

Size distributions, sources and source areas of water-soluble organic carbon in urban background air

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Abstract

This paper represents the results of one year long measurement period of the size distributions of water-soluble organic carbon (WSOC), inorganic ions and gravimetric mass of particulate matter. Measurements were done at an urban background station (SMEAR III) by using a micro-orifice uniform deposit impactor (MOUDI). The site is located in northern European boreal region in Helsinki, Finland. The WSOC size distribution measurements were completed with the chemical analysis of inorganic ions, organic carbon (OC) and monosaccharide anhydrides from the filter samples. During the measurements gravimetric mass in the MOUDI collections varied between 3.4 and 55.0 $\mu\text{g m}^{-3}$ and the WSOC concentration was between 0.3 and 7.4 $\mu\text{g m}^{-3}$. On average, water-soluble particulate organic matter (WSPOM, WSOC multiplied by 1.6) comprised 25 \pm 7.7% and 7.5 \pm 3.4% of aerosol PM₁ mass and the PM₁₋₁₀ mass, respectively. Inorganic ions contributed 33 \pm 12% and 28 \pm 19% of the analyzed PM₁ and PM₁₋₁₀ aerosol mass.

Five different aerosol categories corresponding to different sources or source areas were identified (long-range transport aerosols, biomass burning aerosols from wild land fires and from small-scale wood combustion, aerosols originating from marine areas and from the clean arctic areas). Clear differences in WSOC concentrations and size distributions originating from different sources or source areas were observed, although there are also many other factors which might affect the results. E.g. the local conditions and sources of volatile organic compounds (VOCs) and aerosols as well as various transformation processes are likely to have an impact on the measured aerosol composition. Using the source categories, it was identified that especially the oxidation products of biogenic VOCs in summer had a clear effect on WSOC concentrations.

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1 Introduction

The thorough knowledge on chemistry of atmospheric aerosol particles is needed to understand the effect of multiphase and multicomponent aerosol particles on the earth's radiative budget and climate. During the last few years increasing attention has been focused to the carbonaceous fraction (organic carbon, OC and elemental carbon, EC) of atmospheric aerosols. OC can be directly emitted to the atmosphere in particulate form (POA, primary organic aerosol) or it can be formed by gas-to-particle conversion in the atmosphere (SOA, secondary organic aerosol, Kanakidou et al., 2005). SOA formation is a complex process, involving gas-phase oxidation chemistry, partitioning of oxidation products between the gas and particle phases, and aerosol phase chemistry (Weber et al., 2007; Chan et al., 2007).

The organic compounds in atmospheric aerosols can be further divided to water-soluble compounds (WSOC) and water-insoluble compounds (WISOC). Large fraction of WSOC is assumed to be SOA formed from atmospheric oxidation products of VOCs or via gas-to-particle conversion (e.g. Kondo et al., 2007; Pio et al., 2007). Both processes are generally dependent on the atmospheric conditions like temperature, radiation, photo-oxidants, amount of water vapor and other condensable gases (Fuzzi et al., 2006). According to the results by Decesari et al. (2001) WSOC is composed of highly oxidized species with residual aromatic nuclei and aliphatic chains. WSOC comprises typically 20–70% of OC (Pio et al., 2007). Smallest WSOC to OC ratios are measured near the sources (typically in urban locations near a fossil fuel combustion sources) and larger values are measured for more aged aerosol at more remote locations (Pio et al., 2007). The identified sources or formation mechanisms of WSOC are e.g. biomass burning, soil particles, aged sea salt and in-cloud processing (Huang et al., 2007).

Particulate water-soluble organic matter is expected to affect the chemical and physical properties of aerosols e.g. hygroscopic behavior (the ability of particles to act as CCN), acidity, and radiative properties (Jacobson et al., 2000). Despite the evident

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significance of OC and WSOC in atmospheric chemistry and physics, information concerning their concentration, size distribution and seasonal variation is limited. Also the sources and formation mechanisms of water-soluble organic compounds are not well known.

The size distributions of WSOC have been already studied in different environments, for example in urban and background areas, coastal site and marine environment (e.g. Li et al., 2000; Yu et al., 2004; Decesari et al., 2005; Turšič et al., 2006). The measurements are done by using different types of impactors (e.g. Micro-Orifice Uniform Deposit Impactor (MOUDI) or Berner low pressure impactor) with different filters (PTFE-, tedlar- or quartz fiber filters, Al-foils) and by using different extraction methods (typically ultrasonic or rotating). Also different analyzing techniques (direct analyzes by total organic carbon analyzers or indirect analyses WSOC=OC-WISOC by thermal-optical EC/OC analyzer) has been applied to samples. Comparing the results is difficult due to different collection and analytical methods. Long term measurements on the WSOC size distributions are scarce. Matta et al. (2003) have measured the size distributions of WSOC for one year in Po Valley, Italy. To our knowledge, long term measurements of the WSOC size distributions from the northern European boreal region have not been published, although this region has been recognized as one of the most effective emitters of biogenic volatile organic compounds (VOCs, Tunved et al., 2006; Hakola et al., 2003).

This paper represents the results of one year long measurement period for the size distributions of WSOC, ions and gravimetric mass at an urban background station in northern European boreal region in Helsinki, Finland. The WSOC measurements were completed with the chemical analysis of inorganic ions, OC and monosaccharide anhydrides from the filter samples. The goals of this study were to explore the seasonal variation in WSOC size distributions and evaluate the sources of WSOC by using air mass back trajectories and the results of the chemical analyses and the size distributions of WSOC, mass and ions.

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2 Experimental

2.1 Measurement site

The measurements were conducted in Helsinki (Finland) at the urban background station SMEAR III (60°20' N, 24°97' E, 26 m above sea level). The SMEAR III station is located in the university campus area, 4 km northeast from the Helsinki city center. About 200 m from the station there is a busy road. Due to a forest between the measurement site and road the measurement site is not directly exposed to car exhaust emissions.

2.2 Samples

The size-segregated samples were collected with a MOUDI from February 2006 to February 2007. Altogether 45 collections were made throughout the year, 2–7 collections in each month. The duration of each collection was ranging from 24 to 96 h being typically 72 h. The length of the collection was adjusted according to atmospheric particulate matter mass concentration to avoid overloading or too low mass for chemical analyses. The volume flow rate was $30 \pm 1 \text{ l min}^{-1}$. The cut-off diameters of the impactor stages are 0.056, 0.100, 0.18, 0.32, 0.56, 1.00, 1.8, 3.2 and $5.6 \mu\text{m}$ (Marple et al., 1991). An inlet with a cut-off diameter of $10 \mu\text{m}$ (Liu and Pui, 1981) was used on the top of the sampling line at about five meters above the ground level. The MOUDI samples were collected onto pre-washed 47-mm Al-foil substrates. Each substrate set for nine MOUDI stages had three extra Al-foil substrates which served as a blank control. The average blank value was subtracted from the concentrations of each stage.

