

Seasonal and diurnal changes in inorganic ions, carbonaceous matter and mass in ambient aerosol particles in an urban, background area

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Concentration and composition of the fine particulate matter (PM) was measured using various online methods for 13 months in an urban, background area in Helsinki, Finland. Seasonal differences were found for ions and carbonaceous compounds. Biomass burning was found to increase inorganic ion and elemental carbon (EC) concentrations in winter, whereas organic carbon (OC) contribution was highest during summer due to secondary aerosol formation. Diurnal cycles, with maxima between 06:00 and 09:00, were recorded for EC and nitrate due to traffic emissions. In addition, the concentrations measured with the online and offline PM sampling devices were compared using regression analysis. In general, a good agreement ($r^2 = 0.60\text{--}0.95$) was found. During the year-long measurements, on average 65% of PM_{2.5} was identified by submicron chemical analyses (ions, OC, EC). As compared with filter measurements, the high resolution measurements provided important data on short pollution plumes and diurnal changes.

Introduction

Atmospheric aerosols are produced by several anthropogenic and natural sources. The major constituents of atmospheric aerosol particles are inorganic ions (sulfate, nitrate, and ammonium) and carbonaceous compounds (e.g. Solomon *et al.* 2008 and references therein, Bond *et al.* 2013). Aerosol composition is depending on the source, but it is also affected by the physico-chemical processes like aging in the atmosphere and aerosol removal processes (Jimenez *et al.*

2009). In order to estimate the effects of multi-phase and multi-component aerosol particles on the climate change, human health and ecosystem, concentrations and chemical compositions of aerosol particles should be known (Pope and Dockery 2006, IPCC 2007, Brook *et al.* 2010).

Processes in the atmosphere are rapid and traditional PM-filter collections with long collection times do not provide an adequate picture of the constantly-evolving situation. The new online analyzing methods, such as particle-into-liquid sampler (PILS; Orsini *et al.* 2003), the

aerosol mass spectrometer (AMS; Jayne *et al.* 2000, Allan 2003) or the semi-continuous OC/EC aerosol carbon analyzer (RT-OCEC; Arhami *et al.* 2006) have provided a possibility to study aerosol chemistry and size distribution with high time resolutions. High-time-resolution instruments have also facilitated studies of variety of fast-changing properties like gas/particle partitioning, water solubility and oxygenation state, as well as diurnal changes and sources of ambient aerosol particles (Kondo *et al.* 2007, Hennigan *et al.* 2008, Dunlea *et al.* 2009). The errors and uncertainties in filter collections were extensively studied during the last decades (e.g. Hering and Cass 1999, Pathak and Chan 2005, Viana *et al.* 2006a). Different kinds of sampling artifacts have to be taken into account in online measurements, and due to the short integration times, concentrations to be determined in these online samples are very low and often close to determination limits of the analyzing methods (Parshintsev *et al.* 2009, Timonen *et al.* 2010).

In this study, the chemical composition of ambient fine particulate matter (PM₁) was measured at an urban background station for a year in order to determine PM sources and describe seasonal and diurnal changes of inorganic ions, carbonaceous matter and PM mass (PM_{2.5}) in ambient aerosol particles. In addition, results of the online methods for PM mass and individual compounds were compared with concentrations measured from the traditional filter samples in order to increase the understanding of collection artifacts in both measurements methods.

Material and methods

Measurement site

The SMEAR III station (60°12'N, 24°58'E, 26 m a.s.l.) is situated in an urban, background area approximately 5 km from the Helsinki city center. The SMEAR III station is surrounded by the Kumpula University Campus, small forest area and a road. The aerosol, trace gas and flux measurements have been conducted at the SMEAR III station since it was established in 2004 (Järvi *et al.* 2009). The main local sources of fine particles at SMEAR III are traffic, wood

combustion (residential heating in winter) and secondary aerosol formation (Saarikoski *et al.* 2008, Timonen *et al.* 2008, Järvi *et al.* 2009, Saarnio *et al.* 2010, Saarnio *et al.* 2012). In addition, long-range-transported pollution or biomass-burning emissions from wildfires occasionally elevate PM concentrations (Karppinen *et al.* 2004, Niemi *et al.* 2009). Local meteorological data were obtained from the Finnish Meteorological Institute weather station (Vaisala, Milos 500) situated next to the SMEAR III station.

Online measurements

The Particle-Into-Liquid Sampler (PILS; Table 1) was developed for rapid automated online aerosol collection (Weber *et al.* 2001, Orsini *et al.* 2003). PILS combined with two Dionex ICS-2000 ion chromatographs (Dionex, Sunnyvale, USA) was used to collect aerosol samples directly to the liquid phase and to analyze concentrations of major ions online. A Virtual Impactor (VI; Loo and Cork 1988) with a cut-off size of 1.3 μm was used to remove coarse particles before PILS measurements. Gaseous compounds (ammonia and acidic gases) were removed before PILS measurements with three annular denuders (one coated with 3% phosphoric acid and two with 1% potassium hydroxide). The denuders were changed every second week to ensure that all gaseous compounds were effectively removed. The operation principle of PILS is described in detail in Orsini *et al.* (2003). Briefly, aerosol and water steam is simultaneously fed into PILS, where particles grow as they move across a conical shape cavity. At the other end of the cavity the grown particles impact a quartz-glass surface. The surface is rinsed with water (Milli-Q, Millipore Gradient A10) containing a known concentration of lithium fluoride (LiF) as an internal standard. Liquid from PILS was directly fed into the loops of two Dionex ICS-2000 ion chromatographs (Dionex, Sunnyvale, USA). The 1000 μl loops were used to collect a representative samples for subsequent IC analyzes. With the PILS-IC system the concentrations of Cl⁻, NO₃⁻, SO₄²⁻, Na⁺, NH₄⁺, K⁺, oxalate and methane sulphonate (MSA) could be determined with a 15-min time resolution. The quantification limit for the ions was 2.5 ng ml⁻¹,

which equals the air concentration of $0.05 \mu\text{g m}^{-3}$. The uncertainty of the ion concentrations measured with the PILS-IC system was estimated to be 15% for all analyzed ions.

