

# Organic nitrogen in PM<sub>2.5</sub> aerosol at a forest site in the Southeast US

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**Abstract.** There is growing evidence that organo-nitrogen compounds may constitute a significant fraction of the aerosol nitrogen (N) budget. However, very little is known about the abundance and origin of this aerosol fraction. In this study, the concentration of organic nitrogen (ON) and major inorganic ions in PM<sub>2.5</sub> aerosol were measured at the Duke Forest Research Facility near Chapel Hill, NC, during January and June of 2007. A novel on-line instrument was used, which is based on the Steam Jet Aerosol Collector (SJAC) coupled to an on-line total carbon/total nitrogen analyzer and two on-line ion chromatographs. The concentration of ON was determined by tracking the difference in concentrations of total nitrogen and of inorganic nitrogen (determined as the sum of N-ammonium and N-nitrate). The time resolution of the instrument was 30 min with a detection limit for major aerosol components of  $\sim 0.1 \mu\text{g m}^{-3}$ .

Nitrogen in organic compounds contributed  $\sim 33\%$  on average to the total nitrogen concentration in PM<sub>2.5</sub>, illustrating the importance of this aerosol component. Absolute concentrations of ON, however, were relatively low ( $< 1.0 \mu\text{g m}^{-3}$ ) with an average of  $0.16 \mu\text{g m}^{-3}$ . The absolute and relative contribution of ON to the total aerosol nitrogen budget was practically the same in January and June. In January, the concentration of ON tended to be higher during the night and early morning, while in June it tended to be higher during the late afternoon and evening. Back-trajectories and correlation with wind direction indicate that higher concentrations of ON occur in air masses originating over the continental US, while marine air masses are characterized by lower ON concentrations. The data presented in this study suggests that ON has a

variety of sources, which are very difficult to quantify without information on chemical composition of this important aerosol fraction.

## 1 Introduction

Wet and dry deposition of nitrogen-containing air pollutants, both gaseous and particulate, are important sources of exogenous nitrogen in terrestrial and aquatic ecosystems. Excess nitrogen may lead to soil acidification, aquatic eutrophication, and other stressors that reduce ecosystem health as well as soil and water quality (Moss, 1988; Fenn et al., 1998; Smith et al., 1998). Ambient PM<sub>2.5</sub> aerosol (i.e. particles smaller than  $2.5 \mu\text{m}$  in aerodynamic diameter) contains numerous inorganic and organic nitrogen compounds, which cumulatively can contribute significantly to total atmospheric nitrogen deposition (Erisman et al., 1997; Garstang et al., 1998; Seinfeld and Pandis, 1998; Tolocka et al., 2001; Wittig et al., 2004). The majority of aerosol deposition studies concentrate on quantifying only the inorganic fraction (i.e.,  $\text{NH}_4^+$  and  $\text{NO}_3^-$ ) (Garstang et al., 1998; Yeatman et al., 2001; Morselli et al., 2008; Rojas and Venegas, 2009). However, there is growing evidence that ON can constitute a significant fraction of total nitrogen (inorganic + organic) in ambient aerosol (Zhang et al., 2002; Mace et al., 2003; Duan et al., 2009).

Some of the evidence of ON abundance comes from deposition studies (Cornell et al., 2001; Mace et al., 2003; Sparks et al., 2008). Measurements in the US have shown that 20% to 80% of nitrogen in atmospheric deposition is in an organic form (Zhang and Anastasio, 2001). Organic nitrogen was reported to contribute 20% to 40% to the total annual wet deposition of dissolved nitrogen across the United Kingdom



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(Cape et al., 2004). Other measurements at various marine and continental sites have also shown 20–90% of nitrogen deposition is organic (Nicholls and Cox, 1978; Timperley et al., 1985; Mopper and Zika, 1987; Cornell et al., 1995, 2001). Measurements of ON in fog water have shown that organics contribute 16% of the total nitrogen (Zhang and Anastasio, 2001).

The above cited deposition studies do not directly distinguish between the aerosol and gas contributions, though both gaseous and aerosol compounds contribute to the deposition flux (Zhang et al., 2002a). A few studies have reported ON concentrations measured directly in aerosol. Water-soluble organic nitrogen in PM<sub>2.5</sub> aerosol was shown to account for 30% of total particulate nitrogen mass in Beijing, China (Duan et al., 2009). Organo-nitrogen compounds were estimated to contribute 18% to PM<sub>2.5</sub> mass in Davis, California (Zhang et al., 2002) and between 19 and 25% of total aerosol nitrogen in Cape Grim, Australia (Mace et al., 2003). It should be noted that these data represent the water-soluble fraction of organic nitrogen. The total ON fraction could be higher if the insoluble fraction of ON is significant.

Very little is known about the origin of ON in ambient aerosol, which includes primary and secondary sources. Broad categories of organic nitrogen in aerosol include reduced N, organic nitrates, and biological particulates (see Neff et al., 2002 and references therein). Reduced N compounds include urea, alkyl amines, N-heterocyclic compounds and amino acids that originate from animal husbandry (Schade and Crutzen, 1995), biomass burning (Lobert et al., 1990; Mace et al., 2003; Smith et al., 2009) and ocean air-surface interactions (Milne and Zika, 1993). Organic nitrates (i.e. oxidized forms of organic N) are reaction products involving hydrocarbons and nitrogen oxides (Atkinson, 2007) and may also be present in gas or particulate forms. Reactions of carbonyl containing species and amines have been shown to lead to the synthesis of particulate imine products (Malloy et al., 2009). Photo-oxidation of conjugated dienes under high-NO<sub>x</sub> conditions has been shown to produce nitroxypolyols in the aerosol phase (Sato, 2008). It should be noted that ON itself can participate in photochemical reactions, thus acting as a reservoir of reactive nitrogen in the atmosphere (Zhang and Anastasio, 2003a). Biological particulate includes directly emitted soil, vegetation and skin fragments, pollen, bacteria, etc. (Neff et al., 2002; Jaenicke, 2005) and exists in the atmosphere at sizes ranging from nanometers to millimeters (Baron and Willeke, 2005).

One reason for the lack of data on organic nitrogen in ambient aerosol is measurement difficulty. The few studies that reported direct measurements of ON in ambient aerosol used filter sampling, which requires manual extraction and analysis and is therefore extremely labor intensive. Furthermore, the time resolution of such measurements is low, usually 24 h, which makes it difficult to apply this method to study intra-day dynamics of ON and other transient phenomena involving this aerosol fraction.

In this study, a novel instrumental setup was developed and used to automatically measure organic and inorganic nitrogen in PM<sub>2.5</sub> aerosol with a time resolution of 30 min. The instrument was deployed at the Duke Forest Research Facility, near Chapel Hill, NC. Absolute concentrations and temporal variability of ON were investigated to assess the importance of this aerosol component relative to total PM<sub>2.5</sub> nitrogen and to elucidate its potential sources.

