Atmospheric
Measurement
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High time-resolution chemical characterization of the water-soluble fraction of ambient aerosols with PILS-TOC-IC and AMS

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Abstract

A particle-into-liquid sampler (PILS) was coupled with a total organic carbon analyzer (TOC) and two ion chromatographs (IC) to enable high time-resolution measurements of water-soluble ions and water-soluble organic carbon (WSOC) by a single sampling and analytical set-up. The new high time-resolution measurement system, the PILS-TOC-IC, was able to provide essential chemical and physical information about fast changes in composition, concentrations and likely sources of the water-soluble fraction of atmospheric aerosol. The concentrations of major water-soluble ions and WSOC were measured by the PILS-TOC-IC system from 25 April to 28 May 2009. The data of the PILS-TOC-IC setup was completed with the data from the High-Resolution Time-of-Flight Aerosol Mass Spectrometer (HR-ToF-AMS) data measured from 25 April to 8 May 2009. The measured water-soluble particulate organic matter (WSPOM) concentration varied typically from 0.10 to $8.8\,\mu\text{g}\,\text{m}^{-3}$ (on average $1.5\,\mu\text{g}\,\text{m}^{-3}$). The WSPOM contributed on average 51% to particulate organic matter (POM) measured with the AMS. The correlation between the data of all the online measurement devices (AMS, PILS-TOC-IC, semicontinous EC/OC carbon analyzer and TEOM) was excellent. For sulfate, nitrate and ammonium the correlations between the PILS-TOC-IC and AMS were 0.93, 0.96 and 0.96, respectively. The correlation between WSPOM and POM was also strong ($r=0.88$).

The identified sources of WSPOM were long-range transported biomass burning and secondary organic aerosol (SOA) formation. The WSPOM/POM-ratio followed the trends of the ambient daytime temperature. The temperature dependency of the WSPOM/POM-ratio suggest that in the absence of emissions from biomass burning, the SOA formation was the prevailing source for WSPOM. WSPOM produced in biomass burning was clearly correlated with carbon monoxide, confirming that biomass burning was producing primary WSPOM. In addition, elevated oxalate and potassium concentrations were measured during the biomass burning episode.

1 Introduction

Typically 20–70% of atmospheric aerosol mass comprises of organic compounds, and 40–80% of the organic matter is water-soluble (Jaffrezo et al., 2005; Saxena and Hildeman, 1995). The chemical composition, sources, atmospheric processing, and removal mechanisms of water-soluble organic carbon (WSOC) are inadequately known. The analytical procedure to resolve the chemical composition of water-soluble particulate organic matter (WSPOM) has been typically based on a combination of total organic carbon analysis, chromatographic separations and organic functional group analysis (e.g., Decesari et al., 2000, 2007; Ding et al., 2008). These studies have shown that the WSOC fraction is a complex mixture likely composed of aliphatic structures, oxygenated alkyls, carboxylic acids, and aromatic structures. Typically, the individually identified compounds comprise less than 20% of the total mass of water-soluble compounds (e.g., Yang et al., 2005; Decesari et al., 2006). The recent results indicate that the organic compounds and their precursor gases evolve in the atmosphere (Jimenez et al., 2009). The aging process in atmosphere leads to the formation of organic aerosol, which is increasingly oxidized, less volatile, more hygroscopic and more water-soluble (Jimenez et al., 2009).

According to the recent results, the identified formation of WSOC is connected with e.g. biomass combustion, secondary aerosol formation, long-range transport and in-cloud processing (Huang et al., 2006; Viana et al., 2007; Saarikoski et al., 2008). Biomass burning and secondary organic aerosol (SOA) formation are considered to be the major sources of WSOC (Miyazaki et al., 2006; Kondo et al., 2007). SOA may originate either from anthropogenic or biogenic sources. Traditionally it has been thought that in urban areas most of the SOA is anthropogenic, however, the recent carbon isotope analysis has revealed that more SOA than expected is formed from biogenic precursors (Szidat et al., 2006, 2009). Also hydrocarbon emissions from vegetation have been shown to greatly influence the number and mass concentrations of aerosols in the boreal region (Tunved et al., 2006). According to the calculations made

by Kulmala et al. (2004), the biogenic volatile organic compounds (BVOCs) emitted by forests also enhance the organic aerosol production and growth rate. In addition, Ding et al. (2008) have found a clear correlation between 2-methyltetrols and WSOC during the summer in a rural area, suggesting that isoprene SOA makes an important contribution to WSOC.

Experimental data on WSOC in ambient air is still scarce especially in the boreal region. The emission, transformation, and transport processes of organic aerosols have time-scales ranging from minutes to hours, yet the time-resolution of most of the WSOC data is typically 1–3 days (e.g., Huang et al., 2006; Zhang et al., 2008). This paper describes the new measurement and analyzing system, where one particle-into-liquid sampler was coupled to a total organic carbon analyzer (TOC-V$_{CPH}$) and two ion chromatographs (IC; hereafter the system is called PILS-TOC-IC). PILS-TOC-IC was used for simultaneous high time-resolution chemical measurements of water-soluble fraction (WSOC and ions) of aerosols during field measurement campaign in spring 2009. PILS-TOC-IC results were compared with the results of High-Resolution Time-of-Flight Aerosol Mass Spectrometer (HR-ToF-AMS), gas analyzers, and meteorological measurements. To our knowledge, these measurements are first online-measurements of WSOC in northern Europe.

