

Interactive comment on “Size distributions, sources and source areas of water-soluble organic carbon in urban background air” by H. Timonen et al.

H. Timonen et al.

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Anonymous Referee #3

General comments: Ref. This paper presents new data from measurements over an extended period of time. The data are unique and the papers' main merit is that it provides the climatology of WSOC concentrations at a unique sampling site. However, there are a number of issues with this paper that make it unsuitable for progressing to the next publication step. The most significant concern is that the authors make very strong or specific statements and conclusions that are not explicitly supported by the data. Along this line, another overall weakness is that although there is some discussion of measurement uncertainty in the instrument section, this is never

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applied to the data analysis. No analysis on propagation of errors was considered and no consideration is made of uncertainties when comparisons are made between measurements. Because of this it is not clear if some of the conclusions are valid. Much more care is needed in the interpretation of this data.

Author: the interpretation and discussion of the results have been tried to improve also some discussion is added concerning the uncertainties of the results

Specific points Ref. Page 2849, Line 23-25. There are other identified sources of WSOC, including SOA formation of biogenic and anthropogenic emissions, and oxidation of primary organic aerosol. It would also be appropriate to note what the relative importance of these sources are, although this does depend on location.

AuthorPage 2849, Line 23-25. That sentence has been modified.

Ref. Page 7852 line 20. What is the effect of substrate RH on the weight determined for each impactor stage and filter. For example, was any attempt made to weigh the substrate before and after loading at the same RH to minimize the influence of liquid water.

AuthorPage 7852 line 20. The relative humidity (RH) and temperature was not controlled, but was recorded for each weighing session. RH had a range of 8-64%, and was most of the time below 40%. For the mass of major inorganic ion at the measurement site, ammonium sulfate, the effect of relative humidity is therefore minor, but the effect cannot be completely ruled out for the total mass.

Ref. Page 7853, how were the WSOC and ion uncertainties determined. Does it include consideration of blank variability and artifacts. Statistics on blank values and backup filter concentrations are given, but it would also be of interest to know the magnitude of the blanks and backup filter relative to measured concentrations. Do the uncertainties include any consideration on the propagation of errors? For example, if PM1 WSOC is determined by summing WSOC from a number of impactor stages

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(which is done later in the paper), the total uncertainty associated with this calculated sum could be very high since the total error will be the sum of the absolute error from each stage.

AuthorPage 7853 In each MOUDI run (total 45 runs) includes three blanks and the average value of these blanks was subtracted from each stage of the corresponding impactor. The average WSOC blank value for all Al-foil substrates was $3.6 \pm 0.4 \mu\text{g}/\text{Al-foil}$ (average \pm SD). The maximum and average standard deviation of three blank values in one impactor run was 1.3 and $0.4 \mu\text{g}/\text{Al-foil}$, which equals depending on the sampling time (96-24 h) 0.007-0.03 and 0.003-0.01 $\mu\text{g m}^{-3}$, respectively. The concentrations in the MOUDI stage collecting particles above $5.6 \mu\text{m}$ (highest stage) were about the same as blank values (stage/BL 1.4 ± 0.4), but for other stages the concentration were on average over threefold of the blank values except for some stages during short 24 h sampling.

Most abundant fine particle ions (sulfate, ammonium and nitrate) and most abundant water soluble coarse particle ions (nitrate, chloride, sodium, calcium and sulfate) counted 82 and 93 % of analyzed ions mass in fine and coarse fraction, respectively. The concentrations of these ions were clearly higher than the blank concentrations except for sodium in highest MOUDI stage (particles $> 5.6 \mu\text{m}$). The average ratio (and SD) of sodium in that stage to blank was 1.9 ± 1.4 .

The particulate WSOC and OC concentrations from filter samples were calculated by subtracting the back up filter value from the front filter value to correct the positive gaseous artifact. The average ratios of backup filter to front filter were 0.12 ± 0.05 and 0.27 ± 0.15 for OC and WSOC, respectively. The blank value for OC was $0.08 \pm 0.03 \mu\text{g m}^{-3}$ for 24 h sampling time. The average ratio of WSOC blank to WSOC back-up was 0.95 ± 0.23 .

Ref. Page 7858 line 5, The statement is made that dicarboxylic acids are a major constituent of WSOC (based on a reference to Yao et al 2002). Be quantitative; what is

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the fraction of all measured dicarboxylic acids of WSPOM. If this is based on speciated measurements of various dicarboxylic acids, I doubt this statement since as noted, the most abundant diacid is oxalate and it is only 3%. I would not call that a major constituent.

AuthorPage 7858 line 5, Corrected: Dicarboxylic acids are most abundant constituents of the organic water-soluble fraction in aerosols

Ref. Page 7858 and 7859 regarding Fig 3. I have two major points. First, the statement is made that the shape of the WSPOM/ions graph at the low sizes is due to the dependence of condensation on particle size, ie higher particle surface areas at lower sizes. This does not seem to make sense. Are not most of the ionic species also formed by condensation, similar to what is argued for WSOC. Furthermore, typically the surface area distribution peaks between 0.1 and 1 μm diameter, not below 0.1 μm . Given the extensive aerosol measurements that have been made at this site I suggest this statement be supported by a typical measured surface area distribution, or better, a mass transfer factor that considers the effect of particle size, such as Fuchs/Sutugin. Also, what is the explanation for the high WSPOM/ions ratio at the largest sizes? Surface area explanation likely fails in this case. Second, I wonder if some of the cause for the shape of these curves is due to measurement uncertainty. It appears that WSPOM/ion ratio is generally highest when concentrations are lowest (ie, the two ends of the distributions in Fig 2). If WSOC and ion measurement blanks are fairly independent of concentration (ie constant), then the relative uncertainty of WSOC and ions is highest at lowest measured concentrations and the ratio of the distributions would be highly uncertain in these regions. I suggest some error bars be included in Fig 3 and this issue be discussed. Overall, more detailed explanations are need for the shape of Fig 3. This should also include the point that although the ratios are higher at smallest measured sizes the actual concentrations at these sizes are minor relative to overall accumulation mode and so it may be of minor importance in the overall gas-to-particle conversion leading to WSOC.