## 2 Experimental

### 2.1 Measurement site and time period

The measurements were performed at the Blackwood Division of Duke Forest's Forest-Atmosphere Carbon Transfer and Storage (FACTS-1) research site in Chapel Hill, NC (35.98 N latitude, 79.09 W longitude). Measurements were conducted in the 26 ha Loblolly Pine plantation, which has an average canopy height of approximately 18 m. The site is situated 2.5 km to the southwest of Interstate 40 and adjacent to several secondary roads and is therefore influenced by local mobile sources of particulate matter and nitrogen oxides.

The instruments were housed in an air-conditioned shelter. Ambient air was sampled at 500 Lmin<sup>-1</sup> through a 6" OD pipe from just above the top of the canopy, 25 m above ground level. The organic nitrogen system subsampled from the main 500 Lmin<sup>-1</sup> flow via a manifold attached to the bottom part of the primary sampling pipe. The sampling lines to individual instruments were made of 3/4" copper pipe and were thermally insulated to avoid any evaporation/condensation artifacts during the transport. The measurements presented here were carried out during 1–31 January 2007 and 31 May–30 June 2007.

### 2.2 Organic nitrogen measurements

A general diagram of the instrument is shown in Fig. 1. The instrument sampled at a flow rate of 16.7 Lmin<sup>-1</sup> through a Teflon-coated PM<sub>2.5</sub> cyclone (URG Co.). The air then passed through a denuder which collects water-soluble gases to avoid positive artifact in the aerosol measurements. In the beginning of the study (January 2007), three dry multichannel denuders (activated carbon, Na<sub>2</sub>CO<sub>3</sub>-coated and citric acid-coated) in series were used. No artifact in inorganic or ON measurements was observed (the procedure to determine the artifact is described further in the text). However, the total carbon measurements suffered a high artifact (10 μgm<sup>-3</sup> or higher). Hence, the dry denuders were replaced with a wet annular denuder (Wyers et al., 1993), which considerably reduced the positive artifact in total carbon measurements. Ambient air then flowed into the Steam Jet Aerosol Collector (SJAC) (Khlystov et al., 1995), where both soluble and insoluble particles were collected. The collection efficiency of the SJAC for particles larger than 10 nm and number concentrations up to 65 000 cm<sup>-3</sup> is 99%, thus practically

all aerosol is sampled. The SJAC produces approximately 0.1–0.2 mL min<sup>-1</sup> of particle solution/suspension. The transfer efficiency of insoluble sub-micron particles through the liquid lines of the system was measured in laboratory to be around 85%.

The collected aqueous sample was mixed with a flow of 0.2 mL min<sup>-1</sup> of LiF solution (250 ppb) and transferred by a peristaltic pump (DYNAMAX RP-1) into a glass debubbler. LiF serves to monitor the liquid flow rate from the SJAC and to provide an internal standard for the ion chromatographs (ICs). The sample flow was then split to cation and anion ICs (both Metrohm Model 761 Compact IC), and a high sensitivity TOC/TN (Shimadzu TOC-Vcsh) unit. Two inline filters in series (one 2 μm, the other 0.5 μm pore size; Upchurch Scientific) were installed in the IC line to protect the ICs from suspended insoluble particles. No filters were used in the line to the TOC/TN instrument, which measured both soluble and insoluble material. The ICs measured Li<sup>+</sup>, Na<sup>+</sup>, NH<sub>4</sub><sup>+</sup>, K<sup>+</sup>, F<sup>-</sup>, Cl<sup>-</sup>, NO<sub>3</sub><sup>-</sup>, SO<sub>4</sub><sup>2-</sup>, and small organic ions such as oxalate. 1 mL injection loops were used in both ICs. The eluent for the cation IC was 0.0039 M of L-tartaric acid with 0.0007 M of 2,6-pyridinedicarboxylic acid (Sigma Aldrich). The anion eluent was 0.0032 M of sodium carbonate and 0.0009 M of sodium hydrogen carbonate (Sigma Aldrich). The anion IC was equipped with a suppressor.

The Shimadzu TOC/TN analyzer (Model TOC-Vcsh) uses thermo-catalytic oxidation to determine the total carbon and nitrogen content of the sample. The sample is injected into a combustion tube, which is filled with an oxidation catalyst (fiber platinum on quartz) and heated to 680 °C under a constant flow of ultra-pure air. The combustion gases pass through an electrical dehumidifier for cooling and dehydration, then through a halogen scrubber before being measured by a NDIR detector to determine the total carbon content of the injected sample. It should be noted that both elemental carbon and organic carbon are determined in this instrument and can not be distinguished from each other. Therefore, the instrument measures total carbon (TC), rather than only total organic carbon (TOC). We use the term “TOC” when we refer to the instrument (Shimadzu TOC/TN analyzer), and “TC” when we discuss concentrations measured with this instrument. After passing through the NDIR detector the gas stream is directed to the TN unit, where the nitrogen content is determined by measuring oxides of nitrogen with a chemiluminescence detector. It should be noted that the TN instrument does not discriminate between different compounds in the sample, but provides the total nitrogen content of the sample.

The amount of organic nitrogen was determined by subtracting the inorganic nitrogen concentration (N-NH<sub>4</sub><sup>+</sup> and N-NO<sub>3</sub><sup>-</sup> measured with the ICs) from the total nitrogen concentration (measured with the TOC/TN). The time resolution for the ICs and the TOC/TN was 30 min.

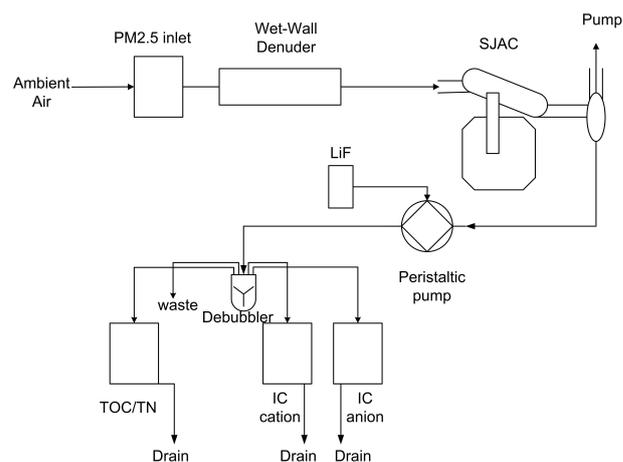


Fig. 1. A general sketch of the instrument setup.