A semi-continuous OC/EC carbon aerosol analyzer (RT-OCEC, Sunset Laboratory Inc., Oregon, US, Table 1) was used to measure the concentrations of elemental and organic carbon with 3-h time resolution. The sample flow was 9.2 l min^{-1} in order to collect a representative sample for the subsequent thermal analysis. A cyclone was used to cut off particles with aerodynamic diameter $> 1 \mu\text{m}$ and a parallel plate carbon denuder (Sunset Laboratory Inc., OR, US) was used in-line before the instrument to remove organic gases. The method is described in detail by Turpin *et al.* (1990) and Birch and Cary (1996). Briefly, during one measurement cycle the instrument collects a sample for 164 minutes. After the sampling period, the deposited particles are heated in a quartz oven where the elemental and organic carbon concentrations are individually quantified. The vaporized carbon compounds formed in the oven are purged to MnO_2 catalyst where they are further oxidized to carbon dioxide and quantified with a non-dispersive infrared (NDIR) detector. In addition the RT-OCEC measures optical EC with one minute time resolution using the laser light transmission values measured before and after the analysis cycle. A predetermined calibration

factor, based on numerous ambient measurements, is used to convert laser attenuation to EC mass on the filter. Due to the small average concentrations in Helsinki, the measurements of total carbon (TC; Thermal EC + OC) and optical EC were considered more reliable and therefore the "Optical OC" concentrations (Optical OC = TC – optical EC) were used in the comparison. The uncertainty of the measured OC and EC concentrations was estimated to be 20%.

A tapered Element Oscillating Microbalance (TEOM[®] 1400a; Rupprecht and Patashnick (1991); *see* Table 1) equipped with a Filter Dynamics Measurement System (FDMS) was used to continuously measure the $\text{PM}_{2.5}$ mass concentration. In FDMS TEOM, the flow is first directed through the Sample Equilibration System (SES) dryer to TEOM and nonvolatile mass is measured. In the next stage, the flow goes through a filter, where PM is removed, and mass volatilized from the collection filter is measured. The mass evaporated from the filter is added to nonvolatile mass to achieve a real $\text{PM}_{2.5}$ concentration. A Virtual Impactor (VI, Loo and Cork 1988) was used before the TEOM to cut off large particles (aerodynamic diameter $> 2.5 \mu\text{m}$). The uncertainty of the PM concentrations measured with TEOM was estimated to be 10%. All TEOM data shown in this article are FDMS TEOM $\text{PM}_{2.5}$ data, i.e., they are corrected for evaporative losses.

Table 1. Used instruments, measurement periods, cutoff sizes, and mean \pm SD and maximum concentrations of each chemical species (OC, EC, BC, major ions, total PM mass) measured with the online instruments during the intensive measurement campaign. Detailed description of the measurement devices and methods are given in the reference articles.

Component/ instrument	Cutoff size (μm)	Measurement period	Mean \pm SD ($\mu\text{g m}^{-3}$)	Maximum ($\mu\text{g m}^{-3}$)	Reference
Total mass /TEOM	2.5	9 Feb. 2006– 28 Feb. 2007	13.8 ± 11.4	178.8	Patashnick and Rupprecht (1991), Allen <i>et al.</i> (1997)
OC, EC/ RT-OCEC	1	17 Jun. 2006– 28 Feb. 2007	OC: 2.0 ± 2.5 EC: 0.74 ± 0.64	41 7.1	Turpin <i>et al.</i> (1990), Bae <i>et al.</i> (2007), Saarikoski <i>et al.</i> (2008)
Major ions/ PILS-IC	1	9 Feb. 2006– 28 Feb. 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	Weber <i>et al.</i> (2001), Orsini <i>et al.</i> (2003), Sorooshian <i>et al.</i> (2006)
BC/aethalometer	2.5	3 Jul.–27 Dec. 2006	1.0 ± 0.8	5.7	Hansen <i>et al.</i> (1984), Weingartner <i>et al.</i> (2003)

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

A single-wavelength aethalometer (model AE-42, Magee Scientific; *see* Table 1) using the wavelength of 880 nm was used to measure the black-carbon concentrations. Time resolution of the measurements was 5 minutes and the flow rate 5 l 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 data using a mass absorption efficiency of 16.6 m² g⁻¹. The uncertainty of the BC concentrations measured with aethalometer was estimated to be 10%.

PM₁ filter measurements

PM₁ filter samples were collected using a filter cassette system. A Berner low pressure impactor (BLPI stages 8–11; Berner and Lürzer, 1980) was used in-line to remove supermicron particles. The flow rate was adjusted to 80 l min⁻¹. Two pre-fired (12 h, 500 °C) quartz-fiber filters (Whatman Q-MA 47 mm) were placed in series to a filter cassette. A sample was collected to the front filter and the backup filter was used to evaluate the sampling artifacts. The collection times were 24 and 72 hours during weekdays and weekends, respectively. During episodes of elevated particle concentrations, a shorter collection time

(12 hours) was used in order to avoid overloading of the filters. Altogether 297 samples were collected during the year-long campaign. In the PM₁ filter collections, denuders were not used in-line.

A 1-cm² piece was cut from each sample for each analyzing method (Table 2). The organic and elemental carbon (OC and EC) concentrations were determined with the thermal-optical carbon analyzer (TOA; Sunset Laboratory Inc., Oregon, US) using the thermal-optical transmittance method (TOT). The method is described in detail by Saarikoski *et al.* (2007). Water-soluble organic carbon (WSOC) was analyzed using Shimadzu's total-organic carbon analyzer TOC-V_{CPH} (Timonen *et al.* 2008). Main inorganic ions (Cl⁻, NO₃⁻, SO₄²⁻, oxalate, NH₄⁺, K⁺) were analyzed using Dionex DX-500 or ICS-3000 ion chromatography systems (Dionex, Sunnyvale, USA; Teinilä *et al.* 2004, Aurela *et al.* 2011). Concentrations measured for the back-up filters were subtracted from those of the front filters for OC and WSOC by assuming that they were only adsorbed gas-phase components of the sample air (positive artifacts) and the adsorption was equal in the front and back-up filters. For WSOC and OC, the backup-to-front-filter ratios were (mean ± SD) 5.6% ± 6.4% and 10% ± 6.6%, respectively. The backup-to-front-filter ratios for ions were 1.3% ± 1.8% (ammonium), 3.9% ± 3.7% (potassium), 4.4% ± 7.1% (sulfate), 4.3%

Table 2. Mean ± SD and maximum concentrations for each chemical species (OC, EC, WSOC, inorganic ions, mass) measured from PM₁ filter samples during the intensive measurement campaign from 9 Feb. 2006 to 28 Feb. 2007. Detailed description of the measurement devices and methods are given in the reference articles.

