

## Water-soluble organic carbon in urban aerosol: concentrations, size distributions and contribution to particulate matter

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The aim of this study was to characterize the concentrations and particle mass size distributions of water-soluble organic carbon (WSOC) in urban aerosols. The sample collection was carried out in spring 2006 at the SMEAR III station in Helsinki, Finland, by using a size-segregating method (MOUDI) and by collecting sub-micrometer fraction of aerosols on the filter. During the three-month measurement period, a major 12-day biomass burning pollution episode was observed. Concentrations of WSOC, organic carbon, monosaccharide anhydrides, inorganic ions and some organic acids (oxalic, succinic and malonic acid) were analyzed from the PM<sub>1</sub> samples. The measured OC and WSOC concentrations varied in ranges 0.67–15.7  $\mu\text{g m}^{-3}$  and 0.26–10.7  $\mu\text{g m}^{-3}$ , respectively. The WSOC/OC concentration ratio was between 0.30 and 0.89 with an average of 0.54. Size distributions of WSOC, inorganic ions and total mass were determined from the MOUDI samples. WSOC had bimodal size distributions with a clear accumulation mode below 1  $\mu\text{m}$  of particle aerodynamic diameter and minor coarse mode at sizes > 1  $\mu\text{m}$ .

### Introduction

Atmospheric particles contain carbonaceous material in the form of organic compounds, elemental carbon (EC), and carbonate minerals. Organic compounds comprise typically 10%–50% and elemental carbon 5%–20% of fine particle mass (Park *et al.* 2005). Carbonate minerals are originating from soil dust and are mainly found in supermicron particles (Park *et al.* 2005). EC is produced only in combustion processes and is therefore always primary material. Organic carbon (OC) can be directly emitted

to the atmosphere in particulate form or it can be formed by gas-to-particle conversion in the atmosphere (Seinfeld and Pandis 1998). Primary organic compounds include plant waxes, resin residues and long-chain hydrocarbons. Secondary organic compounds are typically multifunctional oxygenated compounds, including carboxylic acids, alcohols, carbonyls and nitrates. Some compounds like dicarboxylic acids have both primary and secondary sources. Besides inorganic material, OC is considered to be one of the most important components in atmospheric aerosols (Jaffrezo *et al.* 2005, Kanakidou *et al.* 2005).

The determination of organic particulate matter by quantifying each organic compound in atmospheric particulate matter is difficult because there are hundreds of different organic compounds. The adsorption of gas-phase organic vapors, volatilization and contamination during collection are common problems (Ten Brink *et al.* 2004).

A significant part, typically 10%–70%, of organic matter in atmospheric aerosols is water-soluble (Jaffrezo *et al.* 2005). The water-soluble organic fraction contains usually oxygenated multifunctional compounds like diacids, polyols and amino acids. Recent studies have shown that also humic-like substances (HULIS) are important part of water-soluble organic carbon (WSOC), accounting for 15%–60% of the fine-particle WSOC (Graber and Rudich 2006). The amount of WSOC in atmospheric aerosol particles affects their ability to act as cloud condensation nuclei, which may be important to the Earth's radiative budget. WSOC has also a wide range of poorly-quantified environmental effects ranging from pollution toxicity to visibility degradation (Ten Brink *et al.* 2004).

The objective of this study was to characterize the WSOC in northern European urban or polluted aerosol. The characterization included measurements of concentration levels of submicrometer WSOC during three months, as well as WSOC size distribution measurements. The WSOC measurements were completed with the chemical analysis of water-soluble inorganic ions, organic acids and monosaccharide anhydrides. In addition, OC and EC (not presented here) were analyzed with a thermal-optical analysis.

## Experimental methods

### Measurement site

The measurements were conducted in Helsinki, Finland, at an urban background station (SMEAR III, 60°20'N, 24°97'E, 26 m above the sea level). The measurement site is located in the university campus area, 4 km northeast from the Helsinki city center. About 100 meters from the station there is a busy road. Due to a forest

between the measurement site and road, the site is not directly exposed to car exhaust emissions.

### Sampling

Five sets of samples were collected using a Micro-Orifice Uniform Deposit Impactor (MOUDI). The collections were carried out between February and May 2006. The MOUDI is a nine-stage cascade impactor. The volume flow rate was adjusted to  $30 \pm 1 \text{ l min}^{-1}$ . 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 sampling duration was typically 72 hours. The MOUDI samples were collected onto 47-mm Al-foil substrates that were washed beforehand by dipping them into deionized water (Milli-Q, Millipore Gradient A10). After washing, the foils were dried in an oven at  $120 \text{ }^\circ\text{C}$  and stored in petri dishes until analysed. The foils were weighed before and after the sampling with a Mettler M3 microbalance (Mettler Instrumente AG, Zurich, Switzerland). Quartz fiber filters were used as the after filters in order to collect particles smaller than  $0.056 \mu\text{m}$ . The exposed filters were stored in a refrigerator until the chemical analyzes were made.

