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Monitoring of inorganic ions, carbonaceous matter and mass in ambient aerosol particles with online and offline methods

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Abstract

Year-long high timeresolution measurements of major chemical components in atmospheric sub-micrometer particles were conducted at an urban background station in Finland 2006–2007. Ions were analyzed using a particle-into-liquid sampler combined with an ion chromatograph (PILS-IC), organic and elemental carbon (OC and EC) by using a semicontinuous OC/EC aerosol carbon analyzer (RT-OCEC), and PM_{2.5} mass with a tapered element oscillating microbalance (TEOM). Long time series provides information on differences between the used measurement techniques as well as information about the diurnal and seasonal changes. Chemical mass closure was constructed by comparing the identified aerosol mass with the measured PM_{2.5}. The sum of all components measured online (ions, particulate organic matter (POM), EC) represented only 65 % of the total PM_{2.5} mass. The difference can be explained by the difference in cutoff sizes (PM₁ for online measurements, PM_{2.5} for total mass) and by evaporation of the semivolatile/volatile components. In general, some differences in results were observed when the results of the continuous/semitcontinuous instruments were compared with those of the conventional filter samplings. For non-volatile compounds, like sulfate and potassium, correlation between the filter samples and the PILS was good but greater differences were observed for the semivolatile compounds like nitrate and ammonium. For OC the results of the RT-OCEC were on average 10 % larger than those of the filters. When compared to filter measurements, high resolution measurements provide important data on short pollution plumes as well as on diurnal changes. Clear seasonal and diurnal cycles were observed for nitrate and EC.

1 Introduction

Atmospheric aerosol particles have an effect on a great variety of atmospheric and environmental processes. Particles decrease visibility, change cloud properties, scatter solar radiation (Seinfeld and Pandis, 1998) and they have a yet undefined effect on human health (Brunekreef and Holgate, 2002; Pope and Dockery, 2006). All these effects

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2 Experimental

2.1 Measurement site

All the measurements were conducted in Helsinki at the SMEAR III station ($60^{\circ}12'N$, $24^{\circ}58'E$, 26 m above sea level). The SMEAR III station was built for continuous long-term measurements of basic meteorology, turbulent exchange and chemical and physical properties of atmospheric aerosol particles and gaseous pollutants at an urban background area (Järvi et al., 2009). Helsinki, the capital of Finland, is situated on a fairly flat coastal area by the Baltic Sea. Helsinki together with the neighboring cities of Espoo, Kauniainen and Vantaa forms the Helsinki metropolitan area with more than a million inhabitants. The SMEAR III is located at the Kumpula campus area about five kilometers from Helsinki City centre, next to the University of Helsinki and Finnish Meteorological Institute buildings. Close to the station there is a busy street on the eastern side and a small forested area on the western side. In Finland, the particulate matter concentrations are typically much lower than in Central Europe (Sillanpää et al., 2005), but long-range transported pollution or biomass burning emissions from wild fires elevate concentrations occasionally (Karppinen et al., 2004; Niemi et al., 2004). Based on recent studies, the main local sources of fine particles at SMEAR III are traffic, wood combustion (for residential heating in winter) and secondary aerosol formation (Saarikoski et al., 2008; Timonen et al., 2008; Järvi et al., 2009; Saarnio et al., 2010).

Local meteorological data was obtained from the Finnish Meteorological Institute weather station (Vaisala, Milos 500), situated next to the SMEAR III station. Temperature was measured using Pt100 (Pentronic Ab) sensor, relative humidity with HMP45D (Vaisala Oyj) sensor, and global radiation with CM11 (Kipp & Zonen) sensor.

2.2 Filter samples and chemical analyses

PM_1 filter samples were collected from 9 February 2006 to 28 February 2007 using a filter cassette system. Two pre-fired (12 h, $500^{\circ}C$) quartz fiber filters (Whatman

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2.3 Online methods

Particle-into-liquid sampler combined with two Dionex ICS-2000 ion chromatographs (Dionex, Sunnyvale, USA) was used to collect ambient aerosol samples and to analyze the concentrations of major ions online from 9 February 2006 to 28 February 2007.

- 5 PILS-IC was not measuring from 28 November 2006 to 26 January 2007 due to technical problems. A virtual impactor (VI; Loo and Cork, 1988) with a cut-off size of $1.3\text{ }\mu\text{m}$ was used to remove coarse particles prior to the PILS. Gaseous compounds (ammonia and acidic gases) were removed prior to the PILS with three annular denuders, one coated with phosphoric acid (H_3PO_4 3 %) and two with potassium hydroxide (KOH 1 %).
- 10 The denuders were changed every second week to ensure that all gaseous compounds were effectively removed. The operation principle of the PILS is described in detail in Orsini et al. (2003). Shortly, aerosol and water steam is simultaneously fed to the PILS, where particles grow as they move across a conical shape cavity. On the other end of the cavity the particles are impacted to a quartz glass impaction surface. The surface is rinsed with water (Milli-Q, Millipore Gradient A10) containing a known concentration of lithium fluoride (LiF) as an internal standard. During the campaign the impaction surface was regularly cleaned to remove water-insoluble particles (mainly soot) from the impaction surface. An 8-channel peristaltic pump (Watson Marlow, 205S, USA) was used to maintain the liquid flows (1.25 ml min^{-1} water for steamer, 0.25 ml min^{-1} LiF solution) and to deliver the sample from the debubbler to the ion chromatographs (0.1 ml min^{-1} for each instrument). The liquid from the PILS was directly fed to the loops of two Dionex ICS-2000 ion chromatographs (Dionex, Sunnyvale, USA). Due to short sample collection times (15 min) in PILS-IC system, larger $1000\text{ }\mu\text{l}$ loops were used to collect representative samples for subsequent IC analyzes.
- 20
- 25 With the PILS-IC system the concentrations of Cl^- , NO_3^- , SO_4^{2-} , Na^+ , NH_4^+ , K^+ , oxalate and methane sulphonate (MSA) could be determined with 15 min timeresolution. The quantification limit for the ions was 2.5 ng ml^{-1} , which equals to the air concentration of $0.05\text{ }\mu\text{g m}^{-3}$. The uncertainty of the PILS results was estimated to be 15 % for all analyzed ions.

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OC and EC results was estimated to be 20 %.

