Filterable water-soluble organic nitrogen in fine particles over the southeastern USA during summer

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ABSTRACT

Time integrated high-volume $PM_{2.5}$ samples were collected separately during day and night from 1 August to 10 September 2008 at a paired urban (Atlanta)-rural (Yorkville) sites as part of the August Mini-Intensive Gas and Aerosol Study (AMIGAS). Selected filters ($n = 96$, 48 for each site) were analyzed for a suite of water-soluble chemical species, including major inorganic ions, water-soluble organic carbon (WSOC), water-soluble total and inorganic nitrogen (WSTN and WSIN), and levoglucosan. Semi-continuous analyses of $PM_{2.5}$ mass, soluble ions, WSOC, and gaseous O_3, SO_2, NO, NO_2, NO_y, CO, and meteorological parameters were also carried out in parallel. This study focuses on the characteristics of filterable water-soluble organic nitrogen (WSON), estimated by the difference in the measured concentrations of WSTN and WSIN, determined from aqueous filter extracts. At both sites, WSON varied from below the limit of detection (25 ng-N m^{-3}) to ∼600 ng-N m^{-3} and on average contributed ∼10% to WSTN mass, with the majority of soluble nitrogen being ammonium (∼82%). WSON:WSOC (or N:C) mass ratios ranged between 0 and 27% at both the sites with a median value of ∼5%, similar to what has been reported in another study in the southeastern USA. At both the urban and rural sites median nighttime levels of WSON and N:C were observed to be consistently higher than daytime values. Based on correlation analyses, daytime WSON sources appeared different than nighttime sources, especially at the urban site. Overall, the data suggest the importance of coal-combustion (e.g., link to SO_2), vehicle emissions, soil dust and biomass burning as WSON sources, and that nitrogenous organic compounds are likely a fairly small fraction of the secondary organic aerosol for this location during summer.

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1. Introduction

Reactive nitrogen species, which include oxidized and reduced inorganic and organic forms of nitrogen, are important nutrients in terrestrial and marine ecosystems for the growth of organisms. Formation, transformation, deposition, and transport of inorganic and organic nitrogen species are essential components of the total nitrogen cycle (Duce et al., 2008). Anthropogenic perturbations to the global nitrogen cycle have led to significant environmental degradation (Galloway et al., 2008), mainly through application and run off of fertilizers containing fixed nitrogen. Several studies have documented that the deposition of water-soluble organic nitrogen (WSON) via atmospheric particles has a significant effect on the nitrogen concentration in aquatic and terrestrial ecosystems (Cornell et al., 1995; Duce et al., 2008). The presence of WSON could affect chemical and physical properties of water droplets and aerosol particles by altering their buffering capacity and basicity (Zhang et al., 2002; Laskin et al., 2009). In the past, a lack of direct measurement methods has limited studies of WSON, however, new methods are being developed for organic compounds with nitrate moiety (Rollins et al., 2010).

Possible natural sources of organic nitrogen include terrestrial vegetation, soil dust and marine reservoirs (Mace et al., 2003a,b; Lesworth et al., 2010), while anthropogenic sources include animal husbandry, fertilizers, fossil-fuel and biomass burning (Mace et al., 2003c; Murphy et al., 2007; Laskin et al., 2009). Secondary organic nitrogen compounds, such as alkyl nitrates and amino compounds, produced via the atmospheric reactions of NO_x and volatile organic compounds (VOCs) followed by gas-to-particle condensation are known to produce secondary organonitrate aerosols during day and night (Atkinson, 2000; Lim and Ziemann, 2005; Ng et al., 2008). As a component of secondary organic aerosol (SOA), WSON is of interest

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since SOAs are a significant fraction of total organic aerosols over southeast USA (Weber et al., 2007) and so important for issues relating to human health, visibility and the global radiation balance. Model simulations have lacked skill in predicting SOA, suggesting SOA precursors and chemical formation pathways are not fully identified (Volkamer et al., 2006). Organosulfate (Surratt et al., 2008) and organonitrate (Brown et al., 2009) SOA can be especially important in isoprene-rich environments and it has been suggested that these components may be linked to missing SOA in the southeastern USA (Goldstein et al., 2009).

WSON can account for a significant fraction of the total atmospheric particulate nitrogen, depending upon emission sources. For example, organic nitrogen was found to be >30% of the total nitrogen in clean marine fine mode aerosol collected at Oahu, Hawaii and attributed to gas-to-particle conversions and long-range transport (Cornell et al. 2001). Nakamura et al. (2006) reported that long-range transport of nitrogenous organic aerosols from East Asia was an important source of atmospheric nitrogen in coastal areas of the Pacific Ocean. At the Gulf of Aqaba, organic nitrogen contributed up to 80% of the total aerosol nitrogen (Wedyan et al. 2007). Neff et al. (2002) suggested that the percentage contribution of WSON to total nitrogen abundance varies spatially, and also depends on the measurement methodology, but is consistently roughly a third of the total nitrogen load, with a median value of 30% (standard deviation of 16%). Mace et al. (2003c) documented that WSON accounted for more than 40% of the total particulate nitrogen with substantially higher concentrations in samples collected during the dry season when biomass burning dominated particle abundance in Amazon Basin aerosols, suggesting that biomass burning aerosol is an important source of atmospheric organic nitrogen. Particulate organic nitrogen accounted for ∼20% of the total fine particle mass and a significant component of particulate nitrogen in Davis, California (Zhang et al., 2002). Lin et al. (2010) recorded WSON in aerosols over a forest site in Southeast USA with similar average concentrations (160 ng-N m^{-3}) in summer and winter.

This study investigates the characteristics of WSON in PM$_{2.5}$ ambient aerosols collected simultaneously at an urban (Atlanta) site and a rural (Yorkville) site in southeast USA during August–September 2008 as a part of the August Mini-Intensive Gas and Aerosol Study (AMIGAS) campaign. The relationships between WSON and a large suite of particulate and gaseous chemical species, and day–night differences are investigated.

2. The experiment

2.1. Sampling sites

Aerosol sampling was performed at a paired urban-rural site located in southeast USA, both part of the Southeastern Aerosol Research and Characterization (SEARCH) network (Hansen et al., 2006). SEARCH was chosen due to its location in a region with significant biogenic and anthropogenic emissions. The urban sampling site was located in midtown Atlanta at the Georgia Power facility on Jefferson Street, ∼4 km NW of downtown Atlanta, in a mixed commercial and residential neighborhood within 200 m of a bus maintenance yard and several warehouse facilities. The Yorkville site was located in a rural area of Georgia, approximately 60 km west-northwest of Atlanta.

