

Chemical characterization of the ambient organic aerosol soluble in water: 1. Isolation of hydrophobic and hydrophilic fractions with a XAD-8 resin

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[1] Group separation of the aqueous extract of fine particles bearing water-soluble organic carbon (WSOC) provides unique insights into the sources of organic carbon (OC). XAD-8 resin coupled with a Total Organic Carbon analyzer allows for direct quantification. We term the fraction of WSOC not retained by a XAD-8 resin column at pH 2 as hydrophilic WSOC (WSOCxp); this includes saccharides, amines, and carbonyls and aliphatic monocarboxylic/dicarboxylic/oxocarboxylic acids with less than 4 or 5 carbons. The fraction of WSOC retained by XAD-8, termed the hydrophobic fraction (WSOCxr), include aromatic acids, phenols, organic nitrates, cyclic acids, and carbonyls and monocarboxylic/dicarboxylic acids with greater than 3 or 4 carbons. However, only aromatic compounds (or aromatic-like compounds with similar properties) can subsequently be extracted from XAD-8 with high efficiency. By coupling a Particle-into-Liquid Sampler with this technique, online measurements of WSOC, WSOCxp, and WSOCxr are possible. Urban measurements from St. Louis and Atlanta, on a carbon mass basis, show an increase in the mean WSOC fraction from winter (51%) to summer (61%), due to increases in the WSOCxp/OC from 0.25 to 0.35. During a summer Atlanta PM event, WSOC to OC was 0.75, driven largely by increases in the WSOCxp. The results are consistent with the view that in the summer, there are increased amounts of oxygenated polar compounds, possibly from secondary organic aerosol production, and that these compounds account for an even larger fraction of OC during stagnation events. A companion paper describes a method to further group speciate these XAD-8 isolated fractions.

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1. Introduction

[2] Condensed phase organic compounds are an important component of the atmospheric aerosol, in both remote and anthropogenic-influenced regions they often are a large fraction of the fine atmospheric particle mass. As in other environmental systems containing organic compounds, the atmospheric organic aerosol has been found to be highly chemically complex, making comprehensive chemical characterization by single component identification nearly impossible [Hamilton *et al.*, 2004]. This has confounded comprehensive investigation into sources of the organic aerosol and makes it challenging to relate their atmospherically relevant physical properties to most chemical components. A solution to this problem is to isolate the organic aerosol into broad and comprehensive chemical fractions. This would simplify the complexity and provide samples for further analysis.

[3] One approach is to focus on the fraction of organic aerosol that is soluble in water. The water-soluble organic carbon (WSOC) fraction tends to be an operationally defined quantity since solubility of some (although likely a small) fraction of the organic aerosol may depend on the solution concentrations, which are determined by the experimental procedure, and the pH of all protolyzable compounds. However, by employing a consistent extraction method, significant changes in the water-soluble fraction will provide evidence for changes in aerosol composition. The water-soluble fraction is of interest for a number of reasons. Water is a natural solvent in the atmosphere and its interaction with the aerosol has significant and wide-ranging consequences. WSOC can be a large fraction of the total organic carbon (OC) [Zappoli *et al.*, 1999; Sullivan *et al.*, 2004], and one of its major sources is through secondary organic aerosol (SOA) formation [Saxena and Hildemann, 1996], a process that is not well understood. WSOC can have unique physical properties. Facchini *et al.* [2000] have shown that the WSOC fraction can significantly depress the surface tension of aqueous solutions, which may be one way that organic compounds can affect ambient particle's hygroscopicity and ability to serve as cloud condensation nuclei (CCN) [Saxena

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et al., 1995]. This has implications for issues ranging from visibility impairment to aerosol effects on the Earth's radiation balance.

[4] We have reported on WSOC measurements made at an urban site in St. Louis [Sullivan *et al.*, 2004] in which consistently higher WSOC to OC ratios were observed in summer than in autumn. Under episodes when air quality worsened over periods of 5 to 7 days, a regular diurnal pattern in WSOC/OC was observed, ranging from approximately 0.40 at night to 0.80 at midday. This trend was similar to other secondarily formed products, such as ozone, and consistent with the notion that at least some fraction of the WSOC was formed in the atmosphere by secondary processes.

[5] The organic aerosol fraction that is soluble in water is likely mainly oxygenated compounds with functional groups such as COOH, COH, C = O, COC, CONO₂, CNO₂, and CNH₂ [Saxena and Hildemann, 1996, and references therein]. A variety of different off-line methods have been developed to characterize these various functional groups within the WSOC. Decesari *et al.* [2000] developed a technique involving chromatographic separation of the WSOC using an anion exchange diethylaminoethyl (DEAE)-TSK gel column to give three groups: FR1 (Fraction 1, neutral and/or basic compounds), FR2 (Fraction 2, monocarboxylic and dicarboxylic acids), and FR3 (Fraction 3, polyacidic compounds). On the basis of proton-nuclear magnetic resonance (H-NMR) they suggest that FR1 was composed of polyols or polyethers, FR2 hydroxylated aliphatic acids, and FR3 unsaturated polyacidic compounds of predominately aliphatic character, with minor content of hydroxyl groups. However, Chang *et al.* [2005] found that some compounds are not separated into their expected groups in this method. Decesari *et al.* [2001] observed in the Po Valley, Italy, that the polycarboxylic acids were the most abundant in all seasons, except for the summer when the monocarboxylic and dicarboxylic acids dominated.

[6] Krivácsy *et al.* [2001] have developed a two-step SPE (solid phase extraction) technique using Merck LiChrolut RP-18 SPE columns to give three fractions: Fraction I (slightly hydrophilic, partly acidic, highly polyconjugated), Fraction II (moderately hydrophilic, acidic, moderately polyconjugated), and Fraction III (very hydrophilic, neutral, slightly polyconjugated). This study found that there were two main fractions (each approximately 50% of WSOC): highly polyconjugated weak polyacids (humic-like substances, referred to as HULIS) and slightly polyconjugated, very hydrophilic, neutral compounds.

[7] Kiss *et al.* [2002] employed a one-step SPE on a Waters Oasis HLB column to separate the WSOC into moderately hydrophilic (retained on the column) and strongly hydrophilic (passed through the column). They observed that the hydrophilic fraction that passed through the column contained more polar functional groups than the fraction retained on the column and lacked polyconjugated structures, suggesting a composition of short-chain carboxylic acids, hydroxy-acids, or polyhydroxy compounds.

[8] The speciation methods of Decesari *et al.* [2000], Krivácsy *et al.* [2001], and Kiss *et al.* [2002] have all suggested the presence of humic-like substances (HULIS) in the WSOC aerosol, apparently associated with the

hydrophobic WSOC fraction. These compounds are of interest since they have unique properties, including light absorption and surface activity [Havers *et al.*, 1998; Facchini *et al.*, 2000]. HULIS can be both primary and secondary in nature. For example, evidence for HULIS has been found in biomass burning [Mukai and Ambe, 1986], soot oxidation [Decesari *et al.*, 2002], secondary aerosol formation via heterogeneous reaction of isoprenoid and terpenoid compounds catalyzed by sulfuric acid aerosols particles [Limbeck *et al.*, 2003], and photooxidation of aromatics that leads to polyacids after ~20 hours [Kalberer *et al.*, 2004].

