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

A. S. Wozniak  
*Virginia Institute of Marine Science*

James E. Bauer  
*Virginia Institute of Marine Science*

Rebecca M. Dickhut  
*Virginia Institute of Marine Science*

Li Xu

Ann P. McNichol

Follow this and additional works at: [https://scholarworks.wm.edu/vimsarticles](https://scholarworks.wm.edu/vimsarticles)

Part of the [Oceanography and Atmospheric Sciences and Meteorology Commons](https://scholarworks.wm.edu/vimsarticles)

**Recommended Citation**

Wozniak, A. S.; Bauer, James E.; Dickhut, Rebecca M.; Xu, Li; and McNichol, Ann P., "Isotopic characterization of aerosol organic carbon components over the eastern United States" (2012). *VIMS Articles*. 530.  
[https://scholarworks.wm.edu/vimsarticles/530](https://scholarworks.wm.edu/vimsarticles/530)

This Article is brought to you for free and open access by W&M ScholarWorks. It has been accepted for inclusion in VIMS Articles by an authorized administrator of W&M ScholarWorks. For more information, please contact scholarworks@wm.edu.
Isotopic characterization of aerosol organic carbon components over the eastern United States

Andrew S. Wozniak,1,2 James E. Bauer,3 Rebecca M. Dickhut,1 Li Xu,4 and Ann P. McNichol4

Received 9 November 2011; revised 17 May 2012; accepted 20 May 2012; published 4 July 2012.

[1] Carbon isotopic signatures (δ13C, Δ14C) 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) δ13C values (−27 to −24‰) indicated predominantly terrestrial C3 plant and fossil derived sources. Total solvent extracts (TSE) and their aliphatic, aromatic, and polar OC components were depleted in δ13C (−30 to −26‰) relative to TOC and WSOC. Δ14C signatures of aerosol TOC and TSE (−476 to +25‰) suggest variable fossil contributions (~5–50%) to these components. Aliphatic OC while comprising a small portion of the TOC (<1%), was dominated by fossil-derived carbon (86 ± 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 ± 8%) and fossil (48 ± 8%) OC. The quantitatively significant polar OC fraction (6–25% of TOC) had fossil contributions (30 ± 12%) similar to TOC (26 ± 7%) and TSE (28 ± 9%). Thus, much of both 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.


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., Galiluhn 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 [Lioussse 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 NOx or O3 [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
Table 1. Alphabetical List and Definitions of Acronyms Used in the Paper

<table>
<thead>
<tr>
<th>Acronym</th>
<th>Definition</th>
</tr>
</thead>
<tbody>
<tr>
<td>ANOVA</td>
<td>Analysis of Variance</td>
</tr>
<tr>
<td>BC</td>
<td>Black Carbon</td>
</tr>
<tr>
<td>C1</td>
<td>International Atomic Energy Agency “C1” Carrara marble standard</td>
</tr>
<tr>
<td>DCM</td>
<td>Dichloromethane</td>
</tr>
<tr>
<td>EC</td>
<td>Elemental Carbon</td>
</tr>
<tr>
<td>MeOH</td>
<td>Methanol</td>
</tr>
<tr>
<td>OC</td>
<td>Organic Carbon</td>
</tr>
<tr>
<td>PAH</td>
<td>Polycyclic Aromatic Hydrocarbon</td>
</tr>
<tr>
<td>PM1,2,5,10</td>
<td>Particulate Matter &lt;1.1 μm (or 2.5 or 10)</td>
</tr>
<tr>
<td>SOA</td>
<td>Secondary Organic Aerosol</td>
</tr>
<tr>
<td>TOC</td>
<td>Total Organic Carbon (= OC + BC – inorganic carbonates)</td>
</tr>
<tr>
<td>TSE</td>
<td>Total Solvent Extract</td>
</tr>
<tr>
<td>TSP</td>
<td>Total Suspended Particulates</td>
</tr>
<tr>
<td>VOC</td>
<td>Volatile Organic Compound</td>
</tr>
<tr>
<td>WIOC</td>
<td>Water Insoluble Organic Carbon (= TOC – WSOC)</td>
</tr>
<tr>
<td>WSOC</td>
<td>Water Soluble Organic Carbon</td>
</tr>
</tbody>
</table>

*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., O₃, NOₓ, etc. [Kanakidou et al., 2005; Kroll et al., 2007; Surtratt 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 (¹⁴C) analyses of ambient aerosol particulate OC (using total suspended particulate (TSP) and PM₂.₅ 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.