### 2.3 Supplemental measurements

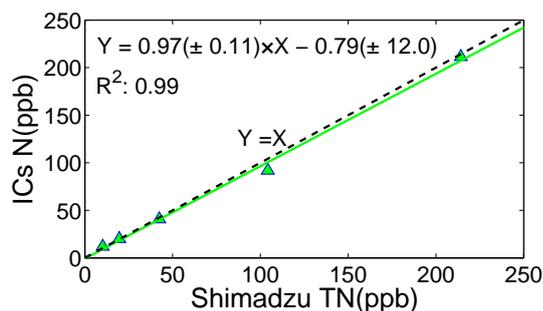
Organic and elemental carbon in PM<sub>2.5</sub> (OC and EC respectively) were quantified using an automated semi-continuous thermal-optical analyzer (Sunset Laboratory) described in detail by Geron (2009). Ambient air was drawn at 8 L min<sup>-1</sup> through a 2.5 μm aerodynamic diameter cut point cyclone (BGI, Inc.) located 3–5 m above the pine canopy. The Sunset instrument sampled through a parallel-plate carbon impregnated fiber denuder (Sunset Laboratory) to remove gas phase organic compounds. Measurements were performed every 3 h (167 min for sampling, 13 min for analysis and cool-down) and corrected for OC charring using the laser transmission technique.

NO<sub>x</sub> concentrations were measured with a Thermo Environmental Instruments Model 42S trace-level chemiluminescence analyzer. The instrument was housed in a climate controlled enclosure and sampled from above the pine canopy through a 1" OD Teflon tubing at a flow rate of 30 L min<sup>-1</sup>. The analyzer was calibrated monthly by mass flow controlled dilution of a certified NO standard (Airgas National Welders). Data were recorded as 30 min averages.

Meteorological data collected at the FACTS-1 site include total precipitation, air temperature in the upper canopy, and wind direction. The data were analyzed as 30 min averages and were from above-canopy instruments.

### 2.4 Quality assurance and quality control

The ICs and the TOC/TN were calibrated monthly with standard solutions in the concentration range 10 ppb–500 ppb (1 ppb=μg L<sup>-1</sup>), which was the range expected during ambient measurements. Good agreement must be obtained between the IC's and TOC/TN nitrogen measurements to avoid bias in ON data. To verify inter-comparability of the IC and TN nitrogen measurements, tests were carried out with



**Fig. 2.** Inter-comparison of nitrogen content measurements with ICs and TOC/TN using  $(\text{NH}_4)_2\text{SO}_4$  standards.

$(\text{NH}_4)_2\text{SO}_4$  (a major ambient aerosol component); the instruments agreed within 3% (Fig. 2).

Concentrations in air were calculated in the following way. The analytical instruments provide concentration data of components in solution in ppb ( $\mu\text{g L}^{-1}$ ). The IN and TN values in ppb were corrected for blanks (see below). Then, the ON concentration in the liquid sample was calculated as the difference between blank-corrected TN and IN concentrations. The IN and ON values were then hourly averaged. The hourly average concentrations in ppb were then converted to concentration in air, expressed as  $\mu\text{g m}^{-3}$ , using the air flow rate and the liquid flow rate. The liquid flow rate is calculated from the flow rate of LiF ( $0.2 \text{ mL min}^{-1}$ ), its original concentration (250 ppb) and the concentration of LiF observed during that hour.

Total instrument blanks were measured twice each month. During the blank measurements, the instrument operated as during ambient measurements, with the only difference being that a HEPA filter was installed in front of the wet denuder. The blank measurements took 2 h in order to obtain at least 4 measurement points. It should be noted that the blanks measured in this way include both the instrument blanks (i.e. of the SJAC, ICs, and TOC/TN) and any positive artifact. Average hourly blanks were 8 ppb, 12 ppb, 288 ppb for IN, TN, and TC, respectively. Under typical conditions, these blanks translated to  $0.17 \mu\text{g m}^{-3}$ ,  $0.31 \mu\text{g m}^{-3}$ , and  $5.82 \mu\text{g m}^{-3}$  for IN, TN, and TC, respectively. All data reported here were corrected for the observed blanks. Due to the high blanks, the TC measurements were discarded. Instead, data from the SunSet OC/EC instrument were used. Blanks in OC measurements with the SunSet instrument were less than  $0.1 \mu\text{g m}^{-3}$ .

The limit of detection (LOD) was defined as two times the standard deviation of the blank measurements. This definition of LOD corresponds to the probability of 97.5% that a single measurement is distinct from the blank. The limits of detection (LOD) for hourly observations are:  $0.09 \mu\text{g m}^{-3}$  for IN,  $0.1 \mu\text{g m}^{-3}$  for TN, and  $0.14 \mu\text{g m}^{-3}$  for ON. The hourly LODs were calculated taking into account that more than one

blank measurement per hour was taken (see the discussion below). The LOD for ON was calculated from those of TN and IN using the propagation of error formula.

Uncertainty of the concentration measured in air was estimated based on the propagation of error from the individual measurements (uncertainty of chemical determination of the analyte and LiF, and uncertainty of the air and liquid flow rates in the system). The calibration uncertainty for the inorganic compounds, estimated as the standard deviation of residuals calculated from the calibration measurements, is 2.5 ppb. For TN the calibration uncertainty is estimated at 5 ppb. Since hourly averages of TN and IN concentrations were used to calculate hourly concentrations of ON, the uncertainty of hourly averages should be used instead of the uncertainty of individual measurements. The average of N measurements has a smaller uncertainty than a single measurement, and in the case of independent measurements the uncertainty is reduced by a factor of square root of N. Therefore, the uncertainty of hourly ON measurements in the liquid sample collected in the SJAC is:

$$\sigma_{\text{ON}_i} = \sqrt{\frac{(\sigma_{\text{IN}_i})^2}{N_{\text{IN}}} + \frac{(\sigma_{\text{TN}_i})^2}{N_{\text{TN}}} - 2 \frac{(\sigma_{\text{IN}_i})^2 (\sigma_{\text{TN}_i})^2}{N_{\text{IN}} N_{\text{TN}}} r_{\text{TN,IN}}} \quad (1)$$

in which  $\sigma_{\text{ON}_i}$  is the uncertainty in hourly concentrations of ON in the liquid sample;  $\sigma_{\text{IN}_i}$  and  $\sigma_{\text{ON}_i}$  are standard deviations of individual IN and ON measurements;  $N_{\text{IN}}$  and  $N_{\text{TN}}$  are the number of observations per hour;  $r_{\text{TN,IN}}$  is the correlation coefficient of TN and IN, which in this study was 0.83. The third term under the square root takes into account that TN and IN are not fully independent, because TN includes IN.

The uncertainties for the TN and IN in the above equation were calculated from:

$$\sigma_l = \sqrt{\sigma_c^2 + \sigma_b^2} \quad (2)$$

in which  $\sigma_l$  is the uncertainty in IN or TN concentrations in the liquid,  $\sigma_c$  is the uncertainty of analytical determination (calibration) of the corresponding component and  $\sigma_b$  is the uncertainty of its blank.