2.2. Sampling and analysis

PM$_{2.5}$ samples were collected simultaneously on pre-combusted tissuquartz filters (8 × 10 in, Whatman) during daytime (10:00–18:00) and nighttime (22:00–06:00 next day,

all Eastern Standard Time) using a high-volume (1.13 m^3 min^{-1}) air sampler during the period from August 1st to September 10th 2008. Loaded filters were wrapped in pre-baked aluminum foil and stored at −20 °C until laboratory analysis. Ninety six filters (48 day and night pairs) were selected from a total of 164 filters (from both sites) for chemical speciation. Filters were chosen so that all types of atmospheric conditions, polluted, moderate and clean (based on the online data), were included. Both at Atlanta and Yorkville, the period from 11 to 19 August was the most polluted (mean TEOM PM$_{2.5}$ mass was 19.3–22.8 µg m^{-3}, respectively) whereas 24–26 August was the cleanest period (mean TEOM PM$_{2.5}$ mass was 2.8–4.3 µg m^{-3}) during the study. Along with the bulk aerosol samples, O$_3$, SO$_2$, NO, NO$_2$, NO$_y$, CO, and PM$_{2.5}$ mass, and meteorological parameters were also measured semi-continuously (5 min frequency) (Hansen et al., 2006). Online measurements of PM$_{2.5}$ were also made at the urban site using a particle-into-liquid sampler (PILS) coupled to ion chromatographs for anions and cations (PILS-IC, Orsini et al., 2003), and to a total organic carbon analyzer (TOC) for WSOC mass concentration measurements (Sullivan et al., 2004).

High-volume filters were analyzed as follows: two circular punches (1 inch diameter) taken from the filter were extracted in high purity water (>18.3 MΩ) for 10 min (3 times) using ultra-sonication and filtered with a 25 mm diameter (0.45 µm pore, Fisher Scientific) disposable syringe filter. The method is identical to that described in detail by Zhang et al. (2010). From this extract, water-soluble anions (Cl$^-$, NO$_2^-$, NO$_3^-$, and SO$_4^{2-}$) and cations (Na$^+$, NH$_4^+$, and K$^+$) were measured on a dual channel Dionex DX-500 ion chromatograph with self-regenerating suppression (SRSULTRA) and conductivity detection (CD20), employing a Dionex AS11-HC anion column and Dionex CS12A cation column, respectively. Analytical protocols were similar to that reported earlier (Baumann et al., 2003). Limits of detection (LOD) for all inorganic ions were between 10 and 50 ng m^{-3} based on the deviation in filter blanks or instrument's detection limit (when filter blanks were not measurable).

Carbohydrates (levoglucosan, mannitol, arabitol, glucose, xylitol, arabinose) were assayed using high-performance anion-exchange chromatography with pulsed ampereometric detection (HPAEC-PAD). The method involved a Dionex DX-500 series ion chromatograph coupled to Dionex ED 50 electrochemical detector with a gold working electrode operating in integrating ampereometric mode, and a Dionex CarboPac PA-1 anion-exchange column with gradient elution of 200 mM NaOH at a flow rate of 0.5 mL min^{-1}. The LOD of various carbohydrate compounds was estimated at 6 ng m^{-3} based on reagent blanks and instrument detection limit. Previous studies reported that the peaks of levoglucosan and arabitol, a sugar alcohol from fungal spores, cannot be fully separated by a CarboPac PA-1 column (Sullivan et al., 2008). Consequently, the integrated peak area of levoglucosan was corrected for this interference by arabitol. Details of this analysis were reported elsewhere (Zhang et al., 2010).

Water-soluble total nitrogen (WSTN) was analyzed by a total nitrogen analyzer (Shimadzu VCSN with TN module) using (NH$_4$)$_2$SO$_4$ as a calibration standard. In the Shimadzu instrument a small aliquot (50–100 µL) of aqueous sample is directly injected into a combustion column containing a Pt catalyst. The catalyzed combustion process converts nitrogen in the sample to NO. The NO is subsequently measured by chemiluminescence following the conversion of NO to radical NO$_2$ using ozonation. The details of method have been reported elsewhere (Cauwet, 1999). The same (NH$_4$)$_2$SO$_4$ standard was also run on the IC and found to be accurate within 5%. The LOD of WSTN was estimated at 13 ng m^{-3}.

The concentration of WSON was determined by difference
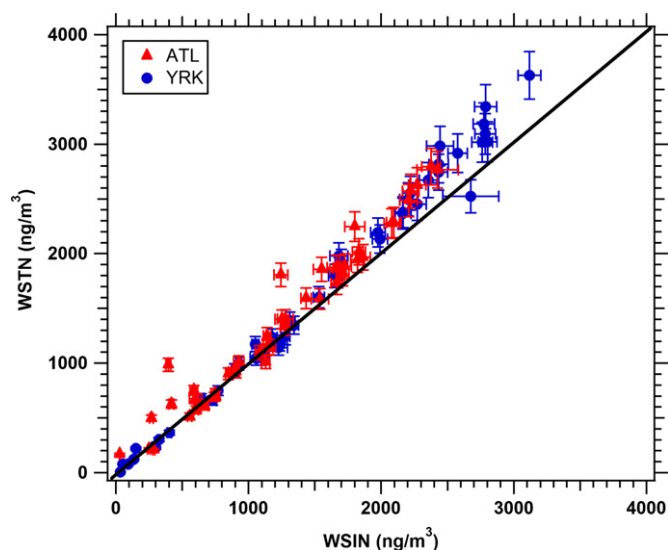
$$WSON = WSTN - WSIN \tag{1}$$

Fig. 1. Water-soluble total nitrogen (WSTN) versus inorganic nitrogen (WSIN). WSTN includes organic nitrogen (WSON) and WSIN and so should always be above the 1:1 line, the distance from the 1:1 line being the WSON concentration. The error bars show the uncertainty associated with WSIN and WSTN measurements.

where WSIN (water-soluble inorganic nitrogen), in terms of nitrogen mass, was determined from the sum of the measured NH_4^+, NO_2^-, and NO_3^- analyzed by ion chromatography ($WSIN = [NH_4^+ \times 14/18] + [NO_2^- \times 14/46] + [NO_3^- \times 14/62]$). Uncertainty associated with the difference method ($(\delta_{WSTN}^2 + \delta_{WSIN}^2)^{1/2}$) can be large when WSTN and WSIN concentrations are large and comparable in magnitude (Cornell et al., 2003; Lin et al., 2010; Lesworth et al., 2010), and was calculated based on the estimated uncertainty associated with each species combined via sum of squares (either on relative or absolute errors depending on the operation; multiplication, division, versus addition, subtraction). Actual uncertainty (%) on WSON data was usually between 5 and 100% but in a few

cases, it was >100%, this occurred when WSON was very low but WSTN and WSIN were relatively high. The LOD of WSON was estimated as 3 times the standard deviation of the average value of the blanks, calculated by the difference between three WSTN and WSIN blanks, and estimated at 25 ng-N m^{-3}. The number of samples with WSON concentrations above the LOD for Atlanta and Yorkville was 32 and 30 (out of 48 in each case), respectively. In cases where WSON and other species were below the LOD, half of the LOD values were used for calculating statistical parameters.