The particulate matter (PM) samples particles with an aerodynamic diameter $< 1 \mu\text{m}$ were collected using a filter cassette system (Gelman Sciences). The four lowest stages of the Berner low pressure impactor (BLPI, Berner and Lürzer, 1980) were used to cut off the particles $> 1 \mu\text{m}$ in aerodynamic diameter to achieve the PM_{10} sample. To collect larger amounts of particulate matter the flow rate of this system was adjusted

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to 80 l min^{-1} . The cut-off diameter corresponding to the new flow rate was calculated to be $1 \mu\text{m}$. The sampling duration was typically 24 h during the working days and 72 h at the weekends. The samples were collected using two quartz fiber filters (Whatman Q-MA with diameter 47 mm) in series. The front filter collects the particulate matter and the back-up filter allows assessing the amount of gaseous species adsorbed on the sampling filter. The back-up filter also collects the compounds evaporated from the front filter, but this cannot be distinguished from the fraction adsorbed from gas phase in the sample flow (Viidanoja et al., 2002; Arp et al., 2007). The PM_{10} samples were collected from the 9 February 2006 to the end of February 2007, altogether 297 samples. WSOC, OC, monosaccharide anhydrides (MA) and inorganic ions were analyzed from the PM_{10} samples.

2.3 Meteorological data

Local meteorological data were recorded at the SMEAR III station. In order to establish potential source areas of the measured aerosol particles during the measurements, 120-h air mass back trajectories were calculated for the sampling periods using FLEX-TRA (Stohl and Wotawa, 1995).

2.4 Chemical analyses

2.4.1 Pretreatment of samples

The gravimetric mass of the MOUDI substrates was measured prior to and after collection with a Mettler M3 microbalance (Mettler Instrumente AG, Zurich, Switzerland). After weighing the samples were stored in a freezer (-20°C) until analyzed. The MOUDI samples were extracted by shaking the filter piece with 20 ml of deionized water (Milli-Q, Millipore Gradient A10) for 15 min. Ions and WSOC were analyzed from the same extraction.

One 1 cm^2 piece was cut from the each PM_{10} filter for the each analytical method

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(WSOC, MA, OC, and ions). The pieces were extracted by shaking the filter piece with 15 ml (WSOC) or 10 ml (ions) of deionized water for 15 min. After the extraction the samples were filtered using the Millex®-LCR (for the WSOC analyses) or the IC Acrodisc syringe filters (for the ion analyses) to prevent the quartz fibers to penetrate the sample lines of the carbon analyzer or the ion chromatograph (IC). The samples subjected to the liquid chromatograph mass spectrometer (LC-MS) for monosaccharide anhydride analyses were extracted to 2 ml of 1:1 volume/volume mixture of tetrahydrofuran and deionized water. The extraction was done in an ultrasonic bath for 30 min. Since quartz filters degrade slightly in water, the samples were filtered with the Millex®-LCR syringe filters. In the IC, WSOC and OC analyses both back-up and front filter was analyzed. The result of the back-up filter was subtracted from that in the front filter to correct for the positive artifacts and to subtract the blank values.

2.4.2 WSOC

The WSOC was analyzed by the total-organic carbon analyzer TOC-V_{CPH} from Shimadzu. The high sensitive catalyst was used to increase the sensitivity of the method. The NPOC-analyzing method has been described in detail by Timonen et al. (2008). Briefly, the sample is extracted to deionized water, which is acidified and injected into an oven. In the oven the carbon is catalytically oxidized to CO₂ at 680°C and the produced CO₂ is detected by a sensitive NDIR-detector. The estimated error of the WSOC results in the MOUDI and PM₁ measurements is 15% for atmospheric concentrations <2 μg m⁻³ and 10% for concentrations >2 μg m⁻³.

2.4.3 IC

The ions (Na⁺, NH₄⁺, K⁺, Mg²⁺, Ca²⁺, Cl⁻, NO₃⁻, SO₄²⁻, oxalate, succinate and malonate) were analyzed using Dionex DX500 or ICS-3000 ion chromatographs. DX500 had AG11/CG12A guard columns, AS11/CS12A analytical columns, 500 μl/300 μl loops, ASRS/CSRS ultra II suppressors and NaOH/MSA eluent for anions and cations,

respectively. The ICS-3000 setup was similar except to anion column (AS17) and the anion eluent (KOH). The uncertainty of the IC analysis of the filters is in order of 5–10% for all of the analyzed ions.

2.4.4 LC-MS

5 The monosaccharide anhydrides (levoglucosan, galactosan and mannosan) were determined by using a LC-MS (Agilent 1100 Series, Trap SL, Agilent Technologies, USA). The used injection volume was 2 μ l and the eluent was deionized water with a flow rate of 0.1 ml min⁻¹. Two LC-columns were used in series (Atlantis dC18 3 μ m, 2.1 mm of inner diameter and 150 mm in length, Waters). A negative electrospray technique was
10 used for ionization. The mass to charge ratio (m/z) of monitored ion was 161. A similar method has been previously used e.g. by Dye and Yttri (2005).

2.4.5 TOA

A thermal-optical carbon analyzer (TOA; Sunset Laboratory Inc., Oregon) was used to determine OC and EC from the PM₁ samples. The TOA is based on the thermal-optical
15 transmittance method (TOT). An optical correction is applied for the separation of pyrolysed OC from EC. The used temperature program was similar to the NIOSH program, except for the last temperature step in the helium phase. The temperature of this last step was decreased from 870°C to 800°C in order to reduce a premature evolution of EC in the helium mode (Subramanian et al., 2006). Inorganic carbon (carbonate carbon)
20 can in some cases interfere with the determination of OC, since it volatilizes in the helium phase concurrently with OC. However, no carbonate carbon was detected in this study when analyzing the thermograms using the method described in detail by Sillanpää et al. (2005a).