The uncertainties of air concentrations were calculated from the uncertainties of concentrations in the liquid and the uncertainties in the liquid and air flow rates:

$$\sigma_a = \sqrt{\left(\frac{\sigma_l}{C_l}\right)^2 + \sigma_{lf}^2 + \sigma_{af}^2} \quad (3)$$

in which  $\sigma_a$  is the relative (percent) uncertainty of air concentration measurements,  $C_l$  is the concentration of the component in the liquid,  $\sigma_{lf}$  is the relative uncertainty of the liquid flow rate (in this study 5% on average), and  $\sigma_{af}$  is the relative uncertainty of the air flow rate (5% on average).

**Table 1.** Descriptive statistics of the parameters observed during the study.

	ON μgm <sup>-3</sup>	NH <sub>4</sub> <sup>+</sup> μgm <sup>-3</sup>	SO <sub>4</sub> <sup>2-</sup> μgm <sup>-3</sup>	OC μgm <sup>-3</sup>	EC μgm <sup>-3</sup>	NO <sub>x</sub> ppb	Temp °C	WS ms <sup>-1</sup>
All:								
Min.	-0.14	-0.09	0.08	0.43	0.03	1.73	-5.23	0.35
1st Qu.	0.04	0.26	1.01	1.30	0.15	3.43	2.78	1.14
Median	0.14	0.40	1.37	2.72	0.21	4.92	17.43	1.53
Mean	0.16	0.42	1.46	2.94	0.25	6.09	14.27	1.71
3rd Qu.	0.24	0.55	1.76	3.93	0.30	7.19	22.97	2.07
Max.	1.13	1.36	4.19	8.74	1.00	33.23	31.64	5.45
January:								
Min.	-0.12	0.01	0.39	0.43	0.06	2.25	-5.23	0.43
1st Qu.	0.02	0.27	1.05	0.85	0.12	4.71	-0.18	1.23
Median	0.12	0.38	1.30	1.28	0.17	6.25	1.77	1.63
Mean	0.15	0.39	1.32	1.51	0.20	6.95	3.43	1.93
3rd Qu.	0.23	0.49	1.53	2.04	0.26	7.93	6.33	2.40
Max.	1.07	1.27	3.33	4.18	0.47	25.66	19.64	5.45
June:								
Min.	-0.14	-0.09	0.08	0.50	0.03	1.73	14.05	0.35
1st Qu.	0.06	0.24	0.99	2.89	0.19	2.87	20.09	1.07
Median	0.15	0.41	1.44	3.69	0.24	3.63	22.61	1.48
Mean	0.17	0.44	1.55	3.97	0.29	5.17	22.94	1.54
3rd Qu.	0.25	0.60	1.98	4.75	0.32	5.14	25.94	1.90
Max.	1.13	1.36	4.19	8.74	1.00	33.23	31.64	3.88

As follows from the above equation, the relative uncertainty of individual points depends on the concentration of the component, being higher at low concentrations and lower at higher concentrations. To give the reader a measure of the uncertainties of concentrations measured in this study, we have calculated the uncertainty for each hourly observation and calculated the grand average for the whole study. The uncertainties are: 8.4% for ON, 12.2% for TN and 8.2% for IN. Even though it is counter-intuitive, the uncertainty in ON is lower than that of TN. This is because TN and IN are highly correlated (correlation coefficient during this study was 0.83), which leads to a lower uncertainty according to Eq.(1).

The consistency of the data was checked by observing the NH<sub>4</sub><sup>+</sup>/SO<sub>4</sub><sup>2-</sup> molar ratio. Because the main ionic components were NH<sub>4</sub><sup>+</sup> and SO<sub>4</sub><sup>2-</sup>, values of the molar ratio outside the 1:1 to 2:1 range (with 20% margin of error) indicate that either the NH<sub>4</sub><sup>+</sup> or SO<sub>4</sub><sup>2-</sup> measurements were questionable. We have excluded such points from the analysis, because accuracy of the NH<sub>4</sub><sup>+</sup> measurements is critical for determining the ON concentration. This procedure excluded approximately 20% of the total number of observations. As will be shown in the Results Section, this data selection criteria does not significantly influence the average concentrations of ON and its contribution to the TN budget of the aerosol. Further, only periods that contain both total and inorganic nitrogen measurements were used to calculate ON concentrations. The

means and other statistical parameters used for comparison of different aerosol species were calculated only for the periods when data for all of the species were available.

### 3 Results and discussion

#### 3.1 Absolute and relative concentrations of ON and other species

Descriptive statistics of the parameters measured during January and June 2007 are listed in Table 1. In January the aerosol was composed of approximately equal fractions of organic and inorganic components, while the organics dominated in summer. The concentration of organic carbon in June was 2.6 times higher than in January, while the concentration of inorganic constituents were only 13–17% higher. The main inorganic components were NH<sub>4</sub><sup>+</sup> and SO<sub>4</sub><sup>2-</sup>. The molar ratio of these species was fairly constant, 1.58 in January and 1.51 in June, which is within the range of previous measurements for this area (Tolocka et al., 2001; Sparks et al., 2008). The molar ratios indicate that the inorganic aerosol was composed mostly of a mixture of ammonium sulfate and ammonium bisulfate. Practically no aerosol NO<sub>3</sub><sup>-</sup> was observed during this study, even in January. This is most likely due to relatively warm ambient temperatures during January 2007, which were 3°C higher than the 50-year average for the study area. The relative humidity was also lower:

64% as compared to 74–76% in the preceding years. Ammonium nitrate is semi-volatile and partitions to the gas phase at higher temperatures and lower relative humidities (Dawson et al., 2007). This in combination with other factors, such as the availability of free NH<sub>3</sub> and HNO<sub>3</sub> could have contributed to the absence of NO<sub>3</sub><sup>-</sup> in our observations. The observed NH<sub>4</sub><sup>+</sup> to SO<sub>4</sub><sup>2-</sup> molar ratio indicate that there was not sufficient ammonia to neutralize sulfate. Such conditions generally do not favor formation of ammonium nitrate. Concentrations of NH<sub>4</sub><sup>+</sup> and SO<sub>4</sub><sup>2-</sup> observed during this study are in general agreement with other studies reported for this area, though NO<sub>3</sub><sup>-</sup> was lower, which could be attributed to year-to-year variations (Tolocka et al., 2001; Sparks et al., 2008). Another explanation for lower NO<sub>3</sub><sup>-</sup> concentrations observed in this study could be volatilization losses in the sampling lines. Even though precautions were taken to avoid such losses by thermally insulating the sampling lines, some losses can not be ruled out. Still, such losses will not influence our measurements of ON, because gases originating from evaporation of ammonium nitrate (NH<sub>3</sub> and HNO<sub>3</sub>) are captured by the wet denuder before reaching the SJAC. However, measured ON/TN ratio in the aerosol could be biased high, because TN will be underestimated due to the losses of ammonium nitrate. It should be also noted that at least a part of ON is probably semi-volatile, which would be also negatively affected by volatilization losses. The combined effect of ON and NH<sub>4</sub>NO<sub>3</sub> volatilization losses, if any, on the ON/TN ratio is very difficult to assess without knowing the semi-volatile fraction of ON.

