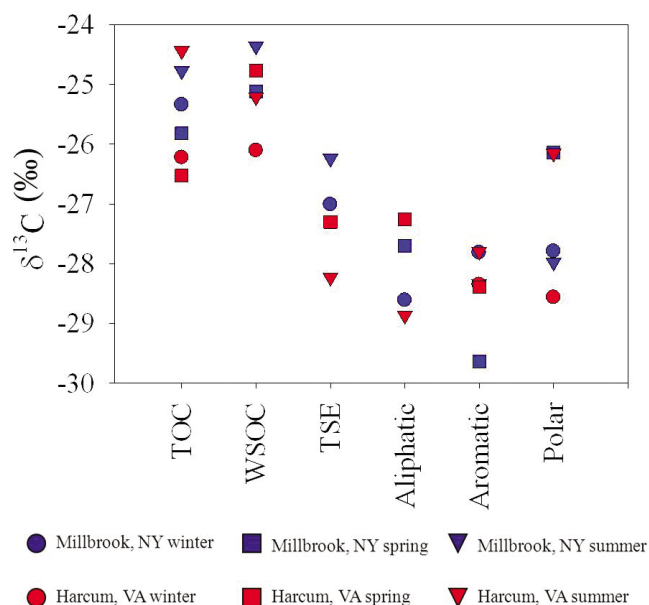
### 2.2.3. Isotopic Analyses

[14] All  $\Delta^{14}\text{C}$  and  $\delta^{13}\text{C}$  analyses were performed at the National Ocean Sciences Accelerator Mass Spectrometry (NOSAMS) facility. For  $\Delta^{14}\text{C}$  analyses, accelerator mass spectrometry measurement errors averaged  $\pm 4\%$  and were never larger than  $\pm 9\%$ . The mean measurement error for  $\delta^{13}\text{C}$  analyses performed using an Optima isotope ratio mass spectrometer was  $\pm 0.1\%$ .

## 2.3. Data Analyses

### 2.3.1. Filter Blanks and Blank Corrections

[15] Blank filters were subjected to the same extraction procedures as sample filters, and corrections for blank contributions to  $\delta^{13}\text{C}$  and  $\Delta^{14}\text{C}$  measurements were made as described elsewhere [Wozniak *et al.*, 2011]. The filter blanks for the aliphatic, aromatic, TSE, and WSOC were all very small (<25  $\mu\text{g C}$ ) and were therefore assessed by diluting these samples with CO<sub>2</sub> derived from the International Atomic Energy Agency C1 “Carrara” marble standard (C1)



**Figure 2.**  $\delta^{13}\text{C}$  signatures of aerosol TOC, WSOC, TSE, and aliphatic aromatic, and polar OC subfractions of the solvent extract in aerosol particulate matter samples collected at Harcum, VA and Millbrook, NY in winter, spring, and summer of 2007. Each data point represents measurement of a single sample.

prior to being measured for isotopic signatures. Isotopic signatures of the blanks were then calculated as

$$X_{\text{blank}} = (X_{\text{measured}} - f_{\text{C1}} * X_{\text{C1}}) / f_{\text{blank}} \quad (1)$$

where  $X_{\text{measured}}$  represents the total  $\delta^{13}\text{C}$  or  $\Delta^{14}\text{C}$  value (i.e., including the blank),  $f_{\text{C1}}$  represents the fraction of the C1 standard in the measured combined blank + C1,  $X_{\text{C1}}$  represents the known isotopic signature of C1 ( $\delta^{13}\text{C}_{\text{C1}} = +2.4\text{‰}$ ;  $\Delta^{14}\text{C}_{\text{C1}} = -1000\text{‰}$ ), and  $X_{\text{blank}}$  represents the  $\delta^{13}\text{C}$  or  $\Delta^{14}\text{C}$  value of the blank alone. In the above, “blank” refers to the blank for each specific OC subfraction (aliphatic, aromatic, TSE, or WSOC) as collected and measured for the blank filter. For aerosol TOC ( $n = 6$ ) and TSE samples ( $n = 4$ ), the fraction of total OC contributed by the filter blank ( $f_{\text{blank}} = \text{OC}_{\text{blank}} / \text{TOC}_{\text{sample}}$ ) was always less than 0.01. WSOC and polar group  $f_{\text{blank}}$  values averaged 0.05 ( $n = 5$ ) and 0.06 ( $n = 5$ ), respectively, while the mean aliphatic and aromatic  $f_{\text{blank}}$  values averaged 0.11 ( $n = 5$ ) and 0.12 ( $n = 6$ ), respectively.

### 2.3.2. Fossil and Contemporary Contributions

[16] Fossil and contemporary biogenic sources of organic matter have characteristic radiocarbon signatures, with fossil  $\Delta^{14}\text{C} = -1000\text{‰}$  [see, e.g., Clayton *et al.*, 1955; Currie *et al.*, 1997] and contemporary OC from terrestrial plant biomass having  $\Delta^{14}\text{C}$  values of  $\sim +55\text{‰}$  (as determined for corn leaves collected in the eastern United States in 2004 [Hsueh *et al.*, 2007]). These two end-member sources may be assumed to be the primary contributors to particulate OC in air from the east coast of North America (see Wozniak *et al.* [2011] for a complete description and justification of the end-member values). The contributions from fossil and contemporary materials to sample  $\Delta^{14}\text{C}$  values were estimated using a 2-source end-member model following previous studies [e.g.,

Lewis *et al.*, 2004; Zheng *et al.*, 2006; Schichtel *et al.*, 2008; Wozniak *et al.*, 2011].

### 2.3.3. Statistical Analyses

[17] Differences in mean isotopic values were analyzed by one-way analysis of variance (ANOVA) using Minitab. When differences were detected by one-way ANOVA, a Tukey-Kramer post-hoc multiple comparisons test was subsequently employed to determine which components were different from each other. The Student's t-test was used to compare isotopic values of aerosol particulate TOC and WSOC. For all statistical comparisons, a p value  $< 0.05$  was considered indicative of a significant difference.

