

A method for on-line measurement of water-soluble organic carbon in ambient aerosol particles: Results from an urban site

A. P. Sullivan,¹ R. J. Weber,¹ A. L. Clements,² J. R. Turner,² M. S. Bae,³ and J. J. Schauer³

Received 9 February 2004; revised 27 April 2004; accepted 9 June 2004; published 14 July 2004.

[1] An instrument for on-line continuous measurement of the water-soluble organic carbon (WSOC) component of aerosol particles is described and results from an urban site in St. Louis are presented. A Particle-into-Liquid Sampler impacts ambient particles, grown to large water droplets, onto a plate and then washes them into a flow of purified water. The resulting liquid is filtered and the carbon content quantified by a Total Organic Carbon analyzer providing continuous six-minute integral measurements with a detection limit of 0.1 $\mu\text{g C/m}^3$. Summer and fall measurements of WSOC and organic carbon (OC) indicated WSOC/OC ratio typically ranged from 0.40 to 0.80. A diurnal variation in WSOC/OC that correlated with ozone was observed over extended periods in June; however, other periods in August had no correlation. The results suggested that WSOC was composed of a complex mixture of compounds that may contain a significant fraction from secondary organic aerosol formation.

INDEX TERMS: 0305 Atmospheric Composition and Structure: Aerosols and particles (0345, 4801); 0345 Atmospheric Composition and Structure: Pollution—urban and regional (0305). **Citation:** Sullivan, A. P., R. J. Weber, A. L. Clements, J. R. Turner, M. S. Bae, and J. J. Schauer (2004), A method for on-line measurement of water-soluble organic carbon in ambient aerosol particles: Results from an urban site, *Geophys. Res. Lett.*, 31, L13105, doi:10.1029/2004GL019681.

1. Introduction

[2] Compounds of organic carbon can comprise a significant fraction of the fine atmospheric aerosol particle mass (10 to 70%) [Andrews *et al.*, 2000]. Due to its chemical complexity, however, little is known about these compounds, and even less is known about the chemical nature and abundance of water-soluble organic compounds in atmospheric aerosol particles. The WSOC fraction is of interest because it could affect the particle's hygroscopicity and ability to serve as cloud condensation nuclei [Saxena *et al.*, 1995]. These processes have implications for regional air quality and global climate.

[3] The WSOC fraction is also important because one of its major sources is thought to be from secondary organic aerosol (SOA) formation in which the oxidation of carbonaceous gases leads to low volatility products that may

condense [Saxena and Hildemann, 1996]. In some regions, SOA can be a significant fraction of the fine particle mass and may have an impact on a region's compliance with air quality regulations [Lim and Turpin, 2002].

[4] Based on studies involving the collection of particles onto integrated filters over periods often in excess of 24 hours, followed by off-line analysis, fine particle WSOC has been found to account for 77, 48, and 65% of the fine particle organic carbon in European background, rural, and polluted sites, respectively [Zappoli *et al.*, 1999]. A seasonal study of WSOC in the Po Valley, Italy found that WSOC in the summer and fall accounted for 50 and 47% of the fine particle organic carbon, respectively [Decesari *et al.*, 2001].

[5] WSOC is likely composed of oxygenated compounds containing functional groups such as COOH, COH, C = O, COC, CONO₂, CNO₂, and CNH₂ [Saxena and Hildemann, 1996, and references therein]. Theoretical and laboratory studies of secondary organic formation through gas-phase reactions [Finlayson-Pitts and Pitts, 1986] indicate this is the main process for the formation of light organic compounds such as carboxylic acids, carbonyls, alcohols, nitrates, and other single and multifunctional oxygenated compounds.

[6] Studies have also found that at times a significant fraction of WSOC is composed of polyacidic compounds (21 to 55%) [Zappoli *et al.*, 1999] analogous to that of naturally occurring macromolecular compounds such as humic and fulvic acids (referred to as humic-like substances or HULIS) [Krivácsy *et al.*, 2000]. Measurements suggest that sources of HULIS could be both primary and secondary, including biomass burning [Mukai and Ambe, 1986], soot oxidation [Decesari *et al.*, 2002], and secondary aerosol formation via heterogeneous reaction of isoprenoid and terpenoid compounds catalyzed by sulfuric acid aerosol particles [Limbeck *et al.*, 2003]. In addition to these components, a myriad of other lesser compounds also likely contribute to the WSOC fraction of fine ambient particles.