Component/ instrument	Mean ± SD (μg m ⁻³)	Maximum (μg m ⁻³)	Reference
OC, EC (Sunset OCEC aerosol carbon analyzer)	OC: 2.5 ± 2.7 EC: 0.91 ± 0.71	OC: 16 EC: 7.1	Turpin <i>et al.</i> (1990), Birch and Cary (1996), Viidanoja <i>et al.</i> (2002)
WSOC (Shimadzu TOC-V _{CPH})	WSOC: 1.5 ± 1.7	10.65	Viana <i>et al.</i> (2006b), Timonen <i>et al.</i> (2008)
Major ions (Dionex ICS-2000)	NH ₄ ⁺ : 0.712 ± 0.632 NO ₃ ⁻ : 0.50 ± 0.58 SO ₄ ²⁻ : 1.88 ± 1.41 K ⁺ : 0.087 ± 0.16 Ox: 0.09 ± 0.09 MSA: 0.03 ± 0.05 Cl ⁻ : 0.01 ± 0.05	NH ₄ ⁺ : 3.96 NO ₃ ⁻ : 3.67 SO ₄ ²⁻ : 6,46 K ⁺ : 2.5 Ox: 0.56 MSA: 0.31 Cl ⁻ : 0.5	Teinilä <i>et al.</i> (2004), Saarikoski <i>et al.</i> (2008), Timonen <i>et al.</i> (2008)
Total mass/calculated = 1.6OC + EC + ions	8.17 ± 6.76	38.53	

$\pm 5.0\%$ (oxalate) and $42\% \pm 33\%$ (nitrate). For ions the backup-to-front-filter ratios were used only to evaluate the magnitude of measurement artifacts in filter collections. 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 ($POM = 1.6 \times OC$; Turpin and Lim 2001, Saarnio *et al.* 2010).

Size-segregated samples were collected with a Micro-Orifice Uniform Deposit Impactor (MOUDI, Marple *et al.* 1991, Timonen *et al.* 2008). Altogether 45 collections were made, approximately one in each week during the campaign. The aerodynamic cut-off diameters of the impactor stages were 0.056, 0.100, 0.18, 0.32, 0.56, 1.00, 1.8, 3.2 and $5.6 \mu\text{m}$. The collection time was typically 72 hours. Gravimetric mass, WSOC and ions were analyzed from the MOUDI samples (Timonen *et al.* 2008)

The ion, carbonaceous compound and PM concentrations of semi-continuous/continuous measurements (RT-OCEC, PILS-IC, TEOM and aethalometer) were compared using regression analysis with those obtained from the PM_{10} filter measurements.

Results and discussion

Comparison between online instruments and filter sampling

Inorganic ions

For main ions, sulfate, nitrate and ammonium

the concentrations were well above the quantification limits and the PILS-IC ion concentrations agreed well with those from the filter samplings ($r^2 = 0.80\text{--}0.87$; Table 3). Sulfate, ammonium and nitrate concentrations were 16%, 14% and 37% lower, respectively, than those measured with PILS. We noted that substantial concentrations of nitrate (front/backup filter ratio 42%) was found from the backup filter in the filter collections.

Ion concentrations measured with PILS-IC were compared with the filter sampling results only in a few other studies. Typically sulfate and ammonium concentrations measured from the filter correlate well with the PILS-IC concentrations, but for nitrate the agreement is poor (Orsini *et al.* 2003, Kuokka *et al.* 2007). Ma *et al.* (2004) compared the ion concentrations measured with a micro-orifice impactor and PILS-IC, and found that the correlation was relatively high, but also the concentrations measured with PILS-IC were lower by $10\% \pm 5\%$, $11\% \pm 8\%$, and $18\% \pm 5\%$ for sulfate, ammonium, and nitrate, respectively. Laboratory tests have shown that the collection efficiency of PILS is good (Orsini *et al.* 2003). However, it has been shown that the collection efficiency depends on volatility of the compounds, since the semi-volatile species evaporate in PILS as a result of latent heat of condensation and convective heating of the sampled air (Sorooshian *et al.* 2006). Sorooshian *et al.* (2006) found that the average collection efficiency for all species from a variety of aerosols exceeded 96% except for ammonium (88%) when compared with simultaneous measurements carried out with a differential

Table 3. Comparisons between ion and carbonaceous matter concentrations of the 24-hour filter samplings (PM_{10}) and the continuous/semi-continuous instruments. Ions were measured with the PILS-IC system, OC and EC with RT-OCEC, and BC with the aethalometer.

Component	Slope	Intercept	r^2	Sample number
SO_4^{2-} (PM_{10} vs. PILS-IC)	0.84	0.45	0.87	214
NO_3^- (PM_{10} vs. PILS-IC)	0.63	0.02	0.80	187
NH_4^+ (PM_{10} vs. PILS-IC)	0.86	0.05	0.82	212
OC (PM_{10} vs. RT-OCEC)	0.77	0.23	0.95	165
EC (PM_{10} vs. RT-OCEC)	0.57	0.27	0.60	167
EC vs. BC (RT-OCEC vs. aethalometer)*	1.31	0.06	0.92	1127

* the cutoffs for EC and BC are PM_{10} and $PM_{2.5}$, respectively. The regression parameters were calculated using 3-h averages.

mobility analyzer (DMA). When compared with other online measurements (e.g. DMA, AMS), PILS-IC has been shown to measure nitrate acceptably (Sorooshian *et al.* 2006, Bae *et al.* 2007, Timonen *et al.* 2010).

It seems likely that evaporation of nitrate compounds from filter samples was the main cause of lower nitrate concentrations measured from filter samples. In addition to volatilization, other differences in the two methods, PILS-IC and PM₁ filters, are likely causing part of the variation seen in the nitrate concentrations in this study. In filter methods, particles remain in the filter material long time after collection. Evaporation of semi-volatile compounds from the filter and adsorption of gases onto the filter material during the collection can have a large effect on the ion concentrations measured from the filter (Hering and Cass, 1999, Viana *et al.* 2006a). In PILS-IC, the sample is mixed with supersaturated water vapor and subsequently impacted onto a quartz plate within seconds (Orsini *et al.* 2003). In addition, it must be noted that at low concentrations (0.05–0.1 µg m⁻³) near the compounds' quantification limits, the ion concentrations measured with IC are also highly uncertain.