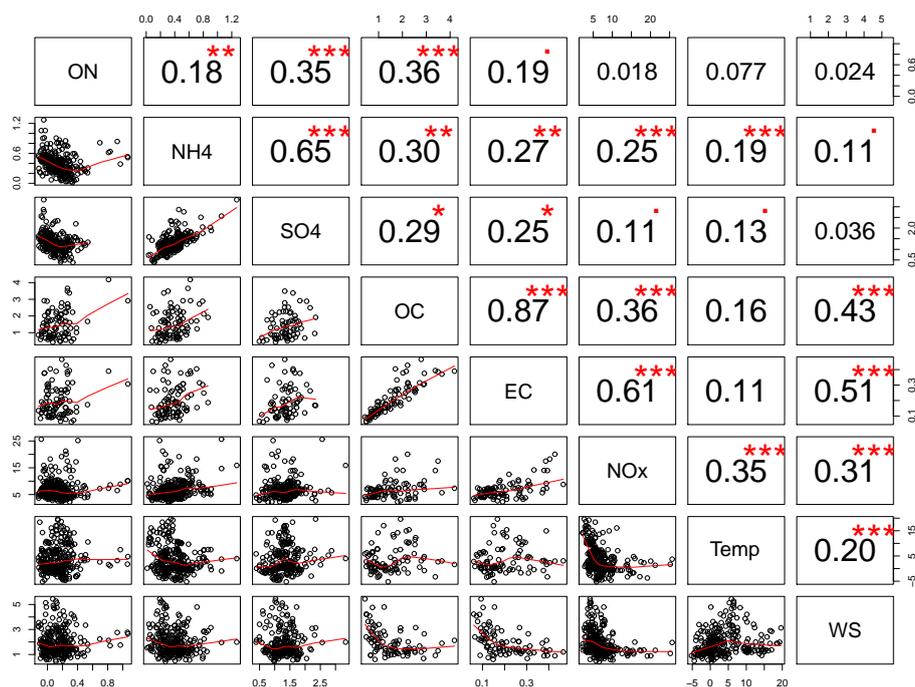
The average concentration of ON during the study was 0.16 μg m<sup>-3</sup> and the contribution of ON to total PM<sub>2.5</sub> nitrogen was fairly constant, 33% on average. Though the absolute concentration of ON was relatively low, its relative contribution to total nitrogen in PM<sub>2.5</sub> was significant. Our observations are similar to other studies, which generally report a 20–30% contribution of ON to the total nitrogen budget of PM<sub>2.5</sub> (Zhang et al., 2002; Mace et al., 2003; Duan et al., 2009).

It should be noted that the observed average concentrations and the contribution of ON to the TN aerosol budget do not change significantly, if the data selection criteria based on the NH<sub>4</sub><sup>+</sup>/SO<sub>4</sub><sup>2-</sup> ratio is not employed (see Sect. 2.4), i.e. when all data points are used. If no discrimination on the basis of ammonium to sulfate ratio is made, the study-mean ON concentration does not change, the mean NH<sub>4</sub><sup>+</sup> concentration is lowered from 0.42 to 0.41, the mean NO<sub>3</sub><sup>-</sup> concentration does not change, SO<sub>4</sub><sup>2-</sup> is lowered from 1.46 to 1.37 μg m<sup>-3</sup>. Therefore, the bias due to our selection appears to be very small and actually slightly increases the ON/TN ratio.

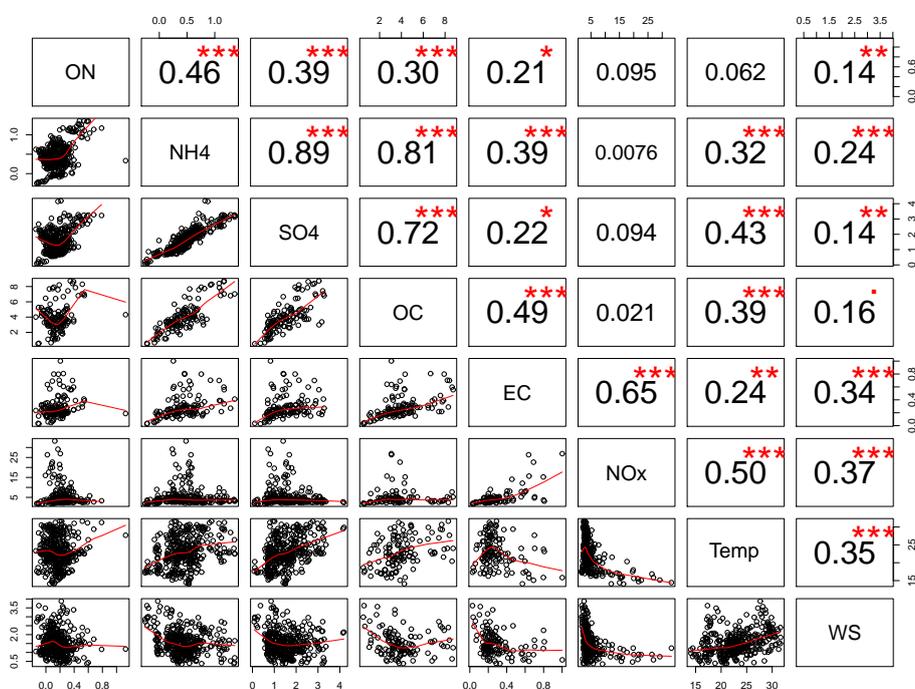
The average atomic C/N ratio for organic nitrogen, calculated as the mean of C/N ratios for each 3-h period when both ON and OC data are available, was 21.4. The C/N ratio exhibited a seasonal trend: it was 11.7 in January and 27.2 in