[7] This report describes a near real-time method for measuring WSOC, followed by results obtained at the St. Louis - Midwest Supersite during the summer and autumn of 2003.

2. Instrumentation

[8] WSOC is operationally defined as the fraction of particulate organic carbon that has been collected in water by the Particle-into-Liquid Sampler (PILS), and at a given liquid concentration, penetrates a 0.5 μm filter and liquid transport tubing and is detected. In this study the liquid concentration ranges from 50 to 250 ppb. A schematic diagram of the method to measure fine particle (PM_{2.5})

¹School of Earth and Atmospheric Sciences, Georgia Institute of Technology, Atlanta, Georgia, USA.

²Chemical Engineering, Washington University, St. Louis, Missouri, USA.

³Water Science and Engineering Laboratory, University of Wisconsin-Madison, Madison, Wisconsin, USA.

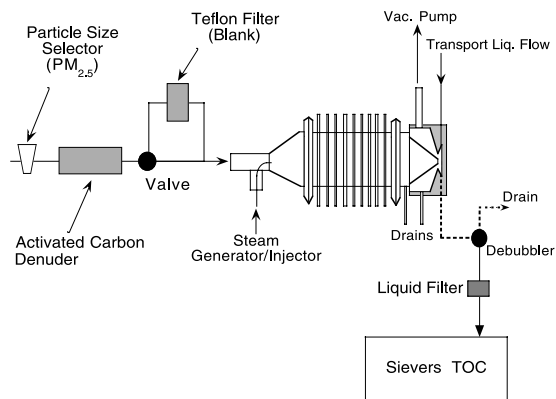


Figure 1. Schematic of the PILS-WSOC with an optional 2.5 μm cut cyclone for PM_{2.5} measurement. A normally open actuated on/off valve controlled by a timer was periodically closed to direct the sample air through the Teflon filter for a particle-free (background) measurement. Typically, a half hour background measurement was conducted every four hours.

WSOC is shown in Figure 1. Ambient particles smaller than 2.5- μm aerodynamic diameter are collected with the PILS by rapidly mixing saturated water vapor with ambient aerosol. The resulting supersaturated water vapor condenses on all ambient particles larger than approximately 10 to 30 nm. These activated particles then grow to 3–5 μm diameter, a size that is readily removed from the air with an inertial impactor. Purified water is pumped over the impaction plate, flows around its perimeter and merges with the liquid from the droplets. The combined flow can then be analyzed by any on-line analytical technique to quantify the aerosol composition. Developed at Georgia Tech, the PILS has been used extensively to measure the inorganic aerosol particle bulk composition by coupling it to ion chromatographs [Orsini *et al.*, 2003]. This paper presents the first results of organic aerosol particle measurements with the instrument.

[9] To measure the WSOC, the PILS effluent is analyzed continuously with a Total Organic Carbon (TOC) analyzer (Sievers Model 800 Turbo, Boulder, CO). The liquid sample is passed through a 0.5 μm PEEK (polyetheretherketone) liquid filter and delivered to the TOC analyzer as a continuous flow via glass syringe pumps (Versa 3, Kloehe Inc.). The TOC measures aqueous carbon by oxidizing organic compounds to form carbon dioxide (CO_2) using UV irradiation and chemical oxidation with ammonium persulfate ($(\text{NH}_4)_2\text{S}_2\text{O}_8$). CO_2 is quantified by membrane separation into a clean water flow followed by conductivity detection. The increase in conductivity of the deionized water (DI Water) is proportional to the concentration of aqueous CO_2 in the sample stream. The instrument has two separate channels to compute total organic carbon by the difference in total carbon and total inorganic carbon (mainly dissolved CO_2 from ambient air) [Clesceri *et al.*, 1989].