In parallel with the MOUDI measurements, particulate matter samples ( $\text{PM}_{10}$ : particles with an aerodynamic diameter  $< 10 \mu\text{m}$ ) were collected using a filter cassette system (Gelman Sciences). The  $\text{PM}_{10}$  sample was achieved by using four stages of the Berner low pressure impactor (BLPI, Berner and Lürzer 1980) to get rid of particles  $> 10 \mu\text{m}$  in diameter. The flow rate of this system was adjusted to  $80 \text{ l min}^{-1}$  instead of the original  $25 \text{ l min}^{-1}$ , which made it possible to collect larger amounts of particulate mass. The cut-off diameter corresponding to the new flow rate was calculated to be  $10 \mu\text{m}$ . The samples were collected using quartz fiber filters (Whatman Q-MA with diameter 47 mm). A back-up filter was used to estimate the positive artifact caused by organic vapours. The sampling duration was about 24 hours during the working days and 72

hours at the weekends. The sampling period was from 9 February to 10 May 2006.

## Chemical analyses

The WSOC, anions, cations and total mass concentrations were analyzed from the MOUDI samples. After the sample collection, the MOUDI substrates were submerged into 20 ml of deionized water (Milli-Q, Millipore Gradient A10) and rotated for 15 minutes prior to the analysis. Both WSOC and ions were analyzed immediately after this procedure from the same extraction. For the MOUDI, the blank value was subtracted from measured concentrations in each impactor stage.

Four 1-cm<sup>2</sup> pieces of each PM<sub>1</sub> sample filter were cut in order to analyze WSOC, total organic carbon, ions and monosaccharide anhydrides. In case of the IC and WSOC analyses, each sample was submerged into 15 ml of deionized water and rotated for 15 minutes prior to the analysis. The samples were filtered using a Millex®-LCR (for WSOC analyses) or IC Acrodisc syringe filters (for IC analyses) to prevent the quartz fibers from going into the sample lines of the carbon analyzer or the ion chromatograph. The pre-treatment and analyses of the samples were done in a cleanroom (ELPIS, class 7 cleanroom) to minimize the contamination. The samples subjected to the LC-MS analyses were extracted to 2 ml of 1:1 v/v mixture of tetrahydrofuran and deionized water. The extraction was done in an ultrasonic bath for 30 minutes. Since quartz filters degrade slightly in water, the samples were filtered with Millex®-LCR syringe filters. In case of IC, WSOC and OC analyses, both back-up and front filters were analyzed. The measured concentration in the back-up filter was subtracted from that in the front filter to correct for the positive artifacts and to subtract the blank values.

## Ion chromatography

Anions (Cl<sup>-</sup>, NO<sub>3</sub><sup>-</sup>, SO<sub>4</sub><sup>2-</sup>, oxalate, succinate, malonate) and cations (Na<sup>+</sup>, NH<sub>4</sub><sup>+</sup>, K<sup>+</sup>, Mg<sup>2+</sup>, Ca<sup>2+</sup>) were analyzed simultaneously using two

Dionex DX-500 ion chromatography systems. The anion system used a NaOH eluent with a flow rate of 1.5 ml min<sup>-1</sup>, 500-μl loop, ASRS 4-mm electrochemical suppressor and 4-mm AG11 and AS11 columns. Cations were measured using a MSA eluent with a flow rate of 1.2 ml min<sup>-1</sup>, 300-μl loop, CSRS 4-mm suppressor and CG12A/CS12A column. The runtime was 12 minutes.

## TOC-V<sub>CPH</sub> organic carbon analyzer

The WSOC analyses were made using a TOC-V<sub>CPH</sub> organic carbon analyzer (Shimadzu) with a high sensitive catalyst. The TOC-V<sub>CPH</sub> was previously used by Viana *et al.* (2006) to analyze the total organic carbon from aerosol samples. The non-purgeable organic carbon (NPOC) method was used. In the NPOC method the sample is first put into deionized water to extract all WSOC from the filter. After that the sample solution is drawn through a plastic tube to the syringe using an 8-way valve. The acid addition (1% 2M HCl) and helium bubbling (1.5 minutes) are done in the syringe. After that all inorganic carbon should have been converted into carbon dioxide and evaporated from the sample solution. After the bubbling the sample is injected into an oven, where it is catalytically oxidized to carbon dioxide at 680 °C. Each sample was measured three times and the average of the three resulting concentrations was calculated. Quite a large injection volume (500 μl) was used because of the relatively small concentrations of WSOC in the samples, especially in the size-segregated impactor samples. The syringe and sample lines were washed two times with the sample solution between the samples. Approximately 10 ml of the sample was needed. The measurement time was approximately 15 minutes.

The NPOC method was used because it is necessary to remove carbonate carbon and carbon dioxide from the samples before the measurements. In the NPOC method it is possible that volatile components evaporate from the sample during the bubbling. The extent of such volatilization is expected to be very minor for aerosol samples because the volatile fraction

escapes from samples already during the collection.

