Organic nitrogen in PM$_{2.5}$ aerosol at a forest site in the Southeast US

M. Lin$^1$, J. Walker$^2$, C. Geron$^2$, and A. Khlystov$^1$

$^1$Department of Civil and Environmental Engineering, Duke University, Box 90287, Durham, NC 27708, USA
$^2$National Risk Management Research Laboratory, US Environmental Protection Agency, Research Triangle Park, NC, 27711, USA

Received: 31 July 2009 – Accepted: 4 August 2009 – Published: 14 August 2009

Correspondence to: A. Khlystov (andrey@duke.edu)

Published by Copernicus Publications on behalf of the European Geosciences Union.
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$_{2.5}$ 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 $\sim 0.1 \mu g \text{ m}^{-3}$.

Nitrogen in organic compounds contributed $\sim 33\%$ on average to the total nitrogen concentration in PM$_{2.5}$, illustrating the importance of this aerosol component. Absolute concentrations of ON, however, were relatively low ($< 1.0 \mu g \text{ m}^{-3}$) with an average of $0.18 \mu g \text{ m}^{-3}$. 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 higher concentrations of ON in continental air than in marine air masses and indicate a variety of potential sources.

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 (Fenn et al.,...
1998; Moss, 1988; Smith et al., 1998). Ambient PM$_{2.5}$ aerosol (i.e. particles smaller than 2.5 µm 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., NH$_4^+$ and NO$_3^-$) (Garstang et al., 1998; Morselli et al., 2008; Rojas and Venegas, 2009; Yeatman et al., 2001). However, there is growing evidence that ON can constitute a significant fraction of total nitrogen (inorganic + organic) in ambient aerosol (Duan et al., 2009; Mace et al., 2003; Zhang et al., 2002).

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 et al., 2002). Other measurements at various marine and continental sites have also shown 20–90% of nitrogen deposition is organic (Cornell et al., 2001, 1995; Mopper and Zika, 1987; Nicholls and Cox, 1978; Timperley et al., 1985). Measurements of ON in fog water have shown that organics contribute 16% of the total nitrogen (Zhang et al., 2002).

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. A few studies have reported ON concentrations measured directly in aerosol particles. Water-soluble organic nitrogen in PM$_{2.5}$ 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$_{2.5}$ 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 can originate from 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\(_x\) conditions has been shown to produce nitroxypolyols in the aerosol phase (Sato, 2008). It should be noted that ON itself exhibits photochemical activity, thus acting as a reservoir of reactive nitrogen in the atmosphere (Zhang et al., 2002). Biological particulate includes directly emitted soil, vegetation and skin fragments, pollen, bacteria, etc. (Jaenicke, 2005; Neff et al., 2002) and exists in the atmosphere at sizes ranging from nanometers to millimeters.

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\(_{2.5}\) 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\(_{2.5}\) and to elucidate its temporal variability and potential sources.
2 Experimental

2.1 Measurement site and time period

The measurements were performed at the Blackwood Division of Duke Forest's Free Atmosphere Carbon Transfer Scheme (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 L min\(^{-1}\) 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 L min\(^{-1}\) 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 L min\(^{-1}\) through a Teflon-coated PM\(_{2.5}\) cyclone (URG Co.). The air then passed through a denuder which collects water-soluble gases to avoid positive artifact in aerosol measurements. In the beginning of the study (January 2007), three dry multichannel denuders (activated carbon, Na\(_2\)CO\(_3\)-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 µg m\(^{-3}\) 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$^{-3}$ is 99%, thus practically all aerosol is sampled. The SJAC produces approximately 0.1–0.2 mL min$^{-1}$ 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$^{-1}$ 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 used to protect the ICs from suspended insoluble particles. The ICs measured Li$^+$, Na$^+$, NH$_4^+$, K$^+$, F$^-$, Cl$^-$, NO$_3^-$, SO$_4^{2-}$, 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 total carbon and nitrogen content of the sample. Because carbon in the aqueous sample from the SJAC is dominated by dissolved CO$_2$, inorganic carbon (carbonates) was removed by the instrument sparging process and therefore not measured. 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 ultrapure air. The combustion gases pass through an electrical dehumidifier for cooling and dehydration, then through a halogen scrubber before being measured by a NDIR de-
tector 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. 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.