[9] These methods have provided unique quantitative information, however, the main sources of these compounds have not been identified and important atmospheric processes that may alter chemical and physical properties remains unknown. Here we describe an online quantitative method that couples a PILS-TOC (Particle-into-Liquid Sampler–Total Organic Carbon) with a XAD-8 column in order to group speciate the WSOC into the hydrophilic and hydrophobic fractions. Ambient results from urban sites are presented. This technique is the first step in a new methodology developed to group speciate the ambient aerosol WSOC and to investigate the atmospherically relevant physical properties of isolated chemical groups. A companion paper [Sullivan and Weber, 2006] describes the second step in this process. Other relevant physical properties of these fractions of the organic aerosol are currently being investigated and will be reported later.

2. Methods

2.1. Particulate Collection

[10] Online sampling was done using a PILS coupled to a TOC analyzer, following the method developed by Sullivan *et al.* [2004]. The PILS captures particles sampled at a flow rate of 16.7 L/min into a liquid flow (1.3 ml/min) of deionized water (DI Water) [Orsini *et al.*, 2003]. This liquid sample is filtered to remove large insoluble particles (0.22 μm pore size), and the carbonaceous material in the sample quantified online with the TOC analyzer (see Figure 1). Typical liquid concentrations range from about 30 to 200 ppb C. Background interferences from absorption of carbonaceous gases and carbonaceous material in the DI water are removed by measurements of a dynamic blank. These blank measurements are performed for 30 min every 3 hours by diverting sample air through a Teflon filter (Zefluor, 47 mm diameter, 2 μm pore size) via an actuated valve controlled by a timer. Bulk measurements of PM_{2.5} WSOC were made through the use of a 2.5 μm sharp cut cyclone (URG) positioned at the sampling line inlet.

2.2. Detector

[11] A Sievers Model 800 Turbo TOC analyzer (Boulder, CO) was used to determine the organic carbon in the aqueous samples containing the soluble components of the ambient aerosol. The TOC analyzer measures the organic carbon content of a liquid sample by converting all organic carbonaceous material to carbon dioxide using chemical oxidation involving ultraviolet (UV) light and ammonium persulfate. The carbon dioxide formed diffuses through a

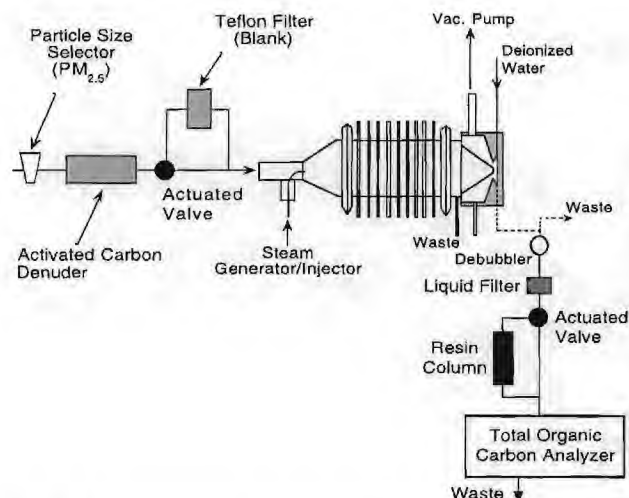


Figure 1. Schematic of the PILS-TOC system coupled with a XAD-8 resin column for sequential online WSOC and WSOCxp measurements. Dynamic blanks are performed every 3 hours for one-half hour via a programmed actuated valve that directs sample air through a Teflon filter prior to sampling. Liquid containing the ambient aerosol is pumped through a $0.22\ \mu\text{m}$ liquid filter and then can either be measured directly by the TOC analyzer for a measurement of WSOC or first conducted through the XAD-8 resin column for a measurement of the WSOCxp fraction. (Abbreviation definitions are listed in the Notation.)

semipermeable membrane into a flow of DI Water and is quantified by conductivity detection. The increase in conductivity of this DI water is proportional to the concentration of aqueous carbon dioxide formed from the sample. The organic carbon is the difference in two channels: a total carbon channel and inorganic carbon channel. Oxidation takes place in the total carbon channel whereas the inorganic carbon channel is unaltered. The analyzer allows for a 6 min integrated measurement when run in online mode and a 3 s measurement when run in Turbo mode. This persulfate-ultraviolet oxidation method produces similar results as methods employing combustion conversion to carbon dioxide gas with infrared detection. However, unlike the combustion method the persulfate-ultraviolet oxidation approach is suitable for concentrations less than 1 ppm C [Clesceri *et al.*, 1989].

[12] The TOC analyzer runs off of an internal calibration performed in the factory. This calibration was periodically verified with an oxalic acid standard. For example, the following are results from a typical calibration: slope = 0.95 ± 0.05 ppb C/ppb C, intercept = -51 ± 20 ppb C (\pm is one standard deviation), and $R^2 = 0.98$.

2.3. XAD-8 Separation Method

[13] Online group separation of WSOC can be performed by solid phase extraction (SPE) with direct TOC analysis, if no carbonaceous eluents are employed. The SPE method employed here involves the partitioning of organic solutes from the polar mobile phase (i.e., aqueous sample with dissolved aerosol components) into a XAD-8 resin, the nonpolar solid phase. This resin's primary partitioning force

is hydrophobic interactions. Therefore the organic compounds retained are the most hydrophobic components of the ambient aerosol particle WSOC. Organic compounds not retained and that penetrate the column are the more hydrophilic fraction. XAD-8 resin is an uncharged but slightly polar resin composed of polymerized methyl ester of polyacrylic acid. It is used extensively by geochemists for extraction of humic substances from natural waters by separating inorganic substances from the humic material [Thurman and Malcolm, 1981].

[14] For this application a 6 mm ID \times 10 cm long glass column hand-packed with resin and fitted on each end with $25\ \mu\text{m}$ polyethylene frits is used. The column is prepared between sample runs via a 1-hour equilibrium period in which no eluent is run over the column, followed by 1 hour of 0.1 M NaOH (sodium hydroxide) and then 15 min of 0.1 M HCl (hydrochloric acid), both at a flow rate of 1.2 ml/min. This regeneration cycle is typically performed after 3.5 hours of online operation since under our operating conditions the maximum sample volume that can be passed over the column before regeneration is necessary is 4 hours. A 10-port actuated valve in combination with syringe pumps performed this regeneration automatically.

[15] Online group separation of the hydrophilic WSOC fraction is determined by coupling in series: a PILS, liquid filter, XAD-8 column, and TOC analyzer (see Figure 1). The flow rate through the column was maintained at 1.2 ml/min. The pH of the sample was adjusted to 2 just prior to sample loading by adding in 0.1 ml/min of 0.1 M HCl via a peristaltic pump. This is done to neutralize most organic compounds so that they are in their free form (i.e., not deprotonated) and able to interact with the neutral XAD-8 resin. The result is that hydrophobic acid and "neutral" compounds are adsorbed to the resin, whereas hydrophobic bases are not. Adsorbed compounds are referred to as the hydrophobic fraction. On the other hand, the compounds that penetrate the XAD-8 column, and are measured online with the TOC analyzer, are hydrophobic bases and all hydrophilic compounds (acids, bases, and neutrals). Here, these compounds are referred to as the hydrophilic fraction. (Note that our experiments to further speciate these fractions [Sullivan and Weber, 2006] show that the contribution of organic bases to the hydrophilic fraction is typically very small (<1%), thus hydrophobic bases have little influence on the hydrophilic fraction.)