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 PM₁₀ [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.

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 [Kulawinska et al., 2004; Stubbins et al., 2010] and concomitantly resistant to microbial degradation [Balduck 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 (δ¹³C and Δ¹⁴C, 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, Δ¹⁴C values of aerosol OC can range from entirely fossil fuel derived (≈−1,000‰) to fully derived from contemporary sources (e.g., newly produced biomass; ≈55‰ [Hsueh et al., 2007]). The very large dynamic range in Δ¹⁴C (≈−1,000‰) and the difference between potential end-member Δ¹⁴C 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, Δ¹⁴C alone is unable to distinguish between different types of fossil materials or contemporary vegetation.

The major contemporary and fossil sources to aerosol OM show typical ranges of δ¹³C values that can aid in source apportionment. δ¹³C signatures for C₄ terrestrial vegetation (e.g., corn, salt marsh plants; δ¹³C ≈−14 to −12‰) and marine (δ¹³C ≈−22 to −18‰) OC sources are distinct from one another and enriched in ¹³C relative to C₃ terrestrial vegetation and fossil fuel OC (δ¹³C ≈−30 to −23‰ for both) [e.g., Fry and Sherr, 1984; Schoell, 1984; Bouton, 1991; Latijha and Marshall, 1994]. Interpretation of δ¹³C signatures in aerosol OC is, however, not always straightforward because C₃ terrestrial vegetation and fossil fuel signatures overlap and combustion and photochemical processes cause isotopic fractionations. OC from biomass combustion shows δ¹³C 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 C$_3$ or fossil fuel origin that appear (incorrectly) to be influenced by marine or 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 m$^3$, ~1.7 m$^3$ 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) and the National Atmospheric Deposition Program site (VA98) in Harcum, VA (37.5312 N, 76.4928 W; http://nadp.sws.uiuc.edu/sites/sitinfo.asp?net=NTRN&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 $\mu$g OC m$^{-3}$; Harcum: 4.33 $\mu$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).$^1$

[9] Air was drawn through pre-ashed (3 h, 525°C) and preweighed high-purity quartz microfilters (20.3 cm × 25.4 cm, nominal pore size 0.6 $\mu$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 (~40–70 h sampling duration, ~60–80 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 (~24 h) and lower face velocities (~30–45 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 $\leq$~10–16% of TOC.

2.2. Laboratory Analyses

2.2.1. TOC and WSOC Preparation

[11] Between one and four filter core plugs (2.84 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 $\mu$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 $\mu$MOC) 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 $\mu$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°C under a stream of ultrahigh purity N$_2$, leaving the dried, operationally defined WSOC in the quartz tube. The WSOC was then oxidized to 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 $\mu$g C.