The detection limit for the  $\text{TOC-V}_{\text{CPH}}$  is  $4 \mu\text{g l}^{-1}$  and the standard deviation of the repeated measurements is smaller than 1.5% (values given by the manufacturer). The measurement error resulting from the TC content in the water (used to make the solutions) and in the blank filters is typically much greater than error resulting from the system blank value. The estimated error in the measurements is 15% for atmospheric concentrations  $< 2 \mu\text{g m}^{-3}$  and 10% for concentrations  $> 2 \mu\text{g m}^{-3}$ .

## TOA

Organic and elemental carbon (OC and EC) were determined with a thermal-optical carbon analyzer (TOA; Sunset Laboratory Inc., Oregon). The TOA is based on the thermal-optical transmittance method (TOT). Shortly, OC is volatilized at four subsequent temperature steps in a pure helium atmosphere, after which EC is determined in a mixture of oxygen and helium by using six temperature steps. The volatilized carbon is catalytically oxidized to  $\text{CO}_2$ , followed by its reduction to  $\text{CH}_4$  in a Ni/firebrick methanator and subsequently quantified as  $\text{CH}_4$  with a FID detector (Birch and Cary 1996). 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 850 to 800 °C in order to reduce a premature evolution of EC in the helium mode (Subramanian *et al.* 2006). Inorganic carbon (carbonate carbon) can 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.* (2005).

The WSOC results given by the  $\text{TOC-V}_{\text{CPH}}$  were compared with the WSOC results based on the measurements with the thermal-optical carbon analyzer (TOA). A total of 11  $\text{PM}_{10}$  samples were tested. For this comparison, two 1-cm<sup>2</sup> pieces were cut from the same  $\text{PM}_{10}$  filter. One

of the pieces was analyzed for OC and EC by the TOA while the other piece was extracted with deionized water for 15 minutes. WSOC was determined from the water solution by the  $\text{TOC-V}_{\text{CPH}}$ , whereas the remaining filter piece was dried in a laminar flow bench and analyzed for OC and EC by the TOA. The amount of OC remaining in the filter after the water extraction was considered to be water-insoluble OC (WISOC). The quartz filter degraded visibly during the water extraction. By assuming that EC was completely water insoluble and that the difference in the concentration of EC between the two filter pieces was only due to the degradation of the filter, individual WISOC values were corrected with the determined EC loss values. On average,  $34\% \pm 9.7\%$  of EC was found to be lost during the extraction.

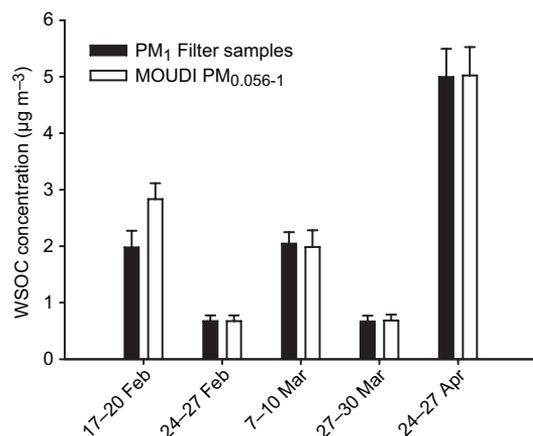
## LC-MS

A Liquid Chromatography combined with mass spectrometry (LC-MS; Agilent 1100 Series, Trap SL, Agilent Technologies, USA ) was used to determine the mass concentrations of three monosaccharide anhydrides in the  $\text{PM}_{10}$  filter samples. The used injection volume was 2  $\mu\text{l}$  and the eluent was deionized water with a flow rate of 0.1  $\text{ml min}^{-1}$ . Two LC columns were used in a series (Atlantis dC18 3  $\mu\text{m}$ , 2.1 mm of inner diameter and 150 mm in length, Waters). A negative electrospray technique was used for ionization. The mass to charge ratio ( $m/z$ ) of the monitored ion was 161. A similar method has been previously used by Dye and Yttri (2005).

## Results and discussion

### Comparison of collection and analytical methods

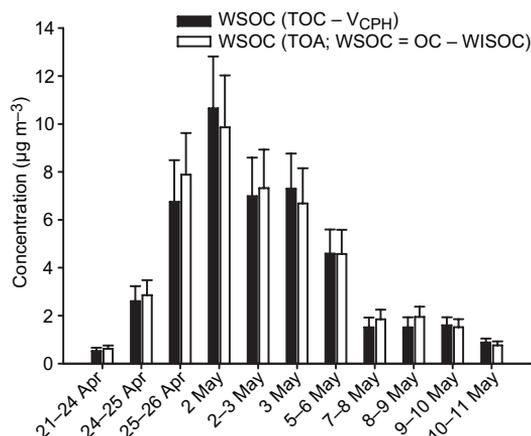
In case of WSOC measurements, the two different collection methods (impactor and filter collections) and the different substrate materials (foil and quartz fiber filter) were compared. Also, for comparison, WSOC was analyzed with two different instruments: the  $\text{TOC-V}_{\text{CPH}}$  and TOA. In order to compare the different collec-