[16] Some components of the retained hydrophobic fraction can be desorbed from the XAD-8 resin off-line and also directly measured with a TOC. This is accomplished by passing a pH 13 eluent of 0.1 M NaOH over the column at 1.2 ml/min for 15 min. Practically all compounds that are desorbed are recovered in the first 5 min of the extraction procedure. Some fraction of the hydrophobic material remains adsorbed to the resin and cannot be recovered by this method. Experiments show that for our column (6 mm ID \times 10 cm long glass column) at least $25\ \mu\text{g C}$ must be loaded onto the column in order to achieve near 100% recovery with pH 13 eluent. Backflushing the column did not improve or change the recovery and therefore was not employed.

[17] To characterize the performance of the XAD-8 resin, recovery tests were performed with a variety of different

Table 1. Results of the XAD-8 Penetration and Recovery Tests for a Variety of Water-Soluble Organic Compounds Listed by Functional Groups, Where WSOCxp = Hydrophilic, WSOCxrr = Hydrophobic Recovered, and WSOCxru = Hydrophobic Unrecovered^a

Functional Group and Compound	Initial Concentration, $\mu\text{g C/L}$	Penetration, %	Recovered in NaOH Wash, %	Comment
Monocarboxylic acid				
Formic acid (1)	51, 100, 131	10, 117, 112		WSOCxp
Acetic acid (2)	45, 55, 82, 84	102, 107, 116, 101		WSOCxp
Butyric acid (4)	70	0		WSOCxru
Caproic acid (6)	87	0	15	WSOCxru
Dicarboxylic acid				
Oxalic acid (2)	23, 105, 148, 149, 150	100, 102, 103, 98, 100		WSOCxp
Malonic acid (3)	58, 69, 76	114, 101, 104		WSOCxp
Succinic acid (4)	29, 46	124, 102		WSOCxp
Maleic acid (4)	77	100		WSOCxp
Fumaric acid (4)	2120	0		WSOCxru
Glutaric acid (5)	87	0		WSOCxru
Adipic acid (6)	2220	0		WSOCxru
Pimelic acid (7)	88	0		WSOCxru
Azelaic acid (9)	80	0	21	WSOCxru
Carbonyls				
Glyoxal (2)	98	100		WSOCxp
Methyl glyoxal (3)	74	100		WSOCxp
Propanal (3)	91	112		WSOCxp
Butanal (4)	58	0	16	WSOCxru
Oxocarboxylic acid				
Glyoxylic acid	2055	102		WSOCxp
Amines				
Ethanolamine	39, 41, 73, 79	133, 102, 100, 96		WSOCxp
Polyols				
1,2-Ethandiol	40, 67	117, 108		WSOCxp
Saccharides				
Levogluconan	45, 86	101, 104		WSOCxp
Inositol	1860	103		WSOCxp
Sucrose	2070	100		WSOCxp
Phenols				
Catechol	90	0	70	WSOCxrr
Vanillin	97	0	78	WSOCxrr
Syringaldehyde	91	0	66	WSOCxrr
Salicylic acid	2100	0		WSOCxrr
3-Hydroxybenzoic acid	107	0	99	WSOCxrr
Aromatic acids				
Benzoic acid	1540, 2000	0	80	WSOCxrr
Phthalic acid	1960	0	87	WSOCxrr
Cyclic acids				
Pinic acid	1960	0	25	WSOCxru
cis-Pinonic acid	1980	0	20	WSOCxru
Humic-like				
Suwannee River fulvic	99, 176, 220, 1577	0, 0, 0, 0	93	WSOCxrr
Suwannee River humic	45, 95, 208, 235, 1477	0, 0, 0, 0, 0	88	WSOCxrr
Organic nitrates				
Isobutyl nitrate	980	0	10	WSOCxru
Isopropyl nitrate	1270	0	8	WSOCxru

^aListed in parentheses is the number of carbon atoms per molecule for the series of monocarboxylic and dicarboxylic acids and carbonyls. Fractions that were not measured are left blank.

water-soluble organic compounds relevant to atmospheric aerosol. Table 1 summarizes the results. Three sets of chemical groups are separated by this method. They include hydrophilic compounds in the WSOC that pass through the column at pH 2 (labeled as WSOCxp, see the Notation), recovered hydrophobic compounds, which are compounds that are retained on the column at pH 2 and subsequently recovered with pH 13 eluent (WSOCxrr), and unrecovered hydrophobic compounds, compounds that are retained on the column at pH 2 but not recovered with high efficiency with pH 13 eluent (WSOCxru). In general the hydrophobic compounds were less soluble than the hydrophilic compounds, which often instantaneously dissolved in water.

[18] The experiments show that for the series of monocarboxylic and dicarboxylic acids and carbonyls, the transi-

tion from hydrophilic to hydrophobic occurs for compounds with approximately 4 to 5 carbons in the chain (see top part of Table 1). On the basis of our limited calibrations, also included in this hydrophilic group are oxocarboxylic acids, amines, polyols, and all saccharides (see Table 1 for compounds identified as WSOCxp).

[19] The bottom part of Table 1 shows organic functional groups that were completely retained at pH 2 (hydrophobic). Some functional groups are subsequently recovered in the pH 13 eluent (NaOH) and some not. Approximately 80% of phenolic compounds could be recovered, 85% of aromatic acids, and 90% of humic substances. These recovered hydrophobic compounds are identified as WSOCxrr in Table 1. Compounds that are retained on the resin at pH 2, but not efficiently recovered at pH 13 (unrecovered

hydrophobics) include monocarboxylic and dicarboxylic acids and carbonyls with at least ~ 4 to 5 carbons, since only approximately 20% or less could be recovered in the pH 13 eluent. In addition to these compounds, organic nitrates and cyclic acids are retained but not efficiently recoverable in pH 13 eluent. All these are grouped as unrecovered hydrophobics and identified as WSOC_{xru} in Table 1. It must be kept in mind that these calibration results should be viewed as a guide to the types of compounds in the ambient aerosol that will be segregated into these three fractions, since much of the WSOC in organic aerosols remains unidentified.

[20] The results of these experiments suggest that all aromatic-containing compounds are hydrophobic (retained at pH 2) and can be recovered with high efficiency in pH 13 eluent. This is consistent with results obtained from solid-state ^{13}C -NMR (^{13}C carbon-nuclear magnetic resonance) performed on ambient aerosols collected via filtration. ^{13}C -NMR was performed on the total WSOC, WSOC_{xp} fraction, and WSOC_{xrr} fraction. Consistent with the calibration results, aromatics were only identified in the WSOC and WSOC_{xrr} fraction, whereas the WSOC_{xp} fraction showed no evidence for aromatics [Sannigrahi *et al.*, 2006]. The ambient WSOC_{xrr} fraction may, however, contain other aromatic-like compounds with similar properties as determined by the interactions with XAD-8 resin. More discussion on the comparisons with ^{13}C -NMR is given by Sullivan and Weber [2006].

[21] The uncertainty for the reported WSOC_{xp} and WSOC_{xrr} fractions is estimated at $\pm 10\%$, obtained by calculating the propagation of all known quantifiable errors. This is similar to what was reported for the uncertainty in the WSOC measurements from the PILS-TOC [Sullivan *et al.*, 2004]. Although there is an additional flow rate of sample over the column and sample dilution volume to account for, the effects of these are minimal because of the high-precision syringe pumps employed. However, unknown processes that could either randomly or systematically bias the separations by this method could lead to significantly higher uncertainties.

