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Simultaneous measurements of particulate and gas-phase water-soluble organic carbon concentrations at remote and urban-influenced locations

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[1] The sources, sinks, and overall importance of water-soluble organic carbon (WSOC) in the atmosphere are not well understood. Although the primary historical focus has been on particulate WSOC (WSOC_P), here we also present results obtained using a newly developed technique that additionally measures gas-phase water-soluble organic carbon (WSOC_G). These first-of-their-kind measurements show that WSOC_G can often be more than ten times larger than WSOC_P at both urban and remote locations. The average fraction of WSOC residing in the gas phase ($f_g = \text{WSOC}_G / (\text{WSOC}_G + \text{WSOC}_P)$) at five various field sites ranged from 0.64 to 0.93, implying significant differences in WSOC phase partitioning between locations. At Houston, TX, and Summit, Greenland, a repeatable diurnal pattern was observed, with minimum values for f_g occurring at night. These trends likely are due, at least in part, to temperature and/or relative humidity related gas-to-particle partitioning. These coincident measurements of WSOC in both the gas and particle phases indicate that a relatively large reservoir of water-soluble organic mass is not taken into account by measurements focused only on WSOC_P. In addition, a significant amount of WSOC_G is available to form WSOC_P or enter cloud droplets depending on the chemical and physical properties of the droplets and/or aerosols present. **Citation:** Anderson, C., J. E. Dibb, R. J. Griffin, and M. H. Bergin (2008), Simultaneous measurements of particulate and gas-phase water-soluble organic carbon concentrations at remote and urban-influenced locations, *Geophys. Res. Lett.*, 35, L13706, doi:10.1029/2008GL033966.

1. Introduction

[2] Organic compounds are emitted by a wide variety of processes, both natural and anthropogenic, and include hundreds to thousands of different types of molecules existing in both the gas and particle phases [Kanakidou *et al.*, 2005]. Of particular importance is the fraction of organic carbon (OC) that is water soluble (WSOC). Water-soluble aerosols, including those dominated by organics, influence cloud formation and lifetime [Intergovernmental Panel on Climate Change, 2001]. Depending on location

and time of year, aerosol-phase WSOC (WSOC_P) can account for between 20 and 80% of the total OC aerosol mass [Saxena and Hildemann, 1996; Jaffrezo *et al.*, 2005; Sullivan and Weber, 2006; Kondo *et al.*, 2007]. In addition, a significant component of WSOC_P is thought to be secondary organic aerosol (SOA) [Sullivan *et al.*, 2006], which is formed from the gas-to-particle transfer of the oxidation products of volatile organic compounds [Pankow, 1994]. SOA production is not well characterized on a global scale, but is thought to represent a large fraction of organic mass missing from global chemical transport models of the free troposphere [Heald *et al.*, 2005]. Some water-soluble organic gases (WSOC_G) can also affect droplet acidity, surface tension, and cloud condensation nuclei activation [Keene and Galloway, 1988; Facchini *et al.*, 1999; Limbeck *et al.*, 2003].

[3] Because of the large number of organic species in the atmosphere, some of which reside in multiple phases, a measurement of WSOC that is comprehensive, phase-specific, and speciated is difficult. Pre-baked quartz filters are commonly used to collect aerosol OC. After sampling, the water-soluble fraction is extracted manually and analyzed by a variety of methods. Attempts to measure individual compounds on a molecular basis typically result in less than 15% of the total organic aerosol mass being identified [Decesari *et al.*, 2006; Fisseha *et al.*, 2006]. Total organic carbon (TOC) analysis allows the total WSOC concentration to be quantified but yields no information about the types of compounds that collectively constitute WSOC. The filter sampling times of several hours to days that are employed commonly also limit the ability to provide details at finer temporal resolution. One method that is able to make real-time measurements of WSOC_P is the Particle-into-Liquid (PILS) total organic carbon (TOC) system [Sullivan *et al.*, 2006]. By making measurements on a short timescale (approximately several minutes), this technique is able to provide important information about the sources, transport, and processing of particulate WSOC.