Tapered Element Oscillating Microbalance (TEOM[©] 1400a, Patashnick and Rupprecht, 1991; Allen et al., 1997) was used to continuously measure the PM_{2.5} mass concentration. The TEOM was equipped with a Filter Dynamics Measurement System (FDMS). In the FDMS, for the first six minutes the flow is directed through the Sample Equilibration System (SES) dryer to TEOM and the nonvolatile mass is measured. For the next six minutes the flow goes through a filter, where all the particles are removed, and the mass volatilized from the collection filter is measured. The mass evaporated from the filter is added to nonvolatile mass to achieve a real PM_{2.5} concentration. A virtual impactor (VI, Loo and Cork, 1988) was used prior to the TEOM to cut off large particles ($D_p > 2.5 \mu\text{m}$). The uncertainty of the TEOM results was estimated to be 10 %.

A single-wavelength aethalometer (model AE-42, Magee Scientific; Hansen et al., 1984) using the wavelength of 880 nm was used to measure the black carbon concentrations. Time-resolution of the measurements was 5 min and the flow rate was 51 min⁻¹. A cyclone was used to remove particles larger than 2.5 μm in aerodynamic diameter. Black carbon equivalent mass concentrations were calculated from the absorption measurements of the aethalometer using a mass absorption efficiency of 16.6 m² g⁻¹. The uncertainty of the results was estimated to be 10 %.

2.4 Comparison between online instruments and filter sampling

The results of semicontinuous/continuous measurements (RT-OCEC, PILS-IC, TEOM and aethalometer) were compared against those obtained from the PM₁ filter measurements. Resulting ratios of PM₁ filter to online collection (r; Pearson correlation) have been collected to Table 1. Sampling time for the PM₁ filters was approximately 24 h during weekdays and 72 h in weekends and therefore the results of the RT-OCEC, PILS-IC and TEOM were averaged to corresponding time periods. Optical EC from RT-OCEC was compared with BC measured with the aethalometer. The measurement period for that comparison was three hours: the timeresolution of RT-OCEC . The results from the comparisons are discussed below.

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3 Results and discussion

3.1 General features of the measurement period

The concentrations of the main chemical components (ions, OC and EC) in aerosol particles, were measured with various online methods (RT-OCEC, PILS-IC, TEOM and aethalometer) at the urban background station for 13 months (9 February 2006–28 February 2007). The TEOM had been operated at SMEAR III since October 2004, but the RT-OCEC measurements did not start before June 2006. Due to technical problems, some of the instruments did not run all the time. Online instruments, their measurement periods and cut off sizes, and the average and maximum values for each measured component are given in Table 2. Daily PM₁ filter samples were collected parallel to the online measurements. The concentrations of ions, WSOC, OC and EC were measured from the filters. Measured components/properties, applied analytical methods, and the average and maximum results for the filter samples are presented in Table 3. The results of the backup filters were subtracted from the results of the front filter in order to take into account the gaseous compounds absorbed on the filters. The backup to front filter – ratios for ions were $1.3 \pm 1.8\%$ (ammonium), $3.9 \pm 3.7\%$ (potassium), $4.4 \pm 7.1\%$ (sulfate), $4.3 \pm 5.0\%$ (oxalate) and $42 \pm 33\%$ (nitrate). For WSOC and OC the backup to front filter -ratios were $5.6 \pm 6.4\%$ and $10 \pm 6.6\%$, respectively. All chemical components investigated are discussed separately in the following sections.

3.2 PM concentrations

TEOM 1400a equipped with the FDMS system was used to measure the PM_{2.5} mass concentrations. PM_{2.5} mass used in the calculations is the FDMS PM_{2.5} mass, i.e. it contains both non-volatile mass and the mass of compounds evaporated from the TEOM filter. PM_{2.5} measurements with the TEOM equipped with both the SES and the FDMS systems have been shown to compare very well with other real-time automatic

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analyzers accounting semivolatile matter (Grover et al., 2006; Wilson et al., 2006). During this campaign (9 February 2006–28 February 2007) the $\text{PM}_{2.5}$ mass concentration was on average $13.8 \pm 11.4 \mu\text{g m}^{-3}$ (average \pm standard deviation, Table 2). Maximum $\text{PM}_{2.5}$ concentrations (up to $180 \mu\text{g m}^{-3}$) were observed during two wild fire burning episodes, first in April–May and the second in August 2006. The details of these episodes have been published by Saarikoski et al. (2007) and Saarnio et al. (2010). The ratio between non-volatile mass and $\text{PM}_{2.5}$ was 0.82 ± 0.52 , suggesting that on average 18 % of mass was volatile at the temperature of the TEOM SES (30°C ; in Finland the temperature is for most of the time below 30°C , thus this represents the maximum value for semivolatile matter). The measured $\text{PM}_{2.5}$ mass concentrations were similar to those measured typically in Finland at urban background sites (Mean $\text{PM}_{2.5}$ values in 2001 in urban and urban background sites were 9.6 and $8.2 \mu\text{g m}^{-3}$; Laakso et al., 2003).

The TEOM results were compared to the 24-h filter measurements carried out in parallel at the SMEAR III. For filter measurements the mass was calculated as a sum of all ions, EC and particulate organic matter (POM), which was calculated from the OC concentration ($\text{POM} = 1.6 * \text{OC}$, Turpin et al., 2001; Saarnio et al., 2010). The average mass concentration for PM_1 was $7.8 \pm 6.5 \mu\text{g m}^{-3}$. The ratio between PM_1 (filters) and $\text{PM}_{2.5}$ (TEOM) was 0.62 ± 0.51 . The difference is caused likely by the evaporation of semivolatile compounds from the PM_1 filter and the difference in the cutoff sizes, PM_1 and $\text{PM}_{2.5}$. The ratio between the PM_1 filter and TEOM $\text{PM}_{2.5}$ nonvolatile mass was 0.70 ± 0.26 . The mass between PM_1 and $\text{PM}_{2.5}$ can be evaluated from the MOUDI results. The mass ratios between $\text{PM}_1/\text{PM}_{1.8}$ and $\text{PM}_1/\text{PM}_{3.2}$ in MOUDI were 0.83 ± 0.10 and 0.68 ± 0.15 , indicating that on average 17 % of $\text{PM}_{1.8}$ mass was between PM_1 and $\text{PM}_{1.8}$ and 32 % of $\text{PM}_{3.2}$ mass between PM_1 and $\text{PM}_{3.2}$. Assuming that the mass is equally distributed between $\text{PM}_{1.8}$ and $\text{PM}_{3.2}$, the mass between PM_1 and $\text{PM}_{2.5}$ would be 25 % of $\text{PM}_{2.5}$ mass that is close to the observed difference between PM_1 and $\text{PM}_{2.5}$ (30 %). Some uncertainty to this approach is due to the fact that the collection efficiency curves in the impactor are not step functions, but this is difficult to

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quantify. The real-time mass closure (constructed for the three hour periods) will be discussed in detail later in this paper.

