Chemical and Source Characterization of Submicron Particles at Residential and Traffic Sites in the Helsinki Metropolitan Area, Finland

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ABSTRACT

Chemical characterization of non-refractory submicron particles (NR-PM1) and source apportionment of organic aerosols (OA) were carried out at four different sites in the Helsinki metropolitan area, Finland, using an Aerodyne Aerosol Chemical Speciation Monitor (ACSM). Two of the sites represented suburban residential areas, whereas the other two were traffic sites, one in a curbside in downtown and the other one in a suburban highway edge. The residential and the curbside measurements were conducted during the winter, but the highway campaign was carried out in the autumn. NR-PM1 were composed mainly of organics (40–68% in the different sites), followed by sulphate (11–34%), nitrate (12–16%), ammonium (7.8–8.5%) and chloride (0.24–1.3%). The mean concentrations of NR-PM1 were quite similar during the winter campaigns (10.1–12.5 µg/m3), but NR-PM1 was clearly lower during the autumn campaign at the highway site (6.0 µg/m3) due to the meteorology (favourable mixing conditions), small concentrations of long-range transported particles and non-intensive heating period locally and regionally. Using a multilinear engine algorithm (ME-2) and the custom software tool Source Finder (SoFI), the organic fraction was divided into two or three types of OA representing hydrocarbon-like organic aerosol (HOA), oxygenated organic aerosol (OOA), and in three sites, biomass burning organic aerosol (BBOA). At the downtown traffic site (Curbside), BBOA could not be found, probably because most of the local wood burning occurs in the suburban areas of the Helsinki region. OOA had the largest contribution to OA at all the sites (50–67%). The contribution of HOA was higher at the traffic sites (25–32%) than at the residential sites (15–18%). At the suburban residential and highway sites, the contribution of BBOA was high (25–30%). Especially during cold periods, very high BBOA contributions (~50%) were observed at the residential sites.

Keywords: Chemical composition; Source apportionment; Fine particles; ACSM.

INTRODUCTION

Atmospheric aerosols play a key role in climate change. Particles scatter and absorb light, and they serve condensation surfaces for water vapour, affecting cloud formation, precipitation rates and indirect climatic effects due to clouds (IPCC, 2013). Some of the particles are semi-volatile, and they can modify the trace gas composition and impact gas-phase reaction pathways through heterogeneous reaction in the atmosphere. Aerosols also have adverse effects on human health, as fine aerosols can penetrate deep into the lungs. Even a short-term exposure to outdoor fine particulate matter is associated with increased risk of death and emergency admission to the hospital (e.g., Atkinson et al., 2014). A 10 µg/m³ increment in particulate matter < 2.5 µm (PM2.5) has been associated with an increase in the risk of death, but the mass concentration alone is not sufficient to evaluate the health effects of particles, as certain chemical components and sources are more harmful than others (Zanobetti et al., 2014). Specific sources like traffic, coal, oil and biomass combustion, soil or road dust have shown positive correlation with mortality or to adverse health effects (Ostro et al., 2011; Dai et al., 2014; Uski et al., 2014; Zanobetti et al., 2014).

Chemical composition of fine particles in urban areas has been studied extensively all over the world. The main contributors to PM are organic materials followed by sulphate, nitrate, ammonium and black carbon (e.g., Putaud et al., 2004; Zhang et al., 2007; Chan and Yao, 2008 and references therein), but the sources for the chemical components may differ depending on local and regional
emissions and how the air masses are drifting. One major source of fine particles in many urban environments is the transportation sector (e.g., Zhang et al., 2005). Biomass burning in fireplaces and stoves is often another significant particulate matter source, especially during winter in residential areas (Glasiou et al., 2006; Szidat et al., 2007), whereas the prescribed burning may have a significant role in agricultural areas also effecting urban areas (Jimenez et al., 2006). Other sources of particulate matter are industry, cooking, power generation, biogenic hydrocarbon emissions and the secondary material formed through chemical reactions (Zhang et al., 2007; Mohr, et al., 2012).

In the Helsinki metropolitan area, vehicular traffic is the most significant local particle source affecting urban air quality (Pirjola et al., 2012; Soares et al., 2014). Also, the effects of wood combustion on local air quality can be considerable, especially during periods of low vertical mixing due to stagnant weather conditions, as the release height of the emissions is typically low and the combustion in domestic heating appliances is incomplete (Saarikoski et al., 2008; Saarnio et al., 2012). Wood combustion is widely used as a supplementary source of heating at detached-housing areas in winter in the Helsinki area. Additionally, a large portion of fine particles originates from long-range transport (LRT) in the Helsinki metropolitan area. The concentrations of LRT particles are highest when aerosols are transported from the polluted areas of Eastern Europe, whereas the lowest LRT levels are observed when air masses originate from the Atlantic Ocean (Niemi et al., 2004, 2005; Saarikoski et al., 2007; Saarnio et al., 2010a).