The amount of organic nitrogen was determined by subtracting the inorganic nitrogen concentration (N-NH$_4^+$, and N-NO$_3^-$ 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.

2.3 Supplemental measurements

Organic and elemental carbon in PM$_{2.5}$ (OC and EC respectively) were quantified using an automated semi-continuous thermal-optical analyzer (Sunset Laboratory, Beaverton, OR, USA) described in detail by (Geron, 2009). Ambient air was drawn at 8 L min$^{-1}$ through a 2.5 µm aerodynamic diameter cut point cyclone (BGI, Inc., Waltham, Massachusetts, USA) located 3–5 m above the pine canopy. The Sunset instrument sampled through a parallel-plate carbon impregnated fiber denuder (Sunset Laboratory, Beaverton, OR, USA) 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$_x$ 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$^{-1}$. The analyzer was calibrated monthly by mass flow controlled dilution of a certified NO standard (Airgas National Welders, Raleigh, NC). Data were recorded at 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, which was the range expected during ambient measurements. To achieve a uniform instrument performance throughout the campaign, a grand-average of all calibrations was used. 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 (NH₄)₂SO₄ (a major ambient aerosol component); the instruments agreed within 3% (Fig. 2).

Total instrument blanks were measured once every month. Blanks were measured by installing a HEPA filter 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 blanks were 0.17 µg m⁻³, 0.31 µg m⁻³, and 5.82 µg 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 µg m⁻³.

Accuracy of the concentration measured in air was estimated based on the propagation of error from the individual measurements (accuracy of chemical analytical determination of the analyte and Li⁺, and accuracy of the air flow rate). The uncertainty is estimated to be 10% for SO₄²⁻, 16% for IN, 25% for TN, 21.5% for TC, and 22% for ON. The limit of detection (LOD), defined as two times the standard deviation of blanks, are: 0.14 µg m⁻³ for ON, 0.8 µg m⁻³ for TC, and 0.1 µg m⁻³ for the inorganic components.

The TN and inorganic data were averaged to one hour intervals to simplify data evaluation. The OC and EC have measurement intervals of three hours. The data were then corrected for blanks. The consistency of the data was checked by observing the
NH$_4^+$/SO$_4^{2-}$ molar ratio. Because the main ionic components were NH$_4^+$ and SO$_4^{2-}$, values of the molar ratio outside the 1:1 to 2:1 range (with 20% margin of error) indicate that either the NH$_4^+$ or SO$_4^{2-}$ measurements were questionable. We have excluded such points from the analysis, because accuracy of the NH$_4^+$ measurements is critical for determining the ON concentration. This procedure excluded approximately 20% of the total number of observations. Further, only periods that contain both organic 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

The average concentrations of ON, NH$_4^+$, NO$_3^-$, SO$_4^{2-}$, EC, OC 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 1.3 times higher. The main inorganic components were NH$_4^+$, and SO$_4^{2-}$. The molar ratio of these species was fairly constant, 1.84 in January and 1.81 in June, which is within the range of previous measurements for this area (Sparks et al., 2008; Tolocka et al., 2001). The molar ratios indicate that the inorganic aerosol was composed mostly of a mixture of ammonium sulfate and ammonium bisulfate. Practically no aerosol NO$_3^-$ 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. Ammonium nitrate is semi-volatile and partitions to the gas phases at higher temperatures (Dawson et al., 2007). Concentrations of the inorganic aerosol components observed during this study are in general agreement with
other studies reported for this area, though slightly lower, which could be attributed to year-to-year variations (Sparks et al., 2008; Tolocka et al., 2001).

The average concentration of ON during the study was 0.18 µg m⁻³ and the contribution of ON to total PM₂.₅ nitrogen was fairly constant, 33% on average, with slightly higher values in January (37% in January and 30% in June). Though the absolute concentration of ON was relatively low, its relative contribution to total nitrogen in PM₂.₅ was significant. Our observations are similar to other studies, which generally report a 20–30% contribution of ON to the total nitrogen budget of PM₂.₅ (Duan et al., 2009; Mace et al., 2003; Zhang et al., 2002).