**Fig. 1.** Comparison of water-soluble organic carbon results from MOUDI ( $\text{PM}_{0.056-1}$ ) and filter-cassette collections ( $\text{PM}_{10}$ ). The measurement errors are indicated by the error bars.

tion methods, the MOUDI samples (duration of sampling 72 h) and  $\text{PM}_{10}$  filter samples (duration of sampling 24–72 h) were collected simultaneously. The  $\text{PM}_{10}$  from the MOUDI samples was calculated by adding together the concentrations of the stages with cut-off diameters  $< 1 \mu\text{m}$ . The WSOC concentrations in the  $\text{PM}_{10}$  filters were  $94\% \pm 14\%$  (average  $\pm$  SD) of those in the MOUDI (Fig. 1), demonstrating that the determination of WSOC is not dependent on the sampling method.

Aluminum foil substrates were used in the MOUDI and quartz fiber filters were used in the filter cassette. The blank values ( $\mu\text{g m}^{-3}$ ) for the collecting substrates were calculated from the measured blank values ( $\mu\text{g}$ ) by dividing the result by the average flow ( $\text{m}^{-3}$ ) in the collections. The blank values for the substrate materials were different. For the quartz filter it was  $0.32 \pm 0.07 \mu\text{g m}^{-3}$  (average  $\pm$  SD), being close to the average amount of WSOC found on the back-up quartz filter ( $0.34 \pm 0.18 \mu\text{g m}^{-3}$ ). On average, the back-up value of WSOC was 12.7% of that in the front quartz filter. For the aluminum foil substrates the blank value was  $0.04 \mu\text{g m}^{-3}$ , which was 1%–15% of the amount of WSOC on impactor stages with the cut-off diameters in the range 0.056–5.6  $\mu\text{m}$ . For the highest impactor stage (the cut-off size of 10  $\mu\text{m}$ ) the blank values were at same level as the WSOC concentrations. It seems that both aluminum foil and quartz-fiber



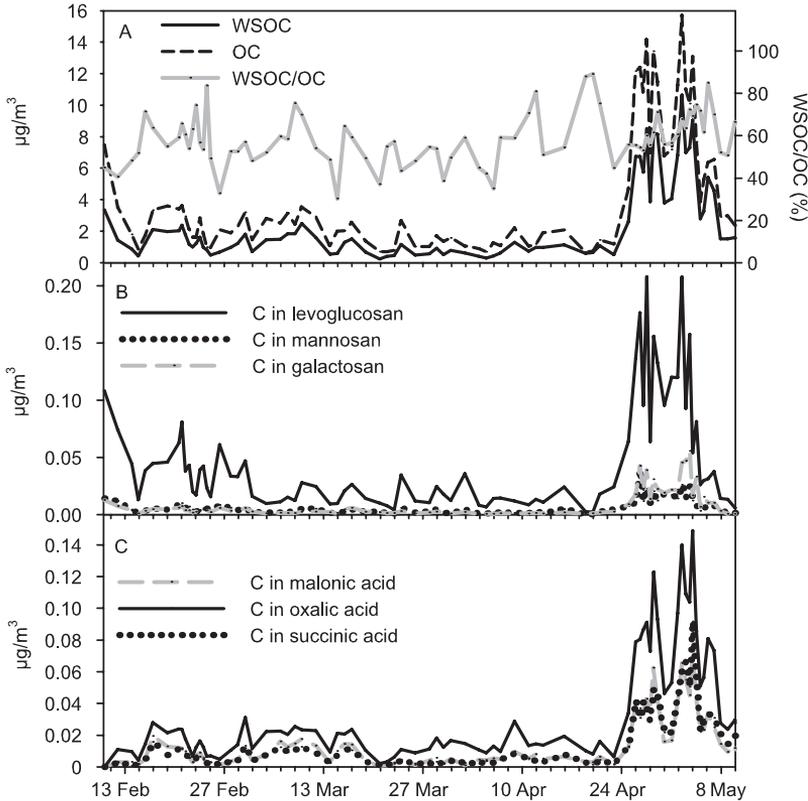
**Fig. 2.** Comparison of measured WSOC concentrations between the TOC- $V_{\text{CPH}}$  and TOA method. For the TOA method WSOC was calculated by subtracting WISOC from OC. The measurement errors are indicated by the error bars.

filters can be used to measure WSOC, provided that corrections for positive artifacts and blanks are being made properly.