The objective of this study was to characterize the chemical composition and sources of submicron particulate matter (PM1) in the Helsinki metropolitan area, Finland, by deploying a relatively new monitoring technique based on aerosol mass spectrometry (Aerodyne Aerosol Chemical Speciation Monitor, ACSM). This study was conducted during the years 2010–2012 at four different sites, including two suburban detached-housing areas (Residential I and Residential II), a curbside site in downtown (Curbside) and a suburban highway edge (Highway). Organic aerosol (OA) data was analysed in detail by applying a multilinear engine algorithm (ME-2, Canonaco et al., 2013) for organic mass spectra in order to explain the main sources of OA in the Helsinki area. So far, the combination of ACSM or AMS (aerosol mass spectrometer) and ME-2 with Source Finder (SoFi) has been used only in few studies (e.g., Canonaco et al., 2013; Crippa et al., 2014).

**METHODS**

**Description of the Sites**

The measurements were conducted at four different sites around the Helsinki metropolitan area (Fig. 1). The population of the Helsinki metropolitan area is about 1 million. The Residential I site was situated approximately 20 km northeast from downtown Helsinki. The site was surrounded by detached houses. It is quite typical to use wood burning as a supplementary heating source in Finnish detached housing areas, and most of the houses have their own fireplaces.

There were no main roads through the area, but the nearest motorway was approximately 1.2 km east of the site. Measurements at the Residential I site were conducted from 17 February to 16 March 2011.

The Residential II site was situated in a low-lying area of detached housing approximately 20 km west from Helsinki downtown. There were no main roads through the area. The closest highway was situated approximately 3 km south of the site. Measurements at the Residential II site were performed from 12 January to 28 February 2012.

The Curbside site was situated in downtown Helsinki beside a quite heavily trafficked road (23000 vehicles/working day). A lot of the vehicles in downtown are related to transportation and work-related drives throughout the day. There were constant rows of buildings on both sides of the road affecting the dispersion of aerosols, although there was one big crossing close to the site. Measurements at Curbside were carried out from 1 December 2010 to 7 January 2011.

The Highway site was situated near a heavily trafficked highway (5 m from the edge of the first lane), which is the inner ring road around Helsinki, approximately 10 km from Helsinki downtown. The traffic density was approximately 69 000 vehicles/working day. Measurements at the Highway site were conducted from 18 October to 5 November 2012.

**Instrumentation**

**Aerosol Chemical Speciation Monitor**

The aerosol chemical speciation monitor (Aerodyne Research Inc., Ng et al., 2011a) is able to routinely characterise non-refractory sub-micron aerosol species (NR-PM1: sum of organics, nitrate, sulphate, ammonium and chloride). The instrument consists of a particle sampling inlet, three vacuum chambers and a residual gas analyser mass spectrometer. In the particle sampling inlet, particles are focussed into a narrow particle beam by using an aerodynamic lens system. After being transmitted through chambers, the beam is directed into a hot tungsten oven (~600°C) where particles are flash- vaporised, ionised with a 70 eV electron impact ioniser and detected with a
quadrupole mass spectrometer. ACSM can measure with a time resolution from 15 minutes upward, and in this study, a time resolution of approximately 30 min was used. The comparison of ACSM to different instruments has been widely studied in the paper of Budisulistiorini et al. (2014). In order to account for the particle losses in the vaporizer, a collection efficiency (CE) of 0.5 has been widely used in aerosol mass spectrometry techniques (Canagaratna et al., 2007). A CE = 0.5 was also used in this study, but it was calculated also based on the Middlebrook et al. (2011). There were some occasions, when high aerosol acidity was achieved. However, most of the time the calculated CE was 0.5. Additionally, there were some uncertainties in the calculation of the acidity of the aerosols. At the time of the measurements campaigns the ACSM was not calibrated for calculation of the acidity of the aerosols. At the time of the measurements campaigns the ACSM was not calibrated for sulfate, only for ammonium and nitrate, and therefore the relative ionization efficiency (RIE) for sulfate was not measured. In this study, the RIE value of 1.2 was used for sulfate that seems to be at the high end, as RIE values of 1–1.2 for sulfate were measured since spring 2013. Uncertainties of the calculations of sulfate concentrations have been presented by Budisulistiorini et al. (2014). There are also other factors like high ammonium nitrate molar fraction or high relative humidity that affects the CE, but in this study they were not present.

**Multi-Angle Absorption Photometer**

The black carbon (BC) concentration was measured using a multi-angle absorption photometer (MAAP, Thermo Electron Corporation, Model 5012). The MAAP determines the absorption coefficient ($\sigma$AP) of the particles deposited on a filter by a simultaneous measurement of transmitted and backscattered light. The $\sigma$AP is converted to BC mass concentrations by the instrument firmware using the mass absorption cross section of 6.6 m$^2$/g (Petzold and Schönlinner, 2004). The inlet cut point for the MAAP was 1 µm (PM$_{1}$). BC concentrations were measured at every site, but due to the poor data coverage caused by technical problems, the data from the Residential I site are not presented here.