3.3 Results of PM₁ measurements versus PILS results

PILS-IC was used to measure the concentrations of major ions with 15 minutes timeresolution from 9 February 2006 to 28 March 2007. Sulfate was the most abundant ion, with an average concentration of $1.74 \mu\text{g m}^{-3}$ (Table 2). The average concentrations for NO₃⁻, NH₄⁺ and K⁺ were 0.77, 0.85 and $0.10 \mu\text{g m}^{-3}$, respectively. The concentrations of ammonium and sulfate correlated strongly ($r = 0.88$). For sulfate the concentrations were well above the quantification limit and the PILS-IC results agreed well with those from the filter samplings ($r = 0.86$; Table 1; Fig. 1). However, for sulfate the results of the filter samples were on average 18 % higher than the PILS-results. Compared to sulfate, substantially larger differences between the PILS and PM₁ results were observed for nitrate and ammonium. The PILS-IC concentrations for nitrate were systematically larger than those in the filters with no clear seasonal variation (Fig. 1). The largest nitrate concentrations were detected in winter and spring, whereas very low concentrations were measured in summer. Sorooshian et al. (2006) has tested the ability of the PILS to collect nitrate by producing ammonium nitrate and collecting it with the PILS. They found that the PILS measurements are within 4 % of the Differential Mobility Analyzer (DMA) derived mass concentrations for nitrate. Additionally, in some studies, where the nitrate concentrations have been measured simultaneously with the AMS and PILS (e.g. Bae et al., 2007; Timonen et al., 2010), a good correlation between the two instruments has been typically observed, indicating that the PILS-IC can be assumed to measure nitrate acceptably. The difference between the PM₁ filter collections and the PILS-IC measurement for nitrate is likely caused by nitrate evaporating from the filters during the collection and storage (in freezer). Also the large amounts of nitrate observed in the quartz backup filter, indicate that substantial amounts of nitrate evaporates from the front filter during the collection. For nitrate the difference between PILS and PM₁ filter results was on average 41 % which is very close to the amount

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of nitrate observed in the backup filter ($42 \pm 33\%$). That percentage is lower than the value of Pakkanen et al. (2001) who found that 66 % of nitrate was evaporated from Teflon filters (nitrate was analyzed from nylon backup filters) in Helsinki. In this study quartz fiber filters were used, which can be assumed to decrease the evaporation of nitrate due to the thicker and more porous texture compared to the Teflon filter material. The average PM_1 filter to PILS-IC ratio for nitrate had large variation from 0.34 to 1.0 (Fig. 2), suggesting that the percentage of nitrate evaporated from the filter varied possibly due to the chemical composition or meteorological conditions like temperature or humidity. The amount of ammonium that was evaporated from filter had very different time trend from that of nitrate. For ammonium the PM_1 filter to PILS-IC ratio was larger during the cold period and smaller in summer (June–August, Fig. 2). On average PM_1 filters gave slightly smaller concentrations for ammonium than the PILS-IC (Figs. 1 and 2).

The concentrations of potassium and oxalate were very low ($0\text{--}0.1 \mu\text{g m}^{-3}$) for most of the year, being in the PILS-IC measurements above the quantification limit only 20 % and 30 % of time, respectively. Elevated potassium concentrations (up to $0.5 \mu\text{g m}^{-3}$; not shown) were measured only during the two biomass burning episodes: in April–May and August (Saarikoski et al., 2007; Saarnio et al., 2010). For potassium the results of the PILS-IC and PM_1 filters agreed very well ($r = 0.9$; Table 1). For oxalate a good correlation was observed only for concentrations above $0.1 \mu\text{g m}^{-3}$ ($N = 15$). For lower concentrations, the results of the PILS-IC were 2–3 times smaller than the PM_1 filter results. At low concentrations ($0.05\text{--}0.1 \mu\text{g m}^{-3}$), near the compounds' quantification limits, the IC results are highly uncertain and therefore it is not possible to draw any conclusions based on them. For sodium and chloride the concentration in the PILS-IC were for most of the time ($>80\%$) below the quantification limit as can be expected for fine PM fraction.

Results of the PILS have been compared with filter samples only in a few other studies. Typically the filter results for sulfate and ammonium correlate well with the PILS, but for nitrate the agreement is poor (Orsini et al., 2003; Kuokka et al., 2007).

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Ma et al. (2004) have compared the ion concentrations collected by a micro-orifice impactor and by the PILS. They found that the correlations between the concentrations measured by the PILS and the impactor were relatively high, but the concentrations measured with the PILS were lower by $10 \pm 5\%$, $11 \pm 8\%$, and $18 \pm 5\%$ for sulfate, ammonium, and nitrate, respectively. In this study the sulfate measured from the filter was 18 % higher whereas ammonium and nitrate concentrations were 9.1 and 39 % lower, respectively, than those in the PILS results.

Laboratory tests have shown that the collection efficiency of PILS exceeds 97 % for olive oil particles in the size range of 30 nm–10 μm (Orsini et al., 2003). However, the collection efficiency in the PILS depends on the volatility of the compounds since the semivolatile species evaporate in the PILS as a result of latent heat of condensation and convective heating of the sampled air (Sorooshian et al., 2006). The collection efficiency has been shown to be lower for ammonium (88 %) that has been theoretically shown to be the most vulnerable to volatilization (Sorooshian et al., 2006). In addition to the volatilization, other differences in the two methods, PILS and PM_1 filters, are likely causing part of the variation seen in the results of this study. In filter methods, particles stay in the filter material long time after collection. Evaporation of semivolatile compounds from the filter and adsorption of gases on the filter material during the collection can have a large effect on the results (Hering and Cass, 1999; Viana et al., 2006). In the PILS the sample is mixed with supersaturated water-vapour and subsequently impacted to quartz impaction plate within seconds (Orsini et al., 2003).