2 Experimental

2.1 Measurement site

The measurements were conducted at the urban background station SMEAR III (60°12′, 24°57′, 30 m a.s.l., Järvi et al., 2009). Long-term measurements of chemical and physical properties of atmospheric aerosols and trace gas concentrations have been conducted at SMEAR III station since it was established 2004. The SMEAR III site is situated in the Helsinki Metropolitan Area, on the coast of the Baltic Sea in Southern Finland. The station is located ca. 5 km northeast from the city centre of Helsinki. It is

surrounded by the buildings of the University of Helsinki and the Finnish Meteorological Institute (FMI) on the northeastern side, and by mainly forested area in the west. At a distance of less than 200 m to the east, there is a major road with heavy traffic (60 000 cars/day).

2.2 Meteorological data and gas-phase components

Local meteorological data were obtained from the Finnish Meteorological Institute Kumpula weather station (Vaisala, Milos 500), 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. To compare with the chemical measurements of this study, one-hour averages were calculated for the meteorological data.

Carbon monoxide (CO) was measured at the SMEAR III station using Horiba APMA 370 analyzer (Horiba, Kyoto, Japan). To establish the potential source areas of the measured aerosol particles, 120-h air mass back trajectories were calculated for the sampling periods using the FLEXTRA model (Stohl and Wotawa, 1995).

2.3 Particle-into-liquid sampler (PILS)

The particle-into-liquid sampler has been developed for rapid automated on-line measurement of ambient aerosol bulk composition (Weber et al., 2001; Orsini et al., 2003). The PILS is typically coupled with either ion chromatograph or total organic carbon analyzer (e.g. Kondo et al., 2007; Saarikoski et al., 2008). Examples of the previous measurement campaigns, where PILS has been used, are collected to Table 1. The campaigns were typically short in duration, from weeks to months and the majority of the measurements has been conducted in the United States. In addition to the stationary measurements, PILS has been often used in mobile measurements e.g. in an airplane (Sorooshian et al., 2007), in a ship (De Gouw et al., 2008) or in a train (TROICA-9 experiment at the Trans-Siberian railway; Kuokka et al., 2007).

2.3.1 Sampling line

A cyclone (sharp cut cyclone SCC 1.829, BGI Inc. US) was used on the top of the sampling line to cut off supermicron particles (particle aerodynamic diameter >1 µm). After the cyclone, the sample flow ($11\,l\,min^{-1}$) was directed to two denuders. A parallel plate carbon filter denuder (Sunset Laboratory Inc., Portland, OR) and an annular denuder (URG-2000, $30\times242\,mm$, Chapel Hill, NC) coated with H_3PO_4 were used to remove gaseous organic components and ammonia from the sample. After the denuders, the line was divided to a sample-line and a blank-line. The sample-line fed the airflow directly to the PILS. In the blank-line the airflow was directed first through a PTFE filter (type FS, diameter 47 mm, pore size 3 µm, Millipore, Ireland) and subsequently fed to the PILS. When the blank values were measured, a valve was used to force the airflow through a PTFE filter. The blank value was measured for approximately 1 h every day during the week days.

2.3.2 Coupling the instruments to the PILS

In this study, a liquid sample from one PILS (Metrohm Peak Inc) was shared by the Shimadzu TOC-V$_{CPH}$ analyzer and two Dionex ICS-2000 ion chromatographs to enable simultaneous high time-resolution measurements of water-soluble organic carbon and water-soluble ions. Figure 1 represents the designed PILS-TOC-IC system. The design and the operating principle of the PILS have been described in detail by Orsini et al. (2003). Shortly, aerosol particles are mixed with water-vapor and after cooling they grow into droplets inside a conical-shaped cavity. After the cavity, the droplets go through a nozzle and are impacted onto a quartz glass impaction plate. The impaction plate is washed off with a steady stream of the transport liquid containing internal standard (lithium fluoride, LiF). During collection, liquid that has been condensed onto aerosol particles and a small amount of water condensing out of the saturated air to the quartz impaction surface dilutes the transport liquid. Based on the LiF concentration prior and after the PILS this dilution is taken into account and the aerosol con-

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centration can be accurately calculated. Since the dilution factor calculation is based on the IC data, it is usually estimated for the PILS-TOC measurements. In the PILS-TOC-IC system developed in this study, the dilution factor for the WSOC samples can be accurately determined from the simultaneous IC data, since the same sample is fed for both instruments. Sudden increases in the dilution factor can also be used to detect the reduced liquid flows e.g. due to the blocked capillary tubes. By using one PILS for both devices instead of two PILS, the amount of liquid consumed was reduced and also the amount of cleaning (e.g. quartz impaction surface) and maintenance work (e.g. replacing dirty and blocked capillary tubes) was reduced. After impaction to the quartz surface, the sample-liquid is delivered into a debubbler to remove air and to divide the liquid-flow into two separate lines.

Two liquid pumps were used to control the liquid flows in the PILS-TOC-IC system, an 8-channel peristaltic pump (Watson Marlow, 205S, USA) and a piston pump (AXP-MS, Dionex, USA). The peristaltic pump was used to feed $1.25\,\mathrm{ml\,min^{-1}}$ of water for the steamer and to deliver the sample from the debubbler to the TOC-V$_{\mathrm{CPH}}$ ($0.22\,\mathrm{ml\,min^{-1}}$) and the ion chromatographs ($0.1\,\mathrm{ml\,min^{-1}}$ for each). The LiF-flow ($0.37\,\mathrm{ml\,min^{-1}}$) was controlled with a separate AXP-MS pump to maintain the flow as stable as possible.