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3 Results and discussion

3.1 Comparison of WSOC results from the different collection methods

The suitability of the different collection methods, MOUDI and filter cassette, with the different collection substrates, Al-foil and quartz fiber filters, was tested for the WSOC analyses. Similar analytical procedures were performed for the samples collected in parallel. For the PM₁ the cut-size was 1 μm, and for the MOUDI the WSOC concentration was calculated by adding together the concentrations of the stages with cut-off diameters ≤1 μm. The corresponding blank values for the Al-foil and quartz fiber filters were calculated. The WSOC blank value for the Al-foil substrates was 0.21±0.06 μgC cm⁻² (average±SD). The blank values were subtracted from the WSOC results in the MOUDI. For the PM₁ quartz fiber back-up filters the average result was 3.1±0.7 μgC cm⁻² (average±SD). For the PM₁ the result of the back-up filter was subtracted from the result of the front filter to subtract the blank value and estimate the amount of gaseous species adsorbed on the front filter.

The WSOC results measured from the different substrates are in good agreement with each other. On average the MOUDI PM₁ WSOC result was 101±19% (average ±SD) of the corresponding PM₁ result. The inorganic ions were also analyzed from the PM₁ filters. The measured sulphate concentration for MOUDI samples was 89±17% of the corresponding PM₁ results.

3.2 Chemical composition of the MOUDI samples

Altogether 45 MOUDI collections were made between February 2006 and February 2007. The size distributions of gravimetric mass, WSOC and ions were analyzed from the collected MOUDI samples. Large variations in the particulate concentration levels were observed in the MOUDI collections. Figure 1 represents the gravimetric mass, concentration of water-soluble particulate organic matter (WSPOM) (μg m⁻³) and sum of inorganic ions (μg m⁻³) for PM₁ and PM₁₋₁₀ for the MOUDI collections. During the

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year long measurement the gravimetric mass in MOUDI collections varied between 3.4 and 55.0 $\mu\text{g m}^{-3}$ and the WSOC concentration was between 0.3 and 7.4 $\mu\text{g m}^{-3}$. The measured carbon concentration (WSOC) has to be multiplied by the assumed organic-matter to organic carbon ratio to achieve the amount of water-soluble particulate organic matter. In this study a multiplier of 1.6 has been used following a recommendation by Turpin et al. (2001). On average $25\pm 7.7\%$ of the aerosol PM_1 mass and $7.5\pm 3.4\%$ of the PM_{1-10} mass comprised of WSPOM. Inorganic ions comprised of $33\pm 12\%$ and $28\pm 19\%$ of the analyzed PM_1 and PM_{1-10} aerosol mass, respectively. Sulphate and ammonium together contributed on average $81\pm 12\%$ and $19\pm 14\%$ of the total inorganic ion content in PM_1 and PM_{1-10} , respectively. The amount of inorganic ions was typically two times larger than the amount of WSPOM, except during biomass burning episodes when the amount of WSPOM exceeded that of the inorganic ions.

During the measurements two major biomass burning episodes were observed. In the first episode (26 April–6 May 2006), most of the particles were long-range transported from the widespread wild land fires in the western parts of Russia (Saarikoski et al., 2007). During the second episode in summer (1–28 August 2006) most of the particles again originated from wild land fires in Russia, but this time from areas closer to Finland. The episodes had a clear effect on the particulate matter and the WSOC concentrations. The highest values in mass and WSOC in MOUDI collections were measured during the biomass burning episode in spring. The episode conditions are described in more detail by Saarikoski et al. (2006, 2007).

3.3 Seasonal differences in WSOC concentrations in ultrafine, fine and coarse particles

The seasonal variation in the WSOC concentrations in fine particles has been examined in many studies. For urban locations the maximum WSOC concentrations in fine particles has been observed to occur in winter and reach minimum values in summer (Viana et al., 2006; Ho et al., 2006) whereas for marine and mountain sites the highest WSOC concentrations have been measured in summer (Pio et al., 2007; Yoon et al.,

2007). This indicates that there might be different sources of WSOC depending of the season and the geographical area.

Recent studies show that biogenic volatile organic compounds emitted by boreal forest might have a large influence to WSOC and OC concentrations in boreal areas (Tunved et al., 2006; Hakola et al., 2003) when the biogenic activity is high in summer time. The published studies of the seasonal variation in the WSOC size distributions are scarce. The seasonal variation in the WSOC size distributions has been measured by Matta et al. (2003) in an urban area in Italy and by Huang et al. (2006) at a coastal urban site in China. To our knowledge, long term measurements of the WSOC size distributions from the northern European boreal region have not been published, although this region has been recognized as one of the most effective emitters of biogenic VOCs (Tunved et al., 2006; Hellén et al., 2004).

The average size distributions of WSOC and mass were calculated for winter (Dec–Feb, $n=14$), spring (Mar–May, $n=13$), summer (Jun–Aug, $n=9$) and autumn (Sep–Nov, $n=9$). The WSOC size distributions measured during the biomass burning episode were excluded from the calculations of the average size distributions for each season, since they deviated substantially from the size distributions measured prior to and after the episodes. Despite the changes in the concentrations between the individual collections, the shapes of the size distributions remained quite stable during each season whereas there are clear differences between the seasons. Figure 2 represents the size distributions of gravimetric mass and WSOC in different seasons. The size distributions of the gravimetric mass were bimodal during all seasons. In winter and autumn the mass concentrations were smaller and the shape of size distribution was clearly different when compared to the mass size distributions of spring and summer. For WSOC the dominant mode was typically the accumulation mode between 0.1 and 1 μm during all seasons. In winter the concentrations of WSOC were small and since the contribution of the coarse mode ($D_p > 1 \mu\text{m}$) to the WSOC was nonexistent, practically all the WSOC during the winter months resided in the accumulation mode. In spring, summer and autumn the accumulation and the coarse modes were clearly ob-

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served in the size distributions of WSOC. In summer and spring more WSOC was observed in ultrafine particles ($D_p < 0.1 \mu\text{m}$) as compared to autumn and winter. Also the accumulation mode ($D_p = 0.1\text{--}1 \mu\text{m}$) concentrations of WSOC were substantially larger in summer and spring.

5 Dicarboxylic acids are major constituents of the water-soluble fraction in aerosols (Yao et al., 2002). Oxalate is the most abundant of dicarboxylic acids, contributing typically 1–3% of fine mode WSOC (Huang et al., 2006). The size distributions of oxalate (not shown) were in all seasons similar to the size distributions of WSOC in the submicron mode ($D_p < 1 \mu\text{m}$) indicating that the oxalate and WSOC were internally
10 mixed. In the coarse mode the shape of the oxalate size distributions were slightly different from that of the WSOC.