**Other Air Quality and Meteorological Data**

PM$_{2.5}$ concentrations were measured with monitors based on β-attenuation (FH 62 I-R, Residential I and Curbside sites), combination of light-scattering and β-attenuation (SHARP 5030, Residential II site) or with a tapered element oscillating microbalance technique (TEOM 1400 AB, Highway site). The PM$_{2.5}$ monitoring data of different instruments was corrected using calibration equations to ensure equivalent results according to European standards (Walldén et al., 2010). NO and NO$_2$ concentrations were measured with a chemiluminescence analyser (Horiba APNA360/370). 24-h filter samples (PM$_{10}$) were collected at the Residential I site every third day (n = 4) and levoglucosan (1,6-anhydro-β-D-glucopyranose), selected ions and benzo(a)pyrene (BaP) were analysed by using a high performance anion-exchange chromatograph coupled with mass spectrometer, an ion chromatograph and a gas chromatograph coupled with mass spectrometer, respectively (Saarnio et al., 2010b; Vestenius et al., 2011; Teinilä et al., 2014). Local meteorological data was recorded at an urban background site (SMEAR III) 5 km northeast from downtown Helsinki.

**ACSM Data Analysis**

The organic aerosol fraction was investigated by using ME-2 and the custom software tool SoFi version 4.6 (Canaco et al., 2013). ME-2 allows exploring the solution place much more widely than positive matrix factorization (PMF). Especially the solutions in ME-2 can be rotated in directions that make sense and not arbitrarily as done with fpeak in PMF. By using the source apportionment method, organic aerosols can be divided into factors representing different particle sources like traffic, biomass burning and cooking, or into factors that represent components with similar chemical characters, such as low-volatility (LV) and semi-volatile (SV) oxygenated organic aerosol (OOA).

The number of factors in the dataset is unknown, and the final number of factors in the ME-2 is defined by the user. The number of factors was selected based on the unexplained variation, changes in the Q-value (the total sum of the squares of the scaled residuals), the comparison of mass spectra with the AMS mass spectra database (Ng et al., 2011b) and/or by using auxiliary species such as BC, inorganic ions, NO, and meteorological information.

In ME-2, the user can constrain factor profiles and/or time series to a chosen extent. According to the guidelines of source apportionment by ME-2, a reference hydrocarbon like organic aerosol (HOA) mass spectrum should be constrained first if the constraint is needed (Crippa et al., 2014). Because primary organic aerosol components (HOA and biomass burning organic aerosol BBOA) were not separated clearly with unconstrained ME-2 analyses in the residential sites, the constrained factor profile of HOA was used.

In the paper of Crippa et al. (2014), reference spectra for constraining were taken from the measurements done in Paris, where HOA and organic aerosol from cooking (COA) were nicely separated (Crippa et al., 2013). As the COA factor has not been identified in Helsinki in earlier studies (Timonen et al., 2013; Carbone et al., 2014), the reference HOA mass spectrum was deployed from the measurement done by Carbone et al. (2014) at an urban background site in Helsinki instead of the reference HOA spectrum from Crippa et al. (2013). In the study of Carbone et al. (2014), high resolution data was presented, but unit mass resolution mass spectrum of HOA was calculated for the purpose of this study. HOA mass spectrum was used as an input data with an a-value of 0.1. The a-value determines the extent to which the output is allowed to vary from the input, i.e. an a-value of 0.1 means that the contributions of the mass spectral ions concentrations are allowed to vary only up to 10%. Different a-values were tested (0.05–0.3) to find the most reasonable one (not shown).

In the Residential I campaign, some periods with very low concentrations (approximately 30% of the data points) were excluded from the factor analyses, as the explained variation over the period with low concentrations was below the reasonable value (< 75%, Canonaco et al., 2013).
RESULTS AND DISCUSSION