3.4 Ion balance in PILS and PM_1 filter collections

The equivalent ratio of cations to anions was calculated for the PM_1 filter samples and the PILS results (Fig. 3). For PM_1 the ratio was quite stable being on average 0.9 ± 0.2 . For PILS the ratio was on average 1.05 ± 0.3 being higher in summer (from July to September) than in winter. The maximum cations/anions -ratio (monthly average 1.4) was observed during the biomass burning episode in August (see Saarnio et al., 2010). The amount of excess ammonium was calculated from the ammonium concentration

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by subtracting first the amount of ammonium sulfate (for simplicity all ammonium is assumed to be ammonium sulphate without contribution of ammonium bisulphate. If part of sulphate would be in the form of ammonium bisulphate the amount of excess ammonium would be larger), then ammonium nitrate and at last ammonium chloride.

- 5 It was observed that for most of the time ammonium was in the form of ammonium sulfate and ammonium nitrate. In summer, from June to September, substantial amount of excess ammonium was observed. The reason why the ammonium results from the PILS are larger than the ammonium measured from the filter in summertime is unclear. It is possible that in summer more ammonium and nitrate is evaporated from the filters than in other seasons, but it does not explain the large cations/anions -ratio.
- 10 Another possible explanation would be the breakthrough of gaseous artifacts if the denuders do not properly remove gaseous ammonia. During the campaign the denuders were changed every two weeks, and this cycle should have been seen in the PILS concentrations if the denuder efficiency had decreased during the two week period.
- 15 Temporal high cation/anion -ratios have been observed also in other studies. Weber et al. (2001) observed that the cation/anion ratio seem to be dependent on the particle source. They measured cation/anion -ratios below one for local pollution episodes and cation/anion -ratios up to four for the clean air masses with low ($10 \mu\text{g m}^{-3}$) ambient aerosol concentrations.
- 20 The amount of excess ammonium increased as the temperature increased (Fig. 4). At the same time as the relative amount of ammonium increased the contribution of nitrate to the total mass decreased (Fig. 4). The temperature dependency of nitrate is likely caused by nitrate partition to the gas phase as the temperature increases.

3.5 Online measurements of OC and EC

- 25 The concentrations of OC and EC were measured continuously using a semicontinuous OC/EC aerosol carbon analyzer (Saarikoski et al., 2008). The average concentrations for OC and optical EC were 2.0 ± 2.5 and $0.74 \pm 0.64 \mu\text{g m}^{-3}$ (average \pm stdev) (Table 2). OC correlated with the PM_{2.5} ($r = 0.70$), but no other correlations between

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the chemical components or between the chemical components and the PM_{2.5} were found. Contrary to the ions, for OC the semicontinuous and the filter sampling methods gave quite similar results. The results of the RT-OCEC were on average 10 % larger than those of the filters for OC (Table 1) but the correlation between the RT-OCEC and the filter sampling was good ($R = 0.98$). Similar behavior for OC has been observed also by Sciare et al. (2010). In both methods (RT-OCEC and PM₁ filters collections) particles were collected on filters, but in the RT-OCEC gas-phase components were removed prior to the filter with a parallel plate carbon denuder. In the filter sampling the absorption of gas-phase compounds on filters was taken into account by subtracting the value of the backup filter from the result of the front filter. In addition to the gaseous compounds, part of the semivolatile organic components evaporated from the front filter were subsequently absorbed on the backup filter and considered as the gas-phase components and subtracted from the particulate-phase OC. That can underestimate the amount of particulate-phase OC determined from the filter samples. In the RT-OCEC semivolatile organic components were included in OC since the two filters were used back to back and analyzed simultaneously. One major difference between online and filter measurements was the storage time. The filter samples were stored in freezer from days to weeks prior to their analysis, whereas the online samples were analyzed directly after the collection. The efficiency of the denuder in front of the RT-OCEC can also explain partly the larger concentrations of OC measured with the RT-OCEC than using the filter sampling. An average of the measured denuder break-through value and the blank values ($0.80 \mu\text{g m}^{-3}$) were subtracted from the RT-OC. However, denuder efficiency may change in time or it can depend on the concentrations of gaseous components. The more detailed analyzes of the sources and the behavior of OC during this campaign has been published by Saarikoski et al. (2008).

For optical EC, the RT-OCEC and the filter measurements gave comparable results with a high correlation coefficient ($r = 0.89$; Table 3). The optically measured EC was compared with black carbon (BC) measured with the aethalometer. On average the concentration of EC was only 78 % of that of BC. This difference is partially due to the

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different cut-off sizes for the RT-OCEC and the aethalometer ($1\text{ }\mu\text{m}$ and $2.5\text{ }\mu\text{m}$, respectively) resulting in slightly different size fraction and possibly in different chemical composition of particles measured. Also the wavelength used was different being 660 nm for the RT-OCEC and 880 nm for the aethalometer. The mass absorption efficiency, needed for calculations, was $16.6\text{ m}^2\text{ g}^{-1}$ for the aethalometer whereas the calibration of RT-EC had been performed by the manufacturer. Despite all the differences in measurements, a good correlation ($r = 0.97$) was observed between the RT-OCEC and the aethalometer.

3.6 Real-time mass closure

Real-time mass closure was constructed by comparing the chemical components measured by online methods (PILS-IC and RT-OCEC) with the $\text{PM}_{2.5}$ measured by the TEOM. Only the major ions (sulfate, nitrate and ammonium) were used to construct the mass closure. The RT-OCEC was measured with a timeresolution of three hours and therefore also the data from the PILS-IC and the TEOM were averaged to corresponding periods: 00:00–03:00, 03:00–06:00, 06:00–09:00, 09:00–12:00, 12:00–15:00, 15:00–18:00, 18:00–21:00 and 21:00–24:00 at local time. Excluding the measurements, when one or more of the instruments was not running properly, the total number of data points was 1225. Similar to the filters, a multiplier equal to 1.6 was used to convert the measured organic carbon to particulate organic matter. Figure 5 represents a month long period when the mass closure was reached well. During February 2007, 90 % of the $\text{PM}_{2.5}$ mass was identified by chemical analyses. During the year-long measurements, on average 65 % of $\text{PM}_{2.5}$ was identified by the chemical analyses. The difference between the analyzed and the measured mass was largest when the $\text{PM}_{2.5}$ concentration was low. Especially for the $\text{PM}_{2.5}$ concentrations $< 5\text{ }\mu\text{g m}^{-3}$ degree of the achieved mass closure varied significantly (0.1–1.95). At that concentration level all the instruments were running close to their detection limits giving a high total uncertainty for the mass closure. When the concentrations were over $15\text{ }\mu\text{g m}^{-3}$, the mass closure was not larger than 1.2, but it could still be as low

as 0.22. For the largest concentrations ($>50 \mu\text{g m}^{-3}$) the mass closure was in range 0.85–1.0, however, the number of data points was very limited ($N = 4$).