2.3.3 Online chemical analysis

The debubbler divided the PILS-sample into two equal fractions. One fraction was fed through an inline PTFE filter to remove the water-insoluble carbonaceous particles from the sample and then collected to a sealed glass bottle for the subsequent WSOC analysis. WSOC was analyzed by a total-organic carbon analyzer (TOC-V$_{\mathrm{CPH}}$, Shimadzu). The non-purgeable organic carbon (NPOC) method was used because it was necessary to remove carbonate carbon and carbon dioxide from the samples before the measurements. The sample that has been fed from the PILS into a bottle was automatically drawn through a tube to a syringe of the TOC-V$_{\mathrm{CPH}}$. To avoid mixing between the consecutive samples, the sample volume was adjusted so that the sample bottle was empty between the samples. In the syringe, the sample was acidified and bubbled

for 5.5 min with helium (grade 5.0) to remove carbonate carbon and carbon dioxide, and then injected into an oven. In the oven, carbonaceous material of the sample was catalytically (platinum on quartz wool high sensitivity catalyst) oxidized to CO_2 at 680 °C and the produced CO_2 detected by a sensitive non-dispersive infrared (NDIR) detector. The estimated error of the WSOC measurement is 15% for atmospheric concentrations <2 µg m^{-3} and 10% for concentrations >2 µg m^{-3}. The limit of quantification for the TOC-V$_{CPH}$ is 4 µg l^{-1}, which equals to an air concentration 0.15 µg m^{-3}. The time-resolution of the measurement was adjusted to six minutes to collect large enough sample for the TOC-V$_{CPH}$ analyzer. In order to estimate the amount of particulate organic matter (WSPOM), the WSOC concentrations were multiplied by the estimated average molecular weight per carbon weight in aerosols. For simplicity, the constant ratio of 1.6 was used in this work, based on calculations published by Turpin and Lim (2001) and Saarnio et al. (2010), but the ratio may vary and likely be higher e.g. depending on the aerosol aging.

The other fraction of the collected PILS sample was further split to two equal fractions by a simple t-shape splitter and fed continuously to the sample loops (1 ml) of the two ion chromatographs to measure anions and cations. The time-resolution of ion measurements was 15 min. The ions (Na$^+$, NH$_4^+$, K$^+$, Mg^{2+}, Ca^{2+}, Cl$^-$, NO$_3^-$, SO$_4^{2-}$, oxalate) were analyzed using the Dionex ICS-2000 (Dionex, Sunnyvale, USA) ion chromatographs. The ion chromatographs had the AG11/CG12A guard columns, AS17/CS12A analytical columns and ASRS/CSRS ultra II suppressors for anion and cation analyzes, respectively. KOH solution, with concentration gradient from 2 to 35 mmol l^{-1}, was used as the eluent for anions. For cations the eluent was 20 mmol l^{-1} methanesulphonic acid. The uncertainty of the IC analysis was of the order of 10–15% for all analyzed ions. The quantification limit for major ions was 2.5 ng ml^{-1}, which equals to the air concentration of 0.1 µg m^{-3}.

Blank values were measured for the PILS-TOC-IC system by directing the air flow through a PTFE filter prior to the PILS. The blank values measured for ions were typically very low compared to the liquid containing dissolved ions from the aerosol par-

ticles. For WSOC the blank values were larger, typically $1.3 \pm 0.5\,\mu g\,m^{-3}$. The blank values of WSOC were subtracted from the corresponding results. The blank concentrations were assumed to be constant between the consecutive background measurements.

2.4 Aerodyne High-Resolution Time-of-Flight Aerosol Mass Spectrometer

The Aerodyne High-Resolution Time-of-Flight Aerosol Mass Spectrometer, previously described by DeCarlo et al. (2006), was used to determine the concentrations of major fine particulate matter species: POM, sulfate, nitrate, chloride, and ammonium. The HR-ToF-AMS consists of a particle sampling inlet, a particle sizing chamber, and a particle composition detection section. Aerosol particles are sampled through an aerodynamic lens, forming a narrow particle beam that is transmitted into the detection chamber where the non-refractory species are flash-vaporized upon impact on a hot surface (600 °C) under high vacuum. The composition is subsequently analyzed via electron impact ionization (70 eV) by the high resolution time-of-flight mass spectrometer. During the measurements, the AMS was alternating between V-mode and W-mode. V-mode is a single-reflection configuration with higher sensitivity and lower resolving power (unit mass resolution) and the W-mode is a two-reflectron configuration with higher resolving power but lower sensitivity (DeCarlo et al. 2006). In this study five minute average results of the unit mass resolution data from V-mode was used. The IGOR 6.11 (Wavemetrics, Lake Oswego, OR) and Squirrel 1.47 (Sueper, 2009) were used to analyze the AMS data. A collection efficiency of 0.5 was used for the data.

2.5 TOA

A semicontinuous EC/OC carbon analyzer (TOA; Sunset Laboratory Inc., Oregon) was used to determine concentrations of organic and elemental carbon (OC and EC). The method is described in detail by Saarikoski et al. (2008). Shortly, a cyclone with cut-off

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at 1 µm was used to remove the coarse particles and a parallel plate carbon denuder (Sunset laboratory Inc., Portland, OR) was used to remove the organic gaseous compounds from the sample air. In the thermal method helium with two temperature steps: 600 °C (80 s) and 840 °C (90 s) was used to determine OC and helium-oxygen mixture with three temperature steps: 550 °C (30 s), 650 °C (45 s) and 850 °C (90 s) was used to determine EC. Charring of OC was corrected optically using the data obtained from the tuned diode laser. The instrumental blank was analyzed daily at 03:00 for three minutes. The blank values were subtracted from the results. The uncertainty of OC and EC results was estimated to be 20%.