The average atomic C/N ratio, calculated as the robust mean of C/N ratios for each 3-h period when both ON and OC data are available, was 19.4. The C/N ratio exhibited a seasonal trend: it was 15.0 in January, 22.5 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) were reported to be a major fraction of organic compounds in ambient aerosol (Kiss et al., 2003; Krivacsy et al., 2000; Samburova et al., 2005). It should be noted that 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 still remarkable. 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; Cornell et al., 2003; Mace et al., 2003; Neff et al., 2002; Zhang et al., 2002). Knowledge of the contributions of these compounds to ON aerosol is highly desirable for understanding the origin and properties of ON.
3.2 Wind direction dependence

Figure 3 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°–270°) sector. However, OC concentrations are relatively higher in the 120°–200° sector, than those of ON. This indicates that these two components may have both similar and different sources. 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 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.

While 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. A low pressure area passed over North Carolina, causing about 1 inch of precipitation on June 3 and a consequent decrease in aerosol concentrations. Figure 4 shows the time evolution of aerosol composition, ambient air pressure, wind direction and precipitation during that week. After precipitation ended, the wind direction changed from N to W-SW, and the concentrations of all of the main aerosol components, including ON, started to increase. At the end of 6 June the wind switched to S-SE, the inorganic components continued to increase in concentration, but the concentration of ON decreased. The difference in the origin of air masses during different stages of this episode is clearly seen in the back-trajectories (Fig. 5).

The trajectory from 5 June originates over an area of the Midwest that is heavily influenced by animal production, which suggests that the concentrations of ON on 5 June may have been influenced by primary emissions from animal manure such as urea and aliphatic amines. After the rain on 6 June and the wind shift to SE, ON concentration followed that of OC (which also lags relative to the immediate increase
of sulfate concentration). Their ratios change dramatically, which may be an indication of a predominance of secondary compounds under this regime. 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. It also demonstrates the power of highly resolved measurements that can capture such transient phenomena and help locate potential sources of ON.

3.3 Diurnal variability

Figure 6 shows the diurnal variability of ON concentration, temperature, OC, EC, and NOx concentrations observed during January and June 2007. In January ON concentrations were relatively high during the night, while low concentrations were observed in the afternoon. ON concentration anti-correlated with 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). While no speciation of the ON was performed in this study, the observed average C/N ratio (19.4) 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).

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).

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 conse-
quent reduction in concentrations due to increased mixing during the day. A comparison of ON and NO$_x$ diurnal profiles in January indicates that these two compounds exhibited diurnal patterns vaguely resembling each other. Similarly to ON, the diurnal patterns of OC and EC showed higher concentrations during the night and lower during the day. Both NO$_x$ and EC are combustion related pollutants and thus suggests the linkage of ON with combustion. The similarity of ON and EC diurnal profiles in January suggests that biomass burning may have a contribution to ON. Heterocyclic nitrogen compounds have been observed in biomass burning aerosols (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. It should be noted that the diurnal pattern of OC 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$_x$ in June showed an opposite trend. This indicates that the ON concentration in June was significantly influenced by photochemical activity. The weekday/weekend difference in July was opposite to that in January, with all the components having higher concentrations during weekdays than during the weekend. ON had the biggest difference, being about 2 times higher during weekdays.

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.

4 Conclusions

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

The ON concentrations in winter and summer were virtually identical and were, on
average, 0.18 µg m\(^{-3}\). In January, the concentration of ON tended to be higher during the night and early morning, following to some extent the trend of combustion-related pollutants, such as NO\(_x\) and EC, which suggests the influence of the combustion sources. In June, ON tended to be higher during the late afternoon and in the evening, following the trend of OC, which suggests it was influenced by photochemical activity. An analysis of back-trajectories and the wind direction dependence of organic nitrogen concentration also indicates a variety of sources of ON.

Our analysis, however, is limited to one site and only to the total organic nitrogen concentration. Chemical speciation would be highly beneficial to better understand the sources and properties of organic nitrogen in ambient aerosol.

**Acknowledgements.** This research was funded by the US Environmental Protection Agency, National Risk Management Research Laboratory, Research Triangle Park, NC. Mention of trade names does not constitute endorsement or recommendation of a commercial product by US EPA or the US Department of Agriculture. The Duke FACE site is supported by the Office of Science (BER), US Department of Energy, Grant No. DE-FG02-95ER62083. We are grateful to Yilin Ma for her contribution to the development of the ON instrument.