[10] The measurement of carbonaceous aerosol particles has been found to be inherently difficult due to errors associated with absorption of gaseous compounds that contribute to the particle measurements (positive artifact) or the loss of semi-volatile particle compounds during

sampling (negative artifact). These issues also apply to this technique. To minimize and account for the positive artifact, an attempt is made to remove some portion of the gaseous organic carbon with a 12 inch long parallel plate denuder comprised of activated charcoal impregnated absorbent surfaces [Eatough *et al.*, 1993]. The measurement background is quantified periodically by passing sample air through a Teflon filter resulting in a measurement of any organic gases absorbed in the PILS and residual organic carbon in our purified water.

[11] Liquid concentrations from ambient measurements in June are shown in Figure 2. The difference between the measured, (includes aerosol carbon plus possible interferences from gaseous compounds and water impurities), and filtered air (background) was interpreted as the ambient aerosol particle WSOC concentration. Our results indicated that the organic carbon in the DI water apparently controls the background, and not the absorption of gases, since periodically injecting DI water directly into the TOC analyzer, independent of the PILS, produced the same background as the filtered air measurements. Moreover, no changes were observed in the background when the denuder was removed (not shown in Figure 2). This suggested that for these data, positive artifacts due to absorption of gases within the PILS during the aerosol particle measurement were likely minimal in the WSOC measurements.

[12] Negative artifacts due to volatility losses of organic compounds during PILS collection have not been quantified. WSOC relative measurement uncertainty is estimated to be between ± 5 to 10% based on the combined uncertainties associated with the sample air and liquid flows and background variability. However, not accounting for the negative artifacts (if any) will lead to a systematic under-measurement of the WSOC.

[13] In addition to the online measurements, WSOC from 24-hr integrated filter sampling and manual extraction was performed for seven days in both June and August. The 24-hour average PILS WSOC was regressed on 24-hour

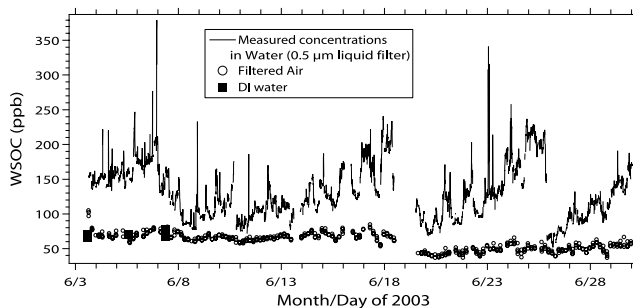


Figure 2. Liquid concentrations recorded by the TOC for measured (ambient) and filtered air (background) for June 2003 in St. Louis. The difference between these curves was the carbon associated with the ambient aerosol. DI water periodically injected directly into the TOC analyzer is also plotted. The data gap was due to routine instrument maintenance and replenishing of the water used to operate the instrument. This resulted in a drop in the filtered air due to water with lower organic carbon concentrations. (Note, the TOC analyzer records liquid concentrations as ppb.)

Table 1. Mean and Standard Deviations (in Parenthesis) of PM_{2.5} EC, OC, WSOC, and the WSOC/OC Ratio for the Months Shown in 2003 at the St. Louis - Midwest Supersite

Month	EC	OC	WSOC	WSOC/OC
June	0.80 (0.57)	4.76 (2.53)	2.87 (1.41)	0.64 (0.13)
August ^a	0.62 (0.51)	4.04 (1.75)	2.40 (0.78)	0.61 (0.16)
October	1.11 (1.01)	4.55 (3.62)	1.33 (0.75)	0.31 (0.11)

Concentrations are reported in $\mu\text{g C/m}^3$.

^aMeasurements averaged over only August 1 to 17.

integrated filter WSOC using a Deming Least Squares fit. The slope and intercept (with 95% confidence intervals) were 1.35 ± 0.20 and -0.07 ± 0.39 , respectively, ($R^2 = 0.71$). Higher PILS WSOC could be due to a number of factors including: differences in sampling artifacts associated with each method (e.g., loss of semi-volatile WSOC from the filter); incomplete filter extraction of all WSOC compounds from the filter; differences in TOC analysis; and differences in solution concentrations affecting the solubility of various organic carbon compounds.