2.6 TEOM

A tapered element oscillating microbalance (TEOM model 1400a) equipped with a Sample Equilibration System (SES) and a Filter Dynamic Measurement System (FDMS, 8500 model series) was used to measure the $PM_{1.3}$ total mass continuously. A $PM_{1.3}$ virtual impactor (VI; Loo and Cork, 1988) was used to cut off the supermicron particles. TEOM collects the sample on the filter placed to the oscillating element. The mass collected on the filter changes the oscillating resonance frequency. The changes in the oscillating resonance frequency are recorded and converted to mass. The uncertainty of the TEOM was estimated to be 10%.

3 Results and discussion

3.1 The origin of air masses

Based on satellite observations deploying MODIS sensor on board of NASA EOS Terra satellite and on the backward trajectories of air masses, smokes from the major forest fire areas in the southern and eastern Europe were transported to the measurement site from 26 April to 29 April 2009. For that period the $PM_{1.3}$ mass concentrations were

high (10–20 µg m^{-3}, not shown) and also elevated sulfate, ammonium, and nitrate concentrations were measured (Fig. 2). The AMS mass to charge ratios m/z 60 and 73, known as biomass burning tracers (Lanz et al., 2007), were elevated (not shown), indicating that the aerosols were originating from biomass burning. Also potassium can be used as a combustion tracer (e.g., Watson et al., 1994). Elevated potassium concentrations (0.3–0.6 µg m^{-3}) were measured with the PILS-TOC-IC during the biomass burning episode (not shown). However, high concentrations of secondary ions in inorganic aerosol composition suggested that biomass burning emissions were mixed with other anthropogenic sources during the transport. Similar long-range transported biomass burning episodes are detected in Finland almost every spring and summer (Sillanpää et al., 2005; Saarikoski et al., 2007; Saarnio et al., 2010).

For the rest of the measurement period (25–26 April and 29 April–28 May) the trajectories showed that air masses came over forested clean areas either from north or west. During that period the PM$_{1.3}$ mass concentration was typically below 10 µg m^{-3} and the concentrations of sulfate, ammonium and nitrate varied from moderate to low (Fig. 2).

3.2 Water-soluble particulate organic matter and ion concentrations

The concentrations of major water-soluble ions and WSOC were measured by the PILS-TOC-IC system between 25 April and 28 May 2009. The WSPOM concentration (using conversion factor 1.6 to convert WSOC to WSPOM) varied from 0.10 to 8.8 µg m^{-3} (Fig. 2). On average, the WSPOM concentration was 1.5 µg m^{-3}. Sulfate was the most abundant ion with an average concentration of 1.5 µg m^{-3}, but with a maxima reaching up to 5.8 µg m^{-3}. The ammonium concentrations ranged from below the limit of quantification (0.1 µg m^{-3}) to 5.0 µg m^{-3}. The concentration of nitrate during the study was rising up to 2.9 µg m^{-3}. During the biomass burning episode, elevated WSPOM values, as high as 8.8 µg m^{-3}, were measured. The ion concentrations also elevated during the biomass burning episode. For the episode period the average

sulfate, ammonium, and nitrate concentrations were 3.7, 1.4, 2.2 $\mu g\, m^{-3}$, respectively.

The HR-ToF-AMS measurements were conducted from 25 April to 8 May 2009. For major ions (sulfate, nitrate and ammonium), the time-series measured by the PILS-TOC-IC and the HR-ToF-AMS followed each other very closely (Fig. 2). The five-minute average POM concentrations measured with the AMS varied from 0.2 to 14 $\mu g\, m^{-3}$ (during biomass burning episode 4.0–14 $\mu g\, m^{-3}$). The WSPOM (PILS-TOC-IC) to POM (AMS)-ratios were calculated. On average 51% of POM consisted of WSPOM. During the biomass burning episode, the WSPOM/POM-ratio was higher, being 69% on average. The major ions, sulfate, ammonium, and nitrate accounted for 30%, 10% and 9% of the total mass, respectively.

The results of the different high-resolution online instruments were compared. All PILS-TOC-IC results correlated closely with the AMS results. For sulfate, nitrate and ammonium the correlations between the PILS-TOC-IC and AMS were 0.93, 0.96 and 0.96, respectively. The total mass (sum of ions and organics, not including EC) calculated from the AMS data was compared to the total mass ($PM_{1.3}$) measured with TEOM (including EC). The time-series of total mass from AMS and TEOM has clearly a similar temporal pattern (Fig. 2). The POM results from the semicontinuous EC/OC-analyzer were compared to POM measured by the AMS. Unfortunately the EC/OC-analyzer oven was broken down during the campaign, and therefore only the results of first week (25 April to 1 May) were available for the comparison. For the first week the correlation was very good (r=0.88).

A good correlation was also observed between POM measured by the AMS and WSPOM measured by the PILS-TOC-IC system (R=0.88), indicating that the WSPOM is major component of POM. This correlation was further studied by dividing the WSPOM data into three subsets on the basis of the AMS data and the air mass back-trajectories: 1) samples influenced by biomass burning (the period from 26 April, 12:00 to 29 April, 11:00, m/z 60 elevated, the trajectories show that the particles originate from wild fire areas), 2) samples influenced by traffic (three separate episodes, from 30 April, 18:00 to 1 May, 07:00, 4 May, 05:00–13:00, from 6 May, 07:00 to 7 May, 11:00,

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when the m/z 57 was elevated above 0.2 µg m^{-3}), 3) the rest of the samples. For biomass burning samples, WSPOM and POM were highly correlated (Fig. 3; r=0.85), but for the periods influenced by traffic, WSPOM didn't correlate with POM. For the rest of the samples there was a correlation between WSPOM and POM, however, the
5   correlation was weaker than for biomass burning.