3. WSOC Speciation Results from Urban Sites

[22] The online system, shown in Figure 1, was used to measure WSOC and the WSOC_{xp} sequentially by either passing the PILS liquid sample containing the dissolved carbonaceous material directly to the TOC or first through the XAD-8 column to strip out the hydrophobic fraction (WSOC_{xr}). A valve was programmed to switch between these measurements to give 4 complete cycles per day, where a cycle was 2.5 hours of WSOC measurements followed by 3.5 hours of column measurements. During WSOC measurements, the XAD-8 column was regenerated. For a period in the summer of 2004, dual PILS-TOC systems were operated in parallel, one dedicated to measurement of WSOC (no XAD-8 column), the other measuring WSOC_{xp} (XAD-8 column in-line). In the following analysis, for both setups, the XAD-8 column was not extracted because the loaded concentrations were insufficient for efficient recovery (see XAD-8 Separation Method above). Here we report the measured WSOC, WSOC_{xp}, and the difference in WSOC and WSOC_{xp} to calculate

WSOC_{xr}. In the companion paper [Sullivan and Weber, 2006], which involves ambient particle collection with integrated filters, the WSOC_{xr} fraction is further divided into WSOC_{xrr} and WSOC_{xru}.

[23] Measurements were made during March 2004 at the St. Louis – Midwest Supersite and then the instrumentation moved to the Environmental Science and Technology Building rooftop laboratory at the Georgia Institute of Technology located in metro Atlanta, where it was operated April through September 2004. We have included measurements from both cities to provide a greater seasonal contrast; from beginning of March to mid-September. At both sites, OC was measured using a field Sunset Labs ECOC analyzer (Forest Grove, Oregon) run with a PM_{2.5} cut cyclone (Sunset Labs cyclone). This instrument determines OC and EC (elemental carbon) using the thermal/optical transmission method [Birch and Cary, 1996]. The ECOC analyzer used the same type of parallel plate carbon denuder [Eatough *et al.*, 1993] as the PILS to minimize positive artifacts. In St. Louis hourly integrated OC was determined at alternate hours [Bae *et al.*, 2004]; in Atlanta 45 min integrated OC was determined starting at the beginning of every hour.

[24] A comparison of the OC, WSOC, WSOC_{xp}, and WSOC_{xr} is made for four periods in these urban environments: winter, a winter event, summer, and a summer event. Both the winter and summer events were chosen on the basis of the presence of stationary high-pressure systems residing over the urban regions. These are likely times when local emissions play a larger role in the measured aerosols compared to other periods. They also provide a contrast to the average conditions during each season. This is especially true for the summer event. Although the summer of 2004 in Atlanta was atypically clean, from about 19 to 24 July a persistent stagnation condition existed resulting in a buildup of ozone and PM_{2.5}. Peak PM_{2.5} levels reached concentrations of 50–60 $\mu\text{g}/\text{m}^3$ in early morning hours, at least twice that measured for most of the summer. During this period the highest PM_{2.5}, ozone, and temperature were recorded for the entire summer, as illustrated in Table 2.

[25] The discussion is based on the following analysis. Time series showing diurnal variability of the organic aerosol and isolated fractions are shown in Figure 2. Pie charts of the WSOC_{xp}, WSOC_{xr}, and water-insoluble fractions of OC (WIOC) based on means for each period are provided in Figure 3, and more details of these statistical results, based on the medians for these periods, are given in Table 3. Scatterplots with linear regression fits for data collected during these periods are also provided. Note that in all cases these results are based on measurements of OC, WSOC, and WSOC_{xp}. Calculated values include: WSOC_{xr} = WSOC – WSOC_{xp} and WIOC = OC – WSOC. Also, for measurements with a single PILS-TOC, WSOC data were linearly interpolated since the WSOC and WSOC_{xp} measurements were made sequentially, not simultaneously.

[26] The time series plots of Figure 2 show clear differences between winter and summer diurnal profiles in OC, WSOC, and WSOC_{xp}. In winter, a prominent feature is the nighttime OC peaks, likely a result of reduced dispersion of emissions due to shallow nocturnal wintertime boundary layers. These nocturnal OC peaks

Table 2. Comparison Between Typical Atlanta Summer 2004 and Summer 2004 Poor Air Quality Event Due to a Stationary High-Pressure System^a

	OC, $\mu\text{g C}/\text{m}^3$	WSOC, $\mu\text{g C}/\text{m}^3$	$\frac{\text{WSOC}}{\text{OC}}$	PM _{2.5} , $\mu\text{g}/\text{m}^3$	Ozone, ^b ppbv	Temperature, °C
Typical summer, 13–27 June	3.22 ± 1.12 (8.23)	1.98 ± 1.00 (6.52)	0.60 ± 0.13 (0.89)	12.54 ± 6.30 (31.71)	22.4 ± 18.4 (75)	25.6 ± 4.0 (32.9)
Summer event, 19–24 July	6.78 ± 2.41 (11.71)	4.76 ± 1.97 (9.30)	0.74 ± 0.08 (0.91)	34.35 ± 14.88 (65.20)	35.1 ± 38.0 (136)	28.9 ± 5.2 (39.8)

^aThe table contains the mean with ± standard deviation (as a measure of the variability), and the maximum value in parenthesis. All ratios are based on carbon mass.

^bOzone data are from a Georgia EPA site in South DeKalb in Atlanta, approximately 20 km southeast of the aerosol measurements.

often occurred near midnight. In the typical summer period of 2004 much of this structure is less distinct, but it is clearly visible again in Figure 2c during the period of the summer event. However, in this summer event the OC peaks tend to occur early in the morning, coinciding with rush-hour traffic, and not near midnight.

[27] The WSOC to OC ratio (based on carbon mass) is generally lower in the winter than summer, but the more averaged data tend not to deviate too significantly from a 50:50 split. In March the medians and standard deviation of the WSOC to OC ratio was 0.56 ± 0.18 compared to June values of 0.58 ± 0.14 . The mean winter and summer WSOC to OC ratios were 0.51 and 0.61 respectively. The nighttime values associated with the peaks in Figure 2a had somewhat lower WSOC to OC ratios, ranging from 0.30 to 0.40 (0.60 to 0.70 WIOC/OC). Although there was only a modest increase in WSOC/OC from March versus June 2004, for the winter and summer events the ratio was much more extreme; in the winter event the mean WSOC to OC ratio was 0.36 compared to 0.75 in the summer event.

[28] The winter WSOCxp and WSOCxr fractions were highly variable but on average about evenly split. (See Table 3 for WSOCxp to WSOCxr ratios and the pie charts of Figure 3. All ratios are based on carbon mass.) However, during the winter event when WSOC/OC was lowest, the WSOCxr fraction was nearly twice the WSOCxp fraction. In the summer as WSOC/OC increased, the WSOCxp fraction becomes the more dominant component and a larger fraction of the fine particle OC. This trend continued into the summer event when the WSOCxp fraction was nearly twice the WSOCxr fraction and composed nearly 50% of the OC (Figure 3d). A noteworthy observation from the pie graphs is that for these data, the mean WSOCxr fractions of OC were similar in all cases studied, at approximately 25% of the OC during both winter and summer.