3. WSOC at an Urban Site

[14] The PILS-WSOC was deployed at the St. Louis - Midwest Supersite during the period June through December 2003. This site is located in East St. Louis, IL in a residential area with some light commercial activity. The field site is periodically impacted by industrial sources within a few kilometers to the south, and is approximately 3 km to the east of the City of St. Louis (MO) central business district.

[15] Along with the PILS-WSOC, there were various other on-line measurements of carbonaceous aerosol properties. Hourly-integrated PM_{2.5} OC and elemental carbon (EC) were measured for alternate hours using a field ECOC analyzer (Sunset Laboratory Inc., Forest Grove, Oregon), which quantifies OC and EC using the thermal/optical transmission (TOT) method [Birch and Cary, 1996]. It was run following the method of Bae *et al.* [2004]. In order to minimize positive artifacts, the ECOC measurements used the same type of denuder as the PILS [Bae *et al.*, 2004].

3.1. Carbonaceous Aerosol Seasonal Trends, June to October

[16] On-going measurements of OC, EC, and WSOC have been conducted at the site since June 2003, here we report on measurements during the months of June, August,

and October (no WSOC measurements were made in September).

[17] Monthly means of EC, OC, WSOC, and the ratio of WSOC to OC for these three months are summarized in Table 1. Mean OC concentrations were fairly similar in June, August, and October, however, the mean WSOC concentration changed significantly. WSOC was approximately 50% lower in October compared to June and August, and thus WSOC/OC was also about 50% lower. This is consistent with the view that much of the WSOC may be from SOA formation, a process that would be less vigorous in the fall when actinic fluxes to drive photochemical activity are lower.

3.2. Diurnal Trends in WSOC/OC

[18] Our measurements show that for the majority of the time WSOC tracks OC (e.g., for June, hourly-integrated OC regressed on hourly-averaged WSOC yields $R^2 = 0.81$). To further demonstrate the observed behavior, Figure 3 shows the OC and WSOC concentration, WSOC/OC ratio, and ozone (O_3) concentration for 14-day periods in June and August. A number of interesting features were observed both within and between these periods.

[19] The time series for OC revealed a 3-to-7 day trend with a diurnal cycle superimposed (EC trends were qualitatively similar to OC trends). The longer-term trend was dictated by precipitation events. Over the multi-day period following a precipitation event (e.g., 6/13/03 and 6/19/03 in Figure 3), the OC increased from approximately $1-4 \mu\text{g C/m}^3$ up to about $10-15 \mu\text{g C/m}^3$; subsequently, the OC concentrations rapidly dropped back to approximately $1-4 \mu\text{g C/m}^3$ apparently due to precipitation scavenging. A steady increase in OC concentrations would resume after the rain event. This cycle was observed three times in June 2003 and has the characteristics of a regional buildup of pollution periodically reset by precipitation events. Superimposed on this multi-day pattern was a distinct diurnal profile with OC concentration exhibiting a maximum during the night and a minimum during the day. These trends are often observed in urban regions and are indicative of the emissions field being attenuated by atmospheric ventilation with strong vertical mixing during the day and a shallow, stably-stratified mixing layer at night. In contrast, for the period August 1-17 there was no discernable day-to-day buildup in the OC concentration and the aforementioned diurnal profiles were only weakly

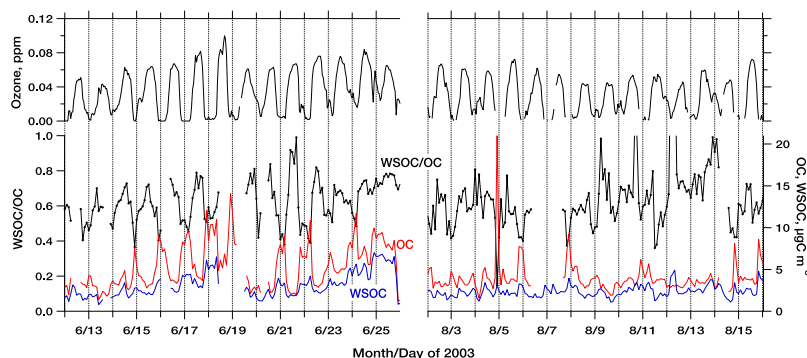


Figure 3. Time series of PM_{2.5} OC, WSOC, the fraction of OC that was water-soluble, and O_3 concentration for two 14-day periods (June and August, 2003). Dashed vertical lines represent midnight CST.