In order to estimate the reliability of the TOC- $V_{\text{CPH}}$  method, concentrations obtained by using this method were compared with those obtained from the TOA method (Fig. 2). For the comparison, OC (TOA), WISOC (TOA) and WSOC (TOC- $V_{\text{CPH}}$ ) were measured from the same sample. The sum of WSOC and WISOC was close to the corresponding OC, being  $97\% \pm 7.6\%$  (average  $\pm$  SD) of OC. The agreement between the two methods was good and independent of the concentration level of carbon on the filter, since the amounts of WSOC and OC ranged from 10.2 to 73.6  $\mu\text{g}$  and from 18.0 to 132  $\mu\text{g}$ , respectively, on the filter piece. As compared with the thermal-optical method, the advantage of the TOC-V analyzer is that the WSOC analysis can be done directly from the water solution. It is easier and more accurate to extract the sample by water and to measure WSOC from a primary water-solution. The direct WSOC analysis also minimizes the contamination risk.

## Concentrations

The concentrations of WSOC, OC, monosaccharide anhydrides and low-molecular weight



**Fig. 3.** (A) Concentrations of WSOC and OC and the WSOC/OC concentration ratio, (B) the concentration of monosaccharide anhydrides, and (C) the concentration of low molecular weight dicarboxylic acids in  $PM_1$  filter samples between 9 February and 10 May 2006.

dicarboxylic acids were measured from 9 February to 10 May 2006. During the three-month measurement period, a major 12-day (26 April–6 May) biomass burning pollution episode was observed. The episode period was considered separately from the reference period, since measured concentrations were quite different between these two periods. The episode conditions have been described in detail by Saarikoski *et al.* (2007).

The concentration of WSOC in spring 2006 was in the range  $0.26\text{--}4.6\ \mu\text{g m}^{-3}$  (Fig. 3). During the biomass burning episode the WSOC concentrations were temporarily as high as  $10.7\ \mu\text{g m}^{-3}$ . The measured OC concentrations varied between  $0.67$  and  $7.5\ \mu\text{g m}^{-3}$  in spring, reaching values of up to  $15.7\ \mu\text{g m}^{-3}$  during the biomass burning episode. The concentrations of both WSOC and OC seemed to decrease during the spring, until the episode began. The contribution of WSOC to OC varied between 30.3% and 89.1%, being on average slightly higher during the biomass burning episode (63.5%) as compared with other

times (54.5%). A statistical summary of these concentrations is presented in Table 1.

The concentration of levoglucosan varied from 4 to  $470\ \text{ng m}^{-3}$ , being clearly the dominant isomer of the three monosaccharide anhydrides (Fig. 3). The concentrations of galactosan and mannosan ranged from 1 to  $125\ \text{ng m}^{-3}$ . Of the measured low-molecular weight dicarboxylic acids, the concentration of oxalic acid varied in the range  $7\text{--}557\ \text{ng m}^{-3}$  and the concentrations of succinic and malonic acid concentrations varied from 1 to  $225\ \text{ng m}^{-3}$ . The highest concentrations of monosaccharide anhydrides and dicarboxylic acids were observed during the biomass burning episode, as one might expect. Monosaccharide anhydrides and dicarboxylic acids are known to be formed during biomass burning (Simoneit *et al.* 1999, Gao *et al.* 2003). Levoglucosan (formed in the thermal breakdown of cellulose) is also a specific tracer for biomass combustion (Simoneit *et al.* 1999).

The concentrations of monosaccharide anhydrides had a clear decreasing trend in spring

similar to those of WSOC (Fig. 3), which indicates that they have a common source or formation mechanism. The higher concentrations of monosaccharide anhydrides in winter can be explained by biomass burning for residential heating during the cold season. Based on this study, biomass burning appears to be an important source of WSOC and dicarboxylic acids.

The sum of carbon in monosaccharide anhydrides and dicarboxylic acids (C1–C3) comprised 2.4%–12.2% of WSOC. During the biomass burning episode this fraction (5.1%) was, on average, slightly lower than outside of the episode (5.8%). A summary of the average concentrations of analyzed monosaccharide anhydrides and dicarboxylic acids, as well as their average contributions to WSOC, is given in Table 2.

### Size distributions of WSOC, inorganic ions and mass

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. Often the concentration of particulate organic matter has been calculated from the concentration of organic carbon by multiplying the result with a factor 1.2–1.4 as suggested by Turpin and Lim (2001). The multiplier 1.2 would be more accurate if organic fraction consisted mostly of saturated, long hydrocarbon chains. In a water-soluble fraction, multifunctional oxygenated groups are very common and therefore a larger multiplier is needed (Zappoli *et al.* 1999). According to Turpin and Lim (2001) the molecular weight per carbon weight for more water-soluble compounds ranges from 1.5 to 3.8. They recommend using the multiplier of  $1.6 \pm 0.2$  for an urban aerosol. According to a recent study by Pang *et al.* (2006), the particulate organic matter to OC ratio can be determined using the organic carbon and organic oxygen data without the knowledge whether the aerosol is fresh or aged. The only problem in this approach is the lack of an easy and fast method to determine the organic oxygen. In order to estimate the amount of WSPOM, we multiplied the WSOC concentration by a factor 1.6 in this study. The measured mass fractions of WSPOM in the submicron and supermicron size

**Table 1.** Measured minimum and maximum values, time-weighted average values for WSOC, OC, WSOC/OC ratio and 10 and 90 percentiles.