[4] To our knowledge, no measurements of WSOC_G have been made, despite the fact that some water-soluble compounds, such as certain carboxylic acids, are semi-volatile and partition between the aerosol and gas phases [Chebbi and Carlier, 1996]. There have been measurements of gas-phase and particulate organic acids, suggesting that gas-phase material is a substantial fraction of the total ambient WSOC budget [Dibb *et al.*, 1994]. In order to gain a better understanding of the partitioning of bulk WSOC between the gas and particle phases, measurements of WSOC_G and WSOC_P were made at a variety of locations including remote (Summit, Greenland; Niwot Ridge, Colorado), urban

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Table 1. Mean and Standard Deviation for WSOC Measurements Made at Five Different Locations^a

Location	Sample Period	Number of Samples	WSOC _G ($\mu\text{gC m}^{-3}$)	WSOC _P ($\mu\text{gC m}^{-3}$)	f_g
Appledore Is., ME	July, 2005	173	17.8 (16.1)	1.4 (1.3)	0.93*
Thompson Farm, NH	October, 2005	87	12.2 (11.4)	2.3 (3.1)	0.88 (0.06)
Niwot Ridge, CO	January, 2006	41	0.46 (0.31)	0.24 (0.18)	0.64 (0.23)
Houston, TX	August/Sept., 2006	1337	9.29 (7.20)	1.48 (2.30)	0.86 (0.14)
Summit, Greenland	June, 2006	206	0.67 (0.23)	0.19 (0.17)	0.78 (0.16)

^aMean concentration values given in table with standard deviations in parentheses.

^bA standard deviation of f_g is not available for Appledore Island due to non-simultaneous measurements of WSOC_G and WSOC_P. The f_g value presented is simply the average WSOC_G divided by the sum of the average WSOC_G and average WSOC_P.

(Houston, TX) and urban influenced (Appledore Island, ME (marine); Thompson Farm, NH (semi-rural)) sites. In this paper, measurements from these sites are presented and compared. In addition, diurnal trends in the partitioning of WSOC at the measurement locations are discussed.

2. Methods

[5] During 2005 and 2006, WSOC measurements were made during field experiments at five locations that represent a diverse set of remote, rural, urban, and marine influenced environments. Niwot Ridge, Colorado (40.05°N, 105.57°W), is a remote location situated at 4000 meters in the Rocky Mountains. Summit, Greenland (72°N, 38°W), is also a remote Arctic location atop 3200 meters of glacial ice and hundreds of kilometers away from the sparsely populated coast. Appledore Island (42.97°N, 70.62°W) is a small, rocky island located 10 km off the coast of the eastern United States along the Maine-New Hampshire border. Thompson Farm (43.11°N, 70.95°W), a semi-rural New England site located 10 km inland from the New Hampshire coast, lies 20 km to the west of Appledore Island. Houston, Texas (29.72°N, 95.34°W), is a large metropolitan area that is also home to a high density of petrochemical plants.

[6] Mist chambers were used to collect WSOC in a small volume, ~30 ml of ultrapure deionized (DI) water. Two measurement channels were used simultaneously, with sample collection times of either 30 or 60 minutes. The longer interval was used when ambient concentrations were expected to be less than roughly $1 \mu\text{g C m}^{-3}$. The DI sample water was injected into the mist chambers using programmed syringe pumps. After the allotted sampling time, the sample water was drawn into a syringe pump and injected into a Sievers 800 TOC Analyzer (General Electric, Boulder, CO). The Sievers instrument was run in Turbo mode, with measurements every 3 s averaged over 1.5 minutes for each sample. One measurement was made for each syringe injection. Detection limits are based upon the variability in the TOC signal of the DI water used to collect samples, which was flushed continuously through the system between samples. The concentration of the DI water used to flush the syringe volume was used to estimate the detection limit. Two times the standard deviation of the mean TOC signal in the DI water is used as the detection limit, which corresponds to an ambient concentration of $\sim 50 \text{ ng C m}^{-3}$.

[7] Isolation of WSOC_G and WSOC_P was achieved by manipulating the inlet configuration. WSOC_G was mea-

sured by sampling through a Fluoropore Teflon[®] filter (Pall Life Sciences, East Hills, NY). Two methods were used to estimate WSOC_P. The denuder method, in which an activated carbon denuder was used to remove WSOC_G, allows for direct measurement of WSOC_P. A denuder removal efficiency must be assumed in this method. The denuder method was used during the first two field studies at Appledore, Island and Thompson Farm. The denuder efficiencies were determined in the field several times daily, and the particulate concentrations were estimated using the average of the efficiency values determined prior to and after a specific sample. It is important to point out that the mean denuder efficiencies at Appledore, Island and Thompson Farm were 81% and 43%, respectively [Anderson *et al.*, 2008]. Given the relatively low gas-phase removal efficiencies, a difference method not involving the denuder was used for subsequent sampling. The difference method, where WSOC_P was calculated as the difference between sample concentrations collected through an unfiltered inlet and a filtered inlet, provided an indirect measurement. In this paper, efforts to measure WSOC_P by both methods are reported. More details on the sampling technique are given by Anderson *et al.* [2008].