June. Since the absolute concentration of ON did not change considerably between the seasons (Table 1), the reason for the higher ratios in the summer months is due to the higher OC concentrations. It is interesting to note, that the average C/N ratio observed in our study is very close to that of humic substances (Schwarzenbach et al., 1993). Humic-like substances (HULIS) have previously been reported to be a major fraction of organic compounds in ambient aerosol (Krivacsy et al., 2000; Kiss et al., 2003; Samburova et al., 2005). However, while several properties of aerosol HULIS are similar to those of humic acids in soil and ground water, they do not necessarily have similar chemical composition (Graber and Rudich, 2006). The comparability of C/N ratios observed in this study with humic substances is remarkable, but possibly coincidental. A number of other nitrogen-containing substances have been identified in ambient aerosol, such as amino compounds, organic nitrates and nitrogen heterocycles (Allen et al., 1994; Neff et al., 2002; Zhang et al., 2002; Cornell et al., 2003; Mace et al., 2003; Zhang and Anastasio, 2003b). Knowledge of the contributions of these compounds to ON aerosol is highly desirable for understanding the origin and properties of ON. In general, the C/N ratio observed in this study is lower than those reported elsewhere. A C/N ratio of 37 was reported during measurements on Whistler Mountain, Canada (Sun et al., 2009). The C/N ratio of 100 was reported for HOA (hydrocarbon-like organic aerosol), OOA (oxygenated organic aerosol), and BBOA (biomass burning organic aerosol); 16.7 for LOA (local nitrogen-containing reduced OA component) in Mexico City (Aiken et al., 2009). It should be noted that these data were obtained with Aerosol Mass Spectrometers (AMS). The C/N ratio measured with the AMS may be overestimated since organo-nitrates can form ions nominally considered to be inorganic (Allan et al., 2004; Aiken et al., 2007, 2008).

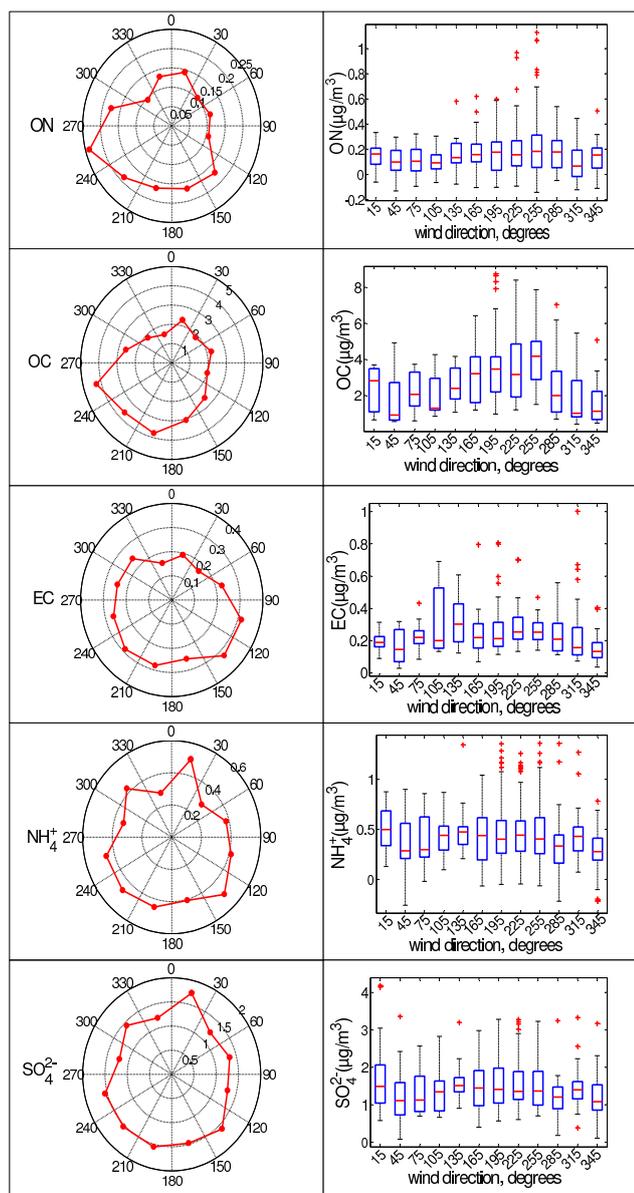
Figures 3 and 4 show inter-correlation between the individual components observed during January and June, respectively. The upper right side of the figures shows the correlation coefficients together with an indication of their statistical significance. In general, ON showed weak but significant correlations with NH<sub>4</sub><sup>+</sup>, SO<sub>4</sub><sup>2-</sup> and OC. In January ON was generally anti-correlated with NH<sub>4</sub><sup>+</sup> and SO<sub>4</sub><sup>2-</sup>, while a positive correlation was observed in June. The exact reason for this difference is unclear. Since sulfate is generally associated with long range pollutant transport, this may indicate that ON in summer was influenced more by long range sources, while in January local sources may have been more pronounced. However, no clear correlation between ON and combustion-related pollutants (EC and NO<sub>x</sub>) was observed. Only a weak correlation (correlation coefficient 0.21, *p*=0.017) between ON and EC was observed in June. No significant correlation was observed between ON and NO<sub>x</sub>. The correlation of ON with OC was positive in both months, significant, but weak. On the other hand, the correlation between OC and EC was very high in January,



**Fig. 3.** Inter-correlation between the components measured in January 2007. The red lines represent loess curves. The upper right corner of the figure shows correlation coefficients and indicates their significance (3 stars :  $p < 0.001$ ; 2 stars:  $0.001 < p < 0.01$ ; 1 star:  $0.01 < p < 0.05$ ; 1 dot:  $0.05 < p < 0.1$ ).



**Fig. 4.** Inter-correlation between the components measured in June 2007. The red lines represent loess curves. The upper right corner of the figure shows correlation coefficients and indicates their significance (3 stars :  $p < 0.001$ ; 2 stars:  $0.001 < p < 0.01$ ; 1 star:  $0.01 < p < 0.05$ ; 1 dot:  $0.05 < p < 0.1$ ).



**Fig. 5.** Wind direction dependence of ON, OC, EC,  $\text{NH}_4^+$ ,  $\text{SO}_4^{2-}$  concentrations. Wind rose graphs show mean values; box-and-whisker plots show median, inter-quartile range, the range of the data, and the outliers (points removed from the median by more than 1.5 times the inter-quartile range).

indicating a strong link between OC and combustion sources during that month. These observations may indicate that if the local sources were influencing ON levels in January, these sources were not directly related to combustion, but were contributing to ON and a relatively small fraction of OC.

