

Characteristics of water-soluble organic carbon associated with aerosol particles in the eastern United States

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ABSTRACT

Desorption kinetics and sources (fossil vs. contemporary) of the water soluble organic carbon (WSOC) component of aerosol particles were examined at two sites on the east coast of the United States. Experiments revealed that WSOC is released either rapidly as one homogeneous pool or via biphasic kinetics with one rapidly and one slowly desorbing pool. The majority (>85%) of WSOC was desorbed within the first 15 min of immersion in water, suggesting that this material can be rapidly incorporated into rainwater pre-depositionally or surface waters post-depositionally and transported through watersheds. Radiocarbon (¹⁴C) measurements showed that on average 12 ± 4% and 14 ± 2% of WSOC from sites in New York and Virginia, respectively, was derived from fossil sources. By contrast, mass balance calculations revealed water-insoluble organic carbon to have significantly greater fossil contributions. These findings suggest that contemporary biogenic aerosol OC is preferentially incorporated into the aqueous phase and may be transported relatively rapidly through watersheds and aquatic systems. In contrast, the more highly aged and fossil aerosol component remains in particulate form and is more likely to be retained on particles or in soils or aquatic sediments.

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1. Introduction

Aerosols and aerosol-associated organic materials play critical roles in atmospheric visibility, human health, and climate (e.g., Ramanathan et al., 2001; Davidson et al., 2005; Highwood and Kinnersley, 2006; Myhre, 2009). Estimates suggest that up to 150 Tg yr⁻¹ of aerosol total organic carbon (TOC = organic carbon + black carbon [OC and BC, respectively]) are emitted to the global atmosphere (Koch, 2001; Bond et al., 2004; de Gouw et al., 2008; Hallquist et al., 2009). Previous work has shown between 9% (Ruellan and Cachier, 2001) and 75% (Zappoli et al., 1999) of TOC to be water soluble organic carbon (WSOC). WSOC has hygroscopic properties that render it effective as cloud condensation nuclei (CCN). Increases in CCN contribute an indirect effect on climate by increasing the number and lifetime of clouds, which reflect radiation back to space (e.g., Novakov and Penner, 1993; Ramanathan et al., 2001). WSOC is also readily taken up by biological systems such as human blood and lungs where it has been suggested as a contributor to cardiovascular and respiratory problems (Swanson et al., 2007; Mills et al., 2009).

In addition to health and climate impacts, aerosol particulate matter is increasingly recognized for its role in biogeochemical cycles, e.g., transporting OC from the atmosphere to land and aquatic settings (e.g., rivers, lakes, estuaries, the coastal ocean; Likens et al., 1983; Velinsky et al., 1986; Jurado et al., 2008; Wozniak et al., 2011). Watershed-scale particulate OC deposition estimates for the east coast of North America are comparable in magnitude to riverine TOC export (Velinsky et al., 1986; Wozniak et al., 2011). While definitive studies of the post-depositional fate of particulate TOC have yet to be conducted, a significant amount of it may be incorporated into soils and sediments, or respired by microbes and reintroduced to the atmosphere as carbon dioxide. Alternatively, WSOC may be more likely to be transported through watersheds to aquatic systems and may be more bioavailable to bacterial heterotrophs.

Radiocarbon measurements suggest that anthropogenic activities (e.g., fossil fuel combustion) can account for up to 80% of aerosol particulate OC in the present-day atmosphere (e.g., Hildemann et al., 1994; Klinedinst and Currie, 1999; Bench and Herckes, 2004; Tanner et al., 2004; Ding et al., 2008; Wozniak et al., 2011). Considerably less work has been done on the relative contributions of fossil fuel-derived and modern-day biogenic materials to aerosol WSOC (Szidat et al., 2004; Weber et al., 2007; Wozniak et al., 2008; Kirillova et al., 2010), and even less is known

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about the dynamics of WSOC desorption into the aqueous phase, which is critical for better understanding the time scales at which atmospherically deposited OC is transported through watersheds. The present study characterizes particulate matter-associated WSOC for both its desorption kinetics and fossil vs. contemporary sources. The findings enhance our understanding of the critical role of WSOC in biogeochemical cycles and budgets at the atmosphere-land-water interface.

2. Methods

2.1. Study sites

Aerosol sampling was conducted at established atmospheric monitoring sites in Millbrook, NY (the Cary Institute of Ecosystem Studies Environmental Monitoring Station; http://www.ecostudies.org/emp_purp.html) and Harcum, VA (the National Atmospheric Deposition Program (NADP) site (VA98)); <http://nadp.sws.uiuc.edu/sites/siteinfo.asp?net=NTN&id=VA98>) (Fig. S1). These sites are located in rural environments within predominantly forested, temperate watersheds along the Atlantic coast of the United States, a region of high population density and higher-than-average fossil fuel consumption (National Research Council 2003). There are no major sources of anthropogenic emissions within 30 km of the sites ensuring that aerosol samples were not biased by fossil fuel point source contributions.

2.2. Field sampling

Field sampling and sample storage details have been reported elsewhere (Wozniak et al., 2011) and can be found in the supplementary information (Appendix A). Briefly, 24-h integrated high-volume total suspended particulate aerosol samples ($\sim 0.8 \text{ m}^3 \text{ min}^{-1}$, $\sim 1150 \text{ m}^3$, Model GS2310 TSP sampler, ThermoAndersen, Smyrna, GA) were collected at both sites during 2006–2007 and stored in carefully cleaned, air-tight polycarbonate desiccators (relative humidity $\leq 10\%$) until analysis. Two samples (Millbrook, NY, 8/18–20/2006 and Harcum, VA, 1/24–26/2007) were collected over 2-day periods at a higher volumetric flow rate ($\sim 1.7 \text{ m}^3 \text{ min}^{-1}$; $>4000 \text{ m}^3$) to attain higher aerosol loadings. Sample collection dates and a list of analyses for each sample are available in the supplementary information (Table S1).

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 (~ 24 – 48 h sampling duration, ~ 30 – 65 cm s^{-1} face velocities). The TOC positive artifact was not measured for the samples in this study; however, samples collected using the same sampling apparatus at similar sampling durations ($\sim 24 \text{ h}$) and face velocities (~ 30 – 45 cm s^{-1}) have shown a TOC positive artifact of 10–15% (unpublished results). The operationally-defined particulate matter samples collected in this study can thus be expected to contain similar levels of adsorbed gas-phase OC (~ 10 – 15% of TOC).