3. Results and Discussion

3.1. Water-Soluble Gas-Phase and Particulate Measurements at Several Sites

[8] Concentrations of WSOC varied significantly between locations (Table 1). The remote settings of Summit, Greenland, and Niwot Ridge, Colorado showed similar mean concentrations for both WSOC_G ($0.67 \mu\text{g C m}^{-3}$ and $0.46 \mu\text{g C m}^{-3}$, respectively) and WSOC_P ($0.19 \mu\text{g C m}^{-3}$ and $0.24 \mu\text{g C m}^{-3}$, respectively), as shown in Table 1. The relatively low values for WSOC_P are within the range of values measured from aircraft in the free troposphere over northeastern North America [Sullivan *et al.*, 2006]. Samples were collected at Niwot Ridge during a short winter campaign that was dominated by strong, westerly flow. In this type of synoptic pattern, air from the free troposphere descends to the sampling site [Greenland, 1989]. A similar degree of isolation from emission sources is found at Summit during the summer season [Kahl *et al.*, 1997; Stohl, 2006].

[9] Appledore Island, Thompson Farm, and Houston are much closer to sources of anthropogenic organic compounds. As a consequence, WSOC concentrations are larger by an order of magnitude than those at Summit and Niwot Ridge. The highest WSOC concentrations were measured at

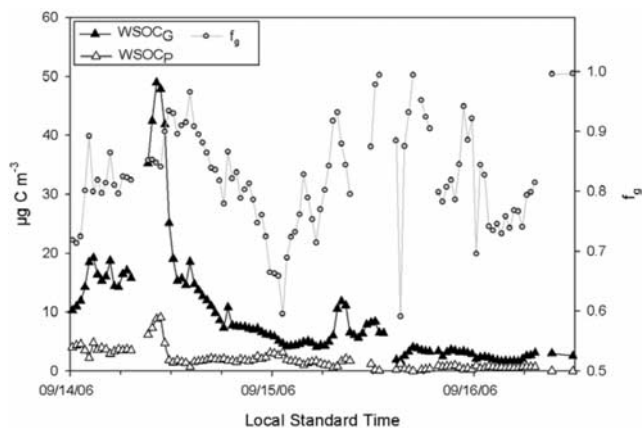


Figure 1. Thirty-minute average time series of WSOC_G , WSOC_P , and f_g in Houston, Texas.

the rural sites of Appledore Island (mean values of $17.8 \mu\text{g C m}^{-3}$ and $1.4 \mu\text{g C m}^{-3}$ for WSOC_G and WSOC_P , respectively) and Thompson Farm (mean values of $12.2 \mu\text{g C m}^{-3}$ and $2.3 \mu\text{g C m}^{-3}$ for WSOC_G and WSOC_P , respectively) with slightly lower, although comparable, values in Houston (mean values of $9.3 \mu\text{g C m}^{-3}$ and $1.5 \mu\text{g C m}^{-3}$ for WSOC_G and WSOC_P , respectively). Finding similar concentrations of WSOC at Thompson Farm and Appledore Island compared to Houston may at first seem surprising. However, Thompson Farm and Appledore Island are downwind of large urban areas in the eastern United States and large industrial centers in the Ohio River Valley and prevailing winds transport plumes of pollution to these sites [Fischer *et al.*, 2006, Ziemba *et al.*, 2007]. It should also be noted that these locations may also be impacted by biogenic emissions of organic compounds from plants.