Fine PM concentrations

The TEOM PM_{2.5} mass concentrations were compared with the PM₁ mass calculated for 24-hour filter measurements that were carried out in parallel at the SMEAR III. The mean ± SD mass concentration for PM₁ was 7.8 ± 6.5 µg m⁻³. The ratio between PM₁ (filters) and PM_{2.5} (TEOM) was 0.62 ± 0.51. The difference can be due to the different cutoff sizes (PM₁ and PM_{2.5}) and possibly also due the evaporation of semi volatile compounds from the PM₁ filter during collection. PM_{2.5} measurements with the TEOM equipped with both the SES and the FDMS systems have been shown to compare very well to other real-time automatic analyzers counting semi-volatile matter (Grover *et al.* 2006, Wilson *et al.* 2006). For this study, the mass between PM₁ and PM_{2.5} can be evaluated also from the MOUDI results. The mass ratios between PM₁/PM_{1.8} and PM₁/PM_{3.2} in MOUDI were (mean ± SD) 0.83 ± 0.10 and 0.68 ± 0.15, indicating that on average 17%

of PM_{1.8} mass was between PM₁ and PM_{1.8} and 32% of PM_{3.2} mass between PM₁ and PM_{3.2}. Assuming that the mass is equally distributed between PM_{1.8} and PM_{3.2}, the mass between PM₁ and PM_{2.5} would be 25% of the PM_{2.5} mass that is close to the difference found between PM₁ and PM_{2.5} (30%). Some uncertainty in this approach is due to the fact that the collection efficiency curves in the impactor are not step functions, but this is difficult to quantify.

Carbonaceous matter

For OC the semi-continuous and the filter sampling methods gave quite similar concentrations. The OC concentrations measured with the RT-OCEC were on average 10% greater than those of the filters for OC (Table 3) but the correlation between the RT-OCEC OC and the filter sampling OC was very good ($r^2 = 0.95$). However, larger differences between the RT-OCEC BC and BC analyzed from the PM₁ filters were found (slope = 0.57, $r^2 = 0.60$). This is likely affected by higher uncertainty associated with small BC concentrations, both in filters and online sampling. Similar behavior for OC was observed also by Sciare *et al.* (2010). In both methods (RT-OCEC and PM₁ filters collections), particles were collected on filters, but in RT-OCEC gas-phase components were removed before the filter with a parallel plate carbon denuder. In the filter sampling, absorption of gas-phase compounds on filters was taken into account by subtracting the OC concentration of the backup filter from the result of the front filter. In addition to the gaseous compounds, part of the semi-volatile organic components that evaporated from the front filter was subsequently absorbed on the backup filter and considered 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, semi-volatile 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 a freezer from days to weeks prior to their analy-

sis, whereas the online samples were analyzed directly after the collection. Also, the efficiency of the denuder in front of the RT-OCEC can partly explain the larger concentrations of OC measured with the RT-OCEC than using the filter sampling. A mean value of the measured denuder break-through and the blank values ($0.80 \mu\text{g m}^{-3}$) were subtracted from the RT-OC. However, denuder efficiency may change with time or it can depend on the concentrations of gaseous components. The more detailed analyzes of the sources of OC during this campaign has been published by Saarikoski *et al.* (2008).

Optically measured EC was also compared with black carbon (BC) measured with the aethalometer. On average the concentration of EC (RT-OCEC) was only 78% of that of BC (aethalometer). This difference is partly due to the different cut-off diameters of the RT-OCEC ($1 \mu\text{m}$) and aethalometer ($2.5 \mu\text{m}$), resulting in a slightly different size fraction and possibly in a different chemical composition of particles measured. Also the used wavelengths were different: 660 nm for the RT-OCEC and 880 nm for the aethalometer. The mass absorption efficiency used to calculation the BC mass 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 very good correlation ($r^2 = 0.92$) was found between the RT-OCEC BC concentration and BC measured with the aethalometer. The BC results from the semi-continuous ECOC carbon analyzer have previously been shown to agree well with the BC results of other online instruments (e.g. Kanaya *et al.* 2008, Solomon *et al.* 2008 and references therein).

Seasonal and diurnal variations in PM concentrations and composition

During this campaign, the $\text{PM}_{2.5}$ mass concentration was $13.8 \pm 11.4 \mu\text{g m}^{-3}$ (mean \pm SD; see Table 1) and the ratio between PM_1 (PM_1 filter samples) and $\text{PM}_{2.5}$ (TEOM $\text{PM}_{2.5}$) was 0.62 ± 0.51 . During this measurement period, 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 TEOM SES

(30°C). In Finland, for most of the time the temperature is below 30°C , thus this represents the maximum value for semi-volatile matter. No clear seasonal variation was found in the PM_1 or $\text{PM}_{2.5}$ mass. The measured $\text{PM}_{2.5}$ mass concentrations were slightly higher than 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 $8.2 \mu\text{g m}^{-3}$; see Laakso *et al.* 2003). The main reason for the slightly higher concentration can be partly explained by the monitoring methods used (FDMS-TEOM in this paper and other monitor types in Laakso *et al.* 2003). Furthermore, also the biomass burning episodes elevated average PM concentrations.

In general, the PM chemical composition followed expected trends in OC, sulfate, nitrate, ammonium, EC being the major components of fine particulate matter (Niemi *et al.* 2004, Siljanpää *et al.* 2005a, 2005b) during the 13 month measurement period (Fig. 1). Sulfate was the most abundant ion, with an average concentration of $1.74 \mu\text{g m}^{-3}$ (Table 1). The average concentrations of NO_3^- , NH_4^+ and K^+ were 0.77, 0.85 and $0.10 \mu\text{g m}^{-3}$, respectively (Table 1). The concentrations of potassium and oxalate in the PILS-IC measurements were very low for most of the year, being above the quantification limit only 20% and 30% of the 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 (Saarikoski *et al.* 2007, Saarnio *et al.* 2010). For sodium and chloride, the concentration in the PILS-IC measurements were for most of the time ($> 80\%$) below the quantification limit as can be expected for a fine PM fraction. The concentrations of OC and optical EC were 2.0 ± 2.5 and $0.74 \pm 0.64 \mu\text{g m}^{-3}$ (mean \pm SD), respectively (Table 1). OC correlated with $\text{PM}_{2.5}$ ($r^2 = 0.70$). Highest 3-h average OC concentrations (up to $41 \mu\text{g m}^{-3}$) were measured during two biomass burning episodes.