Mass Concentrations and Chemical Composition of Fine Particles

The mean concentrations of NR-PM<sub>1</sub> calculated by summing up all chemical species measured by the ACSM (organics, nitrate, sulphate, ammonium, chloride), were quite similar during the wintertime campaigns (Residential I, Residential II and Curbside), whereas the mean NR-PM<sub>1</sub> concentration was clearly lower during the autumn campaign conducted at the Highway site (Table 1; Fig. 2). The low NR-PM<sub>1</sub> concentrations during the highway campaign were mainly caused by the very low level of LRT background aerosol (the small concentrations of typical secondary LRT components such as sulphate, ammonium and nitrate are also visible in Fig. 2). In general, fine particle concentrations during these four campaigns were quite low compared to concentrations measured in large cities like Beijing (Sun et al., 2012, NR-PM<sub>1</sub>: 50 µg/m<sup>3</sup>) or Santiago de Chile (Carbone et al., 2013, NR-PM<sub>1</sub>: 30 µg/m<sup>3</sup>) but comparable to the other observations (e.g., Sun et al., 2012). Different chemical components in filter-based methods, ACSM has deficits in calibrating procedures. The smallest contribution of NR-PM<sub>1</sub> to PM<sub>2.5</sub> was obtained at the Residential I site. The reason for the small contribution could be large BC concentrations at that site due to local wood-burning emissions. Unfortunately, that cannot be confirmed, as the BC data was available only for a short period of the campaign (not shown in Fig. 2). At the other residential site, the ratio of BBOA to BC was on average 0.8, indicating that BC concentrations at Residential I site may be as high as or even higher than BBOA concentrations. A similar value (0.8) has been presented also in the paper Crippa et al. (2013). The source apportionment analysis will be discussed later. The contribution of BC to PM<sub>2.5</sub> was 10, 16 and 17% at the Residential II, Curbside and Highway sites, respectively. By summing NR-PM<sub>1</sub> and BC-PM<sub>1</sub>, the contribution of measured chemical species increased up to 86–99% (excluding Residential I –site). Other components that were not measured by ACSM and can have a minor contribution to the PM<sub>2.5</sub> mass were potassium and calcium, which can be associated with smoke aerosols (Li et al., 2003), sodium and chloride, that are present in sea salt, as well as aluminosilicates (e.g., Si, Al and Fe oxides) that are typical components of street dust particles. However, the difference between the measured chemical species and PM<sub>2.5</sub> was likely to be mostly due to the difference in the size ranges (PM<sub>1</sub> vs. PM<sub>2.5</sub>), the uncertainty in the collection efficiency and the RIE values for chemical species.

The Pearson correlation coefficient, r, between NR-PM<sub>1</sub> and PM<sub>2.5</sub> was high during the winter campaigns (0.87–0.90) and moderate in the autumn campaign conducted at the Highway site (0.80). At the Highway site, BC had quite a high contribution to the PM<sub>2.5</sub> (17%); therefore, the correlation between chemical species and PM<sub>2.5</sub> improved when BC was included in chemical components (r: 0.90). Similar or even higher correlations have been found between ACSM and filter-based method of PM<sub>2.5</sub> and PM<sub>1</sub> in Atlanta (Budisulistiorini et al., 2014).

Source Apportionment of Organic Aerosols

The ME-2 algorithm and SoFi-tool were used to explore the sources and origins of organic aerosol. A three-factor

### Table 1. The concentrations (mean ± stdev) in µg/m<sup>3</sup> during the campaigns.

| Components | Residential I | Residential II | Curbside | Highway |
|------------|--------------|----------------|----------|---------|
| PM<sub>2.5</sub> | 19.3 ± 18.1 | 14.6 ± 9.9 | 14.5 ± 9.7 | 9.19 ± 6.83 |
| NR-PM<sub>1</sub> | 10.1 ± 9.5 | 11.2 ± 8.1 | 12.5 ± 7.6 | 5.96 ± 3.97 |
| BC | 1.55 ± 1.80 | 1.84 ± 1.65 | 1.97 ± 2.16 | |
| organics | 5.25 ± 5.88 | 5.33 ± 4.22 | 6.37 ± 3.92 | 4.01 ± 2.98 |
| sulfate | 1.87 ± 1.67 | 2.37 ± 1.61 | 2.94 ± 2.14 | 0.57 ± 0.37 |
| nitrate | 1.54 ± 1.57 | 1.90 ± 1.93 | 2.01 ± 1.53 | 0.84 ± 0.82 |
| ammonium | 0.77 ± 0.64 | 1.10 ± 0.81 | 0.99 ± 0.67 | 0.49 ± 0.42 |
| chloride | 0.08 ± 0.15 | 0.05 ± 0.06 | 0.18 ± 0.65 | 0.05 ± 0.07 |
| NO<sub>x</sub> | 37.3 ± 41.1 | 33.5 ± 48.3 | 98.7 ± 95.2 | 81.2 ± 85.4 |

*a* sum of organics, sulfate, nitrate, ammonium and chloride measured with the ACSM.
solution was found to represent most reliably the sources of organic aerosol at both the residential sites and at the Highway site. The four-factor solution resulted in split factors, without identifying a unique factor profile. The time series were similar between the two split factors. Factors were identified as OOA, BBOA and HOA based on the reference mass spectra presented in literature (e.g., Ng et al., 2011b). In the Curbside campaign, only HOA and OOA were found, as BBOA could not be extracted from the data. The signal at m/z 60, which is related to biomass combustion, was very noisy without any reasonable time series or diurnal cycle; therefore, constraint of BBOA was not attempted. The average fraction of m/z 60 to organics (f60) was very close to the estimated background level of f60 (0.3%, Cubison et al., 2011) even in higher organic loadings. The reason BBOA was not seen in the Curbside campaign remained unclear. Most of the local wood burning occurs in the suburban areas of the Helsinki region further away from downtown, but it was still expected to extract the BBOA factor in the Curbside campaign.