## 3. Results and Discussion

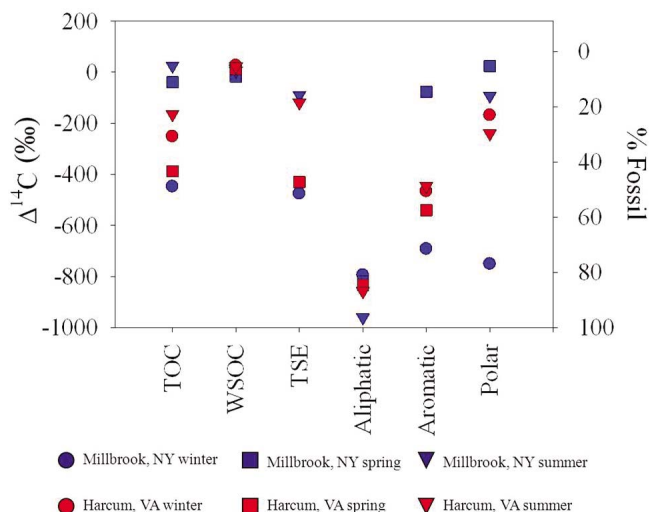
### 3.1. $\delta^{13}\text{C}$ and $\Delta^{14}\text{C}$ Signatures of TOC and WSOC

#### 3.1.1. Aerosol Particulate TOC

[18] Aerosol TOC  $\delta^{13}\text{C}$  values in this study ( $-26.6$  to  $-24.5\text{‰}$ ; Table 2 and Figure 2) were similar to values reported throughout 2006–2007 at the same sites ( $\delta^{13}\text{C} = -26$  to  $-23\text{‰}$  [Wozniak *et al.*, 2011]) and suggest that fossil fuel and/or terrestrial biomass derived sources dominated aerosol TOC [e.g., Fry and Sherr, 1984; Schoell, 1984; Boutton, 1991; Lajtha and Marshall, 1994]. The  $\delta^{13}\text{C}$  values for TOC in this study are on the high end of the range noted for  $\text{C}_3$  terrestrial vegetation/fossil fuel sources ( $\sim -30$  to  $-23\text{‰}$ ) indicating that marine or  $\text{C}_4$  terrestrial vegetation sources could potentially contribute to aerosol OM. However, air mass trajectory analyses (Figure S1) show that only the April ( $\delta^{13}\text{C} = -26.5\text{‰}$ ; Table 2) and August ( $\delta^{13}\text{C} = -24.4\text{‰}$ ; Table 2) samples collected in Harcum were influenced by air masses traveling over the Atlantic Ocean for a portion of the sampling period. Thus, these two samples may be influenced by marine OC sources. Based on air mass trajectory analyses, the remaining samples are not likely to have marine influence. Their slightly enriched  $\delta^{13}\text{C}$  values can be explained by them (1) being derived entirely from fossil fuel and/or  $\text{C}_3$  terrestrial vegetation sources, (2) being OC of fossil fuel or  $\text{C}_3$  terrestrial vegetation origin that has been photochemically altered, or (3) contain small contributions from  $\text{C}_4$  terrestrial sources.

[19]  $\Delta^{14}\text{C}$  values of aerosol TOC covered a broad range ( $-448$  to  $-39\text{‰}$ ; Table 2 and Figure 3) and were also similar to values reported by Wozniak *et al.* [2011] and in previous studies examining  $\text{PM}_{2.5}$  [Hildemann *et al.*, 1994; Klinedinst and Currie, 1999; Bench and Herckes, 2004; Zheng *et al.*, 2006; Ding *et al.*, 2008]. The  $\Delta^{14}\text{C}$  values for TOC suggest that fossil fuel-derived OC contributes between 5 and 50% of particulate TOC at these sites (Table 2), demonstrating significant variability in the relative importance of fossil and contemporary TOC sources depending on site and sampling time. Previous work has shown variability in  $\Delta^{14}\text{C}$  of aerosol TOC to be driven primarily by differences in the amounts of contemporary TOC over a given sampling period, since the amount of fossil TOC was relatively constant throughout the 2006–2007 sampling period [Wozniak *et al.*, 2011]. Here, the variability in TOC  $\Delta^{14}\text{C}$  values enables an examination of whether patterns of fossil and contemporary contributions to OC subfractions are related to or independent of the relative abundance of fossil and contemporary contributions to the TOC.





**Figure 3.**  $\Delta^{14}\text{C}$  signatures of aerosol particulate matter TOC, WSOC, TSE, and aliphatic aromatic, and polar OC subfractions of the solvent extract collected at Harcum, VA and Millbrook, NY in winter, spring, and summer of 2007. Each data point represents measurement of a single sample.

### 3.1.2. Water-Soluble OC

[20] The fraction of WSOC ( $f_{\text{WSOC}} = \text{WSOC}/\text{TOC}$ ) associated with aerosol samples ranged from 0.16 to 0.47 (Table 2), similar to that observed in previous studies of WSOC extracted from  $\text{PM}_{2.5}$  and TSP samples [e.g., Kleefeld *et al.*, 2002; Weber *et al.*, 2007; Wozniak *et al.*, 2012]. WSOC  $\delta^{13}\text{C}$  values ( $-26.1$  to  $-24.4\text{‰}$ ; Table 2 and Figure 2) were similar in overall range to aerosol TOC  $\delta^{13}\text{C}$  values at the high end for  $\text{C}_3$  terrestrial plant and fossil fuel sources. Similar to the TOC samples, fossil and/or terrestrial  $\text{C}_3$  plant biomass again appear to be the major sources of WSOC, with  $^{13}\text{C}$ -enriched sources such as  $\text{C}_4$  plant and marine (April and August Harcum samples) OC likely to be minor [e.g., Fry and Sherr, 1984; Schoell, 1984; Boutton, 1991; Lajtha and Marshall, 1994]. The photochemical processing of  $\text{C}_3$  terrestrial and fossil fuel derived OC may also play a role in these slightly enriched  $\delta^{13}\text{C}$  values [Pavuluri and Kawamura, 2012]. The relatively few previous studies that have measured  $\delta^{13}\text{C}$  signatures of aerosol-associated WSOC have measured them in TSP samples and found similar values to those in the present study (Table 3;  $-25.5$  to  $-24.0\text{‰}$  [Fisseha *et al.*, 2006];  $\sim -25$  to  $-23\text{‰}$  [Fisseha *et al.*, 2009];  $-25\text{‰}$  [Kirillova *et al.*, 2010];  $-25.2 \pm 0.3\text{‰}$  [Wozniak *et al.*, 2012]) and generally attribute them to terrestrial and fossil sources. Two of these studies have shown aerosol WSOC to be enriched in  $^{13}\text{C}$  by up to 2.5‰ relative to aerosol TOC suggesting that  $^{13}\text{C}$ -enriched aerosol TSP components are preferentially soluble [Fisseha *et al.*, 2009; Kirillova *et al.*, 2010]. However, there was no clear pattern of  $^{13}\text{C}$  enrichment in aerosol WSOC relative to TOC in the present study demonstrating that the partitioning of OC components does not appear to have a dependence on  $^{13}\text{C}$  content (Table 2 and Figure 2). TOC  $\delta^{13}\text{C}$  values were found to be both enriched (by 0.8‰) and depleted (by up to 1.7‰) relative to WSOC  $\delta^{13}\text{C}$  values for the same sample suggesting a complex relationship between the  $\delta^{13}\text{C}$

signatures of dominant TOC and WSOC sources on a given sampling date.