Diurnal variation

Since the time resolution for EC and OC was three hours, also the ion and $\text{PM}_{2.5}$ mass concentrations were averaged to the corresponding time

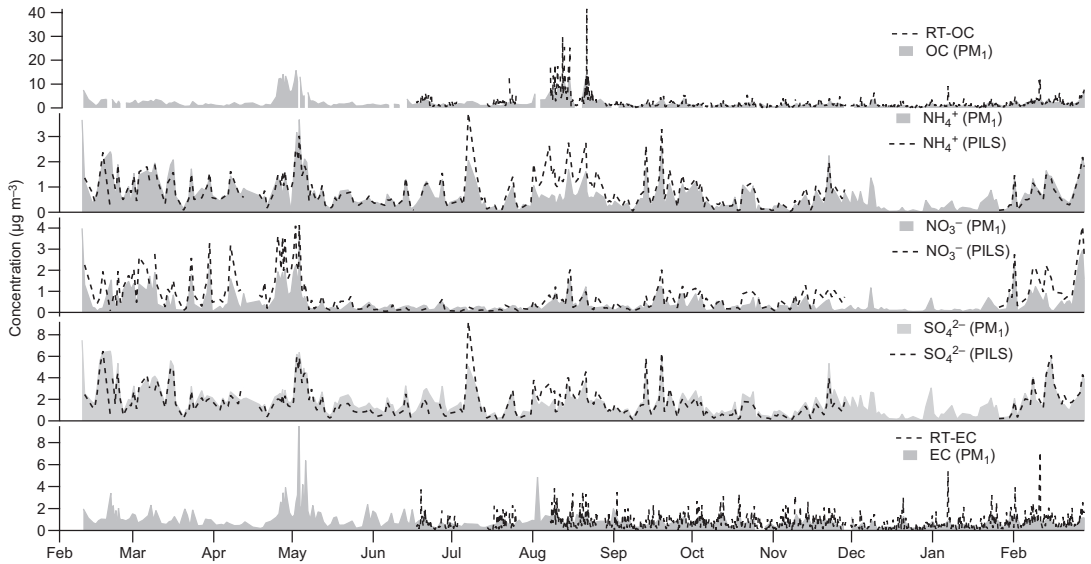


Fig. 1. Comparisons between online and PM_1 filter measurements of OC, ammonium, nitrate, sulfate and EC from 9 February 2006 to 28 February 2007. Sampling time for the PM_1 filters was approximately 24 hours during weekdays and 72 hours on weekends, and the ion results of the online instruments were averaged to corresponding time periods.

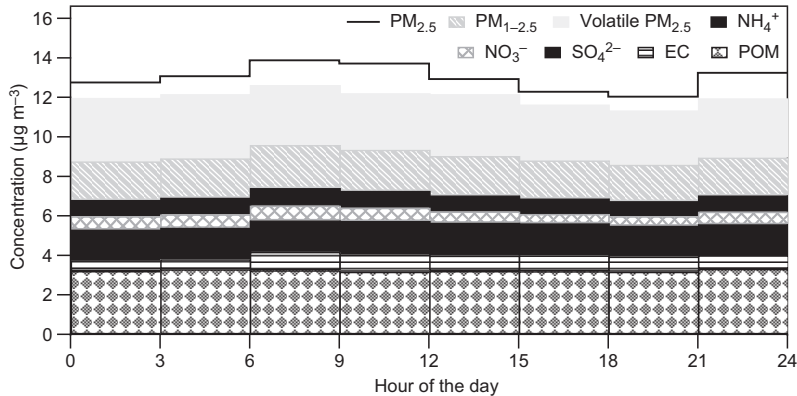
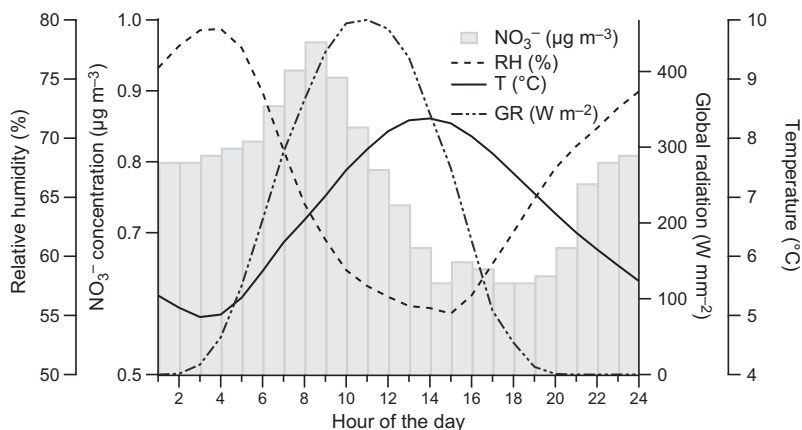


Fig. 2. Measured concentrations of major ions, EC, POM and $PM_{2.5}$ for 3-h averages. The amount of volatile PM is evaluated based on FDMS TEOM results and the mass between PM_1 and $PM_{2.5}$ is evaluated from simultaneous MOUDI collections.

periods. The values measured during biomass burning episodes (April–May and August 2006) were excluded from the data, when seasonal and diurnal variations were studied. No diurnal variation was found for POM, ammonium and sulfate (Fig. 2). The diurnal variation in $PM_{2.5}$ measured with TEOM was weak (Fig. 2). Most evident diurnal variation was recorded for EC which had the highest concentration at 06:00–09:00 and the lowest one at 03:00–06:00 (Fig. 2). Of the ions, only nitrate had the diurnal variation with a peak concentration between 06:00 and 09:00. Diurnal cycles of nitrate depend on available atmospheric

ammonia of the specific location (Seinfeld and Pandis 1998). Similar nitrate behavior to the one found during our experiment was also recorded in previous studies (e.g. Hennigan *et al.* 2008, Poulain *et al.* 2011). It seems that the morning peak of nitrate was not related to changes in meteorological variables (Fig. 3), but was more likely caused by the increased traffic emissions during rush hour. The concentration of nitrate was the lowest in the afternoon and in the evening. The lower concentrations in the afternoon were probably caused by the increased mixing layer height. In the study of Järvi *et al.* (2008)

Fig. 3. Hourly-averaged nitrate (NO_3^-) concentration, global radiation (GR), relative humidity (RH) and temperature for each hour of day from 9 Feb. 2006 to 28 Feb. 2007.



in Helsinki, it was found that also black carbon, which is non-volatile, quite systematically had lower concentrations during afternoon. Concurrently with increased mixing layer height, the ambient temperature was increasing, that may have decreased nitrate concentrations by transferring particle-phase nitrate into the gas-phase.