To gauge a relative contribution of the water-soluble particulate matter in the different size classes the average WSPOM/mass-ratio was calculated for the each size class for each season (not shown). The WSPOM/mass-ratio was largest in summer and smallest in winter. It was also observed that the WSPOM/mass-ratio was larger
15 in submicrometer particles than in coarse particles. A decrease in the contribution of all carbonaceous species to the particulate mass as the particle size increases has been observed also in other measurements made in urban environments (e.g. Bologna, Matta et al., 2003; and Shenzhen, Huang et al., 2006). A smaller WSPOM/mass-ratio
20 in the supermicron particles can be affected by the fact that the mass in large particles is mainly crustal material that is not water-soluble. To further investigate the contribution of WSPOM in the different size classes, an average ratio of WSPOM to inorganic ions was calculated for each season (Fig. 3). Figure 3 clearly demonstrates that also the WSPOM/ions-ratio is largest in summer and autumn and smallest in winter. Larger
25 amount of WSPOM in summer is likely explained by increased photochemical and biogenic activity. The largest WSPOM/mass and WSPOM/ions-ratios were observed in ultrafine particles during all seasons. The different condensable primary and secondary organic gases can condense onto the ambient particles according to the surface area of the pre-existing particles, which obviously favors condensation on smaller particles.

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This phenomenon is one possible explanation to the finding that the WSPOM/ions-ratio (also WSPOM/mass) is especially high for the particles having sizes of about $0.1 \mu\text{m}$ or smaller. These high ratios at ultrafine particles also suggest that a considerable fraction of the measured particulate WSPOM may be of local or regional origin. According to literature, the most likely sources of the observed particulate WSPOM, especially in summer, are atmospheric oxidation processes, which may convert the biogenic and anthropogenic emissions of organic gases to a more water-soluble form (Fuzzi et al., 2006; Kanakidou et al., 2005).

3.4 Seasonal differences in WSOC/OC-ratios

The WSOC/OC-ratios in submicrometer particles were calculated for each season. The WSOC was calculated from the MOUDI results as a sum of lowest stages with cut-size $\leq 1 \mu\text{m}$ and OC was analyzed from the parallelly collected PM_{10} filters. The WSOC/OC-ratios measured during the biomass burning episode were excluded from the calculations of the seasonal WSOC/OC-ratios. The lowest WSOC/OC-ratio was observed in winter (0.46) and the highest (0.70) in summer. The WSOC/OC-ratio was 0.53 in spring and autumn. Comparable seasonal WSOC/OC-ratios has been achieved in previous studies (e.g. Jaffrezo et al., 2005; Decesari et al., 2001). The higher WSOC/OC-ratio indicates that the atmospheric conditions (oxidants, temperature, global radiation) in summer favor the further oxidation of the organic compounds towards higher water-solubility. The same trend has been observed in the aerosol mass spectrometer measurements in Tokyo (Kondo et al., 2007). Oxidation may also happen during cloud processing (Huang et al., 2006).

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3.5 WSOC Source apportionment

3.5.1 Different sources and source areas of aerosol particles observed in Finland

In order to achieve a better understanding of the variability in the size-distributions of WSOC in the sample set, the samples were divided into five categories according to the air-mass back trajectories and the results of the chemical analysis. The categories were chosen to represent the most likely sources of particulate matter and WSOC in Finland. These include 1) long-range transported (LRT) aerosols, 2) biomass burning aerosols originating from wild land fire episodes, 3) local small-scale wood combustion, aerosols in air masses from 4) clean arctic and 5) marine areas. In Finland the anthropogenic emissions of fine particles and their precursor gases are low; the mean $PM_{2.5}$ concentrations in 1999–2001 were typically only $9.6 \mu\text{g m}^{-3}$ at an urban site (Helsinki) and $5.8 \mu\text{g m}^{-3}$ at a rural background site (Hyytiälä; Laakso et al., 2003). In Helsinki typically 50–70% of the $PM_{2.5}$ mass originates from LRT (Niemi et al., 2005). During the LRT pollution episodes, substantially elevated PM concentrations are typically measured (Niemi et al., 2004). Also the long-range transport of emissions from wild land fires from the Baltic countries, Belarus, Ukraine, and Russia raises the PM concentrations in Finland frequently during spring and summer (Niemi et al., 2004, 2005; Sillanpää et al., 2005b; Saarikoski et al., 2007). Low PM concentrations with high sea salt concentrations are typically observed in Finland when the air masses originate from the direction of Arctic and Atlantic oceans (Pakkanen et al., 2001; Tunved et al., 2006). Tunved et al. (2006) also observed that substantial gas-to-particle conversion of biogenic VOC to SOA takes place over the boreal forest in northern Europe in air masses undergoing marine to continental transition. During winter, residential wood burning is a significant particulate emission source in northern Europe (Glasius et al., 2006; Frey et al., 2006). Levoglucosan is commonly used as a tracer for the biomass burning. When the polluted air masses are influenced by biomass burning, such as small-scale combustion or wild land fires, very high levoglucosan mass con-

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centrations are measured (Zdráhal et al., 2002; Sillanpää et al., 2005b; Yttri et al., 2005; Jordan et al., 2006; Saarikoski et al., 2007). Table 1 summarizes the criteria used to classify the measured size distributions to the separate categories according to their primary sources. The average mass, SO_4^{2-} and levoglucosan concentrations, average NaCl/mass-ratios, average temperature and air mass back-trajectories for the each class are represented in Table 1. Following the chosen criteria, 32 of the measured 45 MOUDI size distributions were placed in these categories. The classification remained unclear in 13 cases.

3.5.2 Differences on WSOC concentrations and size distributions according to the origin of aerosol particles

Clear differences in the WSOC concentrations originating from the five different source categories (LRT, wild land fires, small-scale wood combustion, clean arctic, marine areas) were observed (Table 2), although the local conditions and sources of VOCs and aerosols as well as various transformation processes are likely to have an impact on the measured aerosols composition. The amount of WSOC was largest when the particulate matter came from the wild land fire areas or was long-range transported. The WSOC concentrations were different in the two wild land fire episodes observed in spring and in summer. The observed WSOC concentrations were larger during the first episode in spring, $4.9\text{--}7.1 \mu\text{g m}^{-3}$, whereas the measured WSOC concentrations varied in the range of $2\text{--}4.1 \mu\text{g m}^{-3}$ during the second episode in August. The lowest WSOC concentrations were measured in the air masses originating primarily from the clean arctic or marine areas.