[21]  $\Delta^{14}\text{C}$  values of aerosol WSOC provide compelling evidence for both site- and time-dependent differences in the relative importance of fossil versus modern sources of TOC and WSOC (Table 2 and Figure 3). In all cases, aerosol WSOC ( $\Delta^{14}\text{C}$  range:  $-17\text{‰}$  in May at Millbrook to  $+26\text{‰}$  in February at Harcum; Table 2 and Figure 3) was significantly enriched (Student's t-test,  $p < 0.05$ ) compared to aerosol TOC ( $\Delta^{14}\text{C} = -448$  to  $-39\text{‰}$ ). In many cases WSOC was enriched in  $^{14}\text{C}$  by more than 100‰ relative to TOC (Table 2 and Figure 3). Similar to the present study, previous work with aerosol  $\text{PM}_{2.5}$  and TSP has also found contemporary biogenic material to be the predominant contributor to aerosol WSOC (Table 3; 19–33% fossil [Weber *et al.*, 2007]; <25% fossil [Wozniak *et al.*, 2008]; <12% fossil [Kirillova *et al.*, 2010]; 0–25% fossil [Wozniak *et al.*, 2012]). For comparison, using the  $f_{\text{WSOC}}$  values (Table 2) for samples measured in the present study, we estimated the fossil contributions to the WIOC by isotopic mass balance as follows

$$X_{\text{WIOC}} = (X_{\text{TOC}} - f_{\text{WSOC}} * X_{\text{WSOC}}) / f_{\text{WIOC}} \quad (2)$$

where  $X_{\text{WIOC}}$ ,  $X_{\text{TOC}}$ , and  $X_{\text{WSOC}}$  are the  $\Delta^{14}\text{C}$  values for WIOC, TOC and WSOC, respectively, and  $f_{\text{WIOC}}$  is the water-insoluble fraction of TOC ( $f_{\text{WIOC}} = \text{WIOC}/\text{TOC} = 1 - f_{\text{WSOC}}$ ). Calculated WIOC  $\Delta^{14}\text{C}$  values in the present study reveal that this insoluble material is often highly and significantly depleted by as much as 200‰ or more in  $\Delta^{14}\text{C}$  relative to both TOC and WSOC (Table 2). Szidat *et al.* [2004] measured TOC and WIOC  $\Delta^{14}\text{C}$  values in aerosol  $\text{PM}_{10}$  and found similarly elevated fossil contributions for the WIOC (32–45% fossil) and TOC (16–33%) relative to the WSOC (4–24%). Thus, WSOC appears to be enriched in contemporary material across size classes ( $\text{PM}_{2.5}$ ,  $\text{PM}_{10}$ , TSP) of aerosol particulate matter.

[22] Taken together, these findings support a growing body of evidence (Table 3) [see, e.g., Szidat *et al.*, 2004; Wozniak *et al.*, 2012] suggesting fossil fuel-derived aerosol OC to be considerably less soluble than OC from contemporary biogenic sources. It is thus deduced that contemporary-derived SOA and combustion products have a more oxidized molecular composition facilitating their dissolution in water. The findings to date suggest that all aerosol OC becomes oxidized via photochemical aging during its atmospheric lifetime resulting in the highly oxidized molecular composition in ambient aerosols [Jimenez *et al.*, 2009; Kroll *et al.*, 2011]. Because the WSOC is composed of highly oxidized material [Wozniak *et al.*, 2008; Jimenez *et al.*, 2009; Kroll *et al.*, 2011], the primarily contemporary nature of WSOC in these studies may further suggest that photochemical aging creates WSOC from insoluble primary fossil TOC at a slower rate than it is produced for contemporary sources.

## 3.2. Isotopic Signatures of Solvent Extractable Components

### 3.2.1. $\delta^{13}\text{C}$ Signatures

[23] A one-way ANOVA of the  $\delta^{13}\text{C}$  values for TOC and the various OC subfractions showed significant differences among the various components (Table 2). The TSE



**Table 3.**  $\delta^{13}\text{C}$  and  $\Delta^{14}\text{C}$  Values and Sampling Locations for Aerosol OC Components Referenced in This Study<sup>a</sup>