OOA is generally dominated by secondary organic aerosols (SOA) formed in the atmosphere from gas-to-particle conversion. OOA factor could not be further separated to distinct factors in any of the campaigns due to fact that the measurements were done in winter and autumn when ambient temperature and light intensity are low. Typically, more than one OOA component has been found for the datasets collected in summer because of more intense photochemistry, higher ambient temperatures, and larger temperature changes in summer than in winter promote separation (Lanz et al., 2010). The OOA factor at all the sites had very high contributions of m/z 44, which is mainly the CO$_2$ fragment typically from thermal decarboxylation of organic acid groups (Alfarra et al., 2004), and m/z 18, a
fragment of H$_2$O$^+$ implying the thermal breakdown of the carboxylic acid on the vaporizer, indicating highly oxidised organic aerosol that is considered a low-volatility oxidised organic aerosol (Fig. 3).

The mass spectra of individual factors were very similar between the sites, and they correlated well (Pearson correlation $r = 0.92–0.98$). Also, the mass spectra of OOA and HOA were very similar to the reference mass spectra of LV-OOA and HOA presented by Ng et al. (2011b), respectively (Table 2). The BBOA mass spectra had a much higher contribution of $m/z$ 18 and $m/z$ 44 than the mean BBOA mass spectrum in Ng et al. (2011b).

One method to assess the oxidation state of organic aerosol is to plot the fraction of $m/z$ 43 to organics ($f_{43}$) versus the fraction of $m/z$ 44 to organics ($f_{44}$, respectively; Ng et al., 2010; Fig. 4). It can be seen from the figure that, in general, OA has larger $f_{44}$, and therefore is more oxidised, at the Residential I site than at the Highway and Curbside sites. At the Residential II site, on the other hand, OA varied least, especially for $f_{43}$. By looking at the individual ME-2 SoFi factors, it can be seen that OOA had the largest $f_{44}$ (0.21–0.30) and corresponding O:C ratios (0.87–1.2, Ng et al., 2010), with the highest values observed for the residential sites. All OOA are located in the highly oxidised LV-OOA region in the triangle plot where, e.g., fulvic and humic acids are also found. All these $f_{44}$ and O:C ratios for OOA were higher than in multiple field studies (Ng et al., 2010) or even at a very similar site in Helsinki (Timonen et al., 2013; Carbone et al., 2014). The higher ratios may be due to different instruments, as the previous measurements in Helsinki were performed using the high-resolution AMS with time-of-flight detector (ToF). The quadrupole detector used in the ACSM is much less sensitive than the ToF detector in the AMS. However, $f_{44}$ at the Curbside site (0.21) was quite similar to that measured in New York with the ACSM (0.19; Ng et al., 2011a). BBOA had slightly larger $f_{43}$ values than OOA but much smaller $f_{44}$ values. The observed O:C ratios for BBOA (0.4–0.5) were also slightly higher than presented in the literature (e.g., 0.21–0.32; Saarikoski et al., 2012; Timonen et al., 2013; Carbone et al., 2014). It is possible that the BBOA is LRT BBOA (Timonen et al., 2013), a mixture of BBOA and OOA or can be partly processed BBOA (Crippa et al., 2013), as the BBOA factors in all three sites had quite large $f_{44}$ and $f_{18}$, although elevated $f_{44}$ has also been observed for primary wood combustion sources (Alfarra et al., 2007). HOA presented the lowest O:C ratios at all the sites.

### Residential Areas

OOA constituted more than half of organic aerosols at both the residential sites (Residential I 55 ± 22% and

![Fig. 3. Mass spectra of two residential and two traffic sites in the Helsinki metropolitan area in Finland. The reference mass spectrum for HOA was taken from the earlier study carried out in Helsinki and it was used for the constrained factor analysis at the Residential I and II sites.](image)
Table 2. Comparison of factors and auxiliary data calculated as Pearson correlation coefficient r. Means of the factors (*) presented by Ng et al. (2011b). The term “sec ions” is the sum of main inorganic ions (sulfate, nitrate and ammonium) as a unit of an equivalent concentration. Coefficients with values over 0.70 have been bolded.