The WSOC/OC-ratios in submicron particles were calculated for each source category. The WSOC was calculated from the MOUDI results as a sum of lowest stages with cut-size $\leq 1 \mu\text{m}$ and OC was analyzed from the parallelly collected PM_{10} filters. The calculated WSOC/OC-ratios were different for the different source categories. The largest WSOC/OC-ratios were observed in the case of the long-range transported aerosols originating from continental Europe and for the biomass burning aerosols orig-

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inating from the areas of wild land fires. This is probably explained by the atmospheric oxidation processes which increase the water-solubility of organic compounds during the long-range transport. The WSOC/OC-ratios were almost equal for spring and summer biomass burning episodes, 0.64 and 0.63, respectively. The smallest WSOC/OC-ratios were observed in the aerosols affected by small-scale wood combustion which was expected to be local or regional. Small WSOC/OC-ratios are typically observed near their sources (Pio et al., 2007). Small WSOC/OC-ratios were observed also by Frey et al. (2006) in the small-scale wood combustion laboratory experiment.

The normalized WSOC size distributions (Fig. 4) for aerosols from different sources were clearly different. The size distribution of long-range transported WSOC was the narrowest and clearly most of the WSOC mass was observed in the accumulation mode. The size distributions of SO_4^{2-} and WSOC had clearly a similar shape in LRT aerosols, and it was evident that most part of the WSOC was internally mixed with SO_4^{2-} . The amount of the WSOC in ultrafine particles was very small. In the clean arctic air masses the amount of WSOC in ultrafine particles was the largest. Recent studies indicate that this is likely caused by the biogenic volatile organic compounds emitted by boreal forest condensing onto the existing ultrafine particles (Tunved et al., 2006; Anttila et al., 2007) during transport. Also the continuous formation of secondary organic aerosol from biogenic VOCs has been observed to take place during transport over forested areas (Tunved et al., 2006). The size distributions of WSOC in the air masses affected by the wild land fires and small-scale wood combustion were quite similar. The enrichment of WSOC into the ultrafine particles was also observed in the aerosols affected by the wild land fires or by local small-scale wood combustion. For the aerosols originating from the marine areas the WSOC size distribution in ultrafine and accumulation mode was very similar to the size distributions of e.g. biomass burning but more WSOC was observed also in the coarse mode.

The size distribution of WSOC was compared to that of sodium to establish whether the water-soluble compounds condense onto the sea-salt particles. Correlation between the size distributions was not found. This might be due to the fact that the

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coarse mode is a mixture of soil-related and sea-salt particles, and WSOC might be condensing on both kinds of particles. The size distributions of calcium and WSOC were compared to examine if water-soluble organic compounds are condensed on the soil-related particles. The size distributions of calcium and WSOC were clearly similar in the coarse mode, indicating that the water-soluble organic compounds were associated with soil-related particles on the coarse mode rather than with sea-salt particles. Because particulate matter from soil itself usually contains WSOC, the contribution of this mechanism can not be assessed without additional organic speciation which was not available in this study.

To further examine the WSOC fraction, the ratios of WSOC/mass and WSOC/inorganic ions were calculated for the different aerosol sources for each size class (Fig. 5). The WSPOM/mass-ratio (Fig. 5a) was in all cases largest in ultrafine particles. The amount of WSPOM was typically 15–38% of the measured total mass in the ultrafine particles. The WSPOM/mass-ratio decreases as the particle size increases. In the largest particles, the WSPOM accounted only 4–18% of the total mass. To exclude the effect of insoluble materials in the coarse particles, the WSPOM/inorganic ions-ratio was calculated for each size class (Fig. 5b). The largest WSPOM/inorganic ions-ratios were observed in the ultrafine particles, where the amount of WSOC exceeded the amount of inorganic ions. In the accumulation and coarse mode the amount of inorganic ions was larger than the amount of WSPOM.

The enrichment of WSPOM into the ultrafine particles was observed in the biomass burning aerosols transported from the wild land fire areas (Fig. 6), where the WSPOM accounted for 29–38% of the measured total mass in ultrafine particles. The amount of WSPOM was larger than the amount of inorganic ions in all submicrometer particles for the aerosols originating from the wild land fire areas. The WSPOM/mass-ratios were similar for both episodes (Fig. 6a), whereas the WSPOM/ions-ratio in ultrafine particles was clearly larger in the second episode in August (Fig. 6b).

3.5.3 The effect of biogenic VOCs on WSOC concentrations on different size classes

In the recent studies it has been observed that continuous formation of secondary organic aerosol from biogenic VOCs takes place during transport over forested areas (Tunved et al., 2006). Some of the major oxidation products of biogenic VOCs have been observed to be water-soluble compounds (Cavalli et al, 2006; Kourtchev et al., 2005). Anttila et al. (2006) has also observed the enrichment of monoterpene oxidation products into the smallest particles in chamber experiments. The WSOC size distributions measured from air masses originating from clean arctic areas were divided into two new categories, termed summer and winter measurements, to investigate the effect of biogenic VOCs on WSOC concentrations. The calculated WSPOM/mass and WSPOM/inorganic ions-ratios for clean arctic air masses in summer and winter are represented in Fig. 7.

Figure 7 clearly shows that in the clean arctic air masses the amount of WSPOM in the ultrafine particles was larger in summer when the biogenic activity is high, when compared to winter. Also the WSPOM/inorganic ions-ratio was clearly larger in the size distributions measured in summer. Figure 7 indicates that part of the biogenic VOCs condensing onto the pre-existing aerosol particles were most likely water-soluble or they were transformed to water-soluble compounds by oxidation after condensation. This is in agreement with previous findings in chamber experiments by Virkkula et al. (1999), who observed that the oxidation products of α -pinene in the aerosol phase were slightly water-soluble. In the real atmosphere growth of ultrafine particles is due to e.g. condensation of both hygroscopic compounds (e.g. sulfuric acid) and the oxidation products of VOCs. The concentration of sulfuric acid does not completely explain the observed growth of ultrafine particles (Boy et al., 2005). Indirect methods have revealed that the water solubility of the newly formed particles in the boreal forest decreases as the particles grow toward larger sizes (Hämeri et al., 2001; Ehn et al., 2007), but they still remains slightly water soluble. Thus, considering the results of this study it is plausible to conclude that the oxidation products from the biogenic VOCs

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probably contributed largely to the WSOC concentrations in the ultrafine particle size range during clean arctic air masses.