[29] Scatterplots showing ambient concentrations and linear regressions for WSOC versus OC, and WSOCxp and WSOCxr versus WSOC are shown in Figure 4. This linear regression analysis produces similar results to those discussed above based on means and medians. Note that in all cases the WSOC and OC are highly correlated. The lowest WSOC to OC slopes are associated with the winter event, and during this time the WSOCxr component dominated (compare slopes in Figure 4). The WSOCxr fraction is also more highly correlated with WSOC than the WSOCxp fraction. In contrast, the WSOC to OC slope was highest during the summer event, and the fraction of WSOC that was hydrophilic (WSOCxp) was highest during

this period (Figure 4h). This was also the period of highest OC, WSOC, and WSOCxp concentrations.

[30] The seasonal progression in the changing dominance of the WSOCxr to WSOCxp fraction from late winter through summer and into early fall, using combined St.

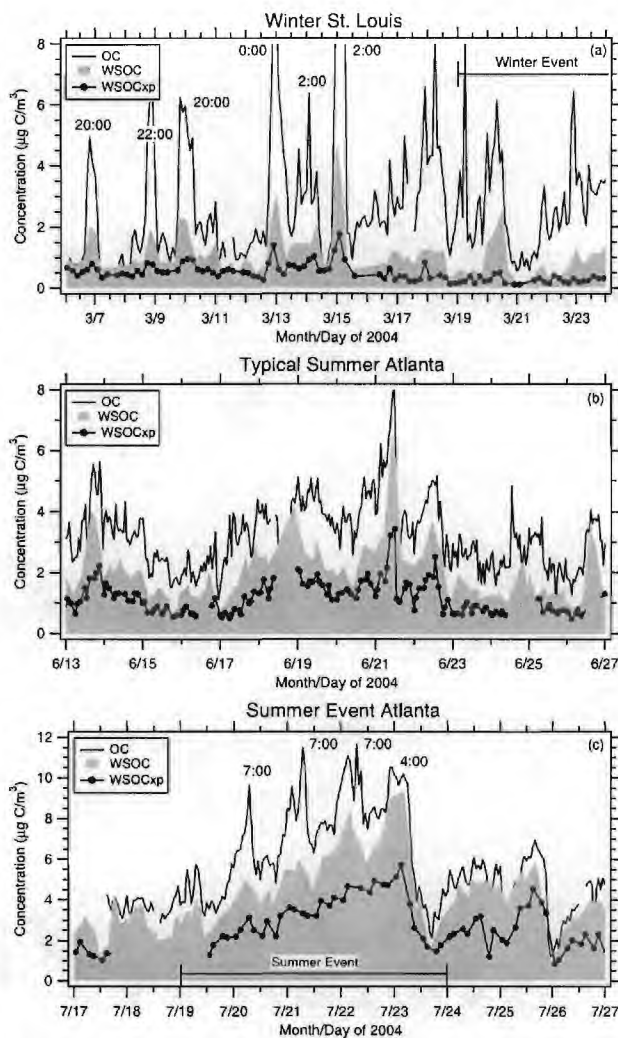


Figure 2. Time series of the OC, WSOC, and WSOCxp for (a) typical winter in St. Louis (6–18 March) and a winter event (19–24 March), (b) typical summer in Atlanta, and (c) a summer event in Atlanta. The WSOCxr is equal to the shaded area bounded by the WSOC and WSOCxp (i.e., $\text{WSOCxr} = \text{WSOC} - \text{WSOCxp}$).

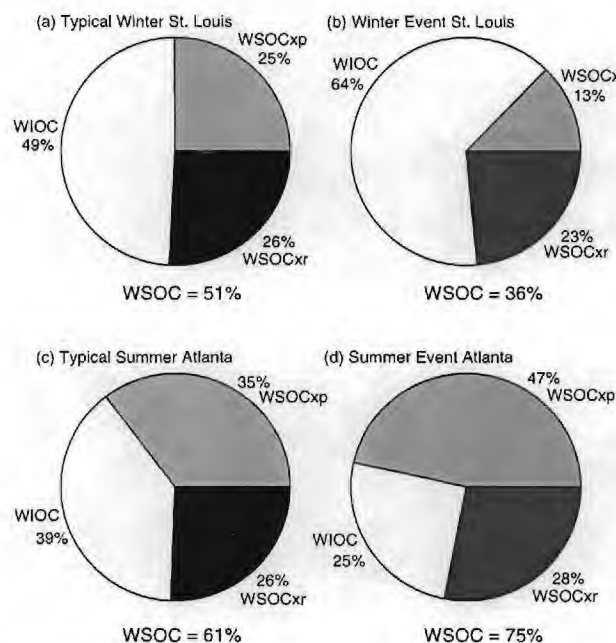


Figure 3. (a–d) Percentage in carbon mass each fraction contributes to total OC, based on means, for the four periods shown in Figure 2. WIOC = water-insoluble OC (i.e., water-insoluble OC = OC – WSOC and WSOC is the sum of WSOCxp and WSOCxr). (Abbreviation definitions are listed in the Notation.)

Louis and Atlanta data, is shown in Figure 5. The short periods analyzed and discussed above fit with the general seasonal trend of Figure 5. The WSOCxr fraction dominated in the winter, but starting roughly in April, the WSOCxp fraction increased relative to the WSOCxr fraction. The fractions were in equal proportions sometime in May, and then the WSOCxp fraction dominated throughout the summer. In late August, the WSOCxp fraction began to steadily decrease relative to the WSOCxr fraction and by September the fractions were back to 50:50 again. Even though there is a seasonality observed, no correlation with temperature for any of the fractions was observed. Observed seasonal trends may depend largely on changes in the dominant sources for each period.

[31] Although the summer of 2004 in Atlanta was unusually clean with only 11 poor air quality days compared to typically 37 (summer averaged from 1987 to 2004), these data do provide evidence for a general shift in fine organic particle sources from winter to summer, and suggest that processes, such as SOA formation, which is likely more vigorous in the summer, produce significant levels of

hydrophilic compounds (WSOCxp) that add substantially to the fine particle fraction of the organic aerosol. Because semivolatile SOA compounds may not be efficiently measured with this approach (this has not been tested), and they are likely to be small hydrophilic species, the WSOCxp fraction of OC may be even more significant during periods of active SOA production. In a companion paper, further chemical speciation of the WSOCxp and WSOCxr fractions provides insights into the sources of these compounds.

4. Summary

[32] Quantifying the carbon mass of broad chemical groupings of the ambient aerosol soluble in water can provide unique insights into the sources of organic aerosols. Aqueous extracts of the water-soluble organic fraction of atmospheric aerosols can be isolated into WSOCxp and WSOCxr fractions (see Notation) by XAD-8 resin. Because no organic eluents are employed, carbon mass can be quantified directly with a Total Organic Carbon analyzer, without intermediate isolation steps, and can be performed online with systems that collect particles into water, such as a Particle-into-Liquid Sampler coupled with a TOC analyzer (PILS-TOC).

[33] Compounds that penetrate the XAD-8 with near 100% efficiency at pH adjusted to 2 are referred to as hydrophilic, whereas compounds that are retained by the XAD-8 have hydrophobic properties. A large fraction of these retained hydrophobic compounds can be extracted via a pH 13 NaOH eluent and directly quantified by a TOC analyzer.