The complexity of the inter-correlations is further revealed by observing the locally weighted scatterplot smoothing (loess) curves, which are shown in red in Figs. 3 and 4. The loess curves represent a form of non-parametric smooth-

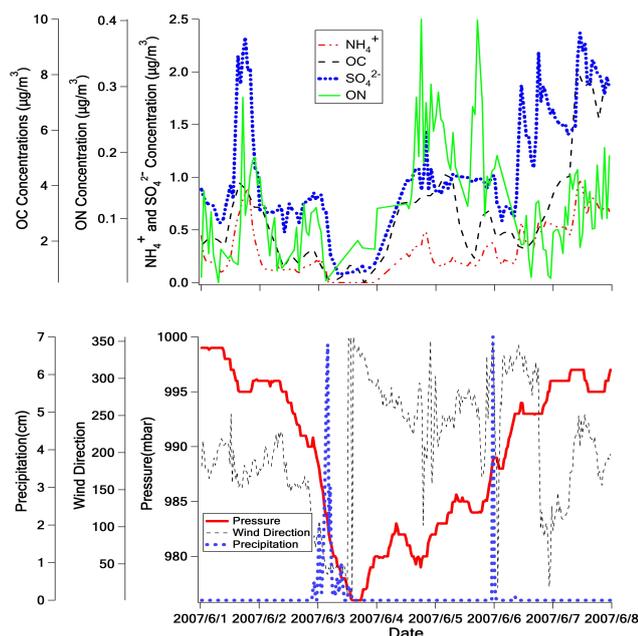
ing, which can help reveal non-linear dependences between two variables (Cleveland, 1993). The loess curves show that the relationship between ON and the other aerosol components is generally non-linear, with often different trends exhibited at low and high concentrations. For example, in June there is a negative correlation between ON and OC at low ON concentration. However, at higher concentrations (at about  $0.2 \mu\text{g m}^{-3}$ ) the correlation reverses to positive. OC has a variety of sources, both local and long-range. The non-linear relationship between OC and ON in June may indicate that some OC sources have very low nitrogen content. For example, OC concentrations in June were 2.6 times higher than in January, while ON showed only a 14% increase. The increase in OC concentrations was probably due to increased biogenic emissions. This suggests that organic aerosol originating from biogenic emissions probably has a relatively low nitrogen content. Similarly to the ON/OC relationship, the correlation between ON and EC in June at ON concentrations  $0.2\text{--}0.6 \mu\text{g m}^{-3}$  also shows a positive trend, which indicates that contribution of combustion-related sources at that ON concentration range can not be ruled out.

These observations demonstrate that ON most probably has a variety of sources. Unfortunately, without information on the chemical composition of ON it is very difficult to assess the relative importance of ON sources.

### 3.2 Wind direction dependence

Figure 5 shows a graph of the concentration of the major aerosol components as a function of wind direction. ON and OC show similar wind roses with the highest concentrations in the southwest ( $240^\circ\text{--}270^\circ$ ) sector. However, ON concentrations are relatively higher in the  $120^\circ\text{--}200^\circ$  sector, than those of OC. This indicates that the relationships between ON and OC are wind direction dependent. To gain insight into the origin of ON, a back-trajectory analysis was performed using the NOAA HYSPLIT model (Draxler, 2007). Back-trajectories showed that relatively high concentrations of ON, as well as of other aerosol components, tended to originate in air masses coming from the continental US, while low ON concentrations were associated with marine air masses coming from the Atlantic. 5% highest and 5% lowest observations were selected from each month and back-trajectories were calculated for the time of those observations. In total, 27 out of 31 (87.1%) of high ON observations originated over the continental US; 19 out of 31 (61.2%) low ON observations originated from the sea.

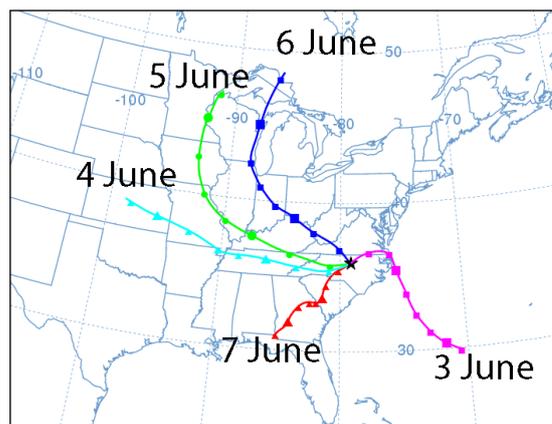
While elevated concentrations of ON and the other major aerosol species were found to be associated with continental air masses, their origin is not necessarily similar. An interesting example occurred during the first week of June 2007 (Fig. 6). On 2 and 3 June 2009, the remnants of Tropical Storm Barry traveled up the mid-Atlantic coastline. During this period, back trajectories from the site originated over the Atlantic Ocean (Fig. 7), and contained low concentrations of



**Fig. 6.** Aerosol composition, ambient pressure, precipitation, and wind direction during passage of a low pressure area in June 2007.

organic nitrogen and other PM components. Following passage of the low pressure system, winds shifted from southeasterly to northwesterly during the period 4 June to 6 June as a cold front approached from the northwest. During this period, back trajectories originated over the Midwest and Great Lakes region and contained higher concentrations of organic nitrogen. Organic nitrogen concentrations decreased again under northerly flow following a precipitation event on 6 June and began to increase along with organic carbon following passage of the cold front as southwest/westerly flow returned on 7 June. This time series illustrates a general pattern of higher organic nitrogen concentrations associated with continental air masses. Elevated organic nitrogen concentrations associated with west/northwest winds and back trajectories passing over the Midwest and Great Lakes regions may reflect the influence of agricultural emissions (urea and aliphatic amines) in the Midwest, biogenic emissions and associated secondary organic aerosol formation, and combustion sources in the Ohio River Valley. Elevated concentrations associated with west/southwest winds and air masses passing over the southeastern US may reflect more strongly the influence of biogenic emissions and secondary organic aerosol formation.

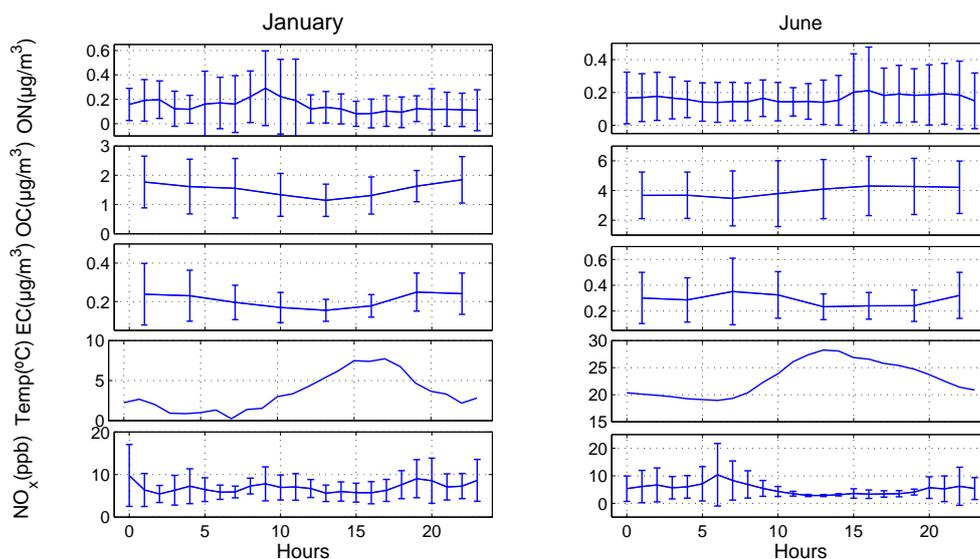
This example shows that while the concentrations of ON and other aerosol species tend to correlate in general, their sources and formation rates are, at times, clearly different, which supports the discussion presented in Sect. 3.1. It also demonstrates the power of highly resolved measurements that can capture such transient phenomena and potentially help locate sources of ON.