2.3. Aerosol-derived WSOC desorption kinetics

For experiments investigating the rates of WSOC desorption from aerosols, triplicate sets of sample filter core plugs (1.9 cm diameter, $n = 15$) were placed in pre-baked (4 h, $525 \text{ }^\circ\text{C}$), 500 mL borosilicate brown bottles, and 200 ml of low-OC water ($<10 \mu\text{M}$)

was added to each bottle. The samples were then capped, swirled gently, and stored at room temperature (~ 22 – $25 \text{ }^\circ\text{C}$) in the dark to allow for WSOC desorption. Sub-samples were removed from each bottle at $t = 15, 30, 60, 120, 240,$ and 480 min and filtered (pre-combusted GF/F, $0.7 \mu\text{m}$ nominal pore size) to obtain the operationally-defined WSOC fraction. Filtered low-OC water was used as the t_0 time point. $30 \mu\text{L}$ of high purity 10% HCl was added to the filtrates ($\text{pH} \sim 2$), which were then sparged for 3 min to remove inorganic carbon, and then measured for WSOC on a Shimadzu TOC analyzer (models 5000A and VCSH) using high temperature ($680 \text{ }^\circ\text{C}$) Pt-catalyzed oxidation coupled to non-dispersive infrared gas detection of CO_2 .

Mean response areas of three replicate injections (coefficient of variation [CV] $< 1.5\%$) for each sample were calibrated to a potassium hydrogen phthalate standard curve. The average CV for these triplicate measurements was 3%. Four samples were re-analyzed in triplicate for WSOC to estimate WSOC measurement variability due to sample storage time. The pooled standard error of the fraction of WSOC ($f_{\text{WSOC}} = \text{g WSOC/g OC}$) for these replicate measurements was 0.07. This variability may be due to 1) filter aerosol OC heterogeneity and/or 2) differences in storage time prior to analysis. The WSOC in triplicate filter blank core plugs was measured along with each set of WSOC analyses, and mean blank WSOC concentrations were subtracted from sample concentrations measured on the same run. Mean blank WSOC contributions were always $<10 \mu\text{M}$ and $<20\%$ of the total WSOC.

2.4. WSOC isotopic analysis

A subset of particulate matter filter samples (Table S1) was chosen for WSOC isotopic ($\delta^{13}\text{C}$ and $\Delta^{14}\text{C}$) characterization. Filter plugs were placed in 150 mL of low-OC ($<10 \mu\text{M}$) water in pre-baked (5 h, $525 \text{ }^\circ\text{C}$) borosilicate brown bottles and stored in the dark (8 h), then filtered through pre-baked (5 h, $525 \text{ }^\circ\text{C}$) $0.7 \mu\text{m}$ GF/F filters. The WSOC samples ($\sim 125 \text{ ml}$) were acidified to $\text{pH} 2.5$ with phosphoric acid and sparged with pure helium for 10 min to remove inorganic carbon. Samples were then saturated with pure oxygen and irradiated for 3 h using a medium-pressure, high-energy (2400 W) UV lamp (Raymond and Bauer, 2001a).

CO_2 from the oxidized WSOC samples was purified cryogenically and isolated on a vacuum extraction line, then quantified using a calibrated Baratron absolute pressure gauge (MKS industries), and collected in 6 mm Pyrex break seal tubes. A portion of each sample was removed prior to vacuum-line processing for WSOC determination on a Shimadzu TOC analyzer as described above. WSOC yields from the two methods (UV oxidation and vacuum line processing vs. TOC analysis) were not significantly different (student's t -test, $p = 0.8$) reflecting the quantitative conversion of WSOC using the UV oxidation method (data not shown). The quantitative nature of this method has been rigorously demonstrated for a variety of soluble OC materials (Raymond and Bauer, 2001a,b; Beaupre et al., 2007). UV-oxidation and vacuum line processing of standard organic compounds (oxalic acid II [OX-II] and acetanilide) also reflected quantitative conversion to CO_2 , and $\Delta^{14}\text{C}$ and $\delta^{13}\text{C}$ analyses were within the measurement error of the known isotopic values ($\Delta^{14}\text{C}_{\text{OX-II}} = 285\text{‰}$, $\delta^{13}\text{C}_{\text{OX-II}} = -17.8\text{‰}$ and $\Delta^{14}\text{C}_{\text{acetanilide}} = -1000\text{‰}$, $\delta^{13}\text{C}_{\text{acetanilide}} = -29.5\text{‰}$) indicating that WSOC oxidation and processing did not bias the isotopic measurements.

The purified CO_2 samples were submitted to the University of Arizona NSF Accelerator Mass Spectrometry laboratory (Arizona) or the National Ocean Sciences Accelerator Mass Spectrometry facility (NOSAMS) for isotopic ($\delta^{13}\text{C}$, $\Delta^{14}\text{C}$) analysis. Measurement error of $\delta^{13}\text{C}$ analyses performed at both NOSAMS and the University of Arizona was $\pm 0.1\text{‰}$. AMS $\Delta^{14}\text{C}$ measurement errors ranged from ± 3 – 11‰ and averaged $\pm 6\text{‰}$ ($n = 19$).

Filter blank contributions to WSOC and isotopic signatures were assessed by distributing duplicate samples of 125 filter blank core plugs among three pre-baked (5 h, 525 °C) bottles with 150 mL of high purity Nanopure water as was done for particulate matter filter samples. The CO₂ from the oxidation of filter blank WSOC was combined to amass duplicate samples of 138 and 139 µg C for δ¹³C and Δ¹⁴C analyses. Filter blanks were found to contribute 1.14 ± 0.26 µg WSOC per core plug with mean δ¹³C and Δ¹⁴C signatures of −29.7 ± 0.2‰ (n = 2) and −603 ± 1‰ (n = 2), respectively. All sample isotopic values were corrected for filter blank contributions as described by Wozniak et al. (2011). The mean *f*_{WSOC} from filter blanks for all samples measured for isotopic analysis was 0.11 and ranged from 0.02 to 0.35. Propagated errors for individual blank-corrected Δ¹⁴C values ranged from ±5–77‰ and averaged ±21‰ (n = 19). These errors correspond to estimated fossil fuel contribution errors of ±1–10% with an average of ±3% (n = 19).