[34] Laboratory calibrations suggest that the hydrophilic fraction (WSOCxp) is composed of compounds that include, saccharides and amines as well as carbonyls and aliphatic monocarboxylic/dicarboxylic acids with less than 4 or 5 carbons. Although it was not tested, it would be expected that the series of polyols and oxocarboxylic acids would follow the same pattern as the carbonyls and monocarboxylic/dicarboxylic acids. Compounds that are retained on the column, referred to as the hydrophobic fraction (WSOCxr), are composed of aromatic acids and phenols, as well as organic nitrates, cyclic acids, and carbonyls and monocarboxylic/dicarboxylic acids with greater than 3 or 4 carbons. However, we have found that only aromatic compounds (or aromatic-like compounds with similar properties) can be extracted from the XAD-8 with high efficiency in the pH 13 eluent (WSOCxr). For the most part, the remaining compounds (WSOCxr; organic nitrates, cyclic acids, and carbonyls and monocarboxylic/dicarboxylic acids with greater than 3 or 4 carbons) are not recovered. This method allows for a comprehensive and quantitative separation of the organic aerosol into distinct

Table 3. Comparisons of Median Ratios With the \pm Standard Deviation for Typical Winter 2004 in St. Louis, Winter Event in St. Louis, Typical Summer 2004 in Atlanta, and Summer Event in Atlanta^a

Event	$\frac{\text{WSOC}}{\text{OC}}$	$\frac{\text{WSOCxp}}{\text{WSOC}}$	$\frac{\text{WSOCxr}}{\text{WSOC}}$	$\frac{\text{WSOCxp}}{\text{WSOCxr}}$
Typical winter, 6–18 March	0.56 ± 0.18	0.49 ± 0.13	0.51 ± 0.13	0.98 ± 0.67
Winter event, 19–24 March	0.36 ± 0.11	0.32 ± 0.21	0.68 ± 0.21	0.47 ± 1.41
Typical summer, 13–27 June	0.58 ± 0.14	0.61 ± 0.13	0.39 ± 0.13	1.53 ± 1.37
Summer event, 19–24 July	0.75 ± 0.08	0.65 ± 0.08	0.35 ± 0.08	1.83 ± 0.65

^aAll ratios are based on carbon mass. Abbreviation definitions are given in the Notation.

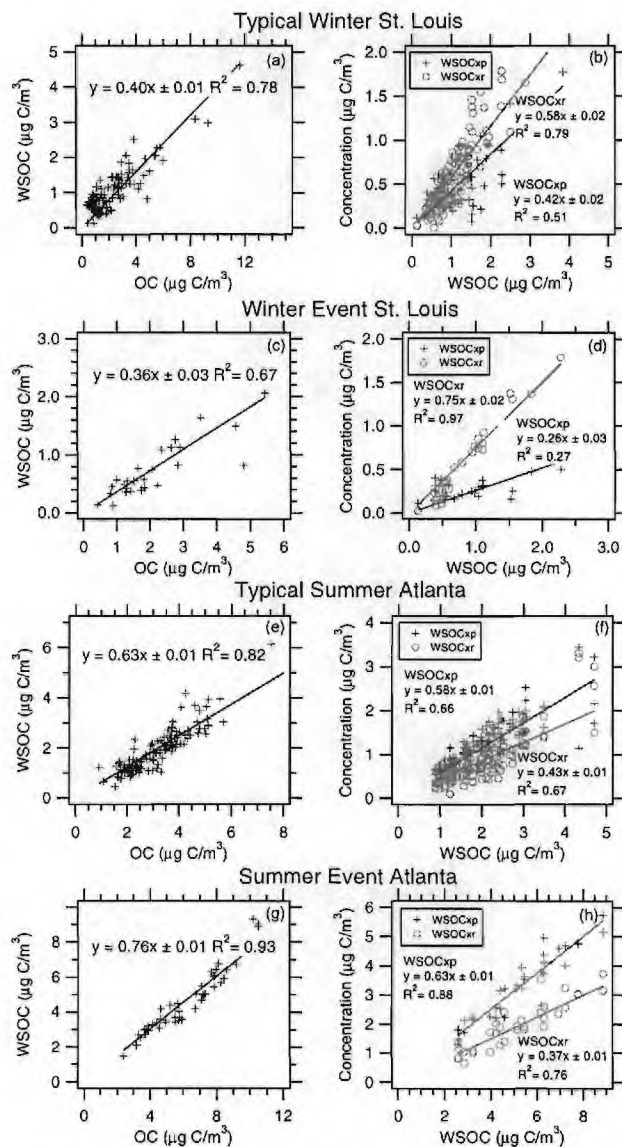


Figure 4. (a–h) WSOC versus OC concentrations and WSOCxp and WSOCxr fractions versus WSOC concentrations for the four periods shown in Figure 2.

fractions from which a range of atmospherically relevant properties could be gained by applying additional analytical techniques.

[35] Urban measurements showed both diurnal and seasonal changes in the WSOC and WSOCxp fractions of OC (on a carbon mass basis) between winter and summer. Overall, there is a general progression of increasing ratios of WSOC to OC and WSOCxp to OC from winter to summer, with highest ratios observed during a summer stagnation event. Mean ratios of WSOC to OC in winter versus a summer PM event were 0.36 and 0.75, respectively, and mean WSOCxp/OC for these two periods were 0.13 and 0.47. However, the WSOCxr fraction showed only a slight increase from 0.23 in winter to 0.28 during the summer event. It follows that the sources for the WSOC fraction of OC, and especially the WSOCxp

fraction of OC, are strongest in the summer and a large contributor to the OC during pollution in urban Atlanta PM events. One possible explanation is SOA production, either from biogenic or anthropogenic emissions, or both.

[36] This measurement technique alone cannot determine which groups of compounds that compose the hydrophilic and hydrophobic WSOC fractions are responsible for the observed trends. In a companion paper a method to further group speciate the hydrophilic and hydrophobic WSOC fractions using size-exclusion chromatography is presented. We show that the increase in the urban Atlanta summertime WSOCxp fraction is driven mostly by increases in the concentrations of short-chain aliphatic carboxylic acids.

Notation

OC	organic carbon.
WSOC	total water-soluble organic carbon (measured with Total Organic Carbon (TOC) analyzer).
WSOCxp	hydrophilic water-soluble organic carbon, compounds that penetrate the XAD-8 column at pH 2 adjusted by 0.1 M HCl (measured with TOC analyzer).
WSOCxr	hydrophobic water-soluble organic carbon, compounds that are retained on the XAD-8 column (calculated from WSOC – WSOCxp).
WSOCxrr	recovered hydrophobic water-soluble organic carbon, compounds that are retained on the XAD-8 column and subsequently recovered from the XAD-8 using 0.1 M NaOH at pH 13 (measured with TOC analyzer).
WSOCxru	unrecovered hydrophobic water-soluble organic carbon, compounds that are retained on the XAD-8 column and are not recovered from the XAD-8 in the 0.1 M NaOH at pH 13 (calculated from WSOC – WSOCxp – WSOCxrr).
WIOC	water-insoluble organic carbon (calculated from OC – WSOC).