**References**


Samburova, V., Szidat, S., Hueglin, C., Fisseha, R., Baltensperger, U., Zenobi, R., and


Organic nitrogen in PM$_{2.5}$ aerosol

M. Lin et al.
Table 1. Average concentrations of the main aerosol components observed during the study, their range and standard deviation.

<table>
<thead>
<tr>
<th>Compound</th>
<th>January</th>
<th>June</th>
<th>All</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>mean</td>
<td></td>
<td></td>
</tr>
<tr>
<td>ON</td>
<td>0.19</td>
<td>0.17</td>
<td>0.18</td>
</tr>
<tr>
<td></td>
<td>STD</td>
<td>0.17</td>
<td>0.14</td>
</tr>
<tr>
<td></td>
<td>min</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>max</td>
<td>1.04</td>
<td>1.10</td>
</tr>
<tr>
<td>NH$_4^+$</td>
<td>0.41</td>
<td>0.52</td>
<td>0.47</td>
</tr>
<tr>
<td></td>
<td>STD</td>
<td>0.20</td>
<td>0.33</td>
</tr>
<tr>
<td></td>
<td>min</td>
<td>0.01</td>
<td>0.05</td>
</tr>
<tr>
<td></td>
<td>max</td>
<td>1.27</td>
<td>1.64</td>
</tr>
<tr>
<td>NO$_3^-$</td>
<td>0.01</td>
<td>0.01</td>
<td>0.01</td>
</tr>
<tr>
<td></td>
<td>STD</td>
<td>0.05</td>
<td>0.02</td>
</tr>
<tr>
<td></td>
<td>min</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>max</td>
<td>0.41</td>
<td>0.50</td>
</tr>
<tr>
<td>SO$_4^{2-}$</td>
<td>1.19</td>
<td>1.53</td>
<td>1.37</td>
</tr>
<tr>
<td></td>
<td>STD</td>
<td>0.62</td>
<td>0.81</td>
</tr>
<tr>
<td></td>
<td>min</td>
<td>0.10</td>
<td>0.08</td>
</tr>
<tr>
<td></td>
<td>max</td>
<td>5.22</td>
<td>8.00</td>
</tr>
<tr>
<td>EC</td>
<td>0.19</td>
<td>0.28</td>
<td>0.23</td>
</tr>
<tr>
<td></td>
<td>STD</td>
<td>0.10</td>
<td>0.15</td>
</tr>
<tr>
<td></td>
<td>min</td>
<td>0.02</td>
<td>0.03</td>
</tr>
<tr>
<td></td>
<td>max</td>
<td>0.67</td>
<td>1.00</td>
</tr>
<tr>
<td>OC</td>
<td>1.44</td>
<td>3.78</td>
<td>2.61</td>
</tr>
<tr>
<td></td>
<td>STD</td>
<td>0.77</td>
<td>1.66</td>
</tr>
<tr>
<td></td>
<td>min</td>
<td>0.34</td>
<td>0.50</td>
</tr>
<tr>
<td></td>
<td>max</td>
<td>4.18</td>
<td>8.74</td>
</tr>
</tbody>
</table>
Fig. 1. A general sketch of the instrument setup.
Fig. 2. Inter-comparison of nitrogen content measurements with ICs and TOC/TN using (NH$_4$)$_2$SO$_4$ standards.
Fig. 3. Wind direction dependence of ON, OC, EC, NH$_4^+$, SO$_4^{2-}$ concentrations. Wind rose graphs show mean values; box-and-whisker plot 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).
Fig. 4. Aerosol composition, ambient pressure and wind direction during a passage of low pressure area during a week in June 2007.
Fig. 5. Back-trajectories obtained with NOAA HYSPLIT model for the first week of June 2007. The dates at the beginning of the trajectory indicate the arrival date at the site of the measurements. The trajectories were calculated for the arrival at 12 p.m. local time.
**Fig. 6.** Diurnal patterns of organic nitrogen, temperature, and NO\(_x\) observed during the three months of the study. The error bars correspond to one standard deviation.