2.5. Data analyses

Student's *t*-tests were employed to test for between-site differences in overall mean *f*_{WSOC}, δ¹³C, and Δ¹⁴C values. All errors are expressed as standard errors of mean values throughout the manuscript.

To describe the kinetics of WSOC desorption from aerosol particulates, the time series of *f*_{WSOC} values were fit to one of two exponential models using Sigma Plot. The first model describes a single rapidly desorbed pool of WSOC and is parameterized as (Tao et al., 2000)

$$f_{\text{WSOC}}(t) = f_{\text{WSOCsat1}}(1 - e^{-k_1(A/V)t}) \quad (1)$$

where *f*_{WSOCsat1} represents the *f*_{WSOC} saturation value, *k*₁ is the mass transfer coefficient (cm min^{−1}), *A* is the area (cm²) of exposed filter added to each bottle, *V* is the volume (cm³) of low OC water added to each bottle, and *t* (min) represents the length of time the sample was immersed in water.

The second model describes a rapidly desorbing and a second slowly desorbing pool of WSOC and is parameterized as (Pignatello and Xing, 1995; Cao et al., 1999; Kan et al., 2000; Chai et al., 2007)

$$f_{\text{WSOC}}(t) = f_{\text{WSOCsat1}}(1 - e^{-k_1(A/V)t}) + f_{\text{WSOCsat2}}(1 - e^{-k_2(A/V)t}) \quad (2)$$

where *f*_{WSOCsat1}, *k*₁, *A*, and *V* represent the same parameters described for the single rapidly desorbed pool in Eq. (1), and *f*_{WSOCsat2} and *k*₂ represent the *f*_{WSOC} saturation value and mass transfer coefficient of the slowly desorbed pool, respectively. For both model fits, the quantities *k*₁(*A*/*V*) and *k*₂(*A*/*V*), were constrained between 0 and 1 in order to eliminate unrealistic non-linear solutions.

Because fossil and contemporary biogenic aerosol OC sources have distinct Δ¹⁴C signatures (Δ¹⁴C_{fossil fuel} = −1000‰; Δ¹⁴C_{contemporary} = ~55‰), Δ¹⁴C signatures were used to estimate contributions from fossil fuels (e.g., combustion of coal, oil, gas, etc.) and contemporary biomass (e.g., biomass burning, biogenic secondary organic aerosols (SOAs), and primary biological materials (e.g., bacteria, viruses, fungi, leaf material)). Source contributions were estimated using a two end-member mixing model (see Appendix B for a detailed justification of this assumption) employing characteristic Δ¹⁴C values for fossil fuel and contemporary biomass derived OC as described elsewhere (e.g., Lewis et al., 2004; Schichtel et al., 2008; Wozniak et al., 2011).

Gas-phase OC adsorbed to quartz filters due to the positive artifact associated with high volume samplers may alter the true

aerosol particulate matter TOC and WSOC radiocarbon signatures, and therefore the calculated fossil and contemporary TOC and WSOC contributions. Without an accounting of the fossil and contemporary OC contributions to the gas-phase OC, its effect on TOC and WSOC can not be established. The positive sampling artifact for this study is estimated to be relatively small (~10–15% of TOC), and the rural locations of the sampling sites suggest that contemporary volatile OC compounds emitted from vegetation, such as monoterpenes (e.g., Guenther, 1997), predominate. We therefore do not expect an overestimation of contributions from fossil OC sources.

3. Results and discussion

3.1. Particulate matter *f*_{WSOC}

Aerosol *f*_{WSOC} values were estimated for WSOC isolated for the desorption kinetics and isotopic analysis experiments and ranged from 0.17 in January 2007 at Harcum to 0.72 in June 2006, also at Harcum (Fig. 1). Mean aerosol *f*_{WSOC} values were similar at the two sites at ~0.35 (Student's *t*-test, *p* > 0.05; Millbrook mean *f*_{WSOC} = 0.35 ± 0.02, *n* = 13; Harcum mean *f*_{WSOC} = 0.36 ± 0.04, *n* = 14; Fig. 1). The range of values reported here (Fig. 1) reflects the

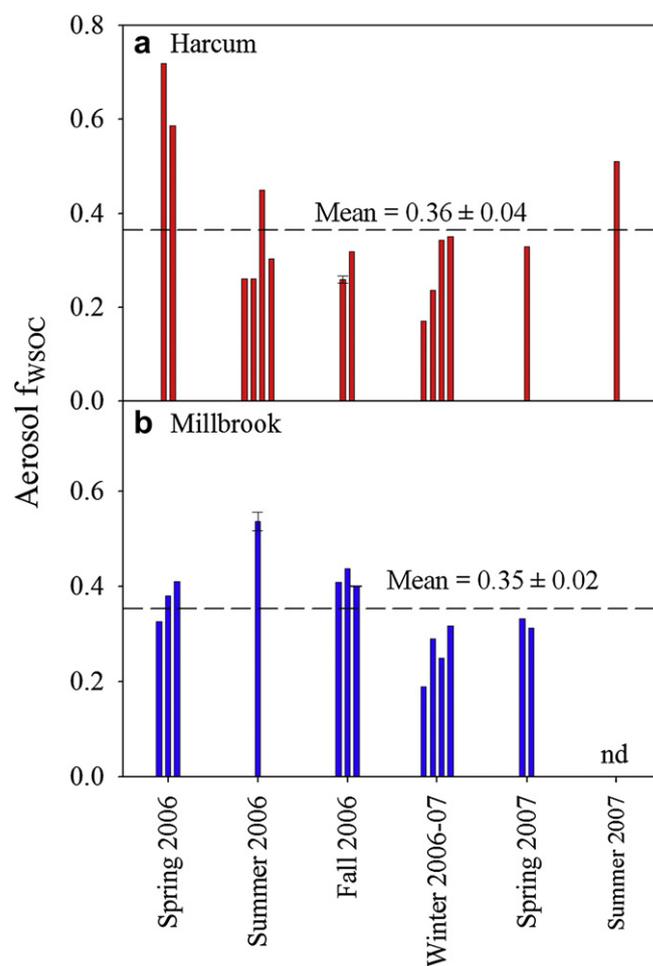


Fig. 1. Aerosol *f*_{WSOC} (= WSOC/OC) for samples collected at (a) Harcum, VA and (b) Millbrook, NY in 2006–2007. Dashed lines represent overall mean aerosol *f*_{WSOC} values calculated for all samples at a given site (Harcum: mean = 0.36 ± 0.04; *n* = 14; Millbrook: mean = 0.35 ± 0.02; *n* = 13). See text for details regarding how samples were differentiated by season. Error bars represent standard errors for repeated WSOC measurements on the same sample. 'nd' denotes time periods when no data for aerosol WSOC was obtained for a given site.