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AuthorPage 7858 and 7859 regarding Fig 3. As the reviewer says, the text about the surface area is confusing, the argument cannot be drawn from the data as it is now; because it is not important for the conclusions of the paper it is removed. The ratios for particles above 5.6 μm (highest stage) had to exclude from the interpretation because of the relative high blank concentrations of WSOC. The values of other stages were verified to be acceptable. The error bars have not been added, because the figure would become too blurry, but sentence of the standard deviations has been added in the text.

Ref. Page 7859 lines 19-20. This statement assumes the sources of WSOC and OC in the summer and winter are somewhat similar. Is there any proof for this?

AuthorPage 7859 lines 19-20. The reviewer is correct. The source contributions will also change.

Ref. Page 7860 line 21. I think the authors should be more precise in their language. I do not believe that it can be claimed that Tunved (2006) observed that substantial gas-to-particle conversion of biogenic VOC to SOA; given that they did not measure VOCs or even any organic aerosol! Tunved et al inferred from measurements of size distributions and estimates of biogenic emissions that SOA from biogenic VOCs was a viable explanation.

AuthorPage 7860 line 21 The Sentence has been changed as follows: Tunved et al. (2006) also observed substantial gas-to-particle conversion in air masses undergoing marine to continental transition which was interpreted to be due to biogenic VOC emissions and subsequent SOA formation over the boreal forest in northern Europe

Ref. Page 7861 top paragraph relating to Table 1. If I am interpreting Table 1 correctly (that is that the second column is the air mass selection criteria) it seems to me that at best the selection criteria provide only a qualitative description of how the air masses were separated into the various sources. Why not use specific criteria, such as ranges in levoglucosan concentrations, air mass back trajectories intersecting fires

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from fire maps, air mass back trajectories from specific geographical sectors in a specified period of time prior to the measurement, etc. This leads to some doubt into the meaningfulness of the analysis that follows.

AuthorPage 7861 top paragraph relating to Table 1. As the reviewer says, the table is confusing. It presents the observed levels. The selected criteria are added to the text and the text in the table has been changed. Categories were mainly identified using levoglucosan concentration level for wood combustion and air mass backward trajectories for other groups. Also some other chemical results were noticed.

Ref. Page 7862 lines 9 and 10. How can it be concluded that the normalized size distributions are clearly different; if there is no consideration given to measurement uncertainty? Error bars are need on this plot.

AuthorPage 7862 lines 9 and 10: Errors bars are included

Ref. Page 7862 line 15, typo (formation formation). AuthorPage 7862 line 15, OK, done

Ref. Page 7863 lines 4 –5, again an imprecise statement. Internal mixing cannot be outright assumed based solely on similar size distributions.

AuthorPage 7863 lines 4 –5 Ok, the sentence has been rephrased.

Ref. Figures 5, 6 and 7. As discussed above it is not clear how much of these ratios as a function of size are due to real differences or systematic measurement uncertainties; include error bars and an uncertainty analysis.

AuthorFigures 5, 6 and 7. The figure 5 has been removed because the discussion of the figure 5 was very rare and more specific figures (Fig 6 and 7) are presented further. The error bars are included with these figures.

Ref. Page 7865 lines 24 and on. It is stated that: In summer the oxidation products of biogenic VOCs were clearly increasing the WSOC concentrations,

2011; How can this statement be made in the conclusions, no data is presented that explicitly showed this, instead it is a conclusion based on expectations. It is strongly recommended that the authors review this paper for these types of over generalizations. From the results presented in this paper it can only be concluded that the differences in summer/winter size distributions for WSOC measured in air masses advecting over forested regions, is generally higher summertime WSOC concentrations, and that this is consistent with higher summertime SOA production from biogenic emissions. This is a very different conclusion than what is currently stated.

AuthorPage 7865 lines 24 and on. The first sentence has been rephrased as follows: In summer the oxidation products of biogenic VOCs may increase WSOC concentrations, especially in the ultrafine particles, but at the urban measurements site also VOCs from other sources, and subsequent secondary aerosol formation are important contributors.

Ref. Page 7866 lines 5, 6,7 and 8 the line starting with 2011; Also the relative amount of water- 2011; This statement is incorrect. Comparing WSCO relative to ion concentrations in biomass burning says nothing about the magnitude of the observed biomass burning WSOC concentrations. It is well known that organic aerosol concentrations are much higher than inorganic compounds in biomass burning plumes.

AuthorPage 7866 lines 5, 6,7 and 8 the line starting with 2011 Ok, the sentence will be removed.

Ref. Page 7866 line 16, the accumulation mode dominated over what, the coarse mode? Only accumulation and coarse modes were measured? This statement must be qualified. Also, as stated above, lines 21 and 22 includes too strong a statement regarding internal mixing. Single particle composition was not measured.

Author Page 7866 line 16: The sentences have been rephrased.

Interactive comment on Atmos. Chem. Phys. Discuss., 8, 7847, 2008.

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