3.3   Correlation of WSPOM with CO and oxalate

Carbon monoxide is often considered as a tracer for urban pollution caused by traffic, but is also formed in incomplete burning of biomass (Ovadnevaite et al., 2006). Clear correlations between CO and WSPOM have been reported in many studies (e.g. Sulli-
10   van et al., 2006; de Gouw et al., 2008). Those studies have been made in places where the urban pollution affects aerosol concentrations significantly. Finland is situated in the boreal region, where biogenic emissions are large (Hakola et al., 2003) and the PM$_1$ concentration is typically low (Laakso et al., 2003). During the measurement period of this study, the total mass concentration (PM$_{1.3}$, measured by the TEOM) was typically
15   below 10 µg m^{-3}. Elevated concentrations (10–20 µg m^{-3}) were measured only when the smokes from forest fires were drifted from the Eastern Europe. To examine the correlation between CO and WSPOM, the measured WSPOM values were divided into three subsets similarly as before: 1) samples influenced by the long-range transported biomass burning smokes, 2) samples influenced by traffic, 3) the rest of the samples.
20   The WSOC versus CO scatter plot (Fig. 4) clearly shows that the WSPOM for periods affected by biomass burning has the strongest correlation (r=0.60) with CO. This suggests that primary WSPOM is produced in biomass burning. The other samples had no clear correlation with CO.
    Oxalate is one of the major components of WSPOM, contributing typically 1–3%
25   of the fine mode WSPOM. Oxalate has various sources such as vehicle emissions, biomass burning, in-cloud processing and atmospheric oxidation of VOCs (Huang et al., 2006; Hsieh et al., 2007). In this study oxalate constituted on average 3.8% of

WSPOM. Typically oxalate concentrations were below quantification limit, $0.1\,\mu g\,m^{-3}$, but during the forest fire episode elevated concentrations (0.1–$0.3\,\mu g\,m^{-3}$) were measured (Fig. 5). The results that were below quantification limit have been plotted to Fig. 5 for qualitative purpose to show the difference between forest fire episode and
5 the rest of the measurement period. However, the error in the concentration measurements close or below quantification limit can be large. The oxalate concentrations during the forest fire episode were clearly correlated with WSPOM ($r=0.82$), indicating that the biomass burning was an important source for oxalate (Fig. 5).

3.4 Secondary organic aerosol

10 In studies made in Tokyo, Japan the secondary organic aerosol formation was estimated to be the dominating source of WSOC in the absence of biomass burning (Fuzzi et al., 2006; Miyazaki et al., 2006; Kondo et al., 2007). Meteorological conditions such as temperature and relative humidity have been found to have an effect on the SOA formation and thus on WSOC formation. Warren et al. (2009) have no-
15 ticed that higher temperature clearly increases the total SOA formation in the chamber experiments made with cyclohexene and α-pinene. Hennigan et al. (2009) have reported that WSOC gas/particle partitioning shows a strong RH dependence that was attributed to particulate liquid water. At elevated RH levels (>70%) they observed an increase in WSOC partitioning to the particle phase. Studies in remote regions (Claeys
20 et al., 2004; Tunved et al., 2006) have proved the importance of biogenic VOCs as the POM precursors.

In this study, the concentrations of WSOC did not directly correlate with temperature, relative humidity, or global radiation. However, the WSPOM/POM-ratio was found to have a similar temporal pattern with the maximum temperature of the day (Fig. 6). The
25 higher the maximum temperature of the day was, the higher was the WSPOM/POM-ratio. The relative humidity or the global radiation did not have the same temporal pattern with the WSPOM/POM-ratio. To further investigate the effect of temperature

on WSOC, the PILS-TOC-IC data was divided into samples measured in daytime (1-h average WSOC results from 06:00 to 18:00) and in night-time (1-h average WSOC results from 06:00 to 18:00). In night-time, there was no correlation between temperature and the WSOC concentrations or the WSPOM/POM-ratio. In daytime no correlation was found between the WSOC concentration and temperature. However, the WSPOM/POM-ratio had a correlation with temperature in daytime (Fig. 7). When the temperatures were below $12\,^\circ$C, the WSPOM/POM-ratios were typically below 50%. For temperatures from $12\,^\circ$C to $18\,^\circ$C the WSPOM/POM-ratios were typically between 50 and 70%. The results of this study are in agreement with the findings of Jaffrezo et al. (2005). They found that the higher WSOC/OC-ratios (>60%) were observed when the temperatures were above $5\,^\circ$C. Also Hennigan et al. (2008) observed that the daily median water-soluble organic matter concentrations were increasing linearly with the increasing temperature.

Based on our data it was impossible to conclude whether the observed temperature dependency in WSPOM/POM-ratio was actually caused by the temperature or some other variable (like changes in boundary layer height or meteorological variables) varying simultaneously with the temperature or even causing the change in WSPOM and the temperature. Anyhow, the SOA formation from biogenic volatile organic compounds emitted by the boreal forests is one possible explanation for the results. The BVOC emissions by boreal forests typically depend on temperature and light (Kulmala et al., 2004, and references therein). The trajectories showed that during the campaign (25 April to 28 May 2009, excluding the forest fire episode during 26–29 April) aerosols came over the forested areas in the west and north. The poor correlation of WSOC with CO and sulfate suggested that neither the anthropogenic secondary aerosol formation nor the long-range transport was the major source during that time. The temperature dependency of the WSPOM/POM-ratio, and the fact that the largest increases in the WSPOM/POM-ratio were seen in daytime, suggested that the SOA formation from biogenic VOC's was a possible source of WSOC in the boreal region in summer.