natural variability in the relative magnitudes of typically soluble (e.g., SOA, acidic primary emissions) and insoluble (e.g., primary hydrocarbon-like emissions) OC components at rural sites throughout the year. Studies conducted at other rural sites have shown f_{WSOC} values as high as 0.70–0.75 (Zappoli et al., 1999; Weber et al., 2007; Ding et al., 2008) and attributed the high values to large contributions from polar, oxygenated biogenic SOAs (e.g., Weber et al., 2007; Ding et al., 2008). The intermediate values for the Millbrook and Harcum sites suggest lower contributions from SOAs and higher inputs from less soluble components such as those from combustion processes (e.g., Rogge et al., 1993, 1997). Very low f_{WSOC} values have been reported for aerosols from urban areas such as near roadways ($f_{WSOC} = 0.09$; Ruellan and Cachier, 2001) and during the winter in large cities (e.g., Tokyo, Japan, $f_{WSOC} = 0.23$; Kondo et al., 2007), and the low mean f_{WSOC} values (~ 0.35 ; Fig. 1) may also reflect the influence of anthropogenic processes even at these rural background sites.

3.2. Desorption kinetics of WSOC

The desorption kinetics of WSOC and various organic contaminants from soils and river sediments have been examined (e.g.; Pignatello and Xing, 1995; Cao et al., 1999; Kan et al., 2000; Tao, et al., 2000; Chai et al., 2007), but to our knowledge there have been no previous studies of WSOC desorption kinetics from aerosol particles. For all particulate matter WSOC desorption kinetics experiments, a minimum of 70% and an average of 87% of the total WSOC desorbed within the first 15 min (Fig. 2a and b).

Five of the eight samples examined for WSOC kinetics were explained by a first-order linear differential equation describing the rapid release of WSOC from aerosols into the aqueous phase with f_{WSOC} approaching $f_{WSOCsat1}$ over the time scale (8 h) of the experiment (Equation (1); Fig. 2a). The remaining three samples displayed kinetics explained by a biphasic first-order linear differential equation that describes two pools of WSOC (Equation (2); Fig. 2b) that desorb at different rates. Model fits for all samples were significant ($p < 0.05$) and had $R^2 > 0.96$ (Table 1). The first pool of aerosol WSOC (mean $f_{WSOCsat1} = 0.30(\pm 0.03)$, $n = 8$) is significantly larger than the second pool (mean $f_{WSOCsat2} = 0.05(\pm 0.04)$, $n = 3$) (Student's t -test, $p < 0.05$; Table 1) and desorbs at a much faster rate (Student's t -test, $p < 0.05$, $k_1 = 0.66(\pm 0.07)$ cm min^{-1} , $n = 8$ vs. mean $k_2 = 0.03(\pm 0.01)$ cm min^{-1} , $n = 3$; Table 1). Total f_{WSOC} saturation values (total $f_{WSOCsat} = f_{WSOCsat1} + f_{WSOCsat2}$ from Table 1) ranged from 0.17 (Harcum 1/24–26/07; Table 1, Fig. 2b) to 0.45 (Harcum 8/1–2/06; Table 1, Fig. 2a) with a mean value of 0.30 that is slightly lower than found for the f_{WSOC} experiments in section 3.1 (Fig. 1) demonstrating the variability of f_{WSOC} for natural particulate matter samples.

Because aerosol WSOC contains thousands of compounds (Reemtsma et al., 2006; Wozniak et al., 2008), the rapidly and slowly desorbing WSOC pools for some of the samples in this study likely represent distinct groups of compounds that desorb at different rates because of their chemical structures and properties. Alternatively, the more slowly desorbing pool of WSOC may be inhibited by components within the aerosol particle matrix, similar to what has been shown for sedimentary components (e.g., BC, clays) (Pignatello and Xing, 1995; Kan et al., 2000; Chai et al., 2007). However, very low contributions of BC to TSP were observed in this study, with one of the samples that exhibited biphasic kinetics containing no measurable BC (Wozniak et al., 2011). The presence of BC, therefore, does not appear to explain the biphasic kinetic behavior for WSOC desorption of these three samples.

Regardless of the kinetic model used, the majority ($\sim 87\%$, Fig. 2) of WSOC clearly desorbs rapidly, generally within 15 min of exposure to water. These findings illustrate how particulate WSOC may