The concentrations of SO_4^{2-} measured in filter extracts were compared to those measured with PILS-IC (integrated over filter sampling time) and found to be strongly correlated ($r^2 = 0.94$) with the slope of 0.67. The significant difference from unity was attributed to systematic error associated with the high-volume sampler flow rate and all filter data at both sites were corrected based on this relationship.

Air samples were not denuded of possible interfering gases prior to passing through the filter. Sampling non-denuded aerosol with a single filter (e.g., non-filter pack) is known to be subject to sampling artifacts (Watson et al. 2009). The likely loss of any semi-volatile organic nitrates restricts our analysis to non-volatile WSON (or referred to here as filterable WSON). Although other nitrogen aerosol components are also likely lost in this analysis method (e.g., NO_3^-), these losses do not affect the calculated WSON since the difference calculation is made based on measurements from the same extract from a single filter. WSOC is another potential component to be affected due to sampling artifacts, such as semi-volatile losses or VOC absorption on filters. Therefore, when comparisons are made between WSON and WSOC, we report ratios using online WSOC data (integrated over filter sampling time), which was available at both sites (from PILS-TOC). However, PILS-NO_3^- was not used because it was not available at the Yorkville site. Comparison between filter and averaged PILS-NO_3^- shows reasonable agreement ($r^2 = 0.82$, slope = 0.84, intercept = 110 ng m^{-3}) over Atlanta. Furthermore, since nitrate levels were minor relative to other N components (NH_4^+, WSON), uncertainties in NO_3^- do not significantly impact the overall N budget analysis. It is also noted that this, and previous studies (based on online data, which are

Table 1
Statistical data for the measured species. All concentrations are in ng m^{-3} for aerosol species (components in bold font) and in ppb for gaseous species (normal font).

Component	Atlanta					Yorkville					Ratio_Median
	Min	Max	Median	Avg	SD	Min	Max	Median	Avg	SD	ATL/YRK
WSTN	bd[a]	2795	1197	1316	774	bd	3629	1366	1636	1055	0.82
WSON	bd	588	106	145	150	bd	556	71	150	161	0.85
NH_4^+	7	2975	1381	1373	828	bd	3705	1596	1767	1099	0.83
NO_3^-	71	3227	291	426	489	bd	4668	298	468	690	1.13
NO_3^-_PILS	54	3763	270	379	530	–	–	–	–	–	–
WSIN	28	2427	1149	1186	681	35	3117	1328	1506	910	0.80
WSOC	901	5380	3600	3146	1147	611	4928	3320	3046	1246	1.05
WSOC_PILS	1005	5634	3082	3181	1137	936	3809	2384	2356	833	1.24
SO_4^{2-}	1496	14,496	5322	5935	3137	868	14,540	6273	6905	3957	0.95
Na^+	62	1473	719	719	365	126	1803	709	709	358	1.01
K^+	bd	201	35	56	50	bd	177	80	76	59	0.76
Cl^-	bd	151	33	33	34	bd	62	5	10	11	3.35
Glucose	bd	68	13	18	15	bd	34	8	11	8	1.42
Levoglucosan	bd	115	9	22	25	bd	68	8	14	14	1.04
Mannitol	bd	44	16	18	11	bd	54	14	16	12	1.19
O_3	0.08	76	24	32	23	11	84	41	42	18	0.82
CO	108	728	205	244	130	100	235	155	153	30	1.29
SO_2	0.12	17	1.1	2.5	4.0	0.05	14	1.3	2.0	2.3	1.07
NO	0.36	54	1.9	6.4	12	0.03	0.57	0.12	0.15	0.13	14.46
NO_2	2.8	36	9.4	14	9.9	0.29	6.5	1.4	1.8	1.3	7.47
NO_y	4.5	88	15	22	20	0.60	8.0	3.1	3.5	1.7	4.99
NO_x	3.6	84	12	20	20	0.40	6.7	1.6	1.9	1.3	8.76
TEOM	6542	46,929	23,584	23,181	9132	3169	36,359	18,537	17,926	8909	1.39

[a] bd: below detection limit.

likely less susceptible to artifacts) show that nitrate and associated ammonium are small fractions of $PM_{2.5}$ at these locations, and that non-volatile NH_4^+, associated with ammonium sulfate, dominates the measured inorganic nitrogen species (Weber et al., 2003).

3. Results and discussion

3.1. Overall comparisons and trends

As a test for data quality, the concentrations of WSTN were compared to WSIN, including estimated measurement errors. Fig. 1 shows that practically all data points were on or above the 1:1 line, (i.e., WSTN > WSIN), indicating reasonably good data quality for estimating WSON by difference, and that WSON was a minor component of the total water-soluble nitrogen (WSTN).

A statistical summary (range, median, mean and standard deviation) of all the species measured at Atlanta and Yorkville is given in Table 1. The WSON concentration ranged from <25 (the LOD) to 588 ng-N m^{-3} (median: 106; mean: 145; SD: 150) over Atlanta whereas at Yorkville, it varied from <25 to 556 ng-N m^{-3} (median: 71; mean: 150; SD: 161) (Table 1) indicating, on average, higher concentrations at the urban site. On average, WSON contributed ∼10% to WSTN with largest contributions from NH_4^+-N

(∼82%) and ∼7% from NO_3^--N at both the sites. Although there are limited studies on aerosol WSON over the USA, our data are of similar magnitude. Lin et al. (2010) measured WSON over North Carolina, USA, and found similar summer and winter concentrations, with levels ranging between below their LOD and 1130 ng-N m^{-3}, with a median of 140 and mean of 160 ng-N m^{-3}. Zhang et al. (2002) reported a yearly median aerosol WSON over Davis, California, of 218 ng-N m^{-3} (mean: 265, SD: 190, range from 43 to 809 ng-N m^{-3}), with relatively higher values during winter and lower during summer. The mean contribution of WSON to WSTN in our study (10%) is, however, lower than that reported by these other studies (∼20–30%) over North Carolina and California (Zhang et al., 2002; Lin et al., 2010). These differences may be related to our measurements being restricted to summer, and possibly higher emissions of SO_2 in our region, leading to more ammonium associated with ammonium sulfate aerosol, which would lower the WSON/WSTN ratio.