4   Summary and conclusions

In this work, a new method for the online measurement of water-soluble fraction of ambient aerosols was developed by combining a PILS with TOC-V$_{CPH}$ and two IC analyzers. The concentrations of water-soluble organic carbon and ions were measured for a month (25 April to 28 May 2009) in southern Finland with the PILS-TOC-IC. The high time-resolution (6 min and 15 min, respectively) of the measurements provided data that could follow the rapid changes in WSOC and ion concentrations. Also, by coupling one PILS simultaneously to two instruments, the amount of work was reduced and the reliability of measurements was increased. The high time-resolution data of WSPOM enables observation of diurnal variations and comparison of the data with gas-phase compounds typically measured continuously as well as with the meteorological data. Additionally an advantage of high-resolution data was that WSPOM can be connected to the potential sources. Moreover, the on-line sample analyzes minimized the contamination risk (common in handling and storage of samples in offline methods) and the sampling artifacts (like evaporation and absorption of organic gases).

The PILS-TOC-IC data was compared to the AMS data measured between 25 April and 8 May 2009. For sulfate, nitrate and ammonium the correlations between the PILS-TOC-IC and AMS were 0.93, 0.96 and 0.96, respectively. Also POM (AMS) and WSPOM (PILS-TOC-IC) results were strongly correlated (r=0.88). The good correlation between the two different instruments shows that both methods can provide high time-resolved, quantitative data. The results of AMS were also strongly correlated with the results of TEOM and semicontinuous EC/OC carbon analyzer.

Biomass burning was pointed out as one of the major individual sources of WSPOM. WSPOM produced by biomass burning was noticed to have a clear correlation with CO, indicating that primary WSOC is produced in biomass burning. More indirectly it was suggested on the basis of this study that biogenic SOA formation also generates water-soluble organic carbon. The suggested source and formation pathway for that is oxidation and particle formation/condensation of biogenic gas-phase emissions,

which in the boreal region in northern Europe is typically high during growing season. The temperature dependency of the WSPOM/POM-ratio and the fact that the largest increases in the WSPOM/POM-ratio were seen in daytime, suggested that the SOA formation from biogenic VOCs was a possible source of WSOC in the boreal region in summer.

The high time-resolution data of the AMS and the PILS-TOC-IC system provided unique insight into the sources and behavior of water-soluble organic carbon and ions. In addition, the high time-resolution data enabled one to study diurnal changes and the correlations between the meteorological data and WSPOM. Although the measurements covered only quite short period representing late spring and early summer, the study showed that real-time observations were valuable in tracking sources and formation routes of atmospheric aerosols.

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Table 1. Main PILS-measurement campaigns reported in the literature.

Author	Detection	Time-resolution	Time/season	Campaign, Place
Orsini et al. (2003)	IC		5 weeks	Field campaign TEXAQS 2000, Houston, TX
Broekhuizen et al. (2006)	IC	15 min	Several weeks, autumn	Downtown Toronto, Ontario, Canada on the University of Toronto St. George Campus
Hennigan et al. (2006)	IC	1.5 min	14 days	NASA INTEX-NA Airplane measurements, centered over the eastern United States and Canada
Miyazaki et al. (2006)	WSOC	6 min	13 days winter, 17 days summer, 15 days fall	Tokyo urban area
Sorooshian et al. (2006)	IC		12 flights	Atmospheric Research on Transport and Transformation (ICARTT) field campaign, 2004. Airplane measurements over Ohio and surrounding areas.
Sullivan et al. (2006)	WSOC	3 s	Large number of flights during one month period in summer	NOAA WP-3D aircraft during the NEAQS/ITCT 2004, northeastern United States
Bae et al. (2007)	IC	15 min	15 days winter, 18 days summer	Urban site in New York City Rural site in southwestern New York state
Kondo et al. (2007)	WSOC	6 min	13 days winter, 15 days summer	Tokyo, Japan
Kuokka et al. (2007)	IC	10 min	14 days autumn	Train between Moscow and Vladivostok
Peltier et al. (2007)	WSOC		5 months	Atlanta, GA, and Riverside, CA
Sorooshian et al. (2007)	IC	5 min	22 flights, 976 samples	GoMACCS, airplane measurements above East Texas and the Gulf of Mexico
De Gouw et al. (2008)	WSOC	1 min	1 month cruise + 18 flights during a month in summer	NEAQS-ITCT 2004, 18 research aircraft (WP-3D) flights above eastern US and the NOAA research ship cruising at Massachusetts and New Hampshire coast
Hennigan et al. (2008)	WSOC	6 min	4 months	Atlanta
Saarikoski et al. (2008)	IC	15 min	1 year (2006–2007)	SMEAR III station Helsinki, Finland
Miyazaki et al. (2009)	WSOC	6 min	26 days	Guangzhou, China
Miyazaki et al. (2009)	WSOC	6 min		PRIDE-PRD campaign, rural site Pearl River Delta region, China
Partshitsev et al. (2009)	GC-MS	2 h	6 days	SMEAR II station at Hyytiälä, Finland