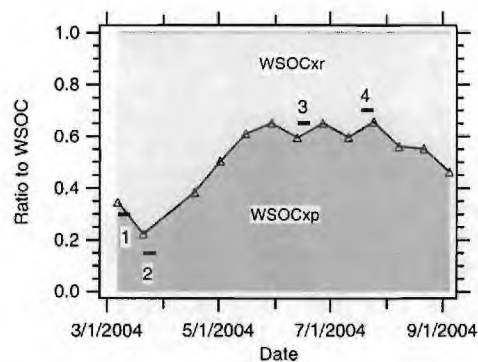


Figure 5. Seasonal trends in the WSOCxp and WSOCxr fractions based on carbon mass. Data were grouped into 14 day periods, and the ratio was determined by linear regression with zero intercept. All data are from urban Atlanta, except for the month of March, where measurements were made in St. Louis. The time periods shown in Figure 2 correspond to 1, typical winter; 2, winter event; 3, typical summer; and 4, summer event.

[37] **Acknowledgments.** This research was made possible by the generous financial support of the U.S. National Oceanic and Atmospheric Administration (NOAA) through contract NA04OAR4310089 and the U.S. National Science Foundation under contract ATM 0454974. We also thank the Air Quality System, Office of Air Quality Planning and Standards, U.S. EPA, for the Atlanta ozone data. The interpretations based on these data are those solely of the authors. We also gratefully thank J. D. Ritchie and E. M. Perdue for their insights regarding the XAD-8 column and procedures. We thank A. L. Clements and J. R. Turner for assistance with the St. Louis–Midwest Supersite measurements and M. S. Bae and J. J. Schauer for the St. Louis–Midwest Supersite OC data.

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Our recent research funded by NSF and other agencies has shown that water-soluble organic carbon (WSOC) in fine particles is mainly from secondary organic aerosol formation or biomass burning emissions. Thus, using tracers to remove instances of biomass burning, SOA can be studied directly by analyzing WSOC. NSF funding of this project was used to characterize and explore sources of WSOC. This research mainly resulted in the publication of two papers describing methods for comprehensive chemical characterization of WSOC, and preliminary investigative work focused on radiocarbon analysis on WSOC extracted from ambient particles. Salient results from this research are summarized below, organized by the two main publications. (These papers are also available at http://www.aerosols.eas.gatech.edu/Papers_List.htm).

Sullivan, A., and R.J. Weber (2006), Chemical characterization of the ambient organic aerosol soluble in water Part 1: Isolation of hydrophobic and hydrophilic fractions with a XAD-8 resin, *J. Geophys. Res.*, *111* (D5), D05314 10.1029/2005JD006485

The approach in this research was to apply existing separation methods, or develop new methods, to comprehensively chemically characterize WSOC. The ability of these approaches to separate specific classes of organic compounds was first tested using known single component laboratory calibration aerosols. These findings were then used as a guide for interpreting results from studies with ambient aerosols.

Extensive calibrations with known compounds showed that the XAD-8 resin classifies carboxylic acids or carbonyls with less than approx. 4 carbons as hydrophilic components, whereas larger molecular weight aliphatic acids and carbonyls (greater than 4 carbons) and aromatic compounds are isolated into the hydrophobic group.

The validity of this isolation method was demonstrated on ambient aerosols collected in a biomass burning plume by measuring surface tension reduction on solutions of hydrophilic versus hydrophobic species: As expected the hydrophilic group was composed of low molecular weight compounds and showed no surface tension depression whereas the hydrophobic group had higher molecular weight compounds and depressed the surface tension [Asa-Awuku *et al.*, 2007]. (Molecular weight and surface tension are critical parameters needed to predict CCN activation and the research group of A. Nenes is using our XAD-8 isolation method to investigate properties of WSOC relevant to formation of CCN, another by product of this research). Further analysis was performed via Carbon-NMR [Sannigrahi *et al.*, 2006], which were consistent with the laboratory calibration results.

We then applies the XAD-8 method for online quantification of hydrophilic and hydrophobic WSOC using the PILS (Particle Into Liquid Sampler) with the goal to gain new insight into the mechanism of SOA formation. A study of ambient particles collected in urban Atlanta showed that during stagnation events, when air quality was poorest and fine PM concentrations highest, the hydrophilic fraction of WSOC increased relative to the hydrophobic group. Since there was little biomass burning influence, (eg, WSOC all from SOA), we conclude that formation SOA larger results from production of low molecular hydrophilic compounds.

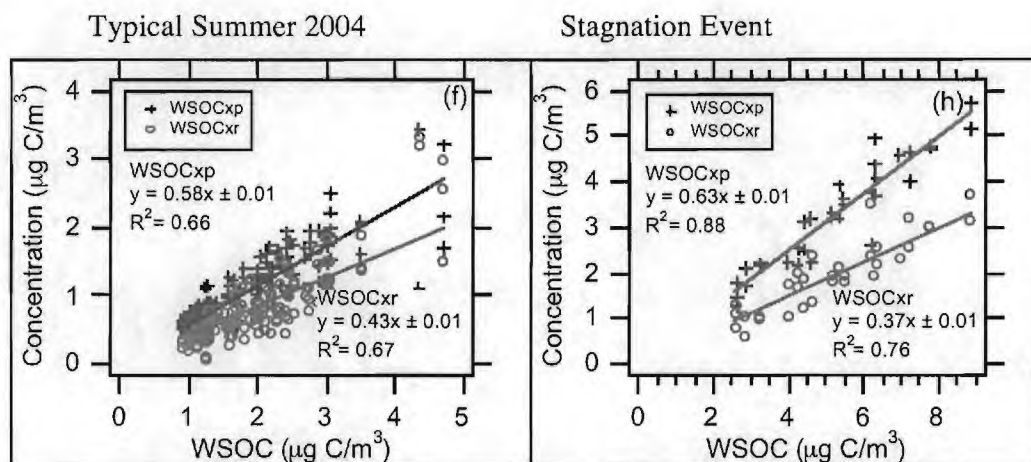


Figure 1, This figure shows that Hydrophilic compounds (blue, WSOCxp) are a greater fraction of WSOC (ie SOA) compared to Hydrophobic species (red, WSOCxr) during photochemical smog events in Atlanta (from Sullivan and Weber, 2004).

Sullivan, A., and R.J. Weber (2006), Chemical characterization of the ambient organic aerosol soluble in water Part 2: Isolation of acid, neutral, and basic fractions by modified size exclusion chromatography, *J. Geophys. Res.*, *111* (D5), D05315 10.1029/2005JD006486.