The difference between weekdays and weekends was also studied. Of all the chemical components only EC varied clearly on the weekday-to-weekend bases. On weekdays, EC concentrations started to raise at 06:00 simultaneously with the increasing traffic volumes. EC concentrations remained at high level until the evening rush hour was over at around 18:00. Minimum EC concentrations were recorded at night between 00:00 and 03:00. During weekends, the diurnal variation of EC was minimal. The diurnal cycle of EC, with maximum at weekdays during the rush hours, indicates that traffic was likely the major source of EC. However, EC had a slightly different diurnal variation in different seasons. In summer and autumn, the concentrations of EC decreased sharply after the morning peak at 06:00–09:00, whereas in winter the concentrations stayed at higher level until the night (Fig. 4), probably because of the more stable boundary layer height during the day. For OC, the diurnal variation was only found in summer (Fig. 4). Similar to nitrate in autumn (Fig. 5), the concentrations of OC in summer were lowest in the afternoon and early evening due to the efficient mixing of pollutants and transfer of particle-phase OC to gas-phase.

Seasonal variation

To study the seasonal differences, one month was chosen to represent each season: February for winter, April for spring, June for summer and September for autumn. Seasonal differences during the measurement campaign were large. The highest ion, EC and OC concentrations were measured during the winter and the highest nitrate concentration during both winter and spring (Figs. 4 and 5). This is in line with the result of Ruoho-Airola (2012) who found a clear seasonal cycle in ambient sulphur and nitrogen concentrations in clean, background areas with a maximum in February. Potassium has been used as a tracer for biomass burning (Khalil and Rasmussen 2003). The concentrations of potassium were highest in winter (excluding the forest fire episodes) and lowest in summer, indicating that the local biomass burning for domestic heating likely increased aerosol concentrations during the winter. Biomass burning has been shown to affect PM concentration during the cold season in Finland (Saarnio *et al.* 2012). In addition to biomass burning, the high secondary ion concentrations recorded during the winter could represent long-range transported aerosol particles.

The lowest concentrations of all compounds, except of OC, were measured during the summer. Therefore, the average contribution of OC was largest during the summer. Also, a clear seasonal cycle was found for the OC/EC ratio. During the summer, the OC/EC ratio was on average 4.5, whereas during the autumn and winter it was

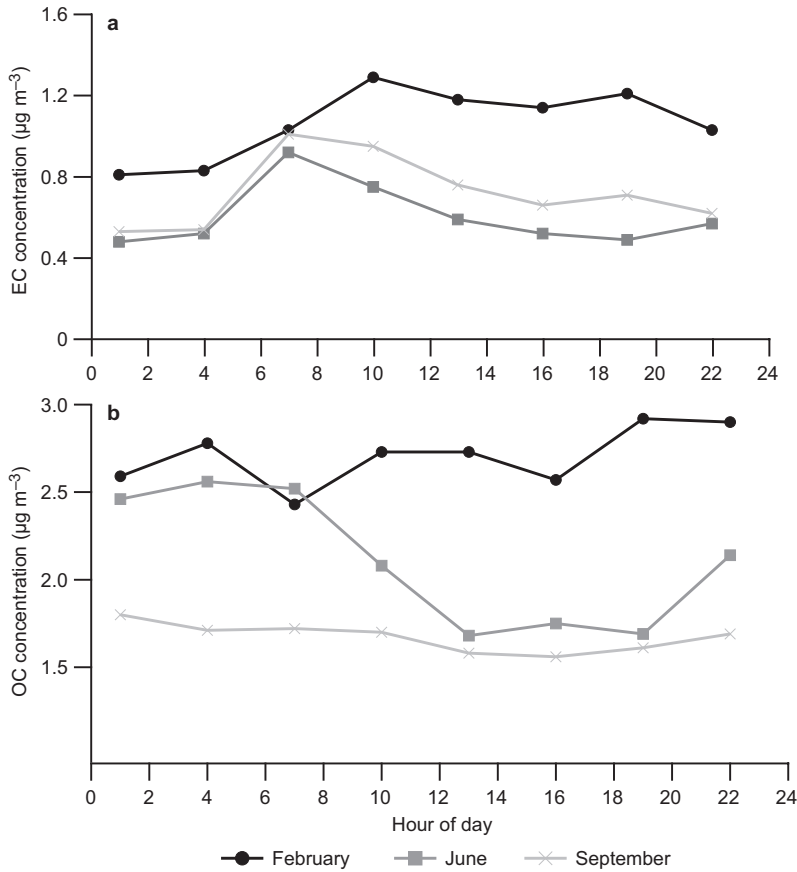


Fig. 4. Average (a) EC and (b) OC and concentrations for eight periods (3-h averages) of day during the measurement campaign (17 June 2006–28 February 2007).

smaller than 3. This is in line with the results of Aurela *et al.* (2011) who found a clear increase in the OC/EC ratio during summer due to biogenic emission at a background site. The EC concentrations were $82\% \pm 41\%$ (mean \pm SD) higher during the winter than during the summer. The high EC concentrations during the winter were likely caused by traffic emissions from the nearby road or biomass burning from domestic heating, amplified by weak atmospheric mixing during the winter. There were clear differences in both nitrate concentrations and its diurnal cycles during the different seasons (Fig. 5). There was a morning peak in the nitrate concentration during the winter and spring. The afternoon decrease in the nitrate concentration was clearly seen in the autumn, whereas in the summer no diurnal cycle was observed. For ammonium, no seasonal or diurnal variation was detected, even though during the summer slightly lower concentrations were recorded in the evening (Fig. 5).