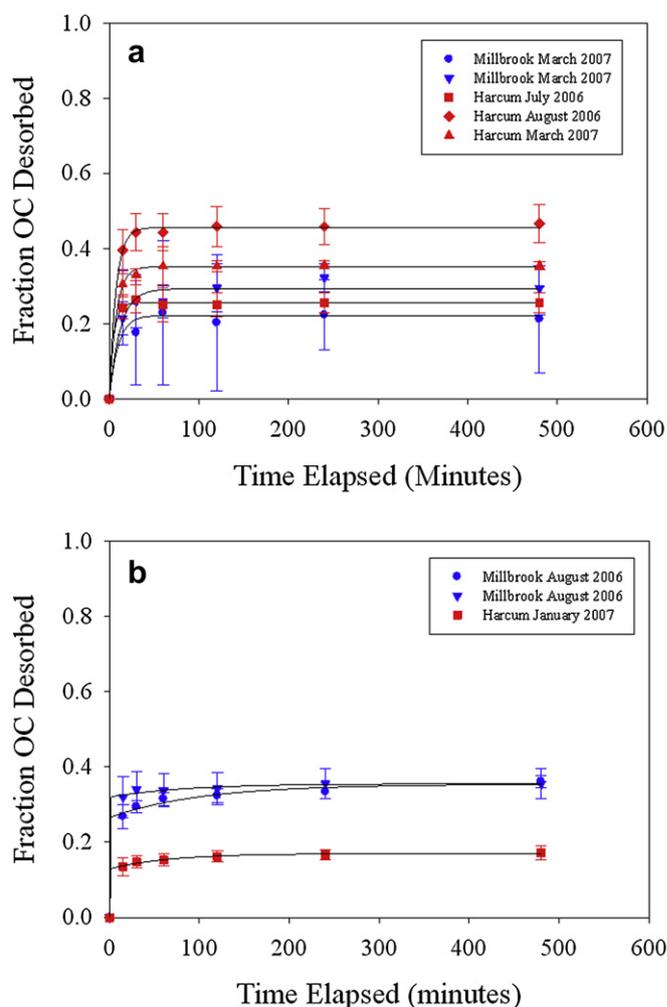


Fig. 2. Aerosol f_{WSOC} desorbed versus time immersed in water for samples collected in Harcum, VA and Millbrook, NY in 2006–07. Trendlines are best curve fits for models describing WSOC desorption following a) a two parameter first-order kinetics model with one rapidly desorbing pool of WSOC or b) a four parameter first-order kinetics model with a rapidly desorbing pool of WSOC and a slowly desorbing pool of WSOC. Error bars represent propagated standard errors for triplicate analyses.

Table 1

Kinetics model parameters for aerosol WSOC desorption for samples collected at Millbrook, NY and Harcum, VA in 2006–2007. Errors represent standard errors for model parameters of best fit curves. See the text for descriptions of the models and model parameters.

Sampling site/date	$f_{WSOCsat1}$	k_1 (cm min^{-1})	$f_{WSOCsat2}$	k_2 (cm min^{-1})	R^{2a}
<i>Millbrook</i>					
5/25–26/06	0.35 ± 0.01	0.63 ± 0.11	0.03 ± 0.01	0.02 ± 0.03	0.999
5/25–26/06	0.31 ± 0.01	0.75 ± 0.08	0.10 ± 0.02	0.01 ± 0.005	0.999
3/6–7/07	0.29 ± 0.01	0.39 ± 0.06	na ^b	na	0.991
3/8–9/07	0.25 ± 0.01	0.48 ± 0.16	na	na	0.961
<i>Harcum</i>					
7/18–19/06	0.26 ± 0.002	0.94 ± 0.14	na	na	0.999
8/1–2/06	0.45 ± 0.004	0.65 ± 0.05	na	na	0.999
1/24–26/07	0.14 ± 0.003	0.88 ± 0.09	0.03 ± 0.003	0.05 ± 0.01	0.999
3/15–16/07	0.35 ± 0.004	0.59 ± 0.05	na	na	0.999
Overall means (both sites) ($n = 8$)	0.30 ± 0.03 ($n = 8$)	0.66 ± 0.07 ($n = 8$)	0.05 ± 0.04 ($n = 3$)	0.03 ± 0.01 ($n = 3$)	na

^a R^2 values represent goodness of fit for sample data to the models defined in equations (1) and (2) (see Methods) using the parameters presented here.

^b 'na' denotes samples for which the parameters presented here are not applicable because the data did not fit the four parameter kinetic model.

be incorporated over short time periods into rainwater, which comprises a significant portion (along with gas-phase atmospheric OC) of the dissolved organic carbon delivered by precipitation to terrestrial and aquatic systems.

3.3. Aerosol $\delta^{13}\text{C}_{\text{WSOC}}$

Mean particulate matter $\delta^{13}\text{C}_{\text{WSOC}}$ values for both sites were similar (Student's *t*-test, $p > 0.05$; Millbrook $\delta^{13}\text{C}_{\text{WSOC}} = -25.2 \pm 0.2\text{‰}$, $n = 9$; Harcum $\delta^{13}\text{C}_{\text{WSOC}} = -25.3 \pm 0.6\text{‰}$, $n = 10$; Table 2) with the majority of samples showing $\delta^{13}\text{C}$ values consistent with a combination of terrestrial C_3 plant (~ -23 to -30‰ ; Fry and Sherr 1984; Boutton, 1994; Lajtha and Marshall, 1994) and fossil fuel (~ -23 to -33‰ ; Yeh and Epstein, 1981; Schoell, 1984) sources as was found for aerosol TOC from the same sites during the study period (Wozniak et al., 2011). With the exception of a single sample at Harcum in summer 2006 ($\delta^{13}\text{C} = -21.1\text{‰}$; Table 2), marine ($\delta^{13}\text{C} = \sim -22$ to -18‰ ; Fry and Sherr, 1984; Boutton, 1994; Lajtha and Marshall, 1994) or C_4 plant ($\delta^{13}\text{C} = \sim -14$ to -10‰ ; Fry and Sherr, 1984; Boutton, 1994; Lajtha and Marshall, 1994) contributions were unlikely to be significant. Similar to the present study, $\delta^{13}\text{C}_{\text{WSOC}}$ values for aerosols collected in Sweden spanned a relatively narrow range ($\delta^{13}\text{C}_{\text{WSOC}} = \sim -25$ to $\sim -26\text{‰}$; Kirillova et al., 2010) and were attributable to a combination of fossil and terrestrial C_3 plant sources. In contrast, a site in Zurich, Switzerland showed slightly enriched values ($\delta^{13}\text{C}_{\text{WSOC}} = \sim -23$ to $\sim -25\text{‰}$; Fisseha et al., 2009) with potential contributions from marine (~ -22 to -18‰ ; Fry and Sherr, 1984; Boutton, 1994; Lajtha and Marshall, 1994) and/or terrestrial C_4 plants ($\delta^{13}\text{C} \sim -14$ to -10‰ ; Fry and Sherr, 1984; Boutton, 1994; Lajtha and Marshall, 1994).