Table 2. Number of Data Points (N), Slope and Intercept (Both With 95% Confidence Limits), and R^2 Value for Linear Regressions of the WSOC/OC Ratio Versus O_3 Concentration for Various Periods During June 2003 in St. Louis

Period in June	N	Slope ^a	Intercept	R^2
Entire Month	328	3.52 ± 0.26	0.53 ± 0.01	0.41
June 15–18	47	2.60 ± 0.30	0.53 ± 0.01	0.72
June 21–25	59	4.09 ± 0.50	0.48 ± 0.02	0.54
June 27–30	39	3.57 ± 0.51	0.57 ± 0.02	0.57

^aUnits are ppm^{-1} .

discernible. October featured a combination of the trends observed for the June and August periods.

[20] WSOC/OC trends also differed between June and August. In June there was a large and consistent variation in the daily WSOC/OC. For extended periods in June, often associated with the aforementioned diurnal OC trends but ~ 12 hours out of phase, there was a clear temporal pattern in WSOC/OC with levels reaching $\sim 80\%$ during the day and dropping to near 40% at night. In several instances the water-insoluble fraction (WIOC) dominated at night (WIOC = OC – WSOC and thus WIOC/OC = 1 – WSOC/OC). In the past most WSOC measurements have been made using 24-hr integrated filter measurements that are incapable of resolving diurnal variability. The elucidation of subdaily WSOC patterns and its coupling to OC and other parameters represents a unique observation for an urban site and demonstrates the insights gained from near real-time measurements.

[21] The site was also periodically influenced by strong local point sources. One event can be seen in Figure 3 just prior to midnight on 8/5/03. At this time, the hourly-averaged OC concentration spiked to over $20 \mu\text{g C/m}^3$, the WSOC concentration, however, did not significantly increase and thus the WSOC/OC ratio was very low, 15%, (i.e., the water-insoluble OC fraction was high) suggesting that most of the carbonaceous aerosol was likely fresh primary OC.

[22] During the June periods of persistent diurnal trends, the WSOC/OC ratio was fairly well correlated with O_3 . Table 2 summarizes linear regression results for the entire month of June, and for each period of OC concentration buildup observed between precipitation events. WSOC/OC to O_3 correlations may suggest that a significant fraction of the June daytime WSOC was associated with SOA. In contrast, diurnal trends in OC and WSOC/OC were not as prominent in August and no correlation was found between WSOC/OC and O_3 ($R^2 = 0.023$). The observed contrasts between June and August could be due to a number of factors, including different atmospheric chemical and meteorological processes, and emissions. Thus, significant chemical differences may exist between the WSOC measured in June and August.

[23] Overall, these results show that online measurements of aerosol WSOC, coupled with equally rapid measurements of aerosol OC, provided unique information about the sources and atmospheric processing of fine particulate organic compounds soluble in water. Extension of the method to chemically speciate WSOC online would provide further insights.

[24] **Acknowledgments.** Although this research has been funded wholly or in part by the United States Environmental Protection Agency through grant X-98722301-0 and R-82897601, it has not been subjected to EPA's required peer and policy review and therefore does not necessarily reflect the views of EPA. The authors gratefully acknowledge the members of the St. Louis – Midwest Supersite consortium and also the field support provided by staff of the Air Quality Laboratory at Washington University in St. Louis (J. R. Turner, director).