**Fig. 7.** Back-trajectories obtained with the NOAA HYSPLIT model for the first week of June 2007. Dates at the beginning of the trajectory indicate arrival (12 p.m. local time) at the measurement site.

### 3.3 Diurnal variability

Figure 8 shows the diurnal variability of ON concentration, temperature, OC, EC, and NO<sub>x</sub> concentrations observed during January and June 2007. In January ON concentrations were relatively high during the night and morning, while lower concentrations were observed in the afternoon. The average ON concentration from midnight to midday was 0.18 µg m<sup>-3</sup> as compared to 0.11 µg m<sup>-3</sup> in the second half of the day. Despite the strong variability in the observations, this difference based on the T-test is statistically significant ( $p = 6.2 \times 10^{-4}$ ). It should be noted that the p-value is probably underestimated, because measurements recorded closely in time are possibly correlated. However, a detailed analysis of this effect on the p-value is beyond the scope of this paper. ON concentration showed an opposite diurnal trend to ambient temperature, which could indicate volatility of some fraction of ON. Organo-nitrates have been identified as products of photochemical reactions and were isolated in ambient particulate matter (Allen et al., 1994). Organo-nitrates are relatively volatile, and only higher alkyl-nitrates (larger than C-18) were estimated to contribute to the aerosol phase (Nielsen et al., 1998). We do not have information on the chemical composition of ON during this study. The C/N ratio observed in January (11.7) suggests that alkyl-nitrates did not contribute significantly to ON in January. Night-time chemistry may be another explanation for the observed diurnal pattern in ON concentrations. For example, reactions of primary amines with nitrate radicals were shown to form imines in the aerosol phase under night-time conditions (Malloy et al., 2009). Nitrooxy organosulfates were observed in night-time aerosol samples in South-Eastern US (Surratt et al., 2008). It should be also noted that the observed C/N ratio, especially that for the whole study (21.4) does not preclude the possibility that at least some of the ON was composed of



**Fig. 8.** Monthly average diurnal profiles of organic nitrogen, OC, EC, air temperature, and NO<sub>x</sub>. Error bars correspond to one standard deviation.

alkyl-nitrates. While no speciation of the ON was performed in this study, the observed average C/N ratio (21.4) makes it plausible to speculate that if all ON was in the form of organo-nitrates it may be found in the aerosol phase and be semi-volatile in nature. It should be noted that (Nielsen et al., 1998) have observed practically equal day and night concentrations of organo-nitrates during their measurements. However, their measurements were rather limited (only two samples) and of rather long duration (12 h).

Yet another explanation could be an influence of local ON sources, which would cause concentration buildup in the shallow night-time boundary layer with the consequent reduction in concentrations due to increased mixing during the day. A comparison of ON and NO<sub>x</sub> diurnal profiles in January indicates that these two compounds exhibited diurnal patterns vaguely resembling each other. However, the average concentration of NO<sub>x</sub> was only 5% higher during the first half of the day than during the second, which does not follow the 66% difference observed in ON concentrations. The diurnal patterns of OC and EC showed night/day differences similar to those of NO<sub>x</sub>, though with a more pronounced decrease in concentrations around noon. No significant correlation was observed in January between ON and NO<sub>x</sub> or EC (Fig. 3). The differences in diurnal profiles and absence of correlation between ON and these components could suggest that combustion sources did not have a strong impact on ON. However, the OC and EC showed a significant correlation (correlation coefficient 0.87); OC and EC also correlated with NO<sub>x</sub>, though with lower correlation coefficients (0.36 and 0.61 respectively). This suggests a link between OC and combustion sources in January. Indeed, OC concentrations at the site of the measurements were shown

to be controlled by primary combustion sources in cool periods of the year (Geron, 2009). ON and OC showed a weak (correlation coefficient 0.36), but significant correlation in January. This leaves the possibility that at least some of ON had combustion origin. For example, biomass burning aerosol were shown to contain heterocyclic nitrogen compounds have been observed in (Mace et al., 2003).

In June however, the ON concentration generally followed the diurnal pattern of OC, increasing during the afternoon and then decreasing during the night and early morning. The average ON concentration in June between midnight and noon was  $0.16 \mu\text{g m}^{-3}$  and  $0.18 \mu\text{g m}^{-3}$  between noon and midnight, demonstrating a 14% increase in the second half of the day. OC showed a similar increase of 16% from  $3.67 \mu\text{g m}^{-3}$  in the first half of the day to  $4.26 \mu\text{g m}^{-3}$  in the second. This suggests that the ON and OC concentrations in June were influenced by photochemical activity. It should be noted that the diurnal pattern of OC and EC observed during this month may not be typical for summertime OC at the site of measurements (Geron, 2009). The diurnal patterns of EC and NO<sub>x</sub> in June showed an opposite trend to that of OC and ON: EC demonstrated a 24% decrease, while NO<sub>x</sub>–53% decrease.

All of these observations indicate that a variety of sources and processes influence ON concentration and stress the importance of chemical speciation of this aerosol fraction for understanding its origin and transformations in the atmosphere.

#### 4 Conclusions

We have developed and deployed a novel instrument for automatic measurements of bulk organic nitrogen concentration in PM<sub>2.5</sub> aerosol with 30 min time resolution. Measurements at the Duke Forest Research Facility near Chapel Hill, NC, during January and June 2007 demonstrated that at this site organic nitrogen comprises a significant fraction (33% on average) of the total nitrogen in PM<sub>2.5</sub>.

ON concentrations were slightly higher in June ( $0.17 \mu\text{g m}^{-3}$ ) than in January ( $0.15 \mu\text{g m}^{-3}$ ). The contribution of ON to the total PM<sub>2.5</sub> nitrogen budget was fairly constant, 33% on average. An analysis of back-trajectories and the wind direction dependence of organic nitrogen concentration showed that higher ON concentrations tend to occur in air masses originating over continental U.S. Inter-correlations between ON and other parameters measured in the study, as well as the diurnal variability of ON, suggest that ON has a variety of sources, which are very difficult to quantify using the information that was obtained in this study. Chemical speciation of ON aerosol would be highly beneficial to better understand the sources and properties of this important aerosol fraction.

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