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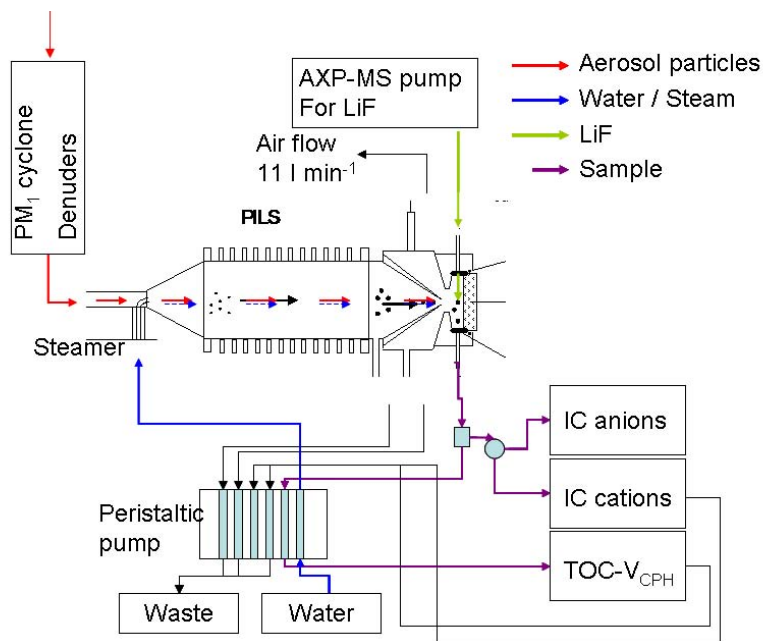
Fig. 1. PILS-TOC-IC measurement device. Arrows represent the flow of the sample and liquids within the system.
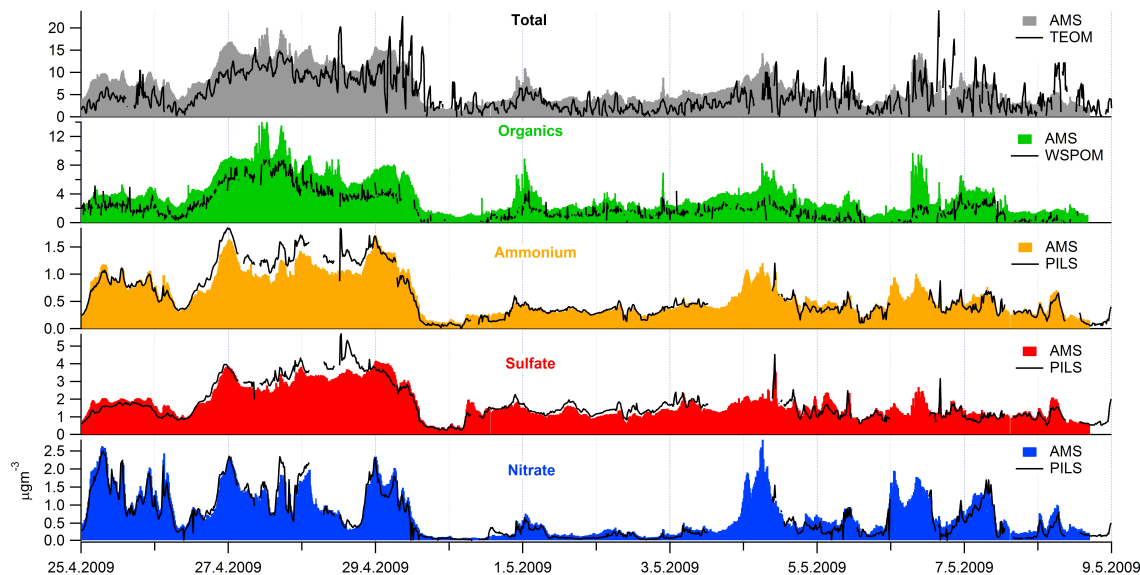
Fig. 2. Concentrations of major ions and WSPOM (using conversion factor 1.6 to convert WSOC to WSPOM) measured by PILS-TOC-IC and AMS from 25 April to 8 May 2009. PILS-TOC-IC (ions, WSPOM) and TEOM (total mass) results are marked with the black line. AMS results are marked with colors (blue = nitrate, red = sulfate, yellow = ammonium, green = total organics, grey = total mass i.e. sum of ions and organics).
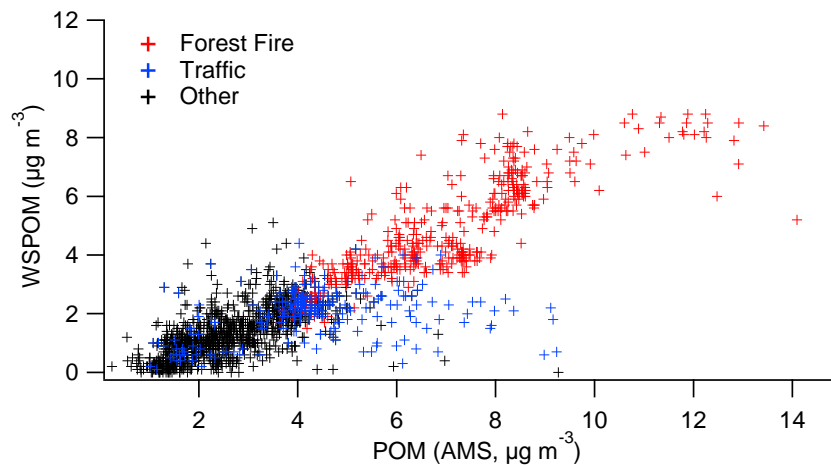
Fig. 3. WSPOM versus POM for different sources of WSPOM.