Only relatively minor differences were observed in the concentrations of the major aerosol species recorded at the urban (Atlanta) and rural (Yorkville) sites (see Table 1). Primary traffic emissions were much higher at the urban site and can account for the elevated CO, NO_x (NO and NO_2) and NO_y levels in Atlanta (Table 1). The biomass burning tracer levoglucosan was low throughout the study at both
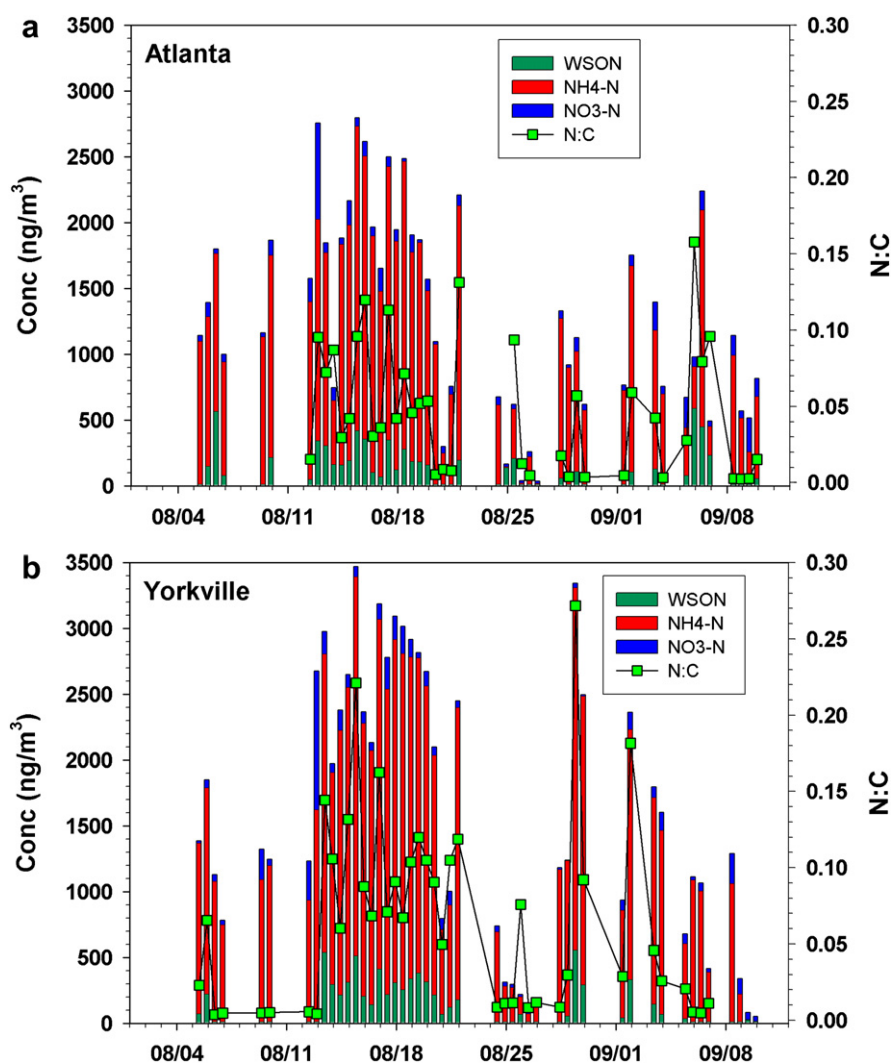

Fig. 2. Temporal variability in water-soluble nitrogenous aerosol components, and WSON/WSOC (or, N:C) ratio over (a) Atlanta and (b) Yorkville.
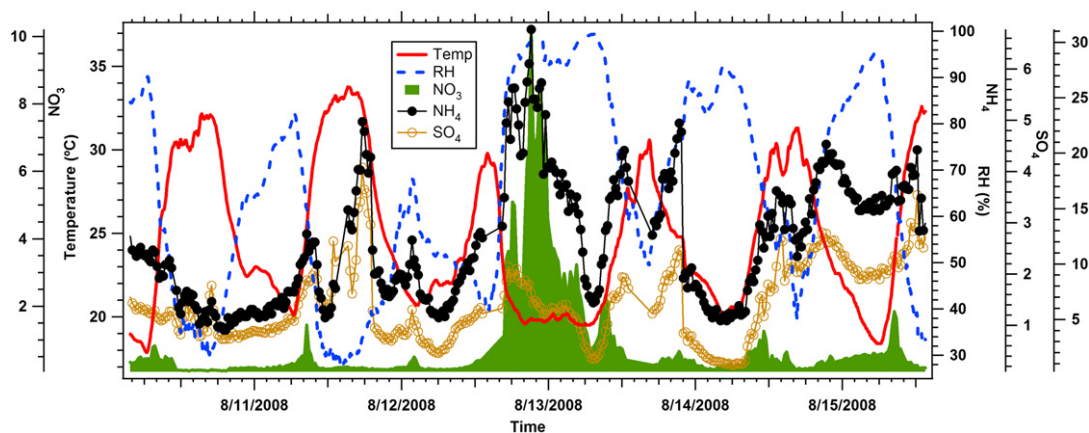
Fig. 3. Temporal variability in NO_3^-, NH_4^+, SO_4^{2-} (concentrations are in mg m^{-3}) along with temperature and relative humidity over Atlanta during August 11–August 15th 2008.

sites (<115 ng m^{-3}) indicating no significant influence from this source during the study period (Zhang et al., 2010).

Temporal variability in nitrogenous components (WSON, NH_4^+-N, and NO_3^--N) over Atlanta and Yorkville is shown in Fig. 2a and b. On a given day, comparable concentrations of chemical species at both the sites can be attributed to their regional source(s) whereas significant difference in concentration would suggest that local source(s) and/or process(es) significantly affect their concentrations. It follows that WSON over Atlanta and Yorkville during August 12–19th was dominated by regional sources (i.e., the more polluted period), whereas during other days of August and September, local sources/processes may have been dominant. Highest concentrations of PM$_{2.5}$ mass as well as most of the species were observed during August 12–19th and the minimum concentrations were observed during August 24–27th, which was a period of unsettled and rainy weather.

3.1.1. Nitrate event on August 12th

An unusually high nitrate concentration was observed during one filter sampling period of the study (night of 12 August). Averaged NO_3^- concentrations over both the sites were typically low (~ 400 ng m^{-3}), but on the night of 12 August, ~ 8–10 times higher concentration of NO_3^- (3227 ng m^{-3} over Atlanta and 4668 ng m^{-3} over Yorkville) were recorded, suggesting that a regional NO_3^- event occurred during the night on 12 August. Semi-continuous measurements of NO_3^- using PILS-IC at Atlanta have been used to investigate this event. The source of elevated NO_3^- is not known but appeared to be secondary NO_3^- formation as a consequence of a sudden change in meteorological conditions. Fig. 3 shows the temporal variability in NO_3^- concentrations along with SO_4^{2-}, NH_4^+, ambient temperature and relative humidity on 12 August and a few days before and after. On the evening of 12 August there was a sudden drop in ambient air temperature (from ~ 28 to 20 °C) and rise in RH (from 40 to 90%) with a major shift in wind direction from easterly to westerly and north-westerly, and relatively calm winds (<1 m s^{-1}), which are favorable conditions (low temperature, high RH) for partitioning of gaseous NH_3 to the aerosol phase in the form of NH_4NO_3 (Russell et al., 1983; Hennigan et al., 2008). The lower temperature and high RH remained more or less uniform for the next ~ 12 h during the daytime sample of 13 August, but NH_4^+ and NO_3^- aerosols concentrations decreased significantly (Fig. 3). This decrease was coincident with a shift in wind direction, again from north-westerly to easterly and therefore may be attributed to relatively low concentrations of NH_3 from the east. The dependence of high ambient aerosol NO_3^- on meteorological conditions are further depicted in Fig. 4 and also indicates that high humidity at

low temperature was the most favorable condition for secondary nitrate formation. During this high NO_3^- event, WSON levels at both Atlanta and Yorkville were not significantly different from the general trend.