|                | Residential I | Residential II | Curbside | Highway  |
|----------------|---------------|----------------|----------|----------|
|                | HOA           | BBOA           | OOA      | HOA      | BBOA    | OOA    | HOA    | BBOA    | OOA    |
| NO             | 0.76          | 0.66           | -0.09    | 0.78     | 0.58     | 0.17    | 0.75   | 0.29     | 0.83   | 0.28   | -0.05 |
| NO₂            | 0.75          | 0.64           | 0.00     | 0.78     | 0.61     | 0.29    | 0.64   | 0.11     | 0.79   | 0.31   | -0.06 |
| NO₃            | 0.82          | 0.70           | -0.06    | 0.84     | 0.64     | 0.23    | 0.74   | 0.24     | 0.84   | 0.30   | -0.05 |
| PM₂.₅          | 0.77          | 0.79           | 0.24     | 0.71     | 0.63     | 0.77    | 0.53   | 0.82     | 0.72   | 0.59   | 0.24  |
| BC             | 0.92          | 0.83           | 0.17     | 0.36     | 0.75     | 0.77    | 0.37   | 0.44      | 0.85   | 0.60   | 0.01  |
| sulphate       | 0.71          | 0.67           | 0.44     | 0.36     | 0.39     | 0.75    | 0.30   | 0.76      | -0.03  | 0.06   | 0.74  |
| nitrate        | 0.76          | 0.62           | 0.56     | 0.76     | 0.62     | 0.74    | 0.62   | 0.74      | 0.33   | 0.40   | 0.61  |
| ammonium       | 0.31          | 0.24           | 0.77     | 0.72     | 0.53     | 0.74    | 0.59   | 0.83      | 0.12   | 0.08   | 0.71  |
| chloride       | 0.71          | 0.76           | 0.14     | 0.74     | 0.71     | 0.38    | 0.38   | 0.20      | 0.30   | 0.26   | 0.25  |
| sec ions       | 0.53          | 0.47           | 0.72     | 0.66     | 0.57     | 0.83    | 0.51   | 0.86      | 0.21   | 0.26   | 0.72  |
| LV-OOA*        | 0.23          | 0.90           | 0.94     | 0.24     | 0.69     | 0.96    | 0.22   | 0.98      | 0.14   | 0.90   | 0.98  |
| HOA*           | 0.99          | 0.26           | 0.08     | 0.99     | 0.33     | 0.13    | 0.98   | 0.15      | 0.96   | 0.37   | 0.20  |
| BBOA*          | 0.70          | 0.76           | 0.36     | 0.72     | 0.85     | 0.42    | 0.76   | 0.76      | 0.63   | 0.81   | 0.50  |

Fig. 4. f43 versus f44 triangle plots for different sites and for the identified ME-2 factors (▲, ● and ■). The dotted lines define the triangular space where ambient OA usually falls. The triangle plot is described detail in Ng et al. (2010).

Residential II 55 ± 19%, Fig. 5). Also, the diurnal patterns of OOA were very similar at both the sites, without any significant trend over the day (Fig. 6). The OOA component has been shown to be a good surrogate of SOA in multiple studies, correlating well with secondary species (e.g., Zhang et al., 2005). In this study, OOA correlated with ammonium at both the residential sites (Fig. 7 and Table 2) and with sulphate at the Residential II site (Table 2). The precursor gas, ammonia, is emitted from agricultural and some natural sources. In Finland, those sources are quite limited in winter; therefore, ammonium can be considered mainly as long-range transported. The good correlation between OOA and ammonium indicates that also OOA originates mostly from LRT. Although the correlation between sulphate and OOA were poor at the Residential I site, it is very likely that part of the sulphate is long-range transported together with ammonia. During the cold period, there was an excess of sulphate up to 70% compared to ammonium, and the inorganic aerosol was acidic (main anion sulphate), referring to some local or regional sulphur dioxide (precursor sulphate) sources. Aerosol at the Residential II site was quite neutral despite the ambient temperature.

The contributions and concentrations of constrained HOA factor were rather similar at both the residential sites: 15 ± 7% of OA and 1.2 ± 1.3 µg/m³ at the Residential I site and 18 ± 9% and 0.92 ± 0.89 µg/m³ at the Residential II site (Fig. 5). The contribution of HOA was very similar to the campaign carried out in January/March 2009 in Helsinki (Carbone et al., 2014), whereas it was higher than during the campaigns done in non-urban environments (Crippa et al., 2014). The ambient temperature did not seem to have any influence on the concentration or contribution of HOA at the Residential II site, whereas at the Residential I site the highest HOA concentrations were detected together with low ambient temperatures (Figs. 5 and 7).