$^1$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

<table>
<thead>
<tr>
<th>Aerosol OC Component</th>
<th>Parameter</th>
<th>Millbrook March 7–10</th>
<th>Harcum May 14–16</th>
<th>Avg 10–12</th>
<th>Mean</th>
<th>Feb 19–21</th>
<th>April 10–12</th>
<th>Aug 6–8</th>
<th>Mean</th>
<th>Overall Mean</th>
</tr>
</thead>
<tbody>
<tr>
<td>TOC</td>
<td>$\delta^{13}$C (%)</td>
<td>25.3</td>
<td>25.8</td>
<td>24.7</td>
<td>25.3</td>
<td>26.2</td>
<td>26.5</td>
<td>26.4</td>
<td>25.7</td>
<td>25.5</td>
</tr>
<tr>
<td></td>
<td>$\Delta^{14}$C (%)</td>
<td>448</td>
<td>39</td>
<td>25</td>
<td>154</td>
<td>252</td>
<td>252</td>
<td>165</td>
<td>268</td>
<td>21.1</td>
</tr>
<tr>
<td>WSOC</td>
<td>$\delta^{13}$C (%)</td>
<td>nd</td>
<td>25.1</td>
<td>24.4</td>
<td>24.7</td>
<td>26.1</td>
<td>25.6</td>
<td>26.8</td>
<td>25.4</td>
<td>25.1</td>
</tr>
<tr>
<td></td>
<td>$f_{WSOC}$</td>
<td>nd</td>
<td>0.78</td>
<td>0.53</td>
<td>0.66</td>
<td>0.71</td>
<td>0.84</td>
<td>0.74</td>
<td>0.76</td>
<td>0.72</td>
</tr>
<tr>
<td>WIOC</td>
<td>$\delta^{13}$C (%)</td>
<td>nd</td>
<td>26.0</td>
<td>25.1</td>
<td>25.6</td>
<td>26.7</td>
<td>26.8</td>
<td>25.9</td>
<td>25.9</td>
<td>25.8</td>
</tr>
<tr>
<td></td>
<td>$f_{WIOC}$</td>
<td>nd</td>
<td>0.03</td>
<td>0.001</td>
<td>0.003</td>
<td>0.003</td>
<td>0.007</td>
<td>0.002</td>
<td>0.004</td>
<td>0.004</td>
</tr>
<tr>
<td>TSE</td>
<td>$\delta^{13}$C (%)</td>
<td>nd</td>
<td>26.2</td>
<td>26.6</td>
<td>nd</td>
<td>27.3</td>
<td>28.2</td>
<td>27.6</td>
<td>27.2</td>
<td>27.2</td>
</tr>
<tr>
<td></td>
<td>$f_{TSE}$</td>
<td>nd</td>
<td>0.03</td>
<td>0.001</td>
<td>0.003</td>
<td>0.003</td>
<td>0.007</td>
<td>0.002</td>
<td>0.004</td>
<td>0.004</td>
</tr>
<tr>
<td>Aliphatic</td>
<td>$\delta^{13}$C (%)</td>
<td>28.6</td>
<td>27.7</td>
<td>nd</td>
<td>28.2</td>
<td>nd</td>
<td>27.3</td>
<td>28.9</td>
<td>28.1</td>
<td>28.1</td>
</tr>
<tr>
<td></td>
<td>$f_{aliphatic}$</td>
<td>0.07</td>
<td>0.09</td>
<td>0.79</td>
<td>nd</td>
<td>0.43</td>
<td>0.74</td>
<td>0.59</td>
<td>0.69</td>
<td>0.69</td>
</tr>
<tr>
<td>Aromatic</td>
<td>$\delta^{13}$C (%)</td>
<td>27.8</td>
<td>29.6</td>
<td>28.3</td>
<td>28.6</td>
<td>28.3</td>
<td>28.4</td>
<td>27.8</td>
<td>28.2</td>
<td>28.4</td>
</tr>
<tr>
<td></td>
<td>$f_{aromatic}$</td>
<td>0.62</td>
<td>0.77</td>
<td>0.446</td>
<td>0.405</td>
<td>0.466</td>
<td>0.540</td>
<td>0.446</td>
<td>0.484</td>
<td>0.444</td>
</tr>
<tr>
<td>Polar</td>
<td>$\delta^{13}$C (%)</td>
<td>27.8</td>
<td>26.1</td>
<td>28.0</td>
<td>27.3</td>
<td>28.6</td>
<td>nd</td>
<td>26.2</td>
<td>27.4</td>
<td>27.3</td>
</tr>
<tr>
<td></td>
<td>$f_{polar}$</td>
<td>0.24</td>
<td>0.039</td>
<td>0.25</td>
<td>0.18</td>
<td>0.063</td>
<td>nd</td>
<td>0.066</td>
<td>0.065</td>
<td>0.13</td>
</tr>
</tbody>
</table>

*All reported $\delta^{13}$C and $\Delta^{14}$C values were corrected for blank contributions following procedures outlined in the text. Values represent the fraction of TOC accounted for by the parameter of interest ($f_{WSOC}$, $f_{WIOC}$, $f_{TSE}$, $f_{aliphatic}$, $f_{aromatic}$, $f_{polar}$). WIOC (water-insoluble organic carbon) values were calculated by mass balance using values for TOC and WSOC (WIOC = TOC - WSOC): $X_{WIOC} = \frac{X_{TOC} - X_{WSOC}}{f_{WOOC}}$, where X represents either $\delta^{13}$C or $\Delta^{14}$C for the component of interest (TOC, WSOC, WIOC). TSE = Total Solvent Extract. Sample was too small for measurement of both $\delta^{13}$C and $\Delta^{14}$C. A value of −25.0‰ was assumed for $\Delta^{14}$C fractionation corrections.
2.2.2. Solvent Extraction and Aliphatic, Aromatic, and Polar OC Subfraction Preparation

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 under a stream of ultrahigh purity N₂, and the remaining OC residue was analyzed for δ¹³C and δ¹⁴C 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 N₂ in pre-ashed 9 mm quartz tubes and subsequently combusted to carbon dioxide and converted to graphite prior to δ¹³C and δ¹⁴C analyses as described elsewhere [Wozniak et al., 2011].