3.4. $\Delta^{14}\text{C}$ of aerosol WSOC

3.4.1. Fossil and contemporary sources of aerosol WSOC

Because the $\delta^{13}\text{C}$ values of terrestrial C_3 plant and fossil fuel-derived materials overlap, it is not possible to distinguish between these two potential OC sources using $\delta^{13}\text{C}$ exclusively. However, the use of natural ^{14}C can help to resolve this ambiguity. $\Delta^{14}\text{C}$ values of WSOC in this study indicate that it was composed primarily of contemporary-aged material. For Millbrook, fossil contributions to aerosol WSOC ranged from 0% (Fall 2006 $\Delta^{14}\text{C}_{\text{WSOC}} = 106 \pm 51\text{‰}$, $n = 2$; Table 2, Fig. 3a) to 25% (Winter 2007 $\Delta^{14}\text{C}_{\text{WSOC}} = -196\text{‰}$; Table 2, Fig. 3a). For Harcum, WSOC fossil contributions ranged from 7% (Winter 2007 $\Delta^{14}\text{C}_{\text{WSOC}} = 2$; Table 2, Fig. 3b) to 21% (Fall 2006 $\Delta^{14}\text{C}_{\text{WSOC}} = -151 \pm 31\text{‰}$, $n = 2$; Table 4–3, Fig. 3b). Overall, mean $\Delta^{14}\text{C}_{\text{WSOC}}$ values were similar for each site ($p > 0.05$, Student's *t*-test; Millbrook mean $\Delta^{14}\text{C}_{\text{WSOC}} = -61 \pm 42\text{‰}$, $n = 9$; Harcum mean $\Delta^{14}\text{C}_{\text{WSOC}} = -73 \pm 17\text{‰}$, $n = 10$; Table 2, Fig. 3) with estimated mean fossil contributions of 12 ± 4 and $14 \pm 2\%$ to WSOC throughout the year at Millbrook and Harcum, respectively.

Fossil carbon contributions to WSOC reported in previous studies conducted at urban (9–24% fossil OC; Szidat et al., 2004; 20–30% fossil OC, Weber et al., 2007) and suburban (Kirillova et al., 2010; 0–12% fossil OC) sites were similar to those found in the present study, indicating that aerosol WSOC is dominated by contemporary-aged material across a variety of settings. Fossil contributions calculated for the entire aerosol OC pool have been reported to cover a much larger range of values (0–80%; e.g., Hildemann et al., 1994; Klinedinst and Currie, 1999; Bench and Herckes, 2004; Tanner et al., 2004; Ding et al., 2008; Wozniak et al., 2011). Despite the smaller relative contributions of fossil OC

Table 2

f_{WSOC} , isotopic values and % fossil contributions for WSOC, TOC, and WINSOC for aerosol particulate samples from Millbrook, NY and Harcum, VA in 2006–2007.^a

Sampling site/date	f_{WSOC}	$\delta^{13}\text{C}$ (‰)	WSOC			TOC ^b			WINSOC ^c		
			$\Delta^{14}\text{C}$ (‰)	F_m ^d	% fossil	$\Delta^{14}\text{C}$ (‰)	F_m ^d	% fossil	$\Delta^{14}\text{C}$ (‰)	F_m ^d	% fossil
<i>Millbrook</i>											
5/23–24/06		-25.8	-187	0.82	24	-190	0.82	24	-191	0.82	25
8/18–20/06 ^e	0.537 ± 0.019	-24.7 ± 0.1	-187 ± 4	0.82 ± 0.01	24 ± 0	-439	0.56	48	-739	0.26	76
12/1–2/06	0.409	-25.0	24	1.03	5	-102	0.90	16	-190	0.82	24
12/3–4/06	0.437	-24.9	101	1.11	0 ^g	ND ^h	ND ^h	ND ^h	ND ^h	ND ^h	ND ^h
12/5–6/06 ^e	0.401 ± 0.001	-25.6 ± 0.7	106 ± 51	1.11 ± 0.05	0 ^g	-260	0.75	31	-505	0.50	54
3/5–6/07	0.190	-23.9	-196	0.81	25	-516	0.49	55	-591	0.41	62
3/9–10/07	0.317	-25.2	38	1.05	3	-527	0.48	56	-789	0.21	80
5/13–15/07	0.332	-26.0	-123	0.88	18	-64	0.94	13	-35	0.97	10
5/15–16/07 ^e	0.313 ± 0.018	-25.7 ± 0.7	-122 ± 59	0.88 ± 0.06	18 ± 6	-26	0.98	9	17	1.02	5
Site mean ^f	0.363 ± 0.033	-25.2 ± 0.2	-61 ± 42	0.95 ± 0.04	12 ± 4	-265 ± 72	0.74 ± 0.07	32 ± 7	-377 ± 112	0.63 ± 0.1	42 ± 10
<i>Harcum</i>											
6/8–9/06	0.586	-25.3	-106	0.90	17	-153	0.83	21	-223	0.78	28
6/20–21/06	0.719	-27.6	-105	0.90	17	-297	0.71	34	-829	0.17	84
7/6–7/06	0.260	-21.1	-14	0.99	8	-95	0.91	16	-123	0.88	18
8/30–31/06	0.304	-23.4	-62	0.94	13	-323	0.68	37	-437	0.57	48
9/26–27/06 ^e	0.259 ± 0.008	-25.6 ± 0.5	-151 ± 31	0.86 ± 0.03	21 ± 3	-410	0.59	45	-500	0.50	53
11/15–16/06	0.318	-25.8	-100	0.91	16	-410	0.59	45	-555	0.45	59
1/4–5/07	0.236	-27.4	-131	0.88	19	-643	0.36	67	-802	0.20	82
2/1–2/07	0.342	-25.7	1	1.01	7	ND ^h	ND ^h	ND ^h	ND ^h	ND ^h	ND ^h
3/22–23/07	0.329	-25.5	-64	1.01	13	-340	0.66	38	-508	0.50	54
5/31–6/1/07	0.511	-25.5	-64	0.94	13	ND ^h	ND ^h	ND ^h	ND ^h	ND ^h	ND ^h
Site mean ^f	0.386 ± 0.051	-25.3 ± 0.6	-73 ± 17	0.93 ± 0.02	14 ± 2	-334 ± 60	0.67 ± 0.06	38 ± 6	-497 ± 88	0.51 ± 0.1	53 ± 8

^a See Appendix A for sample TOC, BC, and WSOC concentrations.

^b The $\Delta^{14}\text{C}$, F_m , and % fossil values directly beneath the TOC heading correspond to TOC data from Wozniak et al., 2011.

^c The $\Delta^{14}\text{C}$, F_m , and % fossil values directly beneath the WINSOC heading correspond to WINSOC data. All WINSOC values were calculated by mass balance based on measured WSOC and TOC values. TOC values are a subset of values reported by Wozniak et al. (2011). See text for details.

^d F_m refers to "Fraction modern" and represents the radiocarbon concentration of the sample divided by that of the "modern" reference standard (National Institute of Standards and Technology standard reference material 4990B, Oxalic Acid I (Stuiver and Polach, 1977)).

^e Samples for which duplicate f_{WSOC} and WSOC isotopic measurements were performed. Errors represent standard errors of the duplicate measurements.