4 Summary and conclusions

This paper presents the results of one-year-long measurements from February 2006 to February 2007 of the size distributions of water-soluble organic carbon, ions and gravimetric mass concentrations at the urban background station (SMEAR III) in northern Europe boreal region in Finland. The WSOC, OC and MA concentrations were determined from the PM₁ filter samples. The gravimetric mass concentrations (PM₁₀) in the MOUDI collections varied between 3.4 and 55 μg m⁻³. On average 25±7.7% of the aerosol PM₁ mass and 7.5±3.4% of the PM₁₋₁₀ mass comprised of water-soluble particulate organic matter. Inorganic ions contributed 33±12% and 28±19% of the analyzed PM₁ and PM₁₋₁₀ aerosol mass. The amount of inorganic ions in submicrometer particles was typically two times larger than the amount of WSPOM, except during the biomass burning episodes when the amount of WSPOM was substantially larger than the amount of inorganic ions.

The collected samples were classified into categories representing the most likely sources of particulate matter and WSOC in Finland. These include long-range transported aerosols, biomass burning aerosols originating from wild land fire episodes and local small-scale wood combustion and aerosols originating from clean arctic and marine areas. Clear differences in the WSOC concentrations and size distributions originating from different source areas were observed, demonstrating that the concentrations and the size distributions of WSOC are dependent on the source area and on the age of aerosol. Also large seasonal differences in the quantities were observed.

In summer the oxidation products of biogenic VOCs were clearly increasing the WSOC concentrations, especially in the ultrafine particles. Higher WSOC/mass and WSOC/OC-ratios in summer indicate that the atmospheric oxidation processes are favoring the condensation of VOCs onto particles surfaces and that the atmospheric conditions are favoring the transformation of organic compounds toward higher water-

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solubility. The observed results support also the idea that the higher biogenic activity will increase condensation growth of aerosol particles and therefore increase the mass of WSOC (Kulmala et al., 2004).

During the large biomass burning episodes larger WSOC concentrations were measured. Also the relative amount of water-soluble organic compounds was elevated compared with the sum of inorganic ions, indicating that large amounts of water-soluble organic compounds were produced during the burning process itself or during the subsequent atmospheric transportation. The enrichment of WSOC in ultrafine particles was observed in the aerosols originating from the wild land fire areas and local small-scale combustion for residential heating. The small-scale combustion is a major source of WSOC in Finland in winter time, when the biogenic activity is very low. Larger WSOC/OC-ratios were observed for aerosols originating from the wild land fires than for aerosols originating from the local small-scale combustion. This is likely caused by to the atmospheric oxidation processes which increase the water-solubility of the organic compounds during the transport.

During LRT episodes the size distribution is typically dominated by accumulation mode particles originating from various primary and secondary sources along the way to the measurement site, which may or may not have been cloud processed. Typically both condensation and cloud processing accumulate material to the accumulation mode as a function of time, which also explains enrichment of the WSOC into a accumulation mode. The size distributions of WSOC and sulphate were similar, indicating that WSOC was clearly internally mixed with SO_4^{2-} in the LRT aerosols.

For aerosols originating from marine areas, the size distributions of sodium and WSOC in coarse mode were compared to see whether the WSOC is likely to condense on the surface of sea-salt particles. The size distributions of sodium and WSOC had clearly different shapes in the coarse mode. According to the results of this study it seems that over the continental area the water-soluble organic compounds in the coarse fraction are more likely associated with the soil-related particles than with the sea-salt particles.

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Table 1. The selected criteria to classify the size distributions to five different classes according to their sources.

Class	Known features	Conc ($\mu\text{g m}^{-3}$)					Air mass origin
		Mass	SO_4^{2-}	Levog.	T ($^{\circ}\text{C}$)	NaCl/mass ^a	
LRT ($n=4$)	High internal mixing High mass concentration Large accumulation mode High SO_4^{2-} concentration	22.95	3.81	0.03	8.8	0.04	Continental areas of Europe and Russia
Wild land fires ($n=8$)	High levoglucosan conc. Back-trajectories from the areas of wild land fires ^b	33.11	2.55	0.18	13	0.01	From known wild land fires in Russia
Clean arctic ($n=7$)	Back-trajectories from arctic sea	10.84	0.89	0.03	8.4	0.14	From arctic sea
Small-scale wood comb. ($n=5$)	Low mass concentration Low temperature -> increased domestic heating High levoglucosan conc.	12.38	2.67	0.11	7.1	0.15	From areas closer to Finland
Marine aerosols ($n=8$)	Back-trajectories High NaCl concentration in coarse mode	11.10	1.45	0.03	7.3	0.71	From Baltic sea

^a NaCl defined as $3.248 \cdot [\text{Na}^+]$ in coarse mode,

^b Saarikoski et al., 2006, 2007.

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Table 2. The WSOC and OC concentrations ($\mu\text{g m}^{-3}$) and WSOC/OC -ratio in selected aerosol source categories.

Source	WSOC (PM ₁) (average±SD)	WSOC (PM _{1–10}) (average±SD)	OC (PM ₁) ^a (average±SD)	WSOC/OC ^a -ratio (PM ₁)
LRT	2.0±0.72	0.44±0.29	2.5±0.40	0.69
Wild land fires	4.3±0.65	0.71±0.23	7.0±2.8	0.64
Clean arctic	0.58±1.0	0.19±0.11	1.3±0.64	0.48
Small-scale wood combustion	1.3±1.0	0.25±0.19	2.3±0.99	0.49
Marine aerosols	0.61±1.1	0.19±0.09	1.2±0.69	0.53

^a OC from the results of PM₁ filter measurements.

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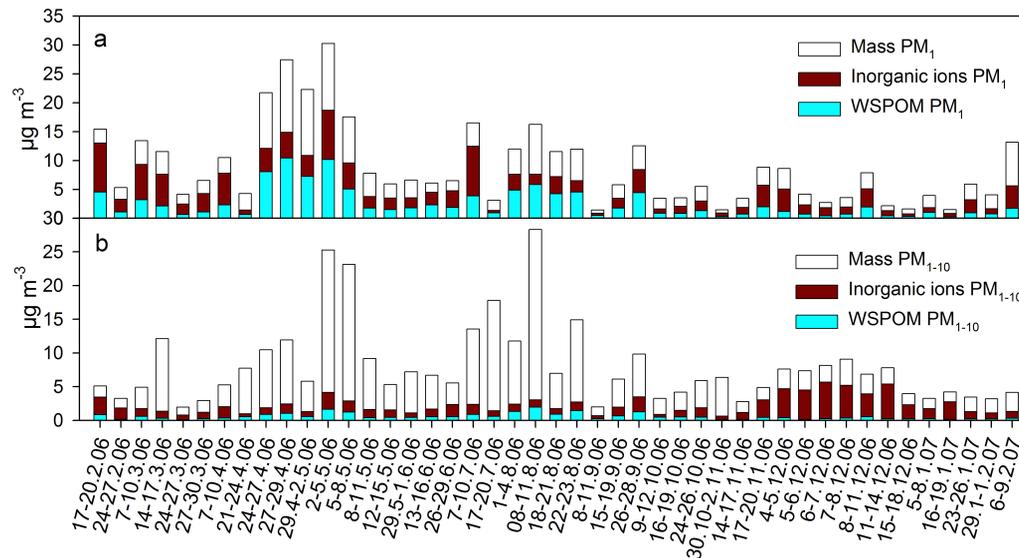