2.2.3. Isotopic Analyses

All δ¹³C and δ¹⁴C analyses were performed at the National Ocean Sciences Accelerator Mass Spectrometry (NOSAMS) facility. For Δ¹⁴C analyses, accelerator mass spectrometry measurement errors averaged ±4‰ and were never larger than ±9‰. The mean measurement error for δ¹³C analyses performed using an Optima isotope ratio mass spectrometer was ±0.1‰.

2.3. Data Analyses

2.3.1. Filter Blanks and Blank Corrections

Blank filters were subjected to the same extraction procedures as sample filters, and corrections for blank contributions to δ¹³C and Δ¹⁴C 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 μg C) and were therefore assessed by diluting these samples with CO₂ derived from the International Atomic Energy Agency C1 “Carrara” marble standard (C1)
prior to being measured for isotopic signatures. Isotopic signatures of the blanks were then calculated as

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

where $X_{\text{measured}}$ represents the total $\delta^{13}C$ or $\Delta^{14}C$ value (i.e., including the blank), $f_{C1}$ represents the fraction of the C1 standard in the measured combined blank + C1, $X_{C1}$ represents the known isotopic signature of C1 ($\delta^{13}C_{C1} = +2.4\%$; $\Delta^{14}C_{C1} = -1000\%$), and $X_{\text{blank}}$ represents the $\delta^{13}C$ or $\Delta^{14}C$ value of the blank alone. In the above, “blank” refers to the blank for each specific OC subfraction (aliphatic, aromatic, TSE, or WSO) 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 ($f_{\text{blank}} = \text{OC}_{\text{blank}} / \text{OC}_{\text{sample}}$) was always less than 0.01, WSO 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 $\Delta^{14}C = -1000\%$ [see, e.g., Clayton et al., 1955; Currie et al., 1997] and contemporary OC from terrestrial plant biomass having $\Delta^{14}C$ values of $\approx +55\%$ (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 $\Delta^{14}C$ 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 WSO. For all statistical comparisons, a p value $<0.05$ was considered indicative of a significant difference.

3. Results and Discussion

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

3.1.1. Aerosol Particulate TOC

[18] Aerosol TOC $\delta^{13}C$ values in this study ($-26.6$ to $-24.5\%$; Table 2 and Figure 2) were similar to values reported throughout 2006–2007 at the same sites ($\delta^{13}C = -26$ to $-23\%$ [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; Lajitha and Marshall, 1994]. The $\delta^{13}C$ values for TOC in this study are on the high end of the range noted for C3 terrestrial vegetation/fossil fuel sources ($\approx 30$ to $-23\%$) indicating that marine or C4 terrestrial vegetation sources could potentially contribute to aerosol OM. However, air mass trajectory analyses (Figure S1) show that only the April ($\delta^{13}C = -26.5\%$; Table 2) and August ($\delta^{13}C = -24.4\%$; 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 $\delta^{13}C$ values can be explained by them (1) being derived entirely from fossil fuel and/or C3 terrestrial vegetation sources, (2) being OC of fossil fuel or C3 terrestrial vegetation origin that has been photochemically altered, or (3) contain small contributions from C4 terrestrial sources.