Seasonal differences in ion balance

The equivalent ratio of cations to anions was calculated for the PM₁ filter samples and PILS-IC ion concentrations (Fig. 6). For PM₁, this ratio was quite stable: 0.9 ± 0.2 (mean \pm SD). For PILS-IC, the ratio was 1.05 ± 0.3 being higher in the summer (from July to September) than in the winter. The maximum cation-to-anion ratio (monthly average 1.4) was found for the biomass burning episode in August (*see Saarnio et al.* 2010). The amount of excess ammonium was calculated from the ammonium concentration by subtracting first the amount of ammonium sulfate (for simplicity all ammonium is assumed to be ammonium sulfate without contribution of ammonium bisulfate; if part of sulfate was in the form of ammonium bisulfate the amount of excess ammonium would be larger), then ammonium nitrate and finally ammonium chloride. It was found that most of the time ammo-

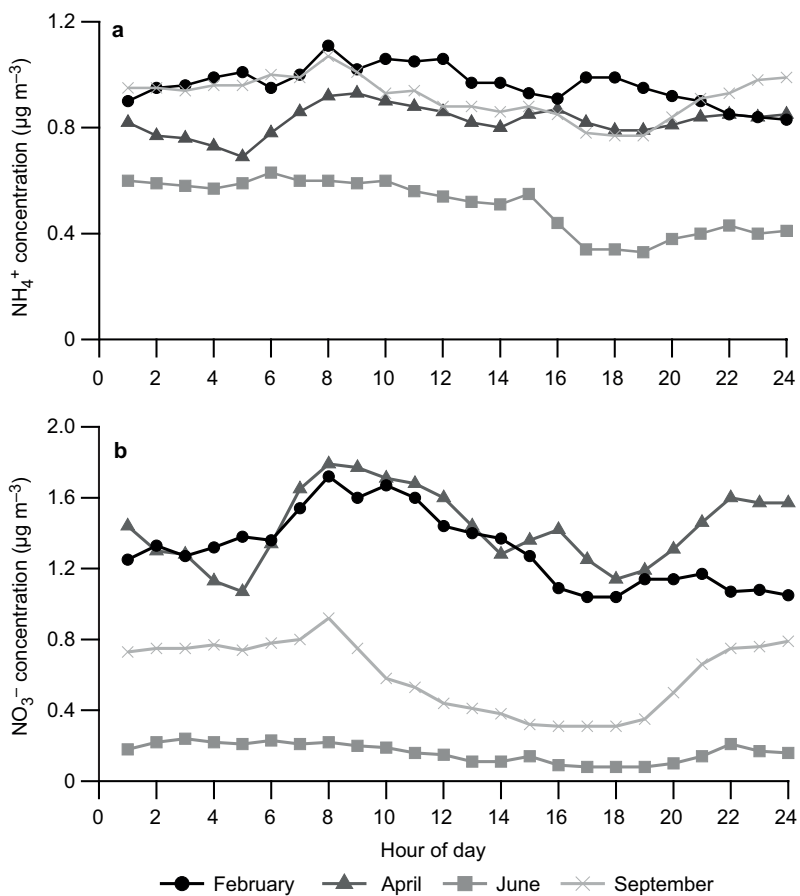


Fig. 5. Average ammonium (a) and nitrate (b) concentrations for each hour of day during the measurement campaign (9 February 2006–28 February 2007)

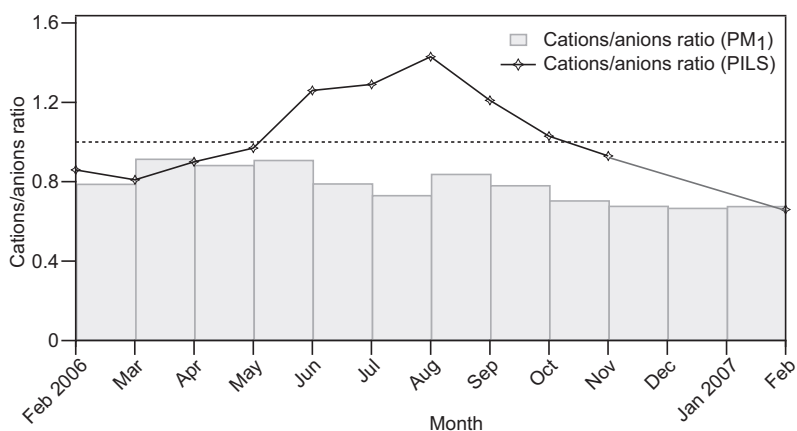


Fig. 6. Monthly average cation-to-anion ratios based on the PILS-IC and PM_{10} filter measurements from February 2006 to February 2007.

nium was in the forms of ammonium sulfate and ammonium nitrate. However, in the summer from June to September, substantial amount of excess ammonium was recorded. The amount of excess ammonium was found to increase as temperatures increased (Fig. 7). At the same time, as

the relative amount of ammonium increased, the contribution of nitrate to the total mass decreased (Fig. 7). The temperature dependency of nitrate was likely caused by nitrate partition into the gas phase with increasing temperature. Occasional high cation-to-anion ratios have also been found

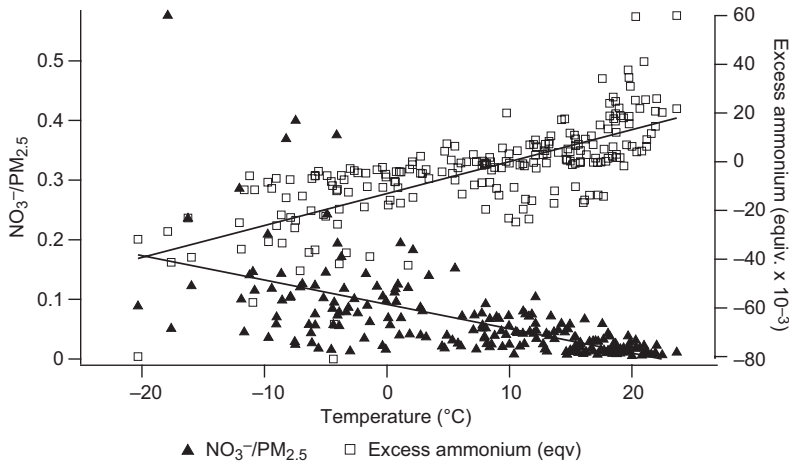


Fig. 7. The nitrate/ $PM_{2.5}$ ratio and amount of excess ammonium as a function of ambient temperature.

in other studies. Weber *et al.* (2001) found that the cation-to-anion ratio seem to be dependent on the particle source. They measured cation-to-anion ratios below 1 for local pollution episodes and ratios of up to 4 for clean air masses with low ($10 \mu\text{g m}^{-3}$) ambient aerosol concentrations.