^f Site means represent parameter mean values for all samples at each site. Errors represent standard errors of the mean. For Millbrook WSOC parameters, $n = 9$, and for TOC and WINSOC parameters, $n = 8$. For Harcum WSOC parameters, $n = 10$, and for TOC and WINSOC parameters, $n = 8$.

^g Samples with 0% fossil contribution have radiocarbon values reflecting $\Delta^{14}\text{C}$ values exceeding current background levels for atmospheric CO_2 and are considered to have modern radiocarbon ages.

^h ND = not determined and denotes samples for which corresponding TOC $\Delta^{14}\text{C}$ measurements were not performed.

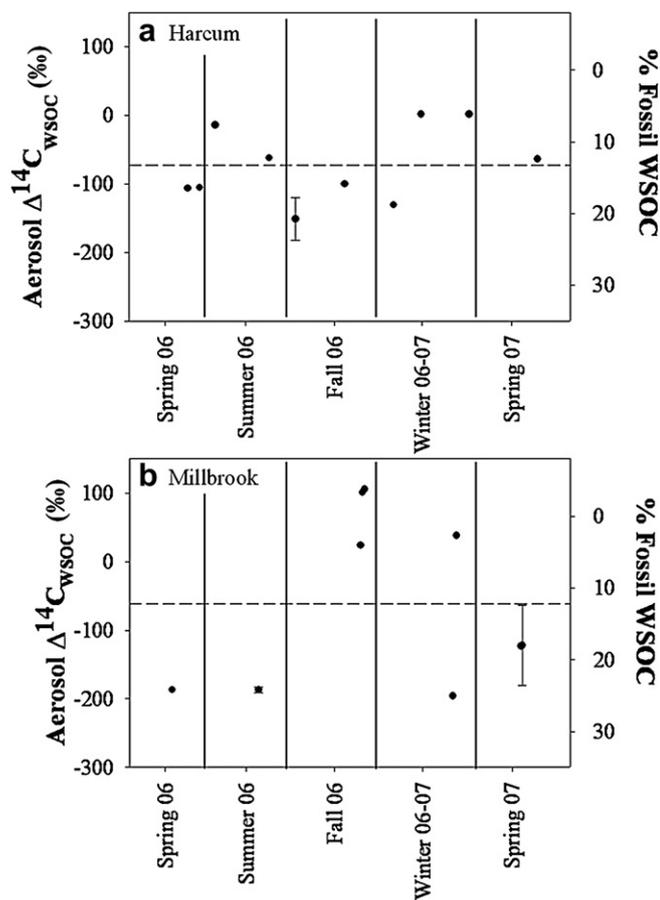


Fig. 3. Aerosol particulate $\Delta^{14}\text{C}_{\text{WSOC}}$ values and % fossil contributions for samples collected in a) Harcum, VA and b) Millbrook, NY in 2006–2007. Error bars represent standard errors for duplicate analyses of the same sample. Black horizontal dashed lines represent mean $\Delta^{14}\text{C}$ values ($n=10$ for Harcum; $n=9$ for Millbrook). Solid vertical lines delineate seasons. See Table S1 for information regarding how samples were differentiated by season.

to WSOC in this and other studies (Table 2, Fig. 3; Szidat et al., 2004; Weber et al., 2007; Wozniak et al., 2008; Kirillova et al., 2010), the findings overall indicate that some portion of the aerosol WSOC is fossil-derived. This WSOC is potentially both mobile and biologically available. The WSOC thus provides a mechanism for fossil fuel-derived OC to be transported through watersheds and contribute to heterotrophic processes in aquatic systems.

3.4.2. Implications of WSOC and WINSOC $\Delta^{14}\text{C}$ differences

$\Delta^{14}\text{C}$ signatures of aerosol TOC from the same two sites during the study period revealed considerably higher fossil contributions to the entire TOC pool ($\sim 33\%$ fossil; Wozniak et al., 2011) relative to the WSOC pool (Table 2, Fig. 3), indicating that the fossil component of particulate TOC is largely insoluble. Using the WSOC isotopic data (Table 2, Fig. 3) along with f_{WSOC} and TOC isotopic data ($\Delta^{14}\text{C}_{\text{TOC}}$, Table 2; Wozniak et al., 2011), $\Delta^{14}\text{C}_{\text{WINSOC}}$ values were calculated for samples for which both WSOC and TOC isotopic measurements were available as

$$X_{\text{WINSOC}} = (X_{\text{TOC}} - f_{\text{WSOC}} * X_{\text{WSOC}}) / f_{\text{WINSOC}} \quad (3)$$

where X_{WINSOC} , X_{TOC} , and X_{WSOC} are the $\Delta^{14}\text{C}$ values for WINSOC, TOC and WSOC, respectively, and f_{WINSOC} is the water-insoluble fraction of TOC ($f_{\text{WINSOC}} = \text{WINSOC}/\text{TOC} = 1 - f_{\text{WSOC}}$).

The relationship between $\Delta^{14}\text{C}_{\text{WINSOC}}$ and $\Delta^{14}\text{C}_{\text{WSOC}}$ (Fig. 4) shows that in nearly every case $\Delta^{14}\text{C}_{\text{WSOC}}$ was greater than the

corresponding $\Delta^{14}\text{C}_{\text{WINSOC}}$ (Table 2; Fig. 4). A paired t -test indicated that $\Delta^{14}\text{C}_{\text{WSOC}}$ values (mean $\Delta^{14}\text{C}_{\text{WSOC}} = -82 \pm 22\text{‰}$, 16% fossil, $n=16$; Table 2) were significantly ($p < 0.05$) higher than corresponding $\Delta^{14}\text{C}_{\text{WINSOC}}$ values (mean $\Delta^{14}\text{C}_{\text{WINSOC}} = -497 \pm 88\text{‰}$, 48% fossil, $n=16$; Table 2). This indicates that the WSOC pool is composed primarily of contemporary-derived OC, and thus fossil TOC is relatively less soluble than contemporary aged TOC.

$\Delta^{14}\text{C}$ measurements of aerosol WINSOC from Zurich, Switzerland showed fossil contributions to WINSOC (32–45% fossil) that were larger than calculated contributions of fossil material to WSOC (9–24% fossil, Szidat et al., 2004), consistent with the findings in the present study (Table 2). The findings therefore collectively suggest a fundamental difference in the partitioning of fossil and contemporary biomass-derived aerosol OC with fossil-derived OC being predominantly insoluble.