[19] $\Delta^{14}C$ values of aerosol TOC covered a broad range ($-448$ to $-39\%$; Table 2 and Figure 3) and were also similar to values reported by Wozniak et al. [2011] and in previous studies examining PM$_{2.5}$ [Hildemann et al., 1994; Klimedinst and Currie, 1999; Bench and Herckes, 2004; Zheng et al., 2006; Ding et al., 2008]. The $\Delta^{14}C$ 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 $\Delta^{14}C$ 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 $\Delta^{14}C$ 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.
3.1.2. Water-Soluble OC

The fraction of WSOC (fWSOC = WSOC/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 PM2.5 and TSP samples [e.g., Kleefeld et al., 2002; Weber et al., 2007; Wozniak et al., 2012]. WSOC δ13C values (−26.1 to −24.4‰; Table 2 and Figure 2) were similar in overall range to aerosol TOC δ13C values at the high end for C3 terrestrial plant and fossil fuel sources. Similar to the TOC samples, fossil and/or terrestrial C3 plant biomass again appear to be the major sources of WSOC, with 13C-enriched sources such as C4 plant and marine (April and August Harcum samples) OC likely to be minor [e.g., Fry and Sherr, 1984; Schoell, 1984; Botton, 1991; Lajtha and Marshall, 1994]. The photochemical processing of C3 terrestrial and fossil fuel derived OC may also play a role in these slightly enriched δ13C values [Pavuluri and Kawamura, 2012]. The relatively few previous studies that have measured δ13C 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‰ [Fisseha et al., 2006]; −25 to −23‰ [Fisseha et al., 2009]; −25‰ [Kirillova et al., 2010]; −25.2 ± 0.3‰ [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 13C by up to 2.5‰ relative to aerosol TOC suggesting that 13C-enriched aerosol TSP components are preferentially soluble [Fisseha et al., 2009; Kirillova et al., 2010]. However, there was no clear pattern of 13C 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 13C content (Table 2 and Figure 2). TOC δ13C values were found to be both enriched (by 0.8‰) and depleted (by up to 1.7‰) relative to WSOC δ13C values for the same sample suggesting a complex relationship between the δ13C signatures of dominant TOC and WSOC sources on a given sampling date.

3.2. Isotopic Signatures of Solvent Extractable Components

3.2.1. δ13C Signatures

A one-way ANOVA of the δ13C values for TOC and the various OC subfractions showed significant differences among the various components (Table 2). The TSE
### Table 3. δ13C and Δ14C Values and Sampling Locations for Aerosol OC Components Referenced in This Study

<table>
<thead>
<tr>
<th>Component</th>
<th>δ13C (%)</th>
<th>Δ14C (%)</th>
<th>Environment and Location</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>WSOOC</td>
<td>−26.1 to −24.4</td>
<td>−17 to 26</td>
<td>Rural; Millbrook, NY/ Harcum, VA, USA</td>
<td>This study[6][7]</td>
</tr>
<tr>
<td>WSOOC</td>
<td>−25.5 to −24.0</td>
<td>−9 to −114</td>
<td>Urban; Zurich, Switzerland</td>
<td>Schefuß et al. [2003][8][9]</td>
</tr>
<tr>
<td>WSOOC</td>
<td>−25.5 to −24.0</td>
<td>−9 to −114</td>
<td>Urban; Zurich, Switzerland</td>
<td>Currie et al. [1997][10][11]</td>
</tr>
<tr>
<td>WSOOC</td>
<td>−25.6 to −25.1</td>
<td>−58 to 125</td>
<td>Grassland/Forest; Stockholm, Sweden</td>
<td>This study[12][13]</td>
</tr>
<tr>
<td>WSOOC</td>
<td>−27.6 to −21.1</td>
<td>−187 to 106</td>
<td>Rural; Millbrook, NY/ Harcum, USA</td>
<td>Kumata et al. [2009][14]</td>
</tr>
<tr>
<td>WSOOC</td>
<td>−26.8 to −24.2</td>
<td>−461 to 42</td>
<td>Rural; Millbrook, NY/ Harcum, USA</td>
<td>Wozniak et al. [2012][15]</td>
</tr>
<tr>
<td>WSOOC</td>
<td>−28.6 to −26.2</td>
<td>−493 to −373</td>
<td>Urban; Zurich, Switzerland</td>
<td>Okuda et al. [2004][16]</td>
</tr>
<tr>
<td>WSOOC</td>
<td>−29.0 to −27.9</td>
<td>−961 to −794</td>
<td>Rural; Millbrook, NY/ Harcum, USA</td>
<td>Okuda et al. [2004][17]</td>
</tr>
<tr>
<td>Odd even numbered</td>
<td>−27.8 ± 0.9</td>
<td>−976</td>
<td>Urban, Washington, DC, USA</td>
<td>Eglinton et al. [2002][18]</td>
</tr>
</tbody>
</table>