3.2. Relationship between WSON and other components

Correlations among measured species over Atlanta and Yorkville were evaluated (at $p < 0.05$) for all the data as well as for daytime and nighttime segregated data (Table 2) to investigate possible major sources of WSON at both sites. A significant relationship between WSON and SO_4^{2-} was observed at Yorkville for all data points ($r^2 = 0.72$, slope $= 0.036$, Fig. 5) as well as for daytime and nighttime data (Table 2), suggesting coal-based thermal power plant (the major source of SO_4^{2-} over this region) was linked in some way to WSON at this rural site. This could be related to direct emissions (e.g., NO_x), or possibly more indirectly through the effect of emissions on aerosol properties (e.g., aerosol pH and possible role of acid-catalyzed SOA formation reactions). At Yorkville, WSON was also found to be strongly ($r > 0.70$) and significantly correlated to NH_4^+ (and so WSTN), Na^+ and TEOM mass, and weakly ($0.30 < r < 0.70$) but still significantly correlated with K^+, mannitol, O_3, CO, SO_2, and WSOC (using all the data, Table 2), possibly an indication of multiple sources or linkages of WSON to SOA formation, soil dust, and power plant emissions. However, among these
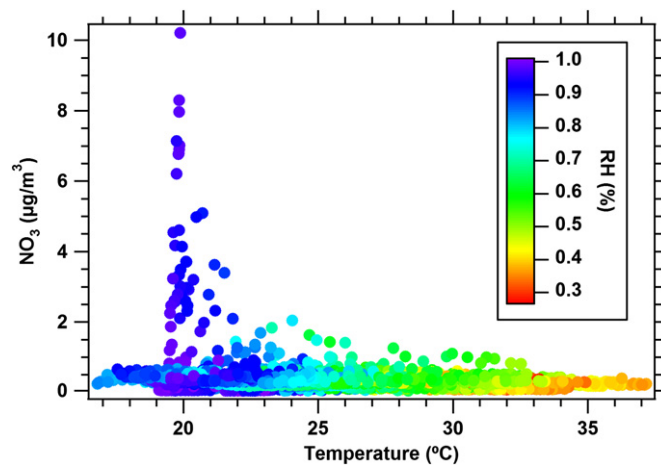

Fig. 4. Relationship between ambient NO_3^- concentrations and temperature. Data points are colored as a function of increasing relative humidity.

Table 2

Correlation coefficients (r) of measured species with WSON (bold values are significant at $p < 0.05$ level). Bold and normal fonts of components are defined in Table 1.

	Atlanta			Yorkville		
	All data	Daytime	Nighttime	All data	Daytime	Nighttime
WSTN	**0.37**	**0.58**	0.18	**0.86**	**0.87**	**0.87**
WSON	1.00	1.00	1.00	1.00	1.00	1.00
NH_4^+	0.17	0.40	−0.10	**0.81**	**0.83**	**0.82**
NO_3^-	0.02	−0.36	0.23	0.19	0.14	0.34
NO_3^-_PILS	0.15	−0.13	0.31	–	–	–
WSIN	0.17	0.37	0.00	**0.81**	**0.81**	**0.83**
WSOC	0.19	0.36	0.07	**0.52**	0.49	**0.60**
WSOC_PILS	**0.43**	**0.58**	0.34	**0.41**	0.30	**0.57**
SO_4^{2-}	0.23	**0.51**	−0.12	**0.85**	0.85	**0.86**
Na^+	0.03	−0.07	0.18	**0.84**	0.95	0.66
K^+	0.06	0.07	0.09	**0.49**	0.47	**0.56**
Cl^-	−0.25	−0.99	0.34	0.06	1.00	0.23
Glucose	0.02	−0.01	−0.04	0.25	0.29	−0.03
Levoglucosan	0.40	0.06	**0.59**	0.46	0.43	0.29
Mannitol	0.18	0.33	−0.03	**0.41**	0.45	0.42
O_3	0.03	−0.04	−0.26	**0.38**	**0.53**	0.41
CO	0.34	−0.27	**0.72**	**0.56**	0.47	**0.74**
SO_2	**0.35**	0.39	**0.51**	**0.51**	**0.65**	0.11
NO	**0.38**	−0.07	**0.68**	−0.15	−0.33	0.13
NO_2	0.07	−0.34	0.44	−0.13	−0.35	−0.16
NO_y	0.27	−0.22	**0.63**	0.17	0.22	0.13
NO_x	0.24	−0.26	**0.63**	−0.15	−0.36	−0.15
TEOM	**0.42**	**0.58**	0.23	**0.74**	**0.73**	**0.79**

correlations a few became even stronger and some became insignificant when only daytime or nighttime data was used. Relationship of WSON (r value) with daytime WSOC, K^+ and CO, and nighttime Na^+, O_3 and SO_2 became stronger whereas corresponding opposite time correlations became insignificant (Table 2), suggesting there was a diurnal variability in primary sources and/or secondary processes of formation of WSON.