Chemical composition was investigated further by classifying 3-h measurements to five different classes according to their $\text{PM}_{2.5}$ concentration (0–5, 5–10, 10–20, 20–30, $>30 \mu\text{g m}^{-3}$) (Fig. 6). Going from the $\text{PM}_{2.5}$ concentration below $5 \mu\text{g m}^{-3}$ to the concentration above $30 \mu\text{g m}^{-3}$ clear differences were found in the chemical composition. The contribution of EC was largest at the $\text{PM}_{2.5}$ of $<5 \mu\text{g m}^{-3}$ and it decreased when $\text{PM}_{2.5}$ concentration increased. The contribution of POM was approximately 47 % when the $\text{PM}_{2.5}$ concentration was below $20 \mu\text{g m}^{-3}$, but started to increase when it was above that value. The contribution of POM was clearly largest when the $\text{PM}_{2.5}$ concentration was above $30 \mu\text{g m}^{-3}$, however, all the large $\text{PM}_{2.5}$ concentrations were measured during the biomass smoke episode in August, and therefore the source for all high concentrations was the same or at least similar. For sulfate, ammonium and nitrate the dependence on the concentration level was similar. The contribution of ions was largest at the $\text{PM}_{2.5}$ level of 0–20 $\mu\text{g m}^{-3}$, whereas it was smallest when $\text{PM}_{2.5}$ was larger than $30 \mu\text{g m}^{-3}$.

3.7 Diurnal and seasonal trends

The campaign-averaged diurnal trends for ions, POM and EC are presented in Fig. 7. Since the timeresolution for EC and OC was three hours, also the ion and $\text{PM}_{2.5}$ mass concentrations were averaged to the corresponding time periods. No diurnal variation was found for POM, ammonium and sulfate. Diurnal variation was insignificant also for the semivolatile $\text{PM}_{2.5}$ measured with the TEOM (Fig. 7). Most evident diurnal variation was observed for EC: it gained highest value in the morning at 6–9 and the lowest in the night at 3–6 (Fig. 7). Of the ions only nitrate had a diurnal trend with a peak concentration in the morning between 6 and 9. Similar behavior for nitrate has been observed by Hennigan et al. (2008) and Poulain et al. (2011). Figure 8 represents the average diurnal cycles of nitrate (one-hour averages), temperature, global

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with maximum at weekdays during the rush hours, indicates that traffic is likely the major source of EC. However, EC had slightly different diurnal trends in different seasons. In summer and fall the concentrations of EC decreased sharply after the peak at 6–9 a.m. whereas in winter the concentrations stayed at higher level until the night

5 (Fig. 10a) probably because of the more stable boundary layer height during the day. For OC a diurnal trend was only found in summer (Fig. 10b). Similar to nitrate in fall (Fig. 9b) the concentrations of OC in summer had lowest values in the afternoon and early evening due to the efficient mixing of pollutants and transfer of particle-phase OC to gas-phase.

10 Nitrate had clear differences in both concentrations and diurnal cycles during different seasons (Fig. 9b). The peak in nitrate concentration in the morning is most pronounced when the nitrate concentrations are large in winter and spring. The decrease in the afternoon can be clearly seen in fall but in summer the nitrate concentrations have no diurnal changes. For ammonium no seasonal or diurnal trends were detected, however, in summer slightly lower concentrations were observed in the evening
15 (Fig. 9a).

4 Conclusions

High timeresolution measurements of major chemical components in fine particles were conducted at urban background station in Finland from February 2006 to February 2007. Long-term measurements provided important information about differences between results of different online methods (PILS-IC, RT-OCEC, TEOM) and the conventional filter measurements. Temporal changes, such as diurnal cycles and short pollution episodes were detected only with online methods. Volatility of measured compound was observed to have an effect to the results in PILS. The results of the PILS agreed well with the results of the filter measurements for non-volatile species, such as sulfate and potassium. Larger discrepancies were observed for semivolatile nitrate

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and ammonium. Sulfate measured from the filters was 18 % higher than that from the PILS-IC whereas nitrate and ammonium were 9.1 and 41 % lower when compared to the PILS results. Many species, like oxalate, sodium and chloride concentrations were most of the time too low and could not be quantified accurately. Larger potassium and oxalate concentration were observed only during biomass burning episodes as could be expected. For EC and OC a strong correlation was observed between filter (PM_1) and online measurements (RT-OCEC). For OC the concentrations measured with RT-OCEC were on average 10 % higher than the concentrations measured from filter samples.

High timeresolution measurements provided important information about the diurnal trends. Nitrate was observed to peak in early morning, during the rush hours. The peak in nitrate concentration in the morning was most pronounced when the concentrations were large in winter and spring. The decrease in the afternoon could be clearly seen in fall but in summer the nitrate concentrations had no diurnal changes. Also EC had a clear diurnal cycle, with maximum during the morning rush hour. A real time mass closure was constructed by comparing the results from the TEOM with those from the PILS-IC and RT-OCEC. The analyzed compounds (PM_1 ; ions, POM, EC) represented on average 60 % of $PM_{2.5}$ mass. The difference in cutoff sizes (PM_1 and $PM_{2.5}$) explained on average 25 % of the unexplained mass whereas the volatilized mass fraction explained the remaining unexplained mass (18 %).

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Table 1. Comparison between the results of 24-h filter samplings (PM_1) and continuous/semitrue instruments. Ions were measured with the PILS-IC system, OC and EC with the RT-OCEC, and BC with the aethalometer. N represents the number of samples available for the comparison.