The HOA factor correlated well with nitrate at the Residential II site and NO₃ (NO + NO₂) at both the sites, which is quite typical, as HOA and NO₃ usually have a common source, traffic (Fig. 7 and Table 2). However, NO₃ also correlated slightly with BBOA at the Residential I site (Table 2), and similar diurnal trends were detected for HOA, BBOA and NO₃ at the Residential I site, with pronounced peaks in the morning and evening (Fig. 6). Similar time series of HOA and BBOA and pronounced morning and evening peaks for BBOA have also been detected during winter inversions in Zürich (Lanz et al., 2008). For HOA and BBOA, the evening peak was clearly higher than the morning peak, whereas NO₃ had a larger peak in the morning. NO₃ also has sources other than traffic, like heating plans and energy production, which, however, were not located in the vicinity. The diurnal profile of HOA at the Residential II site was rather flat, ranging from an early morning value of 0.7 µg/m³ to an evening value of 1.2 µg/m³ at 8 p.m. (Fig. 6). The broad “morning and evening peaks” (7 a.m.–1 p.m. and 3–9 p.m.) were probably a consequence of the combination of rush hours and stable meteorological...
The mean contributions of BBOA to OA were quite similar at both the residential sites (Residential I 30 ± 18% and Residential II 27 ± 17%), but the mean concentration at the Residential I (2.8 ± 4.25 µg/m³) site was almost double that of the Residential II site (1.6 ± 2.2 µg/m³). Some data was excluded from the Residential I site, as the factor analyses could not be performed reliably if all the data were included. Those excluded periods had low mass concentrations and therefore would have decreased the mean BBOA concentration if included in the analysis. Clearly lower contributions of BBOA were achieved in wintertime in Paris, Helsinki (urban background) and Manchester (12–18%; Allan et al., 2010; Crippa et al., 2013; Carbone et al., 2014) than in this study for residential areas.
Temperature had a clear effect on the concentration and the contribution of BBOA at the Residential I site, whereas that kind of behaviour was not seen at the Residential II site. At the beginning of the Residential I campaign, cold and stagnant weather conditions occurred and temperature decreased below –20°C during the nights and stayed below –10°C during the daytime (Fig. 5). The temperature profile for the Residential II site was very different. During the Residential II campaign, the weather was quite mild and rainy (sleeting and snowing), although in the middle of the campaign there were a few days with very low temperatures. The highest BBOA concentrations were measured during those cold days at the Residential II site (Figs. 5 and 7).

Chloride correlated with BBOA at the Residential I site (Fig. 7 and Table 2). It has been noticed earlier that there is potassium chloride (KCl) in young smoke, whereas aged smoke contains more potassium nitrate (KNO$_3$) and potassium sulphate (K$_2$SO$_4$) (Liu et al., 2000; Li et al., 2003). This conversion has been presented to be quite fast (Li et al., 2003). The sources for biomass burning smoke were very close to the Residential I site, as there were several residential houses in the vicinity of the site and smoke from chimneys was regularly seen during the campaign. The clear indication of biomass burning smoke was also seen in the concentrations of levoglucosan, potassium and BaP (Fig. 8). The typical biomass burning tracer, levoglucosan, had higher concentrations during the cold period than right after it when temperature increased. Also, the concentrations of potassium and BaP were elevated at the same time. The correlation between BaP and levoglucosan has been shown to be very strong in small-house areas in Finland (Kousa et al., EAC, 2012).

Sulphate correlated with BBOA at the Residential I site (Table 2). The ratio of BBOA to sulphate increased as the concentration of BBOA increased (not shown), which indicated that BBOA increased relatively more than sulphate, and the main origin of sulphate was probably other than BBOA. The origin of sulphate may be from other heating systems like district heat produced by coal or heavy oil in power plants. The heavy oil is used as an additional heating source during cold weather periods, at least in the Helsinki metropolitan area. Furthermore, sulphate and BBOA are also present in LRT aerosols which are mixed with pollutants from local sources.

Traffic Sites

Similar to the residential sites, OOA had the highest contribution to OA at the traffic sites, (Curbside 67 ± 14% and Highway 50 ± 19%; Fig. 5). The diurnal pattern of OOA was relatively independent of the time of the day (Fig. 6).
Fig. 8. Daily concentrations of benzo(a)pyrene (BaP), levoglucosan and potassium (K) from PM10 filter measurements and biomass burning organic aerosol analyzed by ACSM and ME-2.

The time series of the OOA correlated with ammonium and sulphate at both the traffic sites and with nitrate at the Curbside site (Fig. 7 and Table 2). The ion balance was quite neutral at the Highway site, whereas it was mainly acidic at the Curbside site. There were no local emissions that would have explained the differences observed in acidity at the different sites, but meteorology and variation in emissions of precursor gases likely affected the concentrations of secondary inorganic ions and thus to the ion balance.

The contribution of HOA to OA was 33 ± 14% at the Curbside site and 25 ± 17% at the Highway site, with no correlation between ambient temperature and the concentrations or contributions of HOA. The diurnal trends of HOA, BC and NOx and their time series were similar, indicating common emission sources (Figs. 6 and 7). NOx is strongly associated with vehicle exhaust, and the diurnal pattern at the Highway site was quite typical for other traffic sites (Sun et al., 2011). During the rush hours, the HOA concentrations were elevated, and the morning peak was more pronounced than the evening peak. The morning and afternoon rush hour peaks were not seen at the Curbside site, maybe because the traffic flow near the Curbside site is quite constant throughout the day and/or the dispersion of aerosols was poor.