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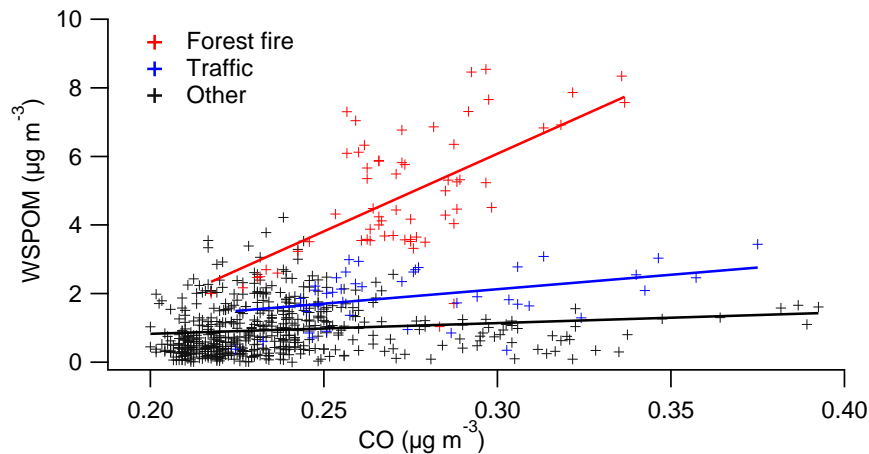
Fig. 4. Concentration of water-soluble particulate organic matter versus carbon monoxide concentration for different sources of WSPOM.
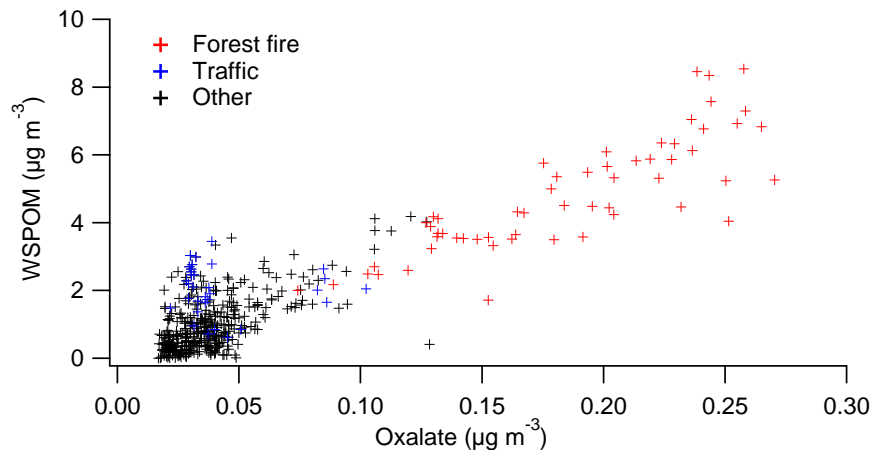
Fig. 5. The concentration of water-soluble particulate organic matter versus concentration of oxalate for different sources of WSPOM.
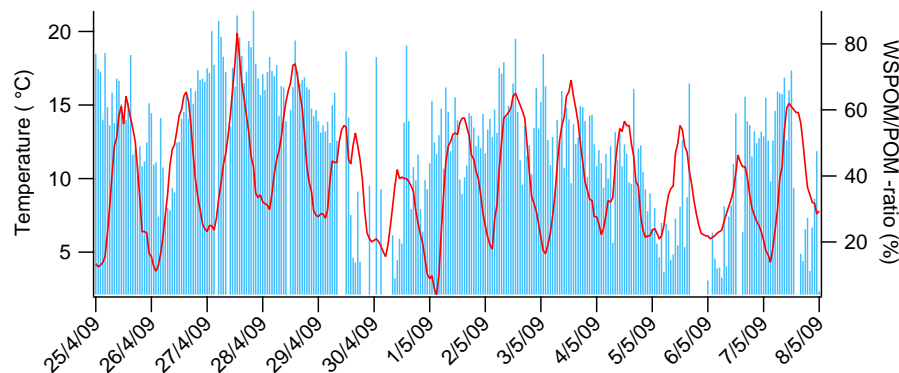
Fig. 6. Time-series of WSPOM/POM-ratio and temperature from 25 April to 8 May 2009.
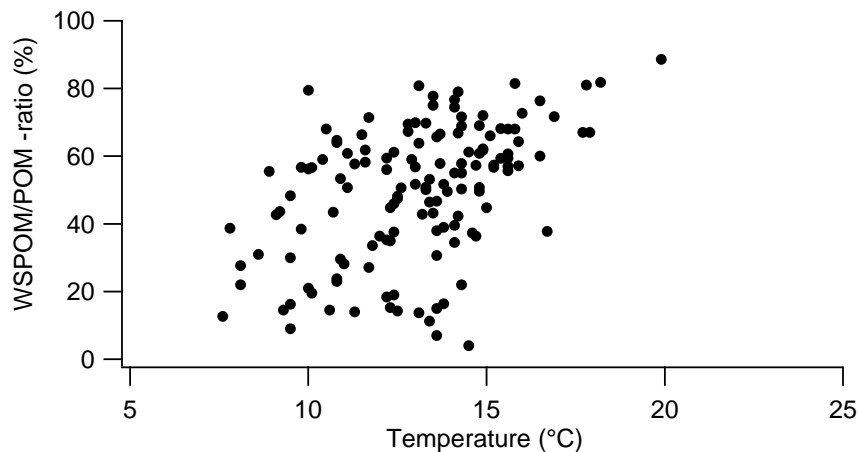
Fig. 7. Temperature dependency of the WSPOM/POM-ratios in daytime (1 h average values from 06:00 to 18:00) between 25 April and 8 May 2009.