References

- Andrews, E., P. Saxena, S. Musarra, L. M. Hildemann, P. Koutrakis, P. H. McMurry, I. Olmez, and W. H. White (2000), Concentration and composition of atmospheric aerosols from the 1995 SEAVS experiment and a review of the closure between chemical and gravimetric measurements, *J. Air Waste Manage. Assoc.*, **50**, 648–664.
- Bae, M. S., J. J. Schauer, J. T. DeMinter, and J. R. Turner (2004), Hourly and daily patterns of particle-phase organic and elemental carbon concentrations in the urban atmosphere, *J. Air Waste Manage. Assoc.*, in press.
- Birch, M. E., and R. A. Cary (1996), Elemental carbon-based method for monitoring occupational exposures to particulate diesel exhaust, *Aerosol Sci. Technol.*, **25**, 221–241.
- Clesceri, L. S., A. E. Greenberg, and R. R. Trussell (1989), *Standard Methods for Examination of Water and Wastewater*, Am. Publ. Health Assoc., Washington, D. C.
- Decesari, S., M. C. Facchini, E. Matta, F. Lettini, M. Mircea, S. Fuzzi, E. Tagliavini, and J.-P. Putaud (2001), Chemical features and seasonal variation of fine aerosol water-soluble organic compounds in the Po Valley, Italy, *Atmos. Environ.*, **35**, 3691–3699.
- Decesari, S., M. C. Facchini, E. Matta, M. Mircea, S. Fuzzi, A. R. Chughtai, and D. M. Smith (2002), Water soluble organic compounds formed by oxidation of soot, *Atmos. Environ.*, **36**, 1827–1832.
- Eatough, D. J., A. Wadsworth, D. A. Eatough, J. W. Crawford, L. D. Hansen, and E. A. Lewis (1993), A multiple system, multi-channel diffusion denuder sampler for the determination of fine-particulate organic material in the atmosphere, *Atmos. Environ., Part A*, **27**, 1213–1219.
- Finlayson-Pitts, B. J., and J. N. Pitts Jr. (1986), *Atmospheric Chemistry: Fundamentals and Experimental Techniques*, John Wiley, Hoboken, N. J.
- Krivácsy, Z., et al. (2000), Study of humic-like substances in fog and interstitial aerosol by size-exclusion chromatography and capillary electrophoresis, *Atmos. Environ.*, **34**, 4273–4281.
- Lim, H.-J., and B. J. Turpin (2002), Origins of primary and secondary aerosol in Atlanta: Results of time-resolved measurements during the Atlanta Supersite Experiment, *Environ. Sci. Technol.*, **36**, 4489–4496.
- Limbeck, A., M. Kulmala, and H. Puxbaum (2003), Secondary organic aerosol formation in the atmosphere via heterogeneous reaction of gaseous isoprene on acidic particles, *Geophys. Res. Lett.*, **30**(19), 1996, doi:10.1029/2003GL017738.
- Mukai, A., and Y. Ambe (1986), Characterization of humic acid-like brown substance in airborne particulate matter and tentative identification of its origin, *Atmos. Environ.*, **20**, 813–819.
- Orsini, D. A., Y. Ma, A. Sullivan, B. Sierau, K. Baumann, and R. J. Weber (2003), Refinements to the particle-into-liquid sampler (PILS) for ground and airborne measurements of water-soluble aerosol composition, *Atmos. Environ.*, **37**, 1243–1259.
- Saxena, P., and L. M. Hildemann (1996), Water-soluble organics in atmospheric particles: A critical review of the literature and application of thermodynamics to identify candidate compounds, *J. Atmos. Chem.*, **24**, 57–109.
- Saxena, P., L. M. Hildemann, P. H. McMurry, and J. H. Seinfeld (1995), Organics alter hygroscopic behavior of atmospheric particles, *J. Geophys. Res.*, **100**, 18,755–18,770.
- Zappoli, S., et al. (1999), Inorganic, organic and macromolecular components of fine aerosol in different areas of Europe in relation to their water solubility, *Atmos. Environ.*, **33**, 2733–2743.

M. S. Bae and J. J. Schauer, Water Science and Engineering Laboratory, University of Wisconsin-Madison, 660 North Park Street, Madison, WI 53706–1484, USA.

A. L. Clements and J. R. Turner, Chemical Engineering, Washington University, One Brookings Dr., Urbauer Hall, Rm. 208, St. Louis, MO 63130, USA.

A. P. Sullivan and R. J. Weber, School of Earth and Atmospheric Sciences, Georgia Institute of Technology, Atlanta, GA, USA. (rweber@eas.gatech.edu)