The mean contribution of BBOA to OA was 25 ± 15% at the Highway site and slightly smaller than at the Residential sites. Highest BBOA concentrations and contributions were measured with low ambient temperature, but such a clear trend as at the Residential I site was not seen (Fig. 5). In general, the weather was quite mild (temperature between −7 and 13°C) during the campaign. Two clear BBOA episodes were detected at the Highway site during the night of October 25–26 and on the evening of October 27 when temperature decreased below 0°C (Figs. 5 and 7). During those periods, the contribution of BBOA to OA was between 60 and 78%. BBOA seemed to be quite fresh during those days, as the concentrations of chloride were elevated together with BBOA. From the Curbside data, BBOA could not be extracted, probably because domestic wood burning is limited in downtown Helsinki and other sources dominate the composition of OA.

SUMMARY AND CONCLUSIONS

The chemistry of non-refractory submicron particles (NR-PM1) was investigated in four measurement campaigns at different environments in the Helsinki metropolitan area, Finland. Two of the campaigns were conducted in the suburban residential areas (Residential I and II sites), one in downtown (Curbside site) and one beside the suburban highway (Highway site). Campaigns were conducted either in winter (Residential I & II and Curbside) or in autumn (Highway). The detailed aerosol chemistry was characterised with approximately 30 min time resolution by using the Aerodyne Aerosol Chemical Speciation Monitor. The sources of organics were further examined by the multilinear engine algorithm (ME-2) and the custom software tool Source Finder (SoFi). Auxiliary aerosol chemical components (inorganics, black carbon) and NOx concentrations were used to interpret the sources and origins of different factors produced by ME-2.

The mean concentrations of NR-PM1, i.e., the sum of components deployed from the ACSM, were quite similar for the campaigns carried out in wintertime (10.1–12.5 µg/m³), whereas the concentration was 40–50% lower during the autumn campaign (6.0 µg/m³) conducted at the Highway site due to the low background concentration levels. The low background levels were likely caused by meteorology, origin of air masses and non-intensive heating period locally and regionally. On the basis of the whole study, organics had the highest contribution to NR-PM1 (54 ± 14%), followed by sulphate (21 ± 11%), nitrate (15 ± 8%), ammonium (9 ± 5%) and chloride (1.0 ± 2.2%). The contribution of black carbon to PM2.5 was 13% on average, having the highest concentrations and contributions at the traffic sites. The sum of NR-PM1 and BC accounted for almost all of PM2.5.

Organic fractions at four sites were divided into two or three distinct types of organic aerosol, representing HOA that was likely to be related to fresh vehicle exhaust, BBOA that mostly originated from local residential wood burning and OOA. The mass spectra of individual factors were very similar between the sites, although different approaches to the ME-2 tool were used: HOA was either constrained (residential sites) or not constrained (traffic sites). It seems that constraining was needed in the environments that were less affected by traffic. BBOA was not constrained, as it was separated without constraining at the Residential and the Highway sites, whereas at the Curbside site the biomass tracer (m/z 60) was not resolved from the background signal.
OOA had the largest contribution to organic aerosol at all the sites (50–67%) correlating with all or some of the secondary inorganic components, which indicates that OOA was mostly regionally distributed and long-range transported. The contributions of HOA were higher at the traffic sites (25–32%) than at the residential sites (15–18%). The time series and diurnal trends of HOA followed those of NOx and BC. The concentration of BBOA was clearly highest at the Residential I site (2.8 µg/m³) due to local wood burning emissions and cold weather. The detection of chloride together with BBOA supported the hypothesis that a significant fraction of BBOA was likely to be fresh and from local sources. BBOA had clear dependency on temperature. The contribution of BBOA was almost half of OA when temperature was low (below −15°C) at the Residential I site and as large as 60–78% during the cold autumn nights (below 0°C) at the Highway site. At the downtown traffic site (Curbside), BBOA could not be found, probably because most of the local wood burning occurs in the suburban small-house areas of the Helsinki region.

This study displayed an extensive chemical characterization of submicron aerosol particles at residential and traffic-related environments. It presented that online monitoring of PM1 chemical composition with ACSM provides new quantitative information on the sources of aerosol. That data is valuable for local authorities dealing with the air quality issues in urban areas. However, this study also showed that in a rather clean urban environment, like in the Helsinki metropolitan area, long-range transported or regionally distributed pollutants often dominate the concentration and the composition of PM, even though the measurements are carried out next to well-known particle sources (traffic, residential wood burning), resulting in relatively similar chemical composition and source apportionment for PM regardless of the location of the measurement site. In those cases, the measurement period needs to be long enough (probably at least several months) to obtain a sufficient amount of data with varying source contributions in order to achieve reliable source apportionment analysis. That can be accomplished by novel, low-maintenance monitoring instruments like the ACSM.

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