Component	Particle size	Filter/online -ratio	N
SO_4^{2-} (PM_1 vs. PILS-IC)	<1 μm	1.18 ± 0.28	214
NO_3^- (PM_1 vs. PILS-IC)	<1 μm	0.59 ± 0.66	187
NH_4^+ (PM_1 vs. PILS-IC)	<1 μm	0.91 ± 0.32	212
OC (PM_1 vs. RT-OCEC)	<1 μm	0.90 ± 0.22	165
EC (PM_1 vs. RT-OCEC)	<1 μm	0.89 ± 0.21	167
EC vs. BC ^b (RT-OCEC vs. Aethalometer)	<1 ^c /2.5 μm^d	0.78 ± 0.33	1127

^a The sum of $\text{PM}_{2.5}$ and the mass volatilized from the TEOM.

^b 3-h average.

^c EC.

^d BC.

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Table 2. Online measurements during the intensive measurement campaign from February 2006 to February 2007.

Component/property	Instrument	Cutoff size (μm)	Measurement period	Average \pm stdev ($\mu\text{g m}^{-3}$)	Maximum ($\mu\text{g m}^{-3}$)
Total mass OC, EC	TEOM RT-OCEC	2.5 1	9.2.2006–28.2.2007 17.6.2006–28.2.2007	13.8 ± 11.4 OC: 2.0 ± 2.5 EC: 0.74 ± 0.64	178.8 OC: 41 EC: 7.1
Major Ions	PILS	1	9.2.2006–28.2.2007 ^a	NH_4^+ : 0.85 ± 0.81 NO_3^- : 0.77 ± 1.0 SO_4^{2-} : 1.7 ± 1.8 K^+ : 0.10 ± 0.07	NH_4^+ : 10 NO_3^- : 15 SO_4^{2-} : 27 K^+ : 2.7
BC	Aethalometer	1	3.7.–27.12.2006	1.0 ± 0.8	5.7

^a Due to technical problems, a break in PILS data from 28 November 2006 to 26 January 2007.

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Table 3. The measured mean and maximum values for each chemical species during the intensive measurement campaign from 9 February 2006 to 28 February 2007.

Component/property		Analytical instrument	Average ($\mu\text{g m}^{-3}$)	\pm stdev	Maximum ($\mu\text{g m}^{-3}$)
PM ₁	OC, EC	Sunset OCEC aerosol carbon analyzer	OC: 2.5 ± 2.7		OC: 16
	WSOC	Shimadzu TOC-V _{CPH}	EC: 0.91 ± 0.71		EC: 7.1
			WSOC: 1.5 ± 1.7		WSOC: 10.65
PM ₁	Major Ions	Dionex ICS-2000	NH ₄ ⁺ : 0.71 ± 0.62		NH ₄ ⁺ : 3.6
			NO ₃ ⁻ : 0.36 ± 0.55		NO ₃ ⁻ : 3.8
			SO ₄ ²⁻ : 1.8 ± 1.4		SO ₄ ²⁻ : 7.4
			K ⁺ : 0.07 ± 0.16		K ⁺ : 2.5
			Oxalate: 0.09 ± 0.09		Oxalate: 0.56
			MSA: 0.03 ± 0.05		MSA: 0.31
PM ₁	Total mass = $1.6 \times \text{OC} + \text{EC} + \text{ions}$	Calculated	7.8	\pm 6.5	30
MOUDI	Total Mass, Ions	Mettler M3 microbalance, Dionex ICS-2000			

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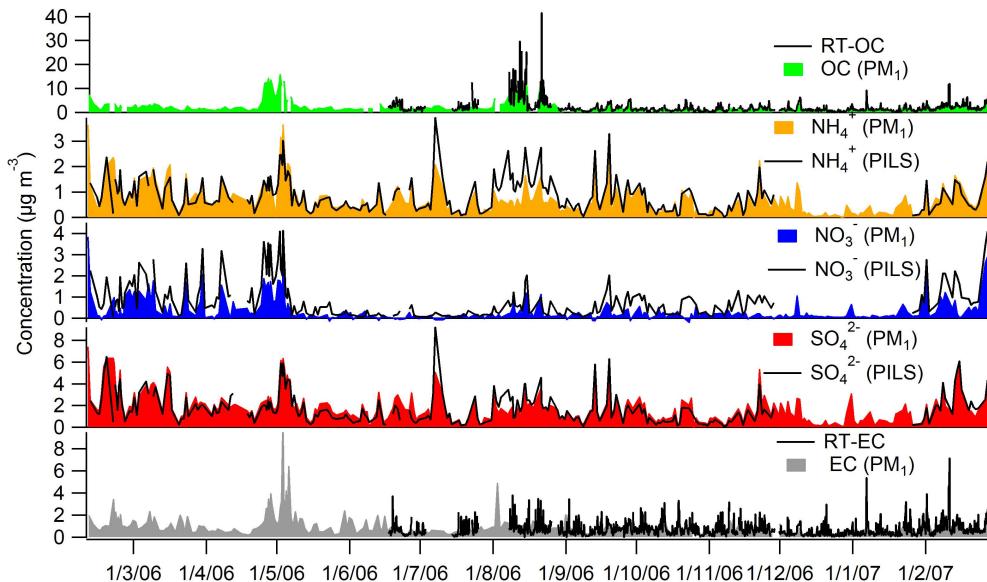


Fig. 1. The comparison between online and PM₁ filter measurements for OC, ammonium, nitrate, sulfate and EC. Sampling time for the PM₁ filters was approximately 24 h during weekdays and 72 h on weekends and the ion results of the online instruments were averaged to corresponding time periods.