(C23, 33) n-alkanes

<table>
<thead>
<tr>
<th>Component</th>
<th>δ13C (%)</th>
<th>Δ14C (%)</th>
<th>Environment and Location</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>C26,31 n-alkane</td>
<td>−31.5 to −27.7</td>
<td>NR</td>
<td>Marine; E Atlantic Ocean off W Africa</td>
<td>Schefuß et al. [2003][19][20]</td>
</tr>
<tr>
<td>Aromatic OC</td>
<td>−27.8 to −29.6</td>
<td>−692 to −77</td>
<td>Rural; Millbrook, NY/ Harcum, USA</td>
<td>This study[21][22]</td>
</tr>
<tr>
<td>Aromatic OC</td>
<td>−27.8 to −29.6</td>
<td>−692 to −77</td>
<td>Rural; Millbrook, NY/ Harcum, USA</td>
<td>Currie et al. [1997][23][24]</td>
</tr>
<tr>
<td>Selected PAHs</td>
<td>−881 to −801</td>
<td>NR</td>
<td>Urban; Washington, DC, USA</td>
<td>Currie et al. [1997][25][26]</td>
</tr>
<tr>
<td>Selected PAHs</td>
<td>−72.7 to −21.1</td>
<td>NR</td>
<td>Beijing, Chongqing, Hangzhou, China</td>
<td>Okuda et al. [2002][27][28]</td>
</tr>
<tr>
<td>Selected PAHs</td>
<td>−25 to −21</td>
<td>NR</td>
<td>Woodburning; Malaysia</td>
<td>Okuda et al. [2002][29][30]</td>
</tr>
<tr>
<td>Selected PAHs</td>
<td>−32 to −27</td>
<td>NR</td>
<td>Urban; Washington, DC, USA</td>
<td>Reddy et al. [2002][31][32]</td>
</tr>
<tr>
<td>Selected PAHs</td>
<td>−963 to −913</td>
<td>NR</td>
<td>Roadside; Tokyo, Japan</td>
<td>Okuda et al. [2004][33][34]</td>
</tr>
<tr>
<td>Selected PAHs</td>
<td>−27.0 to −23.3</td>
<td>NR</td>
<td>Marine; NE Atlantic Ocean off NW Africa</td>
<td>Okuda et al. [2004][33][34]</td>
</tr>
<tr>
<td>Even numbered</td>
<td>−29.2 to −94</td>
<td>NR</td>
<td>Maritime Background; Asprenten, Sweden</td>
<td>Eglinton et al. [2002][35][36]</td>
</tr>
<tr>
<td>Even numbered</td>
<td>−22.6 ± 2.5</td>
<td>NR</td>
<td>Marine; NE Atlantic Ocean off NW Africa</td>
<td>Eglinton et al. [2002][35][36]</td>
</tr>
</tbody>
</table>

(C22, 32) n-alkanols

<table>
<thead>
<tr>
<th>Component</th>
<th>δ13C (%)</th>
<th>Δ14C (%)</th>
<th>Environment and Location</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fatty acids (C16–34)</td>
<td>−30.8 to −23.0</td>
<td>−88 to 83.5</td>
<td>Semi-urban; Hokkaido, Japan</td>
<td>Matsumoto et al. [2004][37][38]</td>
</tr>
</tbody>
</table>

### Notes

aNR denotes references for which δ13C or Δ14C data were not reported for a given OC component.
bData from this study are reported as ranges. For mean values, refer to Table 2.
cComponent measured from samples collecting aerosol TSP. Use Table 2 for mean values.
dWSOC fraction contemporary (fWSOC) values were calculated from measurements on WIOC as described in the reference. fWSOC values were multiplied by 1.077 to convert them to fWSOC convention and converted to Δ14C convention after Stuiver and Polach [1977].

eComponent measured from samples collecting aerosol PM10.
fWSOC data are reported as the average values measured using two different methods.
gData reported for these studies were converted from a reported biogenic fraction to fWSOC by multiplying conversion factors cited in the studies then converted to Δ14C convention after Stuiver and Polach [1977].
hComponent measured from samples collecting aerosol PM1.5.

iWSOC and WIOC δ13C ranges were estimated from error bars on a figure within the reference.

jWIOC data are calculated from data measured for WSOOC as described in the references.