Component	$\delta^{13}\text{C}$ (‰)	$\Delta^{14}\text{C}$ (‰)	Environment and Location	Reference
WSOC	-26.1 to -24.4	-17 to 26	Rural; Millbrook, NY/ Harcum, VA, USA	This study <sup>b,c</sup>
WSOC	NR	-299 to -114	Urban; Zurich, Switzerland	<i>Szidat et al.</i> [2004] <sup>d,e</sup>
WSOC	-25.5 to -24.0	NR	Urban; Zurich, Switzerland	<i>Fisseha et al.</i> [2006] <sup>c,f</sup>
WSOC	NR	-395 to -268	Urban; Atlanta, GA, USA	<i>Weber et al.</i> [2007] <sup>g,h</sup>
WSOC	NR	-230	Rural; Millbrook, NY USA	<i>Wozniak et al.</i> [2008] <sup>c</sup>
WSOC	~-25 to -23	NR	Urban; Zurich, Switzerland	<i>Fisseha et al.</i> [2009] <sup>c,i</sup>
WSOC	-25.6 to -25.1	-58 to 125	Grassland/forest; Stockholm, Sweden	<i>Kirillova et al.</i> [2010] <sup>c</sup>
WSOC	-27.6 to -21.1	-187 to 106	Rural; Millbrook, NY/ Harcum, VA, USA	<i>Wozniak et al.</i> [2012] <sup>c</sup>
WIOC	-26.8 to -24.2	-461 to 42	Rural; Millbrook, NY/ Harcum, VA, USA	This study <sup>b,c,j</sup>
WIOC	-28.6 to -26.2	-493 to -373	Urban; Zurich, Switzerland	<i>Szidat et al.</i> [2004] <sup>g,g</sup>
WIOC	~-27 to -29	NR	Urban; Zurich, Switzerland	<i>Fisseha et al.</i> [2009] <sup>c,i</sup>
WIOC	NR	-829 to 17	Rural; Millbrook, NY/ Harcum, VA, USA	<i>Wozniak et al.</i> [2012] <sup>c,j</sup>
TSE	-28.2 to -26.2	-476 to -90	Rural; Millbrook, NY/ Harcum, VA, USA	This study <sup>b,c</sup>
Aliphatic OC	-28.9 to -27.3	-961 to -794	Rural; Millbrook, NY/ Harcum, VA, USA	This study <sup>b,c</sup>
Aliphatic OC	NR	-976	Urban, Washington, DC, USA	<i>Currie et al.</i> [1997] <sup>c,k</sup>
Odd numbered (C <sub>23-33</sub> ) n-alkanes	-27.8 ± 0.9	NR	Marine; NE Atlantic Ocean off NW Africa	<i>Eglinton et al.</i> [2002] <sup>c,l</sup>
C <sub>29,31</sub> n-alkane	-31.5 to -27.7	NR	Marine; E Atlantic Ocean off W Africa	<i>Schefeuf et al.</i> [2003] <sup>m,m</sup>
Aromatic OC	-27.8 to -29.6	-692 to -77	Rural; Millbrook, NY/ Harcum, VA, USA	This study <sup>b,c</sup>
Aromatic OC	NR	-831	Urban; Washington, DC, USA	<i>Currie et al.</i> [1997] <sup>c,k</sup>
Selected PAHs	NR	-881 to -801	Urban; Washington, DC, USA	<i>Currie et al.</i> [1997] <sup>c,k,n</sup>
Selected PAHs	-27.2 to -21.1	NR	Urban; Beijing, Chongqing, Hangzhou, China	<i>Okuda et al.</i> [2002a] <sup>c,n</sup>
Selected PAHs	-25 to -21	NR	Forest-fire influenced; Malaysia	<i>Okuda et al.</i> [2002b] <sup>c,n</sup>
Selected PAHs	-32 to -27	NR	Woodburning; Malaysia	<i>Okuda et al.</i> [2002b] <sup>c,n</sup>
Selected PAHs	NR	-963 to -913	Urban; Washington, DC, USA	<i>Reddy et al.</i> [2002] <sup>c,k,n</sup>
Selected PAHs	-27.0 to -23.3	NR	Roadside; Tokyo, Japan	<i>Okuda et al.</i> [2004] <sup>c,n</sup>
Selected PAHs	-23.6 to -19.5	NR	Estimated Auto Exhaust; Tokyo, Japan	<i>Okuda et al.</i> [2004] <sup>c,n</sup>
Selected PAHs	-27.7	-381, -388	Semirural Background; Aspvetren, Sweden	<i>Mandalakis et al.</i> [2005] <sup>o,o</sup>
Selected PAHs	-29.2	-888	Adar & Zelebit, Croatia	<i>Mandalakis et al.</i> [2005] <sup>o,o</sup>
Selected PAHs	-29.0	-914	Marine Background; Finokalia, Greece	<i>Mandalakis et al.</i> [2005] <sup>o,o</sup>
LMW and HMW PAHs	-25.4 to -24.3	-514 to -787	Residential; Hachioji, Japan	<i>Kumata et al.</i> [2006] <sup>o,n,p</sup>
Polar OC	-28.6 to -26.1	-750 to 24	Rural; Millbrook, NY/ Harcum, VA, USA	This study <sup>b,c</sup>
Polar OC	NR	-573	Urban; Washington, DC, USA	<i>Currie et al.</i> [1997] <sup>c,k</sup>
Fatty acids (C <sub>16-34</sub> )	-30.3 to -23.3	-518 to 407	Semi-urban; Hokkaido, Japan	<i>Matsumoto et al.</i> [2001] <sup>q,q</sup>
Even numbered (C <sub>22-32</sub> ) n-alkanols	-27.9 ± 2.2	-80.8	Marine; NE Atlantic Ocean off NW Africa	<i>Eglinton et al.</i> [2002] <sup>c,l</sup>
(C <sub>22-32</sub> ) n-alkanoic acids	-22.6 ± 2.5	NR	Marine; NE Atlantic Ocean off NW Africa	<i>Eglinton et al.</i> [2002] <sup>c,l</sup>
Fatty acids (C <sub>16-34</sub> )	-30.8 to -23.0	-89.7 to 83.5	Semi-urban; Hokkaido, Japan	<i>Matsumoto et al.</i> [2004] <sup>c,r</sup>

<sup>a</sup>'NR' denotes references for which  $\delta^{13}\text{C}$  or  $\Delta^{14}\text{C}$  data were not reported for a given OC component.

<sup>b</sup>Data from this study are reported as ranges. For mean values, refer to Table 2.

<sup>c</sup>Component measured from samples collecting aerosol TSP.

<sup>d</sup>WSOC fraction contemporary ( $f_c$ ) values were calculated from measurements on WIOC as described in the reference.  $f_c$  values were multiplied by 1.077 to convert them to  $F_M$  convention and converted to  $\Delta^{14}\text{C}$  convention after *Stuiver and Polach* [1977].

<sup>e</sup>Component measured from samples collecting aerosol PM<sub>10</sub>.

<sup>f</sup>WSOC data are reported as the average values measured using two different methods.

<sup>g</sup>Data reported for these studies were converted from a reported biogenic fraction to  $F_M$  by multiplying by conversion factors cited in the studies then converted to  $\Delta^{14}\text{C}$  convention after *Stuiver and Polach* [1977].

<sup>h</sup>Component measured from samples collecting aerosol PM<sub>2.5</sub>.

<sup>i</sup>WSOC and WIOC  $\delta^{13}\text{C}$  ranges were estimated from error bars on a figure within the reference.

<sup>j</sup>WIOC data are calculated from data measured for WSOC as described in the references.

<sup>k</sup>Data reported for these studies in  $F_M$  convention were converted to  $\Delta^{14}\text{C}$  convention after *Stuiver and Polach* [1977].

<sup>l</sup> $\delta^{13}\text{C}$  data are reported as weighted mean averages ± errors for measurements on individual compounds.