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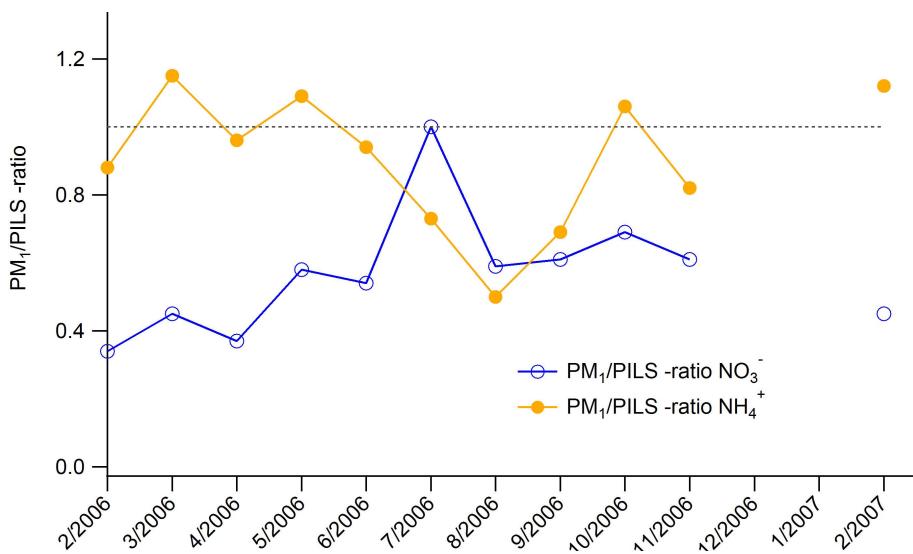


Fig. 2. The monthly average PM₁/PILS -ratios for ammonium and nitrate from 9 February 2006 to 28 February 2007.

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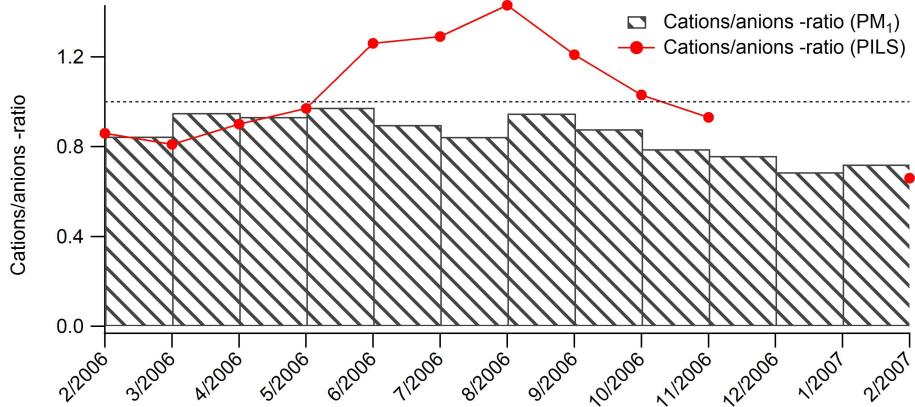


Fig. 3. The monthly average cations/anions -ratios based on the PILS and PM₁ filter measurements.

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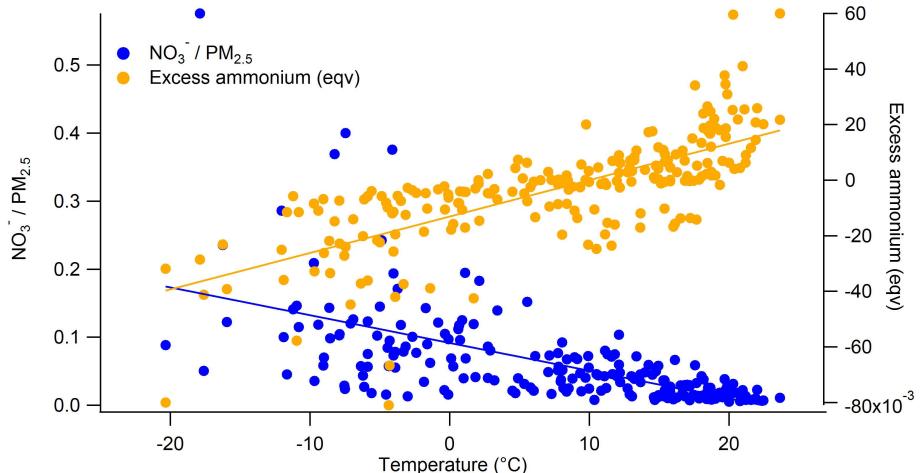


Fig. 4. The nitrate/PM_{2.5} -ratio and amount of excess ammonium (eqv) as a function of temperature.

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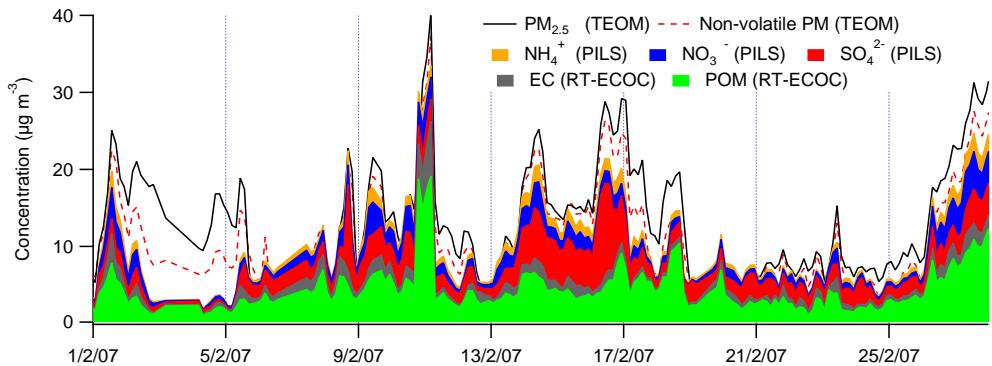


Fig. 5. The timeseries of major ions (sulphate, nitrate and ammonium), particulate organic matter (POM), inorganic carbon and PM_{2.5} and non-volatile PM (TEOM) mass concentration during February 2007.

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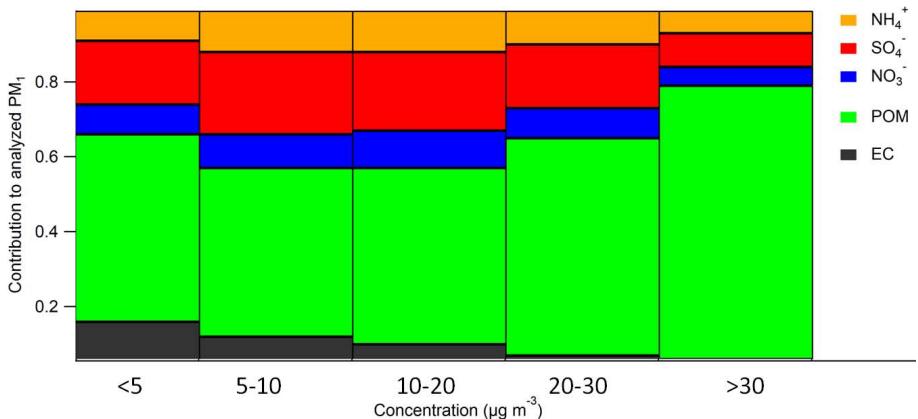


Fig. 6. The relative contribution of ions, POM and EC to analyzed PM₁ at different concentration levels.