The Atlanta data were much more scattered indicating more complexity when all data points were used in a correlation matrix, however, use of only daytime and nighttime data provided better insight into possible sources of WSON (Table 2). Comparing WSON to sulfate for all Atlanta data, it can be seen in Fig. 5 that many data points followed the slope observed at Yorkville, indicating a similar relationship, but a few data points (mainly at lower SO_4^{2-} values) were far above the regression line, suggesting additional significant
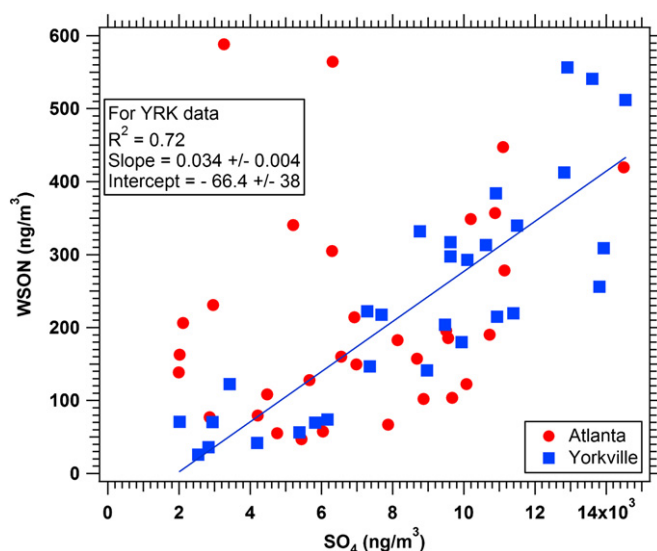

Fig. 5. Relationship between WSON and SO_4^{2-} over Atlanta and Yorkville.

sources/process for WSON at this urban site, even under low sulfate condition. Using all Atlanta data, WSON did not exhibit a strong correlation with any of the measured species, however, it was found to be significantly related ($0.30 < r < 0.40$, $p < 0.05$) to WSTN, SO_2, NO, WSOC and PM mass (Table 2). The relationship between WSON with SO_4^{2-} became significant ($r = 0.51$) when only daytime data were used, and correlations with WSOC, WSTN, and PM mass also became stronger, but the nighttime relationship of WSON with these species became insignificant (Table 2). Interestingly, nighttime WSON data exhibited significant correlations with levoglucosan ($r = 0.59$), CO, ($r = 0.72$), SO_2 ($r = 0.51$), NO ($r = 0.68$), NO_x and NO_y ($r = 0.63$), further suggesting multiple primary sources and secondary processes of WSON formation over the urban site that may include biomass burning, power plant emissions, and mobile sources. Different correlations for daytime and nighttime data also suggest the diurnal variability of WSON was due to different sources. Although biomass burning has been shown as a significant source of WSON (Mace et al., 2003c; Laskin et al., 2009), it was not a major source at Atlanta and Yorkville based on the statistically non-significant relationship between WSON and levoglucosan (marker of biomass burning) over both the sites and given low levoglucosan concentrations (Tables 1 and 2), except nighttime relationship with WSON at Atlanta (Table 2). This suggests that local biomass burning could have contributed to nighttime WSON over Atlanta.

3.3. Water-soluble N:C ratio

For both Yorkville and Atlanta the online WSOC data were averaged to the filter sampling times and the WSON to WSOC ratio calculated (i.e., water-soluble organic N–C mass ratio). Note that this ratio includes N/C of individual compounds plus the overall N and C content of all water-soluble organic components, including soluble organic components containing no N. The online WSOC data was used since it is believed to suffer less from potential sampling artifacts than the filter data. Fig. 2 shows the temporal variability in N:C ratio at both sites. The linear regression parameters for PILS_WSOC and filter_WSOC were: slope = 0.53 and $r^2 = 0.38$ over Atlanta, and slope = 1.39 and $r^2 = 0.85$ over Yorkville. Artifacts associated with semi-volatile WSOC components (mainly in Atlanta) and HiVol sample flow rates (possible cause of difference in Yorkville) likely account for these discrepancies. Similar N:C ratios and trends in ratios at both sites were observed during the more polluted period of 12–20 August, suggesting the dominance of regional sources of WSON. At other times, N/C ratios were more variable between the sites possibly due to more local sources of WSON, since WSOC trends were quite similar over both the sites. The N:C ratio ranged from 0.002 to 0.158 (median: 0.042) over Atlanta and from 0.004 to 0.272 (median: 0.055) at Yorkville, however, median values were significantly different when daytime and nighttime data were used separately (see Table 3, discussed later). These results are somewhat similar to that observed by Lin et al. (2010) over a forest site in Southeast USA in summer (N:C = 0.037). Similar to WSON concentrations, the N:C ratio was found to be weakly but significantly correlated with NO over Atlanta ($r = 0.38$, $p < 0.05$), further suggesting WSON may be linked to vehicle emissions. At Yorkville, the N:C ratio was related to SO_4^{2-} ($r = 0.61$, $p < 0.05$) and SO_2 ($r = 0.48$, $p < 0.05$), and as discussed above, suggests a link between coal-based power plant emissions and WSON over this rural site. Here, N:C was also significantly associated with Na^+ ($r = 0.86$) and K^+ ($r = 0.38$), indicating possible soil dust contributions from the agricultural operations in the vicinity of this site.

The ratio of N:C in WSON may help in broadly identifying the water-soluble organic species and thus, sources of WSON (Neff et al.

Table 3
Comparison WSON (ng-N m^{-3}) and N:C ratios for day (10:00–18:00) and night (22:00–6:00, all on Eastern Standard Time) at the urban and rural site.

Site	Type	WSON				N:C			
		Day		Night		Day		Night	
		Range	Median	Range	Median	Range	Median	Range	Median
Atlanta	Urban	LOD-564	90	LOD-588	131	0.003–0.113	0.030	0.002–0.158	0.042
Yorkville	Rural	LOD-556	58	LOD-413	71	0.004–.272	0.037	0.004–0.182	0.071

LOD is 25 ng-N m^{-3}.

2002). The observed N:C ratios are at the lower end relative to what has been observed in compounds from specific sources. The N:C ratios in atmospheric bacteria typically vary between 0.10 and 0.20 (Neff et al., 2002) (although in soils this ratio can be lower); amino acid N:C ratios vary between 0.33 with lower numbers for aliphatic amino acids in the range of 0.06–0.20; organic nitrates, such as nitric acid esters and hydroxy nitric acid esters, have N:C ratios ranging between 0.08 and 0.5, with most compounds within 0.17–0.50.

N:C ratios over marine atmospheres are significantly higher, for example, ratios of 0.35–0.49 have been reported in the western North Pacific (Miyazaki et al., 2010), indicating a much larger source for nitrogen containing carbonaceous water-soluble compounds relative to WSOC over marine regions, possibly due to much higher non-nitrogen containing SOA over continental regions due to biogenic VOC emissions. However, it is noted that the likelihood of multiple sources of WSON at our urban and rural sites makes it difficult to identify major components contributing to WSON based solely on N:C ratios.

3.4. Day versus night WSON concentrations and N:C ratios

Differences in WSON concentrations and N:C ratios between day and nighttime were investigated since both dark and photochemical reactions may lead to WSON. Table 3 summarizes the results. Comparing the two sites for combined day/night data (Table 1) showed that WSON concentrations were on average higher at the urban site. This is also true for both daytime and nighttime data (Table 3), consistent with more chemical routes to form WSON in the urban atmosphere by both dark and photochemical routes.