<sup>m</sup> $\delta^{13}\text{C}$  ranges are reported for weighted mean averages for measurements on individual compounds.

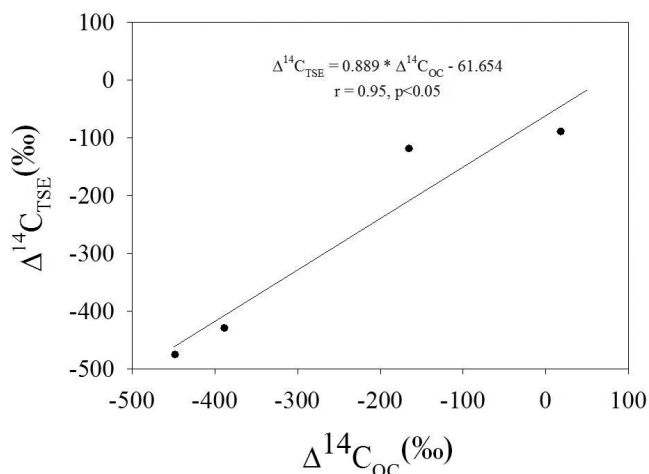
<sup>n</sup>Data ranges are reported for measurements on selected individual PAHs in these references: *Currie et al.* [1997] - fluoranthene, benzo[*a*]anthracene, benzo[*fluoranthene*], benzo[*ghi*]perylene; *Okuda et al.* [2002a] - fluoranthene, pyrene, benzo[*fluoranthene*], benzopyrenes, indeno(1, 2, 3-*cd*)pyrene, benzo[*ghi*]perylene; *Okuda et al.* [2002b] - benzo[*fluoranthene*], benzopyrenes, indeno(1, 2, 3-*cd*)pyrene, benzo[*ghi*]perylene, coronene; *Reddy et al.* [2002] - phenanthrene, fluoranthene, pyrene, benzo[*a*]anthracene, chrysene/triphenylene, benzo[*fluoranthene*], benzo[*ghi*]perylene; *Okuda et al.* [2004] - fluoranthene, pyrene, cyclopenta(*cd*)pyrene/benzo[*a*]anthracene/chrysene, benzo[*fluoranthene*], benzopyrenes, indeno(1, 2, 3-*cd*)pyrene, benzo[*ghi*]perylene, coronene; *Kumata et al.* [2006] - values were reported as LMW and HMW PAHs combined, LMW = anthracene, 3-,2-methylphenanthrene, 9-,1-methylphenanthrene, 2-phenylnaphthalene, fluoranthene, acephenanthrylene, pyrene, benzo[*ghi*]fluoranthene, cyclopenta(*cd*)pyrene/benzo[*a*]anthracene/chrysene/triphenylene. HMW = benzo[*b + j + k*]fluoranthenes, benzo[*e*]pyrene, benzo[*a*]pyrene, indeno(1, 2, 3-*cd*)pyrene, benzo[*ghi*]perylene, coronene.

<sup>o</sup>Several PAHs (dibenzothiophene, phenanthrene/anthracene, 3,2-methylphenanthrene, 4,1-methylphenanthrene, phenylnaphthalene, dimethylphenanthrenes, fluoranthene, pyrene, methylpyrene, benzo[*ghi*]fluoranthene, chrysene/benzo[*a*]anthracene, benzo[*b + k*]fluoranthene, benzo[*a + e*]pyrene, perylene, indeno[1, 2, 3-*cd*]pyrene, benzo[*ghi*]perylene) were pooled for isotopic measurements reported in this reference.

<sup>p</sup>Component measured from samples collecting aerosol PM<sub>1.1</sub>.

<sup>q</sup> $\delta^{13}\text{C}$  values represent the ranges of values for C<sub>16</sub> to C<sub>32</sub> and C<sub>34</sub> fatty acids.  $\Delta^{14}\text{C}$  measurements were reported for samples comprised of 1) C<sub>16</sub>, 2) C<sub>18+20+22</sub>, 3) C<sub>24+26</sub>, and 4) C<sub>28+30+32</sub> fatty acids.

<sup>r</sup> $\delta^{13}\text{C}$  values represent the ranges of values for C<sub>16</sub> to C<sub>32</sub> and C<sub>34</sub> fatty acids.  $\Delta^{14}\text{C}$  measurements were reported for samples comprised of 1) C<sub>16</sub>, 2) C<sub>18</sub>, 3) C<sub>20+22</sub>, 4) C<sub>24+26</sub> and 5) C<sub>28+30+32+34</sub> fatty acids.



**Figure 4.** Relationship between TOC  $\Delta^{14}\text{C}$  and TSE  $\Delta^{14}\text{C}$  for aerosol particulate matter samples collected from Harcum and Millbrook sites. Line and equation represent best fit linear correlation.

( $\delta^{13}\text{C} = -27.2 \pm 0.4\text{‰}$ ,  $n = 4$ ), aliphatic ( $\delta^{13}\text{C} = -28.1 \pm 0.4\text{‰}$ ,  $n = 4$ ), aromatic ( $\delta^{13}\text{C} = -28.4 \pm 0.3\text{‰}$ ,  $n = 6$ ), and polar ( $\delta^{13}\text{C} = -27.3 \pm 0.5\text{‰}$ ,  $n = 5$ ) OC fractions had significantly depleted mean  $\delta^{13}\text{C}$  values (one-way ANOVA,  $p < 0.001$ ; Tukey-Kramer *post hoc* multiple comparisons test,  $p < 0.05$ ) compared to TOC ( $\delta^{13}\text{C} = -25.6 \pm 0.3\text{‰}$ ,  $n = 6$ ; Table 2) and WSOC ( $\delta^{13}\text{C} = -25.2 \pm 0.2\text{‰}$ ,  $n = 5$ ; Table 2). Similar to the present study, various solvent extractable aerosol components (e.g., alkanes, alkanols, alkanolic acids and lignin phenols) in northeast Atlantic Ocean dustfall were depleted in  $^{13}\text{C}$  ( $-27.9$  to  $-22.6\text{‰}$ ; Table 3) relative to TOC ( $-18.9\text{‰}$ ) [Eglinton *et al.*, 2002]. Studies examining the  $\delta^{13}\text{C}$  signatures of aerosol-derived aliphatic OC [Schefuß *et al.*, 2003] and polar OC components (fatty acids [Matsumoto *et al.*, 2001, 2004]) have also shown the majority of  $\delta^{13}\text{C}$  values for these compound classes to be  $< -26\text{‰}$  (Table 3). In addition, the  $^{13}\text{C}$  depleted values of the aliphatic, aromatic, and polar OC components are consistent with findings from studies in other systems that have shown  $\delta^{13}\text{C}$  values for lipids derived from several terrestrial tree and plant species (e.g., alkanes, aldehydes, fatty acids, sterols, lignin [Benner *et al.*, 1987; Collister *et al.*, 1994]) to be depleted compared to the TOC [Benner *et al.*, 1987; Collister *et al.*, 1994]. Such components can contribute to aerosol OC upon release from plants and subsequent entrainment in air masses, and they may therefore comprise portions of the aliphatic, aromatic, and polar OC.