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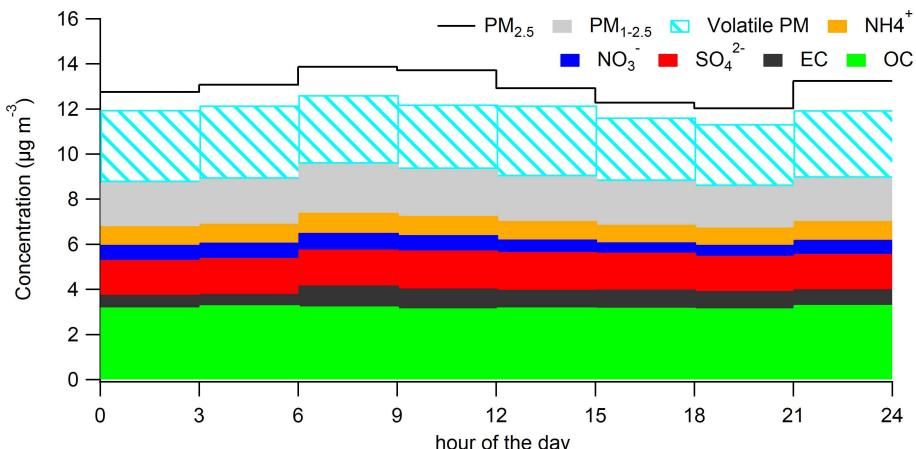


Fig. 7. The measured concentrations for major ions, EC, POM and $\text{PM}_{2.5}$ for three hour averages (0–3, 3–6, 6–9, 9–12, 12–15, 15–18, 18–21, 21–24). The amount of volatile PM is evaluated based on FDMS TEOM results and the mass between PM_1 and $\text{PM}_{2.5}$ is evaluated from simultaneous MOUDI collections.

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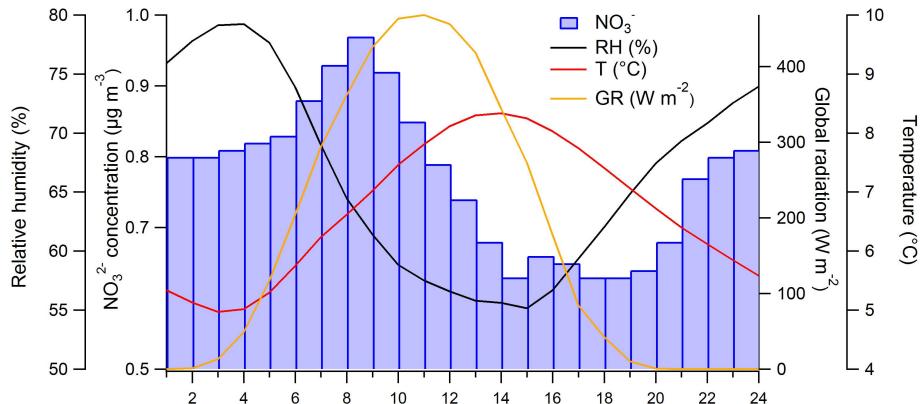


Fig. 8. The hourly-averaged nitrate concentration ($\mu\text{g m}^{-3}$), global radiations (W m^{-2}), relative humidity (%) and temperature for each hour of day from 9 February 2006 to 28 February 2007.

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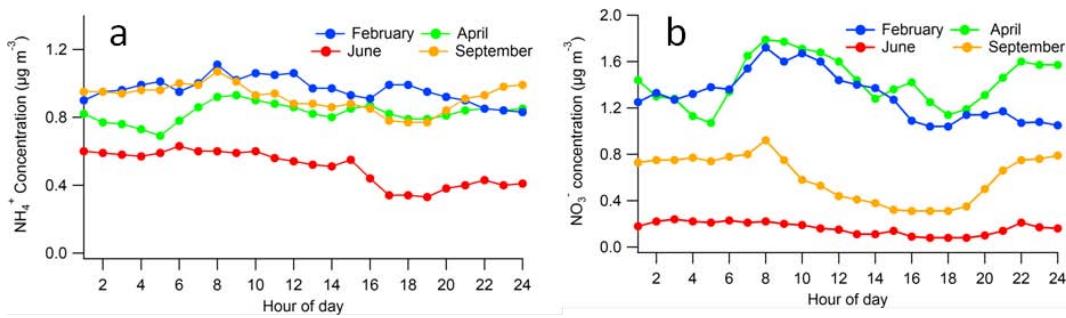


Fig. 9. The average ammonium (a) and nitrate (b) concentrations for each hour of day during the measurement campaign (9 February 2006–28 February 2007).

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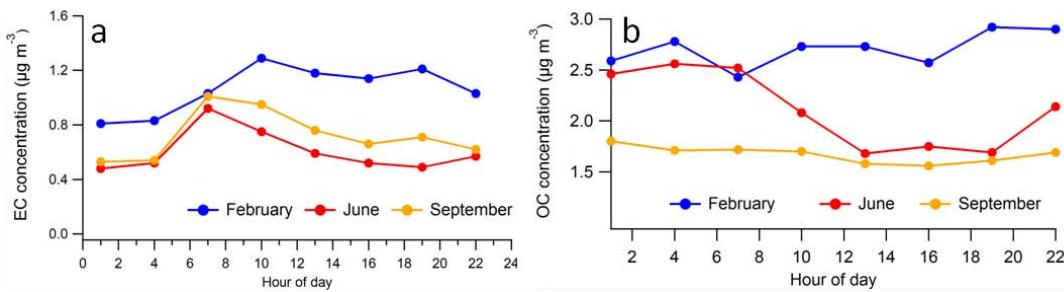


Fig. 10. The average EC (a) and OC (b) and concentrations for eight time periods (three hour averages) of day during the measurement campaign (17 June 2006–28 February 2007).

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