kData reported for these studies in fWSOC convention were converted after Stuiver and Polach [1977].

lδ13C values are reported for aerosol OC components as reported in various studies. For mean values, refer to Table 2.

mδ13C ranges are reported for weighted mean averages for measurements on individual compounds.

nδ13C values represent the ranges of values for C16 to C23 and C34 fatty acids. Δ14C measurements were reported for samples comprised of 1) C16, 2) C18-20,22, 3) C24,26, and 4) C28+30,32 fatty acids.

oδ13C values represent the ranges of values for C16 to C34 fatty acids. Δ14C measurements were reported for samples comprised of 1) C16, 2) C18, 3) C20+22, 4) C24,26, and 5) C28+30,32 fatty acids.

pδ13C values are reported as the average values measured using two different methods.

qComponent measured from samples collecting aerosol PM1.

rΔ14C values represent the ranges of values for C16 to C34 fatty acids. Δ14C measurements were reported for samples comprised of 1) C16, 2) C18, 3) C20+22, 4) C24,26, and 5) C28+30,32 fatty acids.

sδ13C values were calculated from measurements on WIOC as described in the reference. δ13C values were multiplied by 1.077 to convert them to fWSOC convention and converted to Δ14C convention after Stuiver and Polach [1977].

tComponent measured from samples collecting aerosol PM10.

uδ13C values were calculated from measurements on WIOC as described in the reference. δ13C values were multiplied by 1.077 to convert them to fWSOC convention and converted to Δ14C convention after Stuiver and Polach [1977].

vδ13C ranges were estimated from error bars on a figure within the reference.
(δ₁³C = −27.2 ± 0.4‰, n = 4), aliphatic (δ₁³C = −28.1 ± 0.4‰, n = 4), aromatic (δ₁³C = −28.4 ± 0.3‰, n = 6), and polar (δ₁³C = −27.3 ± 0.5‰, n = 5) OC fractions had significantly depleted mean δ₁³C values (one-way ANOVA, p < 0.001; Tukey-Kramer post hoc multiple comparisons test, p < 0.05) compared to TOC (δ₁³C = −25.6 ± 0.3‰, n = 6; Table 2) and WSOC (δ₁³C = −25.2 ± 0.2‰, 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 ¹³C (−27.9 to −22.6‰; Table 3) relative to TOC (−18.9‰) [Eglington et al., 2002]. Studies examining the ¹³C 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 ¹³C values for these compound classes to be <−26‰ (Table 3). In addition, the ¹³C depleted values of the aliphatic, aromatic, and polar OC components are consistent with findings from studies in other systems that have shown ¹³C 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 ¹³C signatures covered a broad range (Table 3; −32 to −21‰) [Okuda et al., 2002a, 2002b, 2004; Reddy et al., 2002; Mandalakis et al., 2005; Kumata et al., 2006]) and were not uniformly ¹³C-depleted relative to aerosol TOC [Reddy et al., 2002]. However, the depleted ¹³C values for aromatic OC reported here (Table 2 and Figure 2; −29.6 to −27.8‰) are consistent with those reported for PAHs from European background sites (Table 3; −29.2‰ to −27.7‰ [Mandalakis et al., 2005]) as opposed to the more enriched values noted from near a roadway in Tokyo (Table 3; −27‰ to −23‰ [Okuda et al., 2004]) and from urban areas in Washington, DC (Table 3; −24.3‰ to −22.4‰ [Reddy et al., 2002]) and China (Table 3; −27‰ to −21‰ [Okuda et al., 2002a, 2002b]). Okuda et al. [2004] estimated the δ¹⁴C value of PAHs from automotive exhaust in Japan to range from −23.6‰ to −19.5‰, while a separate study revealed PAHs from wood burning to be isotopically lighter (Table 3; −32‰ to −27‰ [Okuda et al., 2002b]) suggesting that lighter PAH δ¹⁴C 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 δ¹³C 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] Δ¹⁴C values of TSE were correlated positively with TOC Δ¹⁴C values (Figure 4; r = 0.95, p < 0.05) with a slope (0.89 ± 0.20) not statistically different than 1 (Student’s t-test, p < 0.05). This suggests that the extraction procedure isolated a TSE component (fTSE = TSE OC/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 δ¹³C values, however, were depleted by as much as 4.5‰, (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 δ¹³C 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 δ¹³C 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 δ¹³C values than the TSE (Table 2) supporting the contention that ¹³C-depleted lipids contribute to depleted δ¹³C values of the TSE.