[24] In contrast to aromatic OC in the present study (Table 2 and Figure 2), previously reported aerosol-derived PAH  $\delta^{13}\text{C}$  signatures covered a broad range (Table 3;  $-32$  to  $-21\text{‰}$  [Okuda *et al.*, 2002a, 2002b, 2004; Reddy *et al.*, 2002; Mandalakis *et al.*, 2005; Kumata *et al.*, 2006]) and were not uniformly  $^{13}\text{C}$ -depleted relative to aerosol TOC [Reddy *et al.*, 2002]. However, the depleted  $\delta^{13}\text{C}$  values for aromatic OC reported here (Table 2 and Figure 2;  $-29.6$  to  $-27.8\text{‰}$ ) are consistent with those reported for PAHs from European background sites (Table 3;  $-29.2\text{‰}$  to  $-27.7\text{‰}$  [Mandalakis *et al.*, 2005]) as opposed to the more enriched values noted from near a roadway in Tokyo (Table 3;  $-27\text{‰}$

to  $-23\text{‰}$  [Okuda *et al.*, 2004]) and from urban areas in Washington, DC (Table 3;  $-24.3\text{‰}$  to  $-22.4\text{‰}$  [Reddy *et al.*, 2002]) and China (Table 3;  $-27\text{‰}$  to  $-21\text{‰}$  [Okuda *et al.*, 2002a]). Okuda *et al.* [2004] estimated the  $\delta^{13}\text{C}$  value of PAHs from automotive exhaust in Japan to range from  $-23.6\text{‰}$  to  $-19.5\text{‰}$ , while a separate study revealed PAHs from wood burning to be isotopically lighter (Table 3;  $-32\text{‰}$  to  $-27\text{‰}$  [Okuda *et al.*, 2002b]) suggesting that lighter PAH  $\delta^{13}\text{C}$  values may also be indicative of biomass sources. Compound or compound-specific measurements were not possible in the present study due to the limited sample sizes. Nonetheless, assuming PAH sources are generally representative of the greater aromatic OC subfraction, then the depleted  $\delta^{13}\text{C}$  values for the aromatic OC observed in the present study suggest that it may be composed of considerable biomass combustion derived material.

### 3.2.2. Fossil Versus Biogenic Contributions to Solvent-Extractable Subfractions

#### 3.2.2.1. Total Solvent Extracts

[25]  $\Delta^{14}\text{C}$  values of TSE were correlated positively with TOC  $\Delta^{14}\text{C}$  values (Figure 4;  $r = 0.95$ ,  $p < 0.05$ ) with a slope ( $0.89 \pm 0.20$ ) not statistically different than 1 (Student's *t*-test,  $p < 0.05$ ). This suggests that the extraction procedure isolated a TSE component ( $f_{\text{TSE}} = \text{TSE OC}/\text{TOC} = 0.43 - 0.91$ ) of the TOC that is representative of the fossil and modern components of the aerosol TOC in general. The TSE  $\delta^{13}\text{C}$  values, however, were depleted by as much as  $4.5\text{‰}$ , (one-way ANOVA, Tukey-Kramer *post-hoc* multiple comparisons test,  $p < 0.05$ ) relative to TOC (Table 2). The lack of correlation between TOC and TSE  $\delta^{13}\text{C}$  values likely reflects isotopic partitioning among lipid components extracted by these methods as has been observed for plant lipid components (e.g., fatty acids, alkanes, sterols, lignin, etc.) which often exhibit depleted  $\delta^{13}\text{C}$  values relative to the total plant biomass [Benner *et al.*, 1987; Collister *et al.*, 1994; Canuel *et al.*, 1997]. The purified aliphatic, aromatic, and polar OC components from this study were found to have even more depleted  $\delta^{13}\text{C}$  values than the TSE (Table 2) supporting the contention that  $^{13}\text{C}$ -depleted lipids contribute to depleted  $\delta^{13}\text{C}$  values of the TSE.

#### 3.2.2.2. Aliphatic OC

[26] The aliphatic component was quantitatively the smallest OC constituent ( $< 1\%$  of TOC; Table 2) and had  $\Delta^{14}\text{C}$  signatures that were significantly lower (mean  $\Delta^{14}\text{C}_{\text{aliphatic}} = -853 \pm 29\text{‰}$ ,  $n = 5$ ; one-way ANOVA with Tukey-Kramer *post hoc* multiple comparisons test,  $p < 0.05$ ; Table 2 and Figure 3) than all other forms of OC measured in this study. These  $\Delta^{14}\text{C}$  values correspond to a mean contribution from fossil carbon sources of  $86\%$  (Table 2). Alkanes are aliphatic OC constituents that are also relatively abundant components of contemporary-derived leaf abrasion products ( $13$ – $19\%$  OC [Rogge *et al.*, 1993b]) but represent a considerably smaller fraction of OC emissions from fossil carbon ( $1$ – $3\%$  [Rogge *et al.*, 1993a, 1993c, 1997]) and contemporary wood ( $< 0.001\%$  [Rogge *et al.*, 1998]) combustion. Estimates of  $f_{\text{aliphatic}}$  in the present study were always less than  $0.01$  (Table 2), representing a very small contribution to aerosol particulate TOC and consistent with the fossil fuel combustion emission estimates [Rogge *et al.*, 1993a, 1993c, 1997, 1998].