Fig. 1. Concentrations of mass, inorganic ions and WSPOM ($\mu\text{g m}^{-3}$) in PM_1 (a) and PM_{1-10} (b) in the MOUDI collections between February 2006 and February 2007.

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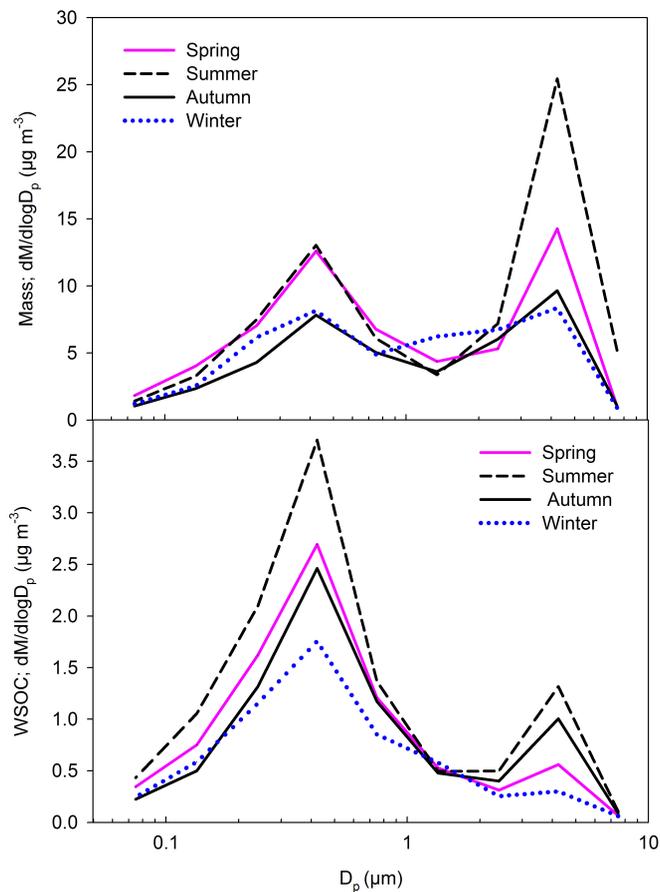


Fig. 2. The mass and WSOC size distributions for each season: spring (Mar–May), summer (Jun–Aug), autumn (Sep–Nov), and winter (Dec–Feb).

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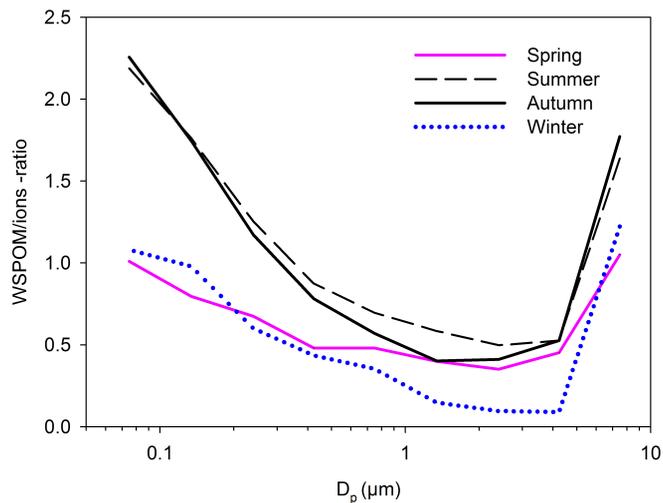


Fig. 3. The WSPOM/inorganic ions-ratio in different size classes in MOUDI collections for each season: spring (Mar–May), summer (Jun–Aug), autumn (Sep–Nov), and winter (Dec–Feb).

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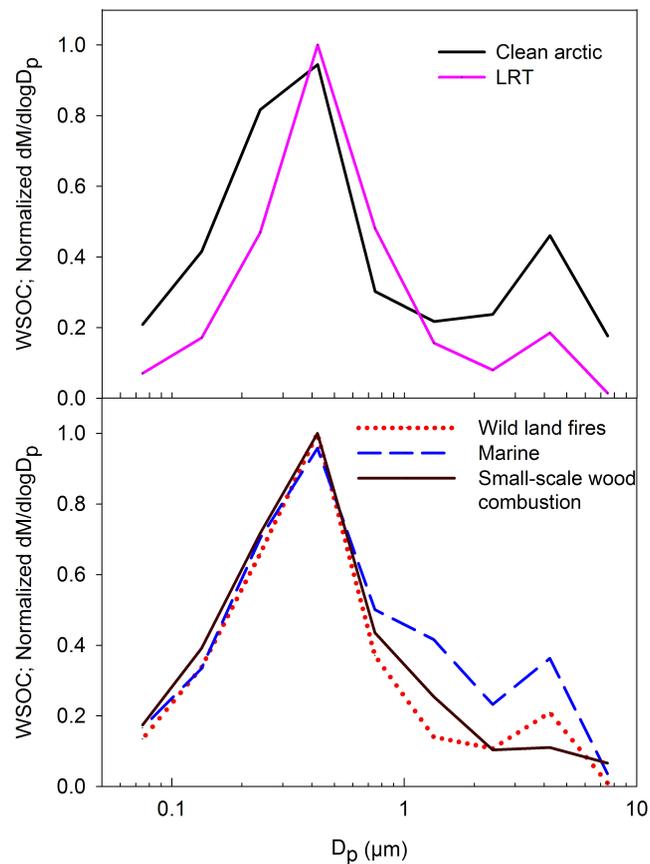


Fig. 4. The normalized WSOC size distributions representing the five different types of sampled air masses; LRT, clean arctic, wild land fires, marine and small-scale wood combustion.