Chemical characterization of aerosol WSOC has shown it to consist of highly oxygenated, polar compounds such as mono- and di-carboxylic acids and polyconjugated acids (e.g.; Mayol-Bracero et al., 2002; Yang et al., 2004; Duarte et al., 2007; Wozniak et al., 2008). Approximately half of WSOC compounds identified by gas chromatography–mass spectrometry in aerosol OC from Amazonia were carboxylic acid species (Mayol-Bracero et al., 2002), and 57–64% of WSOC collected from a rural-coastal site in Portugal was characterized as having acidic character (Duarte et al., 2007). The prevalence of acidic species in WSOC has been attributed to contributions from SOA that form via oxidation reactions involving naturally (contemporary) and anthropogenically (fossil) emitted semi-volatile and volatile organic compounds (VOC; Jang and Kamens, 2001; Gao et al., 2004; Jaoui et al., 2005; Kanakidou et al., 2005). The incomplete combustion of fossil fuels also produces acidic, soluble OC byproducts in addition to insoluble compounds such as polycyclic aromatic hydrocarbons (PAHs) and alkanes (Rogge et al., 1993, 1997). Biomass burning OC (contemporary) byproducts have been shown to be highly water-soluble (29–64% for redwood and eucalyptus; Novakov and Corrigan, 1996) and have been implicated as major sources of aerosols having a large WSOC component (Zappoli et al., 1999; Mayol-Bracero et al., 2002).

Molecular characterization of aerosol WSOC was not the focus of this study so it is not possible to distinguish the relative importance of these specific WSOC sources. However, the WSOC radiocarbon findings for the Millbrook and Harcum sites suggest that for the eastern United States contemporary biomass burning and SOA are

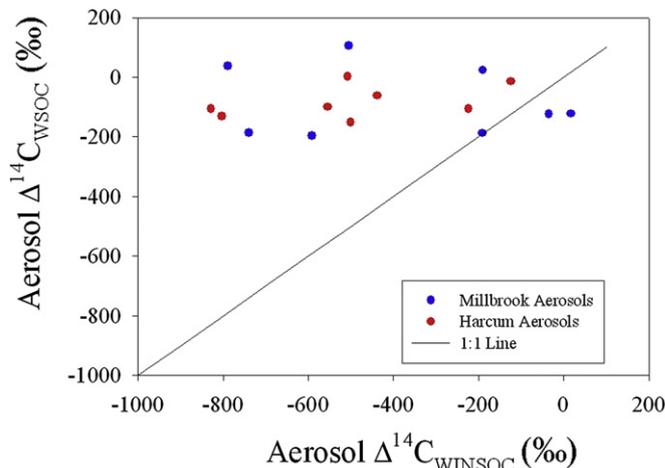


Fig. 4. Measured aerosol particulate $\Delta^{14}\text{C}_{\text{WSOC}}$ vs. calculated $\Delta^{14}\text{C}_{\text{WINSOC}}$ for samples collected in Harcum, VA and Millbrook, NY in 2006–2007. The line represents the 1:1 relationship. See text for details of $\Delta^{14}\text{C}_{\text{WINSOC}}$ calculations.

more prevalent sources to aerosol WSOC than fossil fuel derived SOA and combustion byproducts. Fossil sources represented approximately one-third of TOC (Table 2; Wozniak et al., 2011), and WSOC was similarly estimated as approximately one-third of TOC (Fig. 1) making the two OC pools (WSOC and fossil TOC) roughly the same size. However, <15% of WSOC was fossil-derived, and because the WSOC and fossil TOC pools are the same size, fossil WSOC also accounts for less than 15% of the fossil TOC. Therefore, the majority (>85%) of the fossil TOC partitioned as WINSOC, a finding that suggests that the majority of the fossil component of aerosol TOC in the eastern United States is made up of hydrophobic components (e.g., alkanes, PAHs).

The relatively small contributions to aerosol TOC of fossil WSOC compared to WINSOC observed in the present (Table 2; Fig. 4) and previous studies (Szidat et al., 2004; Weber et al., 2007; Wozniak et al., 2008; Kirillova et al., 2010) suggests a relatively larger contribution of contemporary carbon to the water soluble component of aerosol TOC. Nonetheless, previously published positive relationships between WSOC and concentrations of fossil fuel compounds such as acetylene, isopropyl nitrate, and carbon monoxide (de Gouw et al., 2005; Weber et al., 2007) suggest a possible direct link between fossil fuel combustion and WSOC concentrations. Positive correlations between WSOC concentrations and the fossil fuel tracers carbon monoxide ($r^2 = 0.80$) and acetylene ($r^2 = 0.60$; Weber et al., 2007) in urban Atlanta suggest a fossil source to WSOC. Yet radiocarbon analyses revealed fossil contributions of just 20–30%, indicating that the increase in WSOC was fossil-influenced but not due to fossil C in WSOC. Thus, fossil fuel combustion appears to influence WSOC concentration through some other mechanism, possibly via the co-emission of inorganic species which can initiate SOA formation (e.g., Jang and Kamens, 2001; Kanakidou et al., 2005) or organic aerosol aging (e.g., Kanakidou et al., 2005; Hallquist et al., 2009).

4. Conclusions

Particulate matter-derived WSOC from two background sites in the eastern United States desorbed rapidly and accounted for ~35% of the total OC pool. Contemporary biomass-derived sources represented >85% of the WSOC, in contrast to the WINSOC which was ~50–60% contemporary-derived. These findings suggest major differences in the hydrophilic nature of fossil fuel and contemporary aerosol OC and have significant potential impacts for the biogeochemical cycling of this material. The lower solubility of fossil fuel derived aerosol OC compared to contemporary biomass-derived aerosol OC suggests it is more likely to become incorporated in soils or sorb to vegetation than is the pool of contemporary-derived aerosol OC. Nonetheless, up to 24% (Table 4-3) of WSOC associated with aerosol particles is fossil-derived and needs to be considered in studies of atmosphere-land-water carbon exchanges. In addition, fine aerosol particulates (<10 μm , Warneck, 2000) such as the predominantly fossil WINSOC may be readily eroded and transported through watersheds as part of the particulate load.

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Appendix. Supplementary data

Supplementary data associated with this article can be found in the online version, at doi:10.1016/j.atmosenv.2011.10.001.

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