A comparison of day to night at each site shows that although the range in day versus night WSON concentrations were somewhat similar, the median WSON concentration was consistently higher during nighttime, especially for the urban site (Table 3). Nighttime concentrations were roughly 22% and 45% higher at the rural and urban sites, respectively. Median N:C ratios were also higher during nighttime: ~40% higher at the urban site, and almost double (~92%) at the rural site. Nighttime chemistry combined with lower dispersion associated with the shallow nighttime boundary layer could produce higher nighttime concentrations relative to day. In the northeastern USA, Brown et al. (2009) found ambient evidence for nocturnal SOA formation involving isoprene (the dominant VOC in the southeast USA) primarily through reactions involving the nitrate radical; although the resulting organo-nitrate SOA was a rather small fraction of the total SOA ranging between 1 and 17% (highest percentage in the cleaner regions), and similar to our N:C ratios. Hennigan et al., (2009) found little nighttime SOA (which we assume would form WSON, a subset of SOA) relative to daytime levels.

4. Conclusions

Filterable water-soluble organic nitrogen (WSON) was estimated in ambient aerosols collected over an urban site (Atlanta) and a rural site (Yorkville) located in southeast USA during August–September 2008 as a part of AMIGAS study. WSON concentration exhibited large variability at both sites. On average, WSON contributed ~10% to water-soluble total nitrogen (WSTN) with largest contribution from NH_4^+-N (~82%) and a minor contribution from NO_3^--N (~7%) at both sites. The N:C ratio ranged between 0 and 0.27 at both sites with somewhat similar median ratios of ~0.05, indicating nitrogenous organic compounds are not a substantial fraction of SOA over southeast USA during summer. Based on comparisons between the sites, it is concluded that the sources of WSON were local and regional on different days. Higher nighttime median WSON relative to daytime, and differences in daytime/nighttime relationships with other species provide evidence of different sources of WSON during day and night and likely include dark reactions for secondary WSON formation. A significant association between WSON and sulfate aerosol at Yorkville (and to a lesser extent in Atlanta) point to linkage with coal-fired power plant emissions, possibly via an acid-catalyzed WSON formation pathway. Multiple sources such as secondary formation, biomass burning, power plant emissions and soil dust contribute to WSON over both sites.

References

Atkinson, R., 2000. Atmospheric chemistry of VOCs and NO$_X$. Atmospheric Environment 34, 2063–2101.

Brown, S.S., deGouw, J.A., Warneke, C., Ryerson, T.B., Dubé, W.P., Atlas, E., Weber, R.J., Peltier, R.E., Neuman, J.A., Roberts, J.M., Swanson, A., Flocke, F., McKeen, S.A., Brioude, J., Sommariva, R., Trainer, M., Fehsenfeld, F.C., Ravishankara, A.R., 2009. Nocturnal isoprene oxidation over the northeast United States in summer and its impact on reactive nitrogen partitioning and secondary organic aerosol. Atmospheric Chemistry and Physics 9, 3027–3042.

Baumann, K., Ift, F., Zhao, J.Z., Chameides, W.L., 2003. Discrete measurements of reactive gases and fine particle mass and composition during the 1999 Atlanta supersite experiment. Journal of Geophysical Research 108, 8416. doi:10.1029/2001JD001210.

Cauwet, G., 1999. Determination of dissolved organic carbon and nitrogen by high temperature combustion. In: Grasshoff, K., Kremling, K., Ehrhardt, M. (Eds.), Methods of Seawater Analysis. Wiley, Weinheim, pp. 407–420.

Cornell, S.E., Rendell, A.R., Jickells, T.D., 1995. Atmospheric deposition of organic nitrogen. Nature 376, 243–246.

Cornell, S., Mace, K., Coeppicus, S., Duce, R., Huebert, B., Jickells, T., Zhuang, L.-Z., 2001. Organic nitrogen in Hawaiian rain and aerosol. Journal of Geophysical Research 106, 7973–7983.

Cornell, S.E., Jickells, T.D., Cape, J.N., Rowland, A.P., Duce, R.A., 2003. Organic nitrogen deposition on land and coastal environments: a review of methods and data. Atmospheric Environment 37, 2173–2191. doi:10.1016/S1352-2310(03)00133-X.

Duce, R.A., La Roche, J., Altieri, K., Arrigo, K.R., Baker, A.R., Capone, D.G., Cornell, S., Dentener, F., Galloway, J., Ganeshram, R.S., Geider, R.J., Jickells, T., Kuypers, M.M., Langlois, R., Liss, P.S., Liu, S.M., Middleburg, J.J., Moore, C.M., Nickovic, S., Oschlies, A., Pedersen, T., Prospero, J., Schlitzer, R., Seitzinger, S., Sorensen, L.L., Uematsu, M., Ulloa, O., Voss, M., Ward, B., Zamora, L., 2008. Impacts of

atmospheric anthropogenic nitrogen on the open ocean. Science 320, 893–897. doi:10.1126/science.1150369.

Galloway, J.N., Townsend, A.R., Wrisman, J.W., Bekunda, M., Cai, Z., Freney, J.R., Martinelli, L.A., Seitzinger, S.P., Sutton, M.A., 2008. Transformation of the nitrogen cycle: recent trends, questions, and potential solutions. Science 320, 889–892.

Goldstein, A.H., Koven, C.D, Heald, C.L. and Fung, I.Y., 2009. Biogenic carbon and anthropogenic pollutants combine to form cooling haze over the southeastern United States. Proceedings of the National Academy of Sciences 106, 8835–8840. 8810.1073/pnas.0904128106.

Hansen, D.A., et al., 2006. Air quality measurements for the aerosol research and inhalation epidemiology study. Journal of Air Waste Management Association 56 (10), 1445–1458.

Hennigan, C.J., Sullivan, A.P., Fountoukis, C.I., Nenes, A., Hecobian, A., Vargas, O., Hanks, A.T.C., Huey, L.G., Lefer, B.L., Russell, A.G., Weber, R.J., 2008. On the volatility and production mechanisms of newly formed nitrate and water soluble organic aerosol in Mexico City. Atmospheric Chemistry and Physics 8, 3761–3768.

Hennigan, C.J., Bergin, M.H., Russell, A.G., Nenes, A., Weber, R.J., 2009. Gas/particle partitioning of water-soluble organic aerosol in Atlanta. Atmospheric Chemistry and Physics 9, 3613–3628.

Laskin, A., Smith, J.S., Laskin, J., 2009. Molecular characterization of nitrogen-containing organic compounds in biomass burning aerosols using high-resolution mass spectrometry. Environmental Science and Technology 43, 3764–3771. doi:10.1021/es803456n.

Lesworth, T., Baker, A.R., Jickells, T.D., 2010. Aerosol organic nitrogen over the remote Atlantic Ocean. Atmospheric Environment 44, 1887–1893.

Lim, Y.B., Ziemann, P., 2005. Products and mechanism of secondary organic aerosol formation from reactions of n-alkanes with OH radicals in the presence of NO_x. Environmental Science and Technology 39, 9229–9236.