[10] One consistent finding at all locations is that average WSOC_G is always significantly larger than average WSOC_P . The WSOC_G concentrations are generally two to five times greater than those observed for WSOC_P at both Summit and Niwot Ridge, indicating a significant pool of organic material available to partition to the particle phase given the appropriate conditions. The fractions of total WSOC in the gas phase (f_g) are smaller at Summit and Niwot Ridge than at the more temperate locations (Table 1). One potential reason for this is the closer proximity of the low altitude locations to anthropogenic sources of volatile organic compounds (WSOC and precursors). In addition, less aged air masses impacting the semi-rural and urban location would have had less time for WSOC_G to be removed by precipitation scavenging and/or partitioning to the aerosol phase. Lastly, colder temperatures at Summit and Niwot Ridge may result in the partitioning of WSOC to the particle phase.

3.2 Diurnal Variability of WSOC_G and WSOC_P

[11] In Houston the concentrations of WSOC in both the aerosol and gas phase varied by nearly an order of magnitude on a timescale of several hours (Figure 1). This was due in part to transport from the Gulf of Mexico that intermittently brought air masses nearly as clean as those impacting the high altitude stations. The concentrations are also influenced by a wide variety of local sources as is

evidenced by the relatively high concentrations observed during the sampling period. In addition to these meteorological/emissions driven changes in concentrations, a potential phase-partitioning of WSOC between the gas and aerosol based on an observed diurnal cycle with peaks in f_g in early afternoon and minima around midnight (Figure 1) likely affects phase-specific concentrations. It should be noted that filter artifacts, such as the evaporation of deposited particles with increasing ambient temperature and lowering RH, can potentially influence our measurements. Although it is very difficult to assess the influence of artifacts given our lack of knowledge of the specific organic compounds present on the aerosol particles.

[12] Similar trends in WSOC partitioning were observed at Summit, Greenland (Figure 2), during a six-week campaign. Measurements during late June display consistent minimum f_g values at night and early morning (a few hours later than in Houston in local solar time). Coincident decreases in WSOC_G and increases in WSOC_P occur on four out of the five nights shown. These events are correlated with temperature, and it is likely that gas-to-particle partitioning of WSOC, modulated by exchange of WSOC_G between the air and surface snow, is responsible for the observed trends [Anderson *et al.*, 2008]. It is probable that a combination of decreased temperature and increased relative humidity (which dictates the amount of condensed water associated with the particles) during the nights favors particulate phase WSOC. In fact during the sampling days the day time RH was typically 60% with night time values often greater than 90%. It should be noted it is extremely difficult to verify the RH dependency of phase-partitioning since we do not have chemical composition information on the WSOC_G .

[13] The Houston and Summit observations show that in both remote and densely populated regions, the gaseous fraction dominates WSOC. Further, the values of f_g vary substantially with a similar diel pattern at both sites on several days. The larger amplitude of the daily variation of f_g at Summit (up to 70%) compared to Houston (maximum on the order of 40%) may reflect the lack of local sources influencing Summit, Greenland as well as the more consistent day-to-day meteorology of the site. It appears that a

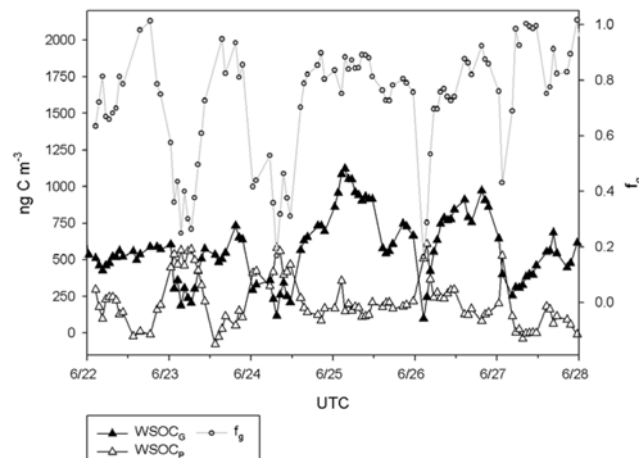


Figure 2. Hour-average time series of WSOC_G , WSOC_P , and f_g at Summit, Greenland.

large part of the diurnal variation in f_g at Summit reflects temperature and/or relative humidity driven gas to particle exchange. In contrast, Houston is subject to a wide range of local sources of organic gases and particles and much more diverse meteorological conditions. However, it appears gas/particle partitioning of WSOC may still be important in modulating f_g . Overall, this research indicates a relatively large reservoir of WSOC_G is available across urban and rural locations. This material may play a significant role in determining the concentrations of particulate organic carbon.

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