3.2.2.2. Aliphatic OC

[25] The aliphatic component was quantitatively the smallest OC constituent (<1% of TOC; Table 2) and had Δ¹⁴C signatures that were significantly lower (mean Δ¹⁴C_aliphatic = −853 ± 29‰, 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 Δ¹⁴C 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 δ¹³C_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]*

<table>
<thead>
<tr>
<th>Component</th>
<th>This Study (2007)</th>
<th>Currie et al. [1997]</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Contemporary OC (%)</td>
<td>Fossil OC (%)</td>
</tr>
<tr>
<td>TOC</td>
<td>74 ± 7</td>
<td>26 ± 7</td>
</tr>
<tr>
<td>WSOC</td>
<td>94 ± 1</td>
<td>6 ± 1</td>
</tr>
<tr>
<td>TSE</td>
<td>72 ± 9</td>
<td>28 ± 9</td>
</tr>
<tr>
<td>Aliphatic OC</td>
<td>14 ± 3</td>
<td>86 ± 3</td>
</tr>
<tr>
<td>Aromatic OC</td>
<td>52 ± 8</td>
<td>48 ± 8</td>
</tr>
<tr>
<td>Polar OC</td>
<td>70 ± 12</td>
<td>30 ± 12</td>
</tr>
</tbody>
</table>

*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>a</sup>Contemporary OC values were calculated from “Modern-C” values which were not originally corrected for the 42% excess 14C 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>b</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 (Δ<sup>14</sup>C = −77‰; Table 2 and Figure 3), the aromatic OC isolates were strongly 14C-depleted (Δ<sup>14</sup>C of −692 to −446‰; Table 2 and Figure 3), with a mean Δ<sup>14</sup>C value of −444‰. This average Δ<sup>14</sup>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 Δ<sup>14</sup>C content of aerosol-derived PAHs, and have reported Δ<sup>14</sup>C values ranging from −381‰ at a background site in Sweden [Mandalakis et al., 2005] to <−900‰ 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 Δ<sup>14</sup>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 Δ<sup>14</sup>C signature of the aromatic fraction reported for the May 14–16, 2007 Millbrook sampling (−77‰; 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 Δ<sup>14</sup>C value (−39‰ 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 Δ<sup>14</sup>C signature for the aromatic fraction (Table 2 and Figure 3). This 14C-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 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 Δ<sup>14</sup>C (−240 to 24‰; 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 Δ<sup>14</sup>C (−750‰; 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 $\Delta^{14}C$ analyses of aerosol polar OC components such as alkanols (Table 3; $\Delta^{14}C = -80.8\%$, 14% fossil [Eglinton et al., 2002]) and fatty acids ($\Delta^{14}C = -518$ 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.

[35] 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 $\Delta^{14}C$ 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 $\Delta^{14}C$ value was $-168\%$, reflecting a 22% contribution from fossil OC.

[36] 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 $^{14}C$ 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 $^{14}C$ 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 $\Delta^{14}C$ 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., $\Delta^{14}C$ aerosol WSOC is greater than all other components; aerosol aromatic, aliphatic, and WIN SOC $\Delta^{14}C$ 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.

[37] Acknowledgments. ASW was partially supported by a Graduate Fellowship from the Hudson River Foundation during the course of this study. Additional funding for this work came from a NOSAMS student internship award, a fellowship award from Sun Trust Bank administered through the VIMS Foundation, a student research grant from VIMS, and the following NSF awards: DEB Ecosystems grant DEB-0234533, Chemical Oceanography grant OCE-0327423, and Integrated Carbon Cycle Research Program grant EAR-0403949 to JEB; and Chemical Oceanography grant OCE-0727575 to RMD and JEB. We thank Willy Reay for field assistance in Virginia, Jon Cole, Heather Malcom, and Vicky Kelly for field assistance in New York, and Mary Lardie, Al Gagnon, and Dana Gerlach for laboratory assistance. This paper is contribution 3237 to the Virginia Institute of Marine Science.

References

Aceves, M., and J. O. Grimault (1993), Seasonally dependent size distributions of aliphatic and polycyclic aromatic hydrocarbons in urban aerosols.