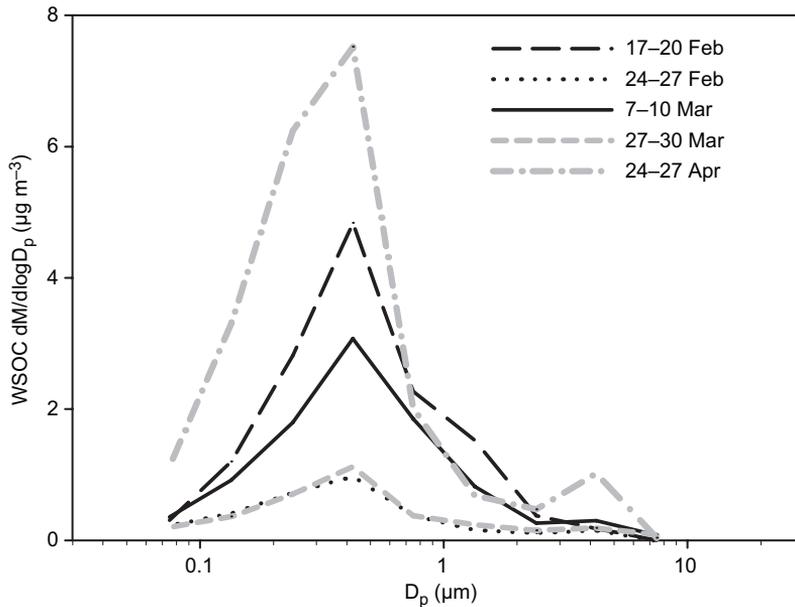
	Time-weighted average	Max	Min	10 percentile	90 percentile
WSOC normal <sup>1</sup> ( $\mu\text{g m}^{-3}$ )	1.16	4.59	0.26	0.45	2.02
WSOC episode <sup>2</sup> ( $\mu\text{g m}^{-3}$ )	6.04	10.7	2.78	3.63	8.66
OC normal ( $\mu\text{g m}^{-3}$ )	2.13	7.48	0.67	0.86	3.52
OC episode ( $\mu\text{g m}^{-3}$ )	9.59	15.7	3.88	6.05	13.6
WSOC/OC normal (%)	54.5	89.1	30.3	42.0	74.3
WSOC/OC episode (%)	63.5	84.9	53.0	55.2	73.0

<sup>1</sup> Normal refers to period 9 February–25 April and 7–10 May 2006.

<sup>2</sup> Episode refers to observed biomass burning episode between 26 April and 6 May 2006.

**Table 3.** The total mass and water-soluble particulate organic matter concentrations ( $\mu\text{g m}^{-3}$ ) and the amount of water-soluble particulate organic matter (%) in submicron ( $\text{PM}_{10}$ ) and supermicron particles ( $\text{PM}_{1-10}$ ).

Date	Total mass $\text{PM}_{10}$ ( $\mu\text{g m}^{-3}$ )	Total mass $\text{PM}_{1-10}$ ( $\mu\text{g m}^{-3}$ )	WSPOM $\text{PM}_{10}$ ( $\mu\text{g m}^{-3}$ )	WSPOM $\text{PM}_{1-10}$ ( $\mu\text{g m}^{-3}$ )	WSPOM (% of $\text{PM}_{10}$ )	WSPOM (% of $\text{PM}_{1-10}$ )
17–20 Feb	15.44	5.12	4.53	0.84	29	17
24–27 Feb	5.32	3.26	1.08	0.16	20	5
7–10 Mar	13.41	4.90	3.18	0.59	24	12
27–30 Mar	6.55	2.95	1.27	0.40	19	14
24–27 Apr	21.72	10.48	8.04	0.88	37	8



**Fig. 4.** Size distributions of WSOC in MOUDI samples collected between 17 February and 27 April 2006.

fractions varied in the ranges 19.4%–37.1% and 5.0%–16.5%, respectively (Table 3).

The gravimetric mass, ions and WSOC were determined from the MOUDI samples collected between 17 February and 27 April. Bimodal size distributions were observed for the gravimetric mass, the dominant mode being usually the accumulation mode between 0.1 and 1  $\mu\text{m}$ . The last MOUDI collection was made during the major biomass burning episode on 24–27 April. The size distribution of the gravimetric mass for this period was different compared with those

measured earlier in that spring. In addition to the bigger accumulation mode, also the coarse mode was substantially bigger, which is probably due to the biomass burning episode. For WSOC and sum of inorganic ions, bimodal size distributions were observed as well. In case of WSOC the dominant mode was the accumulation mode and only a small coarse mode was observed (Fig. 4). During the biomass burning episode (24–27 April), the accumulation mode of WSOC was shifted slightly toward smaller particle sizes and the concentration was substantially higher than that prior to the episode (Fig. 4). The shift toward smaller particle sizes of the WSOC size distribution was also evident in the first MOUDI collection (17–20 February). This shift might be explained partly by biomass burning for residential heating, since also the levoglucosan concentrations were elevated at that time (Fig. 3).