**Table 4.** Comparison of Mean Percent Contributions of Contemporary and Fossil OC Reported for TOC and Various Subfractions of OC for All Samples Collected From the Rural Millbrook and Harcum Sites in this Study and in Urban Aerosol as Reported in Currie et al. [1997]<sup>a</sup>

Component	This Study (2007)		Currie et al. [1997]	
	Contemporary OC (%)	Fossil OC (%)	Contemporary OC <sup>b</sup> (%)	Fossil OC (%)
TOC	74 ± 7	26 ± 7	43	57
WSOC	94 ± 1	6 ± 1	nd <sup>c</sup>	nd <sup>c</sup>
TSE	72 ± 9	28 ± 9	nd <sup>c</sup>	nd <sup>c</sup>
Aliphatic OC	14 ± 3	86 ± 3	2	98
Aromatic OC	52 ± 8	48 ± 8	12	88
Polar OC	70 ± 12	30 ± 12	30	70

<sup>a</sup>For details on the urban aerosol (National Institute of Standards and Technology SRM-1941), see Currie et al. [1997]. Errors reported for this study are standard errors of the mean.

<sup>b</sup>Contemporary OC values were calculated from “Modern-C” values which were not originally corrected for the 42% excess <sup>14</sup>C abundance in the 1973 (date of sample collection in Currie et al. [1997]) atmosphere due to nuclear testing. As a result, the “Modern-C” values from Currie et al. [1997] were divided by 1.42 to obtain Contemporary OC values presented here as Contemporary OC (%) = Modern-C (%) / 1.42. Refer to text for additional details.

<sup>c</sup>nd-not determined.

[27] Aliphatic OC was similarly found to be almost entirely (98%) fossil-derived in urban dust from Washington, DC (Table 4) [Currie et al., 1997] though the sample examined in that study was collected in 1976–77 during a time of much less efficient fossil fuel combustion. In the present study, aliphatic OC had a consistently highly fossil derived character even in samples showing highly contemporary TOC (Table 2 and Figure 3; see Millbrook May, August samples). The predominance of fossil sources to aliphatic OC even at the rural background sites sampled in the present study therefore further emphasizes that anthropogenic sources dominate this hydrophobic component and suggests that aliphatic components from leaf waxes and other biogenic sources are minor constituents of east coast United States aerosols.

### 3.2.2.3. Aromatic OC

[28] Similar to the aliphatic fraction, the aromatic OC fraction was a quantitatively small component of the TOC, representing less than 1% on average (Table 2). With the exception of the May 2007 Millbrook sample ( $\Delta^{14}\text{C} = -77\text{‰}$ ; Table 2 and Figure 3), the aromatic OC isolates were strongly <sup>14</sup>C-depleted ( $\Delta^{14}\text{C}$  of  $-692$  to  $-446\text{‰}$ ; Table 2 and Figure 3), with a mean  $\Delta^{14}\text{C}$  value of  $-444\text{‰}$ . This average  $\Delta^{14}\text{C}$  value corresponds with 48% of aromatic OC being derived from fossil sources (Table 4). For comparison, Currie et al. [1997] showed a much higher contribution to aromatic OC from fossil sources (88%; Table 4) in a sample collected in 1976–77 in an urban setting. Our findings suggest that anthropogenic sources of aromatic OC are significantly diluted by contemporary sources in rural background eastern United States air.

[29] PAHs, which can have both contemporary biogenic (e.g., diagenetic processes, forest fires/biomass burning [e.g., Laflamme and Hites, 1978; Wakeham et al., 1980; Rogge et al., 1993b, 1998; Lima et al., 2005]) and fossil-derived (e.g., oil spills, fossil fuel combustion [Laflamme and Hites, 1978; Tan and Heit, 1981; Rogge et al., 1993a,

1993c, 1997; Gustafson and Dickhut, 1997; Lima et al., 2005]) sources, have been the most commonly studied aromatic OC components in previous studies. Several of the previous studies have examined the <sup>14</sup>C content of aerosol-derived PAHs, and have reported  $\Delta^{14}\text{C}$  values ranging from  $-381\text{‰}$  at a background site in Sweden [Mandalakis et al., 2005] to  $<-900\text{‰}$  for a background site in Greece [Mandalakis et al., 2005] and for urban aerosol particulate matter from Washington, DC [Reddy et al., 2002] (Table 3). The higher  $\Delta^{14}\text{C}$  values found in Sweden corresponded to a 43% fossil contribution and were attributed to dilution by large contributions from modern biomass burning sources [Mandalakis et al., 2005]. The findings from the present study (Table 2 and Figure 3), also from background sites, similarly suggest a combination of modern biomass burning and fossil fuel combustion sources and reflect important differences in the composition of aromatic OC in urban versus background sites.

[30] The  $\Delta^{14}\text{C}$  signature of the aromatic fraction reported for the May 14–16, 2007 Millbrook sampling ( $-77\text{‰}$ ; Table 2 and Figure 3) was highly enriched relative to the other samples (Table 2 and Figure 3), revealing significant isotopic heterogeneity within the aromatic OC fraction at different sampling times. This sampling date also showed a relatively enriched aerosol TOC  $\Delta^{14}\text{C}$  value ( $-39\text{‰}$ ) that was likely influenced by unusually high inputs of pollen that were readily observable on the aerosol filter (personal observation). While not major contributors to pollen, aromatic compounds have been identified as pollen constituents [Guilford et al., 1988; Watson et al., 2007; Schulte et al., 2008] and may have been major contributors to the aromatic OC in this sample as evidenced by the elevated  $\Delta^{14}\text{C}$  signature for the aromatic fraction (Table 2 and Figure 3). This <sup>14</sup>C-enriched sample further illustrates that variability in the relative magnitudes of fossil and contemporary aromatic OC sources can have both spatial (urban versus background sites) and temporal features.

[31] Even in this pollen influenced sample, the aromatic OC always showed a consistently higher fossil content than the TOC demonstrating its higher relative abundance in fossil versus contemporary sources. Thus, aromatic OC, which is thought to be microbially resistant [see, e.g., Baldock and Smernik, 2002; Kim et al., 2006] and will therefore persist in the environment if it escapes photochemical degradation, may be derived from both fossil and contemporary sources but has a strong fossil anthropogenic component. Further, while PAHs are components of aromatic OC derived from contemporary biomass or fossil fuel combustion, the May 2007 Millbrook sample suggests that additional non-combustion sources (e.g., pollen) must at times be important in delivering refractory aerosol OC to terrestrial and aquatic environments.