Real-time mass closure

A real-time mass closure (i.e. the ratio between chemically analyzed compounds and gravimetric mass) was constructed by comparing the chemical components measured by online methods (PILS-IC and RT-OCEC) with $PM_{2.5}$ measured by TEOM. Only the major ions (sulfate, nitrate and ammonium) were used to construct the mass closure. The RT-OCEC was measured with a time resolution of 3-h and therefore also the data from PILS-IC and TEOM were averaged over the same periods. 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 filter collections, a multiplier of 1.6 was used to convert the measured organic carbon to particulate organic matter.

During February 2007, 90% of the $PM_{2.5}$ mass was identified by chemical analyses (Fig. 8). During the year-long measurement period, on average 65% of $PM_{2.5}$ was identified by the chemical analyses of PM_{1} . No seasonal differences in the degree of the achieved mass closure results were found. However, the difference between the analyzed and measured mass was

largest when the $PM_{2.5}$ concentration was low. Especially for the $PM_{2.5}$ concentrations below $5 \mu\text{g m}^{-3}$, the 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 high total uncertainty for the mass closure. When the concentrations were $> 15 \mu\text{g m}^{-3}$, the mass closure result 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 ($n = 4$). The used multiplier to convert carbon to particulate organic matter has an effect on the results of mass closure. The OM/OC ratio depends on the source and age of aerosols and can range typically from 1.2 to 2.5 (Turpin and Lim, 2001, Jimenez *et al.* 2009, Saarnio *et al.* 2010). An estimated value 1.6 was used based on the previous studies and recommendation of Turpin and Lim (2001). The reconstruction of mass measured by TEOM has previously been studied e.g. by Schwab *et al.* (2006) in US. They found that the difference between mass reconstructed from filter samples and measured by TEOM was on average less than 10%. But similarly to our case, they recorded a large variation in how the mass closure was reached.

Summary and conclusions

Long time-series of the PM chemical composition determined with high-time-resolution meas-

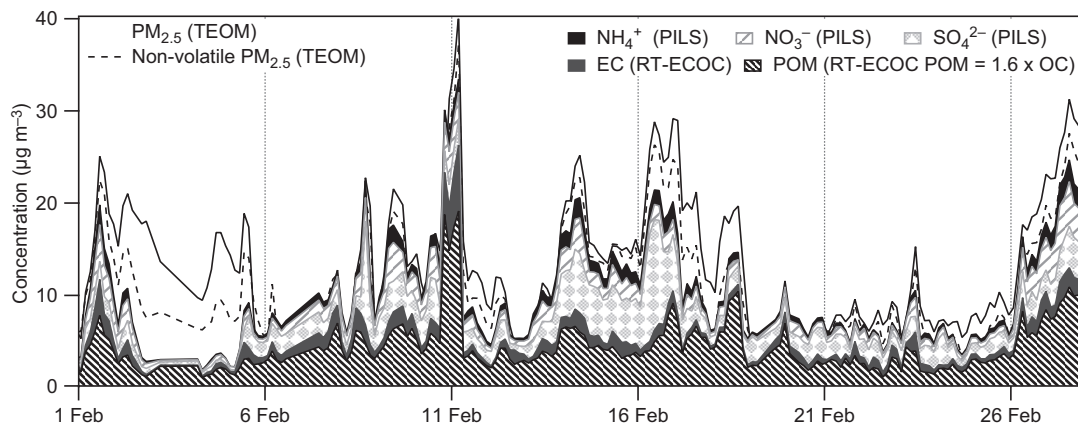


Fig. 8. Time series of major ions (sulfate, nitrate and ammonium), particulate organic matter (POM), inorganic carbon and PM_{2.5} and non-volatile PM (TEOM) mass concentration in February 2007.

urement devices in sub-arctic conditions are rare. In this study, measurements of major chemical components in fine particles were conducted at an urban, background station in Finland from February 2006 to February 2007 in order to investigate diurnal and seasonal changes in the PM concentration and composition. In addition, concentrations obtained from online measurement devices were compared with those from the traditional filter collections in order to increase the understanding of collection artifacts in both measurement approaches.

In addition to regional and long-range transported aerosols, the sources of PM during the measurement were biomass burning, SOA formation and traffic. The contribution of ions and EC were largest in the winter due to emissions from biomass burning that is used for domestic heating during the cold season. The contribution of OC was largest during the summer, likely due to more pronounced SOA formation. The PM ion balance was 1.05 ± 0.3 (mean \pm SD), being higher during the summer (from July to September) than winter. During the summer from June to September, substantial amount of excess ammonium was recorded. The amount of excess ammonium was found to increase as temperatures increased, whereas the contribution of nitrate to the total mass decreased, likely due to changes in nitrate partitioning between the gas and aerosol phases.

The aerosol chemical composition measured from the PM₁ filter samples compared well with

the concentrations measured with the online instruments. Volatility of the measured compounds and differences in the measurement techniques were the main reasons for the differences between the online and offline methods. Also, a different cutoff sizes used in the measurements (PM₁ and PM_{2.5}) affected the measured concentrations. The ratio between PM₁ (filter) and PM_{2.5} (TEOM) was 0.62 ± 0.51 . The difference in the cutoff sizes (PM₁ and PM_{2.5}) explained on average 25% of the unexplained mass, whereas the volatilized mass fraction ($\leq 18\%$) explained the remaining unexplained mass. A real-time mass closure was constructed by using the PM_{2.5} mass concentrations from TEOM, ion concentrations from PILS-IC and carbonaceous matter concentrations measured with the RT-OCEC. The analyzed submicron compounds (ions, POM, EC) represented on average 65% of the PM_{2.5} mass.

Nitrate concentrations were found to peak in early morning, during the rush hours. There was a morning peak in the nitrate concentration during the winter and spring. The afternoon decrease in the nitrate concentration could be clearly seen during the autumn, whereas no diurnal cycle was found during the summer. Also EC had a clear diurnal cycle, with a maximum during the morning rush hour.

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