Lin, M., Walker, J., Geron, C., Khlystov, A., 2010. Organic nitrogen in $PM_{2.5}$ aerosol at a forest site in the Southeast US. Atmospheric Chemistry and Physics 10, 2145–2157.

Mace, K.A., Duce, R.A., Tindale, N.W., 2003a. Organic nitrogen in rain and aerosol at Cape Grim, Tasmania, Australia. Journal of Geophysical Research 108 (D11), 4338. doi:10.1029/2002JD003051.

Mace, K.A., Kubikay, N., Duce, R.A., 2003b. Organic nitrogen in rain and aerosol in the eastern Mediterranean atmosphere: an association with atmospheric dust. Journal of Geophysical Research 108 (D10), 4320. doi:10.1029/2002JD002997.

Mace, K.A., Artaxo, P., Duce, R.A., 2003c. Water-soluble organic nitrogen in Amazon Basin aerosols during the dry (biomass burning) and wet seasons. Journal of Geophysical Research 108, 4512. doi:10.1029/2003JD003557.

Miyazaki, Y., Kawamura, K. and Sawano, M., 2010. Size distributions of organic nitrogen and carbon in remote marine aerosols: evidence of marine biological origin based on their isotopic ratios. Geophysical Research Letters 37, L06803. doi:06810.01029/02010GL042483.

Murphy, S.M., Sorooshian, A., Kroll, J.H., Ng, N.L., Chhabra, P., Tong, C., Surratt, J.D., Knipping, E., Flagan, R.C., Seinfeld, J.H., 2007. Secondary aerosol formation from atmospheric reactions of aliphatic amines. Atmospheric Chemistry and Physics 7, 2313–2337.

Nakamura, T., Ogawa, H., Maripi, D.K., Uematsu, M., 2006. Contribution of water soluble organic nitrogen to total nitrogen in marine aerosols over the East China Sea and western North Pacific. Atmospheric Environment 40, 7259–7264. doi:10.1016/j.atmosenv.2006.06.026.

Neff, J.C., Holland, E.A., Dentener, F.J., McDowell, W.H., Russell, K.M., 2002. The origin, composition and rates of organic nitrogen deposition: a missing piece of the nitrogen cycle? Biogeochemistry 57–58, 99–136. doi:10.1023/A:1015791622742.

Ng, N.L., Kwan, A.J., Surratt, J.D., Chan, A.W.H., Chhabra, P.S., Sorooshian, A., Pye, H.O.T., Crounse, J.D., Wennberg, P.O., Flagan, R.C., Seinfeld, J.H., 2008. Secondary organic aerosol (SOA) formation from reaction of isoprene with nitrate radicals (NO_3). Atmospheric Chemistry and Physics 8, 4117–4140.

Orsini, D., Ma, Y., Sullivan, A., Sierau, B., Baumann, K., Weber, R.J., 2003. Refinements to the particle-into-liquid sampler (PILS) for ground and airborne measurements of water soluble aerosol composition. Atmospheric Environment 37, 1243–1259.

Rollins, A.W., Smith, J.D., Wilson, K.R., Cohen, R.C., 2010. Real time in situ detection of organic nitrates in atmospheric aerosols. Environmental Science and Technology 44, 5540–5545.

Russell, A.G., McRae, G.J., Cass, G.R., 1983. Mathematical modeling of the formation and transport of ammonium nitrate aerosol. Atmospheric Environment 17, 949–964.

Sullivan, A.P., Weber, R.J., Clements, A.L., Turner, J.R., Bae, M.S., Schauer, J.J., 2004. A method for on-line measurement of water-soluble organic carbon in ambient aerosol particles: results from an urban site. Geophysical Research Letters 31 (L13105). doi:10.1029/12004GL019681.

Sullivan, A.P., Holden, A.S., Patterson, L.A., McMeeking, G.R., Kreidenweis, S.M., Malm, W.C., Hao, W.M., Wold, C.E., Collett Jr., J.L., 2008. A method for smoke marker measurements and its potential application for determining the contribution of biomass burning from wildfires and prescribed fires to ambient $PM_{2.5}$ organic carbon. Journal of Geophysical Research 113, D22302. doi:10.1029/2008JD010216.

Surratt, J.D., Gmez-González, Y., Chan, A.W.H., Vermeylen, R., Shahgholi, M., Kleindienst, T.E., Edney, E.O., Offenberg, J.H., Lewandowski, M., Jaoui, M., Maenhaut, W., Claeys, M., Flagan, R.C., Seinfeld, J.H., 2008. Organosulfate formation in biogenic secondary organic aerosol. Journal of Physical Chemistry 112, 8345–8378.

Volkamer, R., Jimenez, J.L., Martini, F.S., Dzepina, K., Zhang, Q., Salcedo, D., Molina, L.T., Worsnop, D.R. and Molina, M.J., 2006. Secondary organic aerosol formation from anthropogenic air pollution: rapid and higher than expected. Geophysical Research Letters 33(17), L17811. doi:17810.11029/12006GL026899.

Watson, J.G., Chow, J.C., Chen, L.-W.A., Frank, N.H., 2009. Methods to assess carbonaceous aerosol sampling artifacts for IMPROVE and other long-term networks. Journal of Air Waste Management Association 59, 898–911.

Weber, R.J., et al., 2003. Intercomparison of near real-time monitors of $PM_{2.5}$ nitrate and sulfate at the EPA Atlanta supersite. Journal of Geophysical Research 108 (D7). doi:10.1029/2001JD001220.

Weber, R.J., Sullivan, A.P., Peltier, R.E., Russell, A., Yan, B., Zheng, M., de Gouw, J., Warneke, C., Brock, C., Holloway, J.S., Atlas, E.L., Edgerton, E., 2007. A study of secondary organic aerosol formation in the anthropogenic influenced southeastern United States. Journal of Geophysical Research 112, D13302. doi:10.1029/2007JD008408.

Wedyan, M.A., Fandi, K.G., Al-Rousan, S., 2007. Bioavailability of atmospheric dissolved organic nitrogen in the marine aerosol over the Gulf of Aqaba. Australian Journal of Basic Applied Sciences 1, 208–212.

Zhang, Q., Anastasio, C., Jimenez-Cruz, M., 2002. Water-soluble organic nitrogen in atmospheric fine particles ($PM_{2.5}$) from northern California. Journal of Geophysical Research 107 (D11), 4112. doi:10.1029/2001JD000870.

Zhang, X., Hecobian, A., Zheng, M., Frank, N., Weber, R.J., 2010. Biomass buring impact on $PM_{2.5}$ over the southeastern U.S.: integrating chemically speciated FRM filter measurements, MODIS fire counts and PMF analysis. Atmospheric Chemistry and Physics 10, 6839–6853.