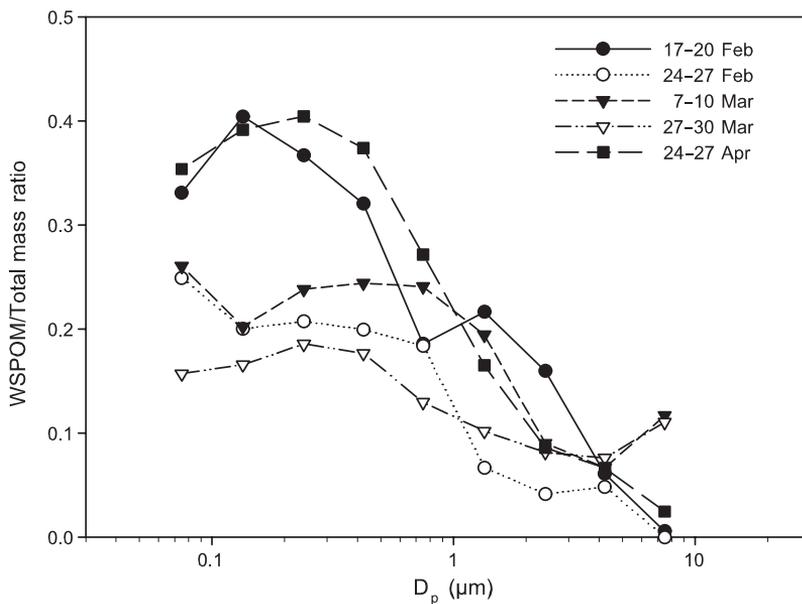
**Table 2.** Concentrations of monosaccharide anhydrides and dicarboxylic acids (C1–C3) compared to the total mass of water-soluble organic carbon in PM<sub>10</sub> samples. The results of episode period (26 April–6 May 2006) are reported in parenthesis after the average value of rest of the period.

Component	Average concentration <sup>1</sup> (ng m <sup>-3</sup> )	Average contribution of C in compound/total WSOC <sup>1</sup> (%)
Levoglucosan	26.0 (103.4)	2.5 (1.7)
Galactosan	2.90 (23.7)	0.3 (0.40)
Mannosan	3.97 (14.4)	0.4 (0.25)
Oxalic acid	16.2 (84.4)	1.5 (1.4)
Malonic acid	6.73 (37.6)	0.6 (0.62)
Succinic acid	6.01 (41.2)	0.5 (0.68)

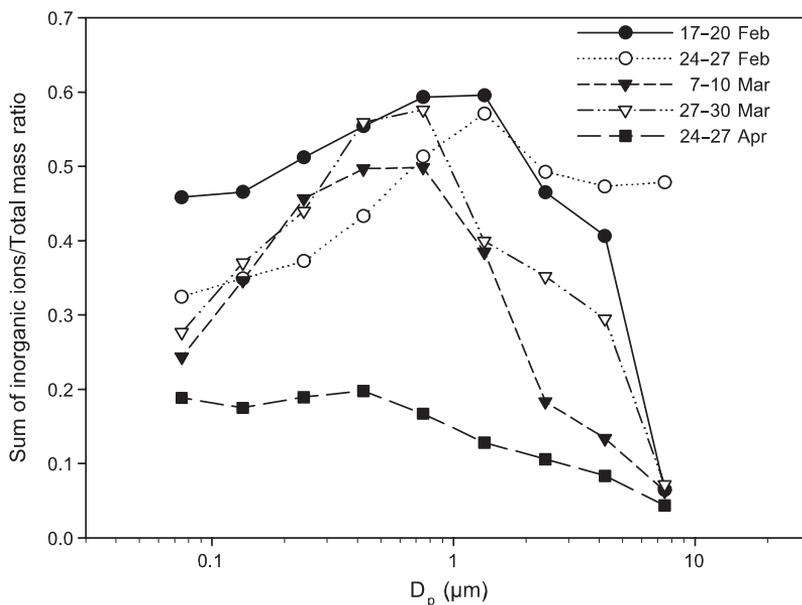
<sup>1</sup> Time-weighted average value.

In order to further investigate the distribution of WSPOM between the different size classes, the ratio of WSPOM to total particulate mass was calculated for each size range measured by the MOUDI (Fig. 5). The highest ratios were observed in the smallest classes (< 0.56  $\mu\text{m}$ ) and the lowest ones in the largest sizes (> 5.6  $\mu\text{m}$ ). Figure 5 clearly shows the shift of the WSOC size distribution towards smaller sizes in the MOUDI collection done during the biomass burning episode and also in the first collection

**Fig. 5.** Ratio of water-soluble particulate organic matter to total mass in different size classes in the MOUDI collections.