To further investigate the chemical nature of isolated hydrophilic and hydrophobic fractions of WSOC, under funding from this grant we next developed a method to quantify the acid and neutral fractions of organic compounds in aqueous solutions. The method involves a novel application of Size Exclusion Chromatography (SEC) that uses the polar interactions between WSOC compounds in the mobile phase with the stationary phase. These interactions are typically suppressed in normal SEC applications. Applying this analysis to WSOC samples collected in Atlanta in summer, winter, and a biomass-burning plume the acid, neutral and basic components of WSOC, and hydrophilic and hydrophobic fractions were investigated (see Fig 2 below). In the figure, which shows the chromatographic separations, the vertical line separates acids to the left, (which come off the column first) and neutral compounds to the right (come off the column after acids). Note the little peak at $\sim 00:40$ is the contribution from basic compounds, which as expected are minor. Also as expected, but never shown before in a comprehensive way,

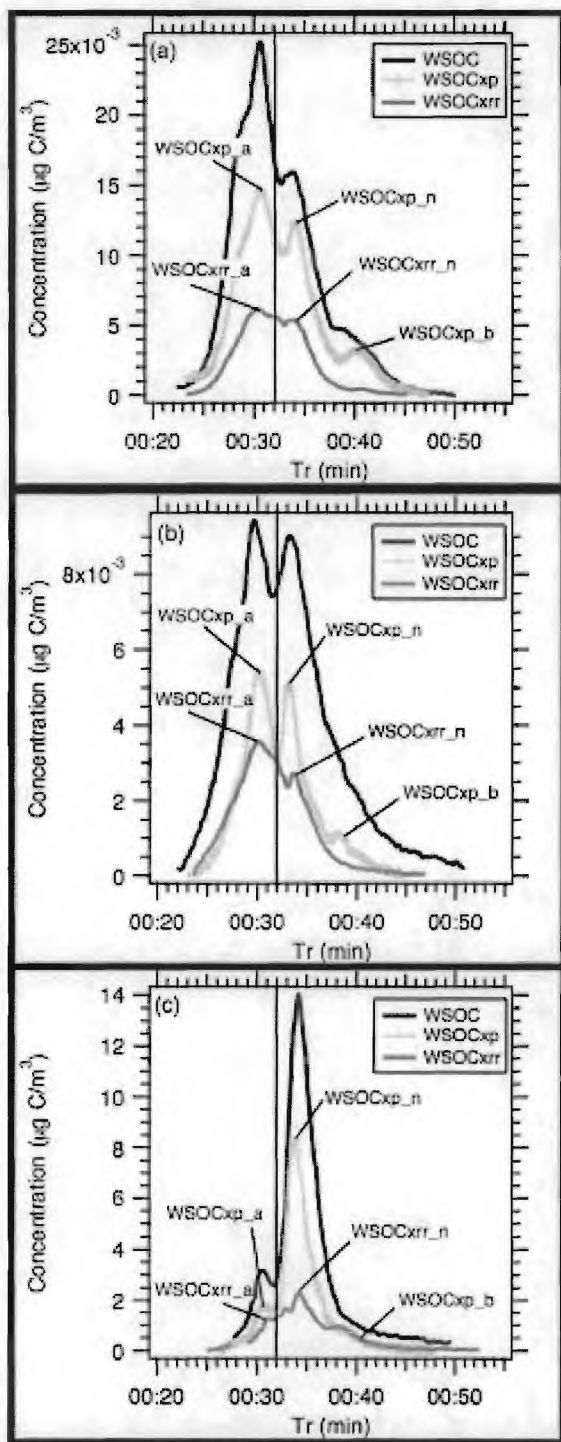


Figure 2. Chromatographs of WSOC, hydrophilic and hydrophobic WSOC for samples collected in Atlanta in the summer and winter, and a biomass smoke sample. Acids are to the left of the vertical line, neutral compounds to the right.

acid components of SOA in the summer are generally higher than neutral components (see peak in WSOC curve to left of vertical line in plot (a) of Figure 2). In winter WSOC is composed of approximately 50:50 acid and neutral compounds. In contrast, for biomass-burning smoke, known to be composed of significant amounts of sugars (levoglucosan is the most prevalent), neutral compounds dominate the WSOC fraction of fine PM. During polluted stagnation events we found three main classes of compound lead to higher WSOC and hence are the major SOA components in Atlanta: hydrophobic acids (likely aromatic and long chain aliphatic acids), hydrophilic acids (likely small $< C_4$ aliphatic acids), and hydrophilic neutral compounds (likely small $< C_4$ carbonyls), where of these three groups the latter two dominate.

Overall, these findings provide new and valuable comprehensive insights into the process of SOA formation in urban Atlanta. Based on our findings, and consistent with findings from our studies, our hypothesis is that photochemical processes that produce SOA predominately lead to the formation of low molecular weight compounds that over time may form more stable oligomers.

We are currently developing methods to further chemical characterize these isolated groups by: 1) Studying the thermal volatility of each isolated group (lower molecular weight

hydrophilic compounds should be less volatile than higher molecular weight hydrophobic species. 2) Applying LC-MS to identify more specific compounds in each group. In addition, the one year extension on this project was used to begin to develop methods for radiocarbon analysis (^{14}C) on WSOC and these isolated groups (hydrophilic and hydrophobic) to gain insights into contributions from biogenic and anthropogenic species.

Asa-Awuku, A., A. Nenes, A. Sullivan, C. Hennigan, and R.J. Weber (2007), Investigation of molar volume and surfactant characteristics of water-soluble organic compounds in biomass burning aerosol, *Atm. Chem. Phys.*, *submitted*.
Sannigrahi, P., A. Sullivan, R.J. Weber, and E.D. Ingall (2006), Characterization of water-soluble organic carbon in urban atmospheric aerosols using ^{13}C NMR spectroscopy, *Environ. Sci. Tech.*, *40*, 666-672.

Overall, funding from this 1-year (with one year extension) ~\$50k project focused on developing new comprehensive methods for determining the chemical composition of the water-soluble fraction of ambient fine aerosol particles. These methods were applied to analysis of the Atlanta aerosol with the goal to investigate mechanisms involved in secondary organic aerosol (SOA) formation. The approach was to develop a method to quantify through a broad categorization most of the chemical compounds produced via SOA formation processes in urban Atlanta. These isolated broad groups could then be further chemically characterized by various methods, such as C-NMR, LC-MS, radiocarbon analysis, and measurements of physical properties such as depression of solution surface tension and inferred molecular weights. Our method is in contrast to most current approaches, which attempt detailed chemical speciation, yet only quantify a small portion (eg, 20% or so) of the total organic aerosol.

Our research focused on development and application of separation methods for liquid samples. We developed methods to separate and quantify the hydrophilic and hydrophobic fractions of water-soluble compounds extracted from the ambient aerosol, and to further isolate and quantify these fractions into acid or neutral groups. In addition, work in collaboration with other researchers in our department built on method development by applying C-NMR and surface tension analysis on our samples to further investigate chemical properties.

As a result of this funding, a graduate student (Amy Sullivan) published two papers, which comprised a major portion of her PhD thesis [*Sullivan and Weber, 2006a; Sullivan and Weber, 2006b*]. Two other graduate students working on analysis of our samples have also published or submitted papers [*Asa-Awuku et al., 2007; Sannigrahi et al., 2006*].

Amy Sullivan was invited to the 2006 ACCESS conference to present the results of this work and is now a Post Doc at Colorado State. All three of the students directly (eg A. Sullivan), or indirectly (eg A. Asa-Awuu, P. Sannigrahi) involved in this work have presented their findings at a number of conferences.

- Asa-Awuku, A., A. Nenes, A. Sullivan, C. Hennigan, and R.J. Weber (2007), Investigation of molar volume and surfactant characteristics of water-soluble organic compounds in biomass burning aerosol, *Atm. Chem. Phys.*, *submitted*.
- Sannigrahi, P., A. Sullivan, R.J. Weber, and E.D. Ingall (2006), Characterization of water-soluble organic carbon in urban atmospheric aerosols using ¹³C NMR spectroscopy, *Environ. Sci. Tech.*, *40*, 666-672.
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