### 3.2.2.4. Polar OC

[32] Four of the five polar OC isolates were enriched in  $\Delta^{14}\text{C}$  ( $-240$  to  $24\text{‰}$ ; Table 2 and Figure 3) relative to the aromatic and aliphatic OC. This finding is similar to that for the National Institute of Standards and Technology urban dust reference material [Currie et al., 1997]. In contrast, the polar OC component from the March 2007 Millbrook sample was highly depleted in  $\Delta^{14}\text{C}$  ( $-750\text{‰}$ ; Table 2 and Figure 3). The March 2007 sample notwithstanding, polar OC in general showed significantly lower fossil contributions compared to the aliphatic and aromatic fractions

(Table 4), similar to findings from compound-specific  $\Delta^{14}\text{C}$  analyses of aerosol polar OC components such as alkanols (Table 3;  $\Delta^{14}\text{C} = -80.8\%$ , 14% fossil [Eglinton *et al.*, 2002]) and fatty acids ( $\Delta^{14}\text{C} = -518$  to  $+407\%$ , 0–55% fossil [Matsumoto *et al.*, 2001, 2004]). The observed consistency in the relative contributions of polar versus aromatic and aliphatic OC demonstrates that contemporary aerosol OC sources are consistently more prevalent in polar compared to aromatic and aliphatic OC.

[33] The mean estimate of fossil carbon contribution to the polar OC component was heavily influenced by the March 7–10, 2007 (Table 2 and Figure 3) Millbrook sampling when 77% of the polar OC was fossil-derived. This sample also had the most depleted TOC  $\Delta^{14}\text{C}$  value (Table 2 and Figure 3) of all the samples. It thus appears that polar OC can at least at times be dominated by fossil sources, again illustrating the variability in the relative fossil and modern contributions to these operationally defined OC subfractions. The median polar OC  $\Delta^{14}\text{C}$  value was  $-168\%$ , reflecting a 22% contribution from fossil OC.

[34] Highly oxygenated polar compounds with acidic functional groups can form via photochemical transformation of biogenic [e.g., Gao *et al.*, 2004; Kanakidou *et al.*, 2005; Bhat and Fraser, 2007; Heaton *et al.*, 2007] and anthropogenic [e.g., Odum *et al.*, 1997; Kleindienst *et al.*, 1999, 2002; Kanakidou *et al.*, 2005; Song *et al.*, 2007] volatile, semi-volatile, and non-volatile organic compounds and would likely be extracted as part of the polar OC component. The polar OC was not consistently enriched or depleted in  $^{14}\text{C}$  relative to TOC suggesting that neither fossil nor contemporary sources preferentially partitioned into the polar OC component. This is in contrast to the aerosol WSOC which is likely to be a component of polar OC and was consistently enriched in  $^{14}\text{C}$  relative to TOC (Table 2 and Figure 3). Because of the highly oxygenated nature of SOA, WSOC has been used as a proxy for SOA [Weber *et al.*, 2007]. The  $\Delta^{14}\text{C}$  data presented here for WSOC and polar OC (Table 2 and Figure 3) suggest that SOAs dominated by contemporary material may have been important contributions to WSOC and polar OC in this study as has been suggested in other work [Weber *et al.*, 2007]. However, the polar OC appears to contain a fossil source of OC that is non-water soluble and may reflect the greater hydrophobic nature of fossil fuel [e.g., Odum *et al.*, 1997; Kleindienst *et al.*, 1999, 2002; Kanakidou *et al.*, 2005; Song *et al.*, 2007] relative to biogenic [e.g., Gao *et al.*, 2004; Kanakidou *et al.*, 2005; Bhat and Fraser, 2007; Heaton *et al.*, 2007] SOA precursors. As water solubility is expected to make aerosol OC both more mobile within a watershed and available for bacterial degradation, fossil fuel derived polar OC may be more likely to be retained within watersheds.

#### 4. Summary and Implications

[35] Fossil and contemporary sources were found to have variable contribution to aerosol particulate OC components, with the exception of aliphatic OC and WSOC which were predominantly fossil and contemporary-derived, respectively. The variable nature of these fossil and contemporary contributions to other aerosol TOC components merit further consideration in order to understand the spatial, temporal, and

anthropogenic factors determining fossil and contemporary sources of these materials. Still, in spite of the different sampling locations and times, many of the observed patterns in isotopic composition are generally consistent across these temporal and spatial scales (e.g.,  $\Delta^{14}\text{C}$  aerosol WSOC is greater than all other components; aerosol aromatic, aliphatic, and WINSOC  $\Delta^{14}\text{C}$  is consistently depleted relative to aerosol TOC, polar OC, and WSOC.), suggesting that these patterns may be relatively independent of environmental conditions. The overwhelming fossil source for the aliphatic component for both urban [Currie *et al.*, 1997] and background (present study) sites suggests it may be useful as a potential fossil aerosol OC proxy for characterizing and perhaps even quantifying fossil aerosol sources (e.g., using molecular markers). Isolation and molecular characterization of the aliphatic fraction may therefore be an excellent means of assessing fossil sources of ambient aerosol OC in the absence of considerable contemporary OC contributions.

[36] Wet and dry deposited aerosol OC constitute major inputs of OC to terrestrial watersheds that may be transported hydrologically to aquatic systems and contribute to watershed and aquatic biogeochemical cycles through biotic and abiotic degradation, burial, and transport. The findings presented here suggest that the potentially more refractory and immobile portions of aerosol OC, aliphatic and aromatic OC, have large fossil fuel sources, while polar and WSOC, which are likely to be more bioavailable and mobile, are predominantly contemporary in origin. Emissions of fossil aerosol OC appear to take the form of relatively insoluble aromatic and aliphatic components, while aerosol OC derived from contemporary biomass is more likely to be water-soluble as reflected by the smaller fossil contributions to WSOC and the polar constituent (Table 4). Some fossil OC is also water-soluble, accounting for a mean of 6% of WSOC (Table 4) in the present study and up to 30% of WSOC in other studies [Weber *et al.*, 2007; Wozniak *et al.*, 2012] and thus may be input to aquatic systems where it will be a previously unrecognized component of aquatic OC cycling. However, fossil-derived aerosol OC is more often insoluble, suggesting its contribution to aquatic systems and carbon budgets may be more generally dependent on the erodibility of aerosol particles from within a watershed. With further work to more fully characterize the susceptibility of OC compound classes to biogeochemical processes, the results from this study may be used to more fully assess the impacts of aerosol OC sources to aquatic and terrestrial biogeochemistry.

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