**Fig. 6.** Ratio of inorganic ions to total mass in different size classes in the MOUDI collections.



(17–20 February). The ratio between the sum of inorganic ions and total particulate mass was also calculated for each MOUDI stage (Fig. 6). The highest ratios were observed in the size range 0.32–3.2  $\mu\text{m}$ , whereas the lowest ratios were typically observed in the largest particles ( $> 5.6 \mu\text{m}$ ). Together, Figs. 5 and 6 demonstrate that the contributions of WSPOM and inorganic ions to the total particulate mass differed clearly from each other between the different size classes. The

contribution of WSPOM was clearly at its largest in the smallest sizes (0.056–0.32  $\mu\text{m}$ ), whereas that of inorganic ions was at its largest in the size range 0.56–1  $\mu\text{m}$ . Also the ratio of WSPOM to the sum of inorganic ions was calculated for each size range (not shown). This ratio was typically smaller than one in the most of the size ranges, indicating that the sum of inorganic ions was larger than the amount of WSPOM. However, the MOUDI collection conducted during the

episode (24–27 April) was different. In that collection the amount of WSPOM was larger than the sum of inorganic ions in all the size classes below 1.8  $\mu\text{m}$ .

### Comparison with other studies

So far, most of the WSOC measurements have been conducted during short measurement campaigns (e.g. Matta *et al.* 2003, Yu *et al.* 2004, Viana *et al.* 2006, Huang *et al.* 2006). Furthermore, different collection methods and substrates have been used in different studies, which makes the comparison of the results difficult. Jaffrezo *et al.* (2005) and Decesari *et al.* (2001) have reported a long time series of WSOC measurements in French Alps and Po Valley, Italy, respectively. They observed higher WSOC concentrations in winter and as compared with those in spring and summer. In this study OC and WSOC concentrations were measured on a daily basis during a three-month period in spring 2006. The decrease in the WSOC concentration from winter to spring was obvious also in this study. To our knowledge, other long-term measurements on WSOC concentrations have not been conducted in northern Europe.

Data on size distributions of water-soluble organic carbon are scarce. Huang *et al.* (2007) used a MOUDI with quartz fiber filters and Li *et al.* (2000) used a MOUDI with teflon filters to measure WSOC size distributions in China. Decesari *et al.* (2005) published results of WSOC size distributions measured at Jeju Island, Korea, with a five-stage Berner low pressure impactor. Yu *et al.* (2000) measured WSOC size distributions by using an eight-stage impactor with quartz fiber filters in Hong Kong. In Europe data on WSOC in size-segregated samples have been published from Hyytiälä (QUEST 1 and 2 campaigns: Cavalli *et al.* 2006, Allan *et al.* 2006), from Maze Head (O'Dowd *et al.* 2004) and from Slovenia (Turšič *et al.* 2006). In all of the published studies, the WSOC was found predominantly in sub-micron particles. Matta *et al.* (2003) and Huang *et al.* (2006) observed a decrease in the contribution of all carbonaceous species to the particulate mass as the particle size increased. The same pattern was observed also in this study.

## Summary and conclusions

In this study, concentration time series of WSOC, OC, inorganic and some organic ions, low-molecular weight dicarboxylic acids and monosaccharide anhydrides were measured from February to May 2006. The WSOC/OC ratio was 0.54 on average, which clearly indicates that a significant fraction of organic carbon consists of water-soluble compounds. Monosaccharide anhydrides and low-molecular weight dicarboxylic acids constituted an important fraction of water-soluble organic carbon. According to this study, on average 5.8% of WSOC was made of these compounds. On average, levoglucosan, galactosan and mannosan contributed 2.5%, 0.27% and 0.40%, respectively, to the total WSOC. For oxalic, malonic and succinic acid the corresponding contributions were 1.5%, 0.57% and 0.50%. The trends in the concentrations of monosaccharide anhydrides and WSOC were similar, suggesting that they had a common source or formation mechanism. For monosaccharide anhydrides, the higher concentrations in winter can be explained by biomass combustion for residential heating during the cold season. Based on this study, biomass burning appears to be an important source of dicarboxylic acids and WSOC in general.

A procedure to analyze the size distributions of WSOC from size-segregated atmospheric aerosol samples was developed in this study. Bimodal size distributions with a dominant accumulation mode were observed for WSOC. The coarse mode was small. The size distributions of WSOC differed slightly from those of inorganic ions, which may be an indication that they were partly externally mixed. Also, the size distributions of WSOC were different from those of gravimetric mass. The measured WSOC concentrations from the MOUDI were comparable to those from the  $\text{PM}_{10}$  filter samples collected during same time.

Only a limited amount of information is available on size distributions of water-soluble organic carbon. The still ongoing study completes the knowledge of water soluble organic aerosol fraction in urban particulate matter in northern Europe.

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