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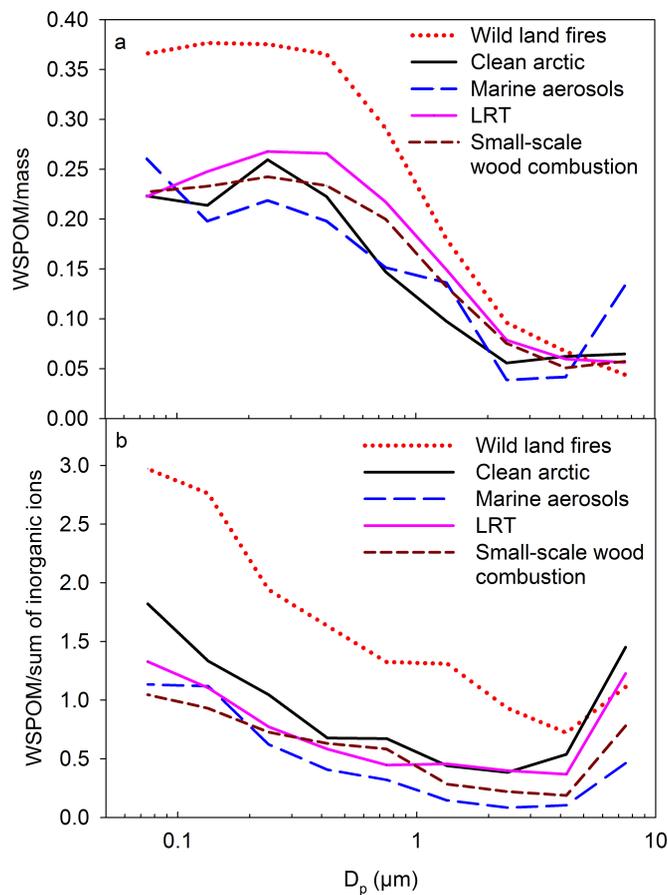


Fig. 5. The WSPOM/mass -ratio (a) and WSPOM/inorganic ions -ratio (b) for collections representing the five different aerosol sources; LRT, clean arctic, wild land fires, marine and small-scale wood combustion.

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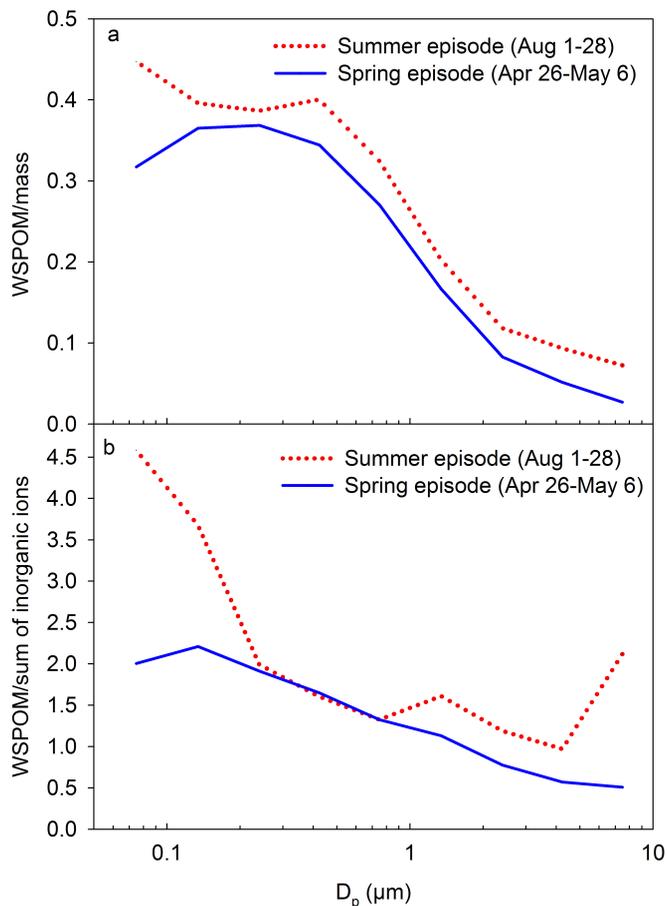


Fig. 6. The calculated WSPOM/mass-ratio (**a**) and WSPOM/inorganic ions ratio (**b**) for biomass burning aerosols originating from the wild land fire areas in spring (26 Apr– 6 May 2006) and in summer (1–28 Aug 2006).

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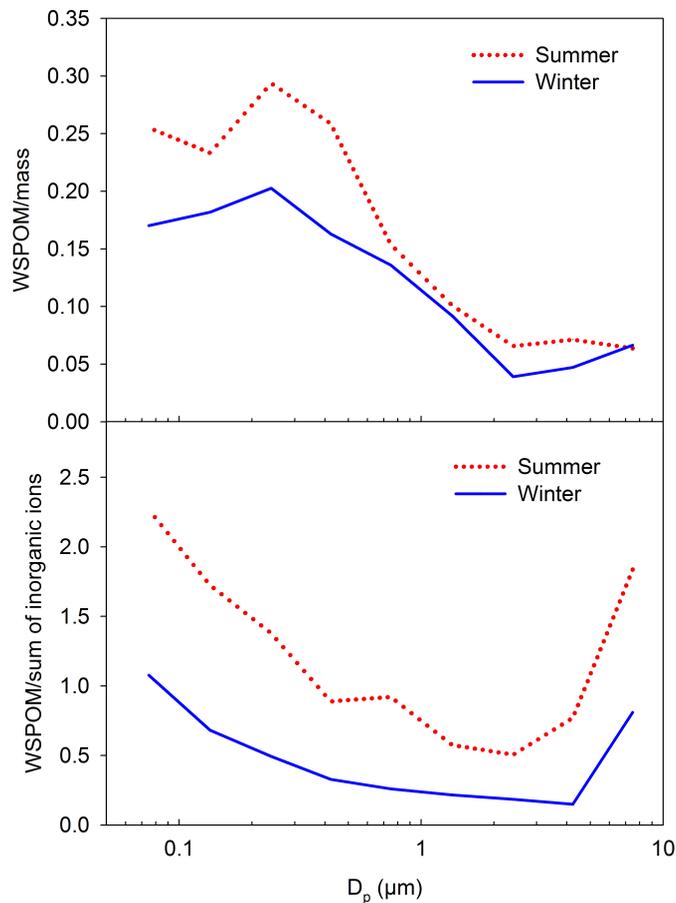


Fig. 7. The calculated WSPOM/mass-ratio and WSPOM/inorganic ions ratio for aerosols originating from clean arctic areas in summer and in winter.

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