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Comment

## ***Interactive comment on “High time-resolution chemical characterization of the water-soluble fraction of ambient aerosols with PILS-TOC-IC and AMS” by H. Timonen et al.***

**H. Timonen et al.**

hilkka.timonen@fmi.fi

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We are grateful to Reviewer #2 for taking time to comment on the manuscript. His suggestions resulted in a clearer and better revised version of the original manuscript. For clarity, we first list the referee comment, and then our response (Authors' Response) in the following.

Reviewer #2. This paper presents a new approach which combines three analytical techniques (PILS, TOC, IC) to obtain high time-resolution data of water-soluble OC. The technique is highly interesting and useful for atmospheric aerosol research, and it is therefore of interest for the readers of AMT. In addition, the results presented show

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a very good agreement with AMS data. Unfortunately, the manuscript tends to over-interpret the data with regard to the discussion of the sources of the aerosol, which I believe should not be the purpose of the manuscript. The authors seem to extract more conclusions about sources than are really evident from the data presented, due to the fact that the dataset is probably too small. I would recommend that the authors put more focus on the technique and the comparison with the AMS results than on the interpretation of the data on sources of WSPOM. AR: We have revised the manuscript and more focus is put on the new technique rather than on interpretation.

Specific comments: page 1776, line 23: "suggest" should be "suggests"

AR: The change has been made according to the suggestion

page 1778, line 13: "water soluble fraction" should be "the water soluble fraction"

AR: The change has been made according to the suggestion

line 14: "during measurement campaign" should be "during one measurement campaign"

AR: The change has been made according to the suggestion

line 18: it would be interesting to briefly mention the online WSOC studies in other regions of the world (e.g., US, referenced in Table 1)

AR: A following comment was added on the end of introduction "The online WSOC measurements have been conducted in the North and South America and in Japan previously, but to our knowledge, these measurements are first online-measurements of WSOC in northern Europe."

line 22: please describe the "measurements", provide the dates, duration, time resolution, etc.

AR: following summary of measurements was added on chapter 2.1. "The online-measurements (PILS-TOC-IC from April 25 to may 28, AMS from April 25 to May 8,

Semicontinuous EC/OC April 25 to May 1) were conducted at the urban background station SMEAR III (60° 12', 24° 57', 30 m a.s.l.)” The more detailed description is given in following chapters (2.3 Particle-into-liquid sampler (PILS), 2.4 Aerodyne High-Resolution Time-of-Flight Aerosol Mass Spectrometer, 2.5 TOA, 2.6 TEOM).

page 1779, line 4: it would be useful to add mean PM values to provide an estimation of the aerosol load.

AR: A sentence describing the mean PM<sub>2.5</sub> and PM<sub>10</sub> concentrations measured in Helsinki was added to chapter 2.1. "In Finland the anthropogenic emissions of fine particles and their precursor gases are low, the average annual the PM<sub>2.5</sub> and PM<sub>10</sub> concentration at an urban background station (in Helsinki1999-2001) were 9.6 and 18.7  $\mu\text{g m}^{-3}$ , respectively. Similar results have been later measured by Saarikoski et al. 2007 and Järvi et al. 2009."

line 23: "has been" should be "have been"

AR: The change has been made according to the suggestion

page 1780, line 3: were any tests carried out to verify the denuder efficiency? And to ensure that there was no particle loss in the denuder system?

AR: During this campaign the denuder efficiency was not tested. Anyhow, if the efficiency of the denuders would have decreased we would have observed it in the blank values. During the blank measurements (once a day) the particles were removed with a filter that was placed between the denuders and sampler and blank values were measured for approximately 30-60 minutes. If the denuders would not remove all the gaseous compounds, elevated blank values would be observed. All the blank values for ions were below detection limits and did not change during the campaign, so the annular denuders (coated with H<sub>3</sub>PO<sub>4</sub>) seem to work very well. The organic gases were removed with parallel plate carbon denuder. The efficiency of the carbon plate denuder can be less than 100%, allowing some organic gases to penetrate through the

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denuder (breakthrough). For the WSOC measurements the blank values were larger and they were subtracted from the results. Even if there was breakthrough of organic gases from denuders, it should not have major influence to the results. The measured blank value for WSOC includes possible breakthrough from the denuders as well as the impurities in water, sampler and lines, and therefore it is not possible evaluate the quantity of breakthrough. Anyhow, based on the results of Arhami et al. 2006, the breakthrough in the parallel plate denuders should be very small. If there were major particle loss in the denuders, we would have observed it in the results. The results of aerosol mass spectrometer (where we did not use denuders) and PILS-TOC-IC were very close to each other, therefore it seems likely that there were no major particle loss in the denuders. A following sentence was added to chapter 2.3.1. “The blank value was measured for approximately 1 hour every day during the week days to evaluate the influence impurities in solvents and system as well as the breakthrough of gases from denuders to the results.”

page 1784, line 9: please provide reference for the 20% uncert, e.g., Peltier et al. (2010)

AR: Unfortunately we were not able to find the article you are referring (peltier et al. 2010), and therefore we had to use previously published articles. Following references were added as references for the method uncertainty: Arhami, M., Kuhn, T., Fine, P. M., Delfino, R. J. and Sioutas, C. Effects of Sampling Artifacts and Operating Parameters on the Performance of a semicontinuous Particulate Elemental Carbon/Organic Carbon Monitor, *Environ. Sci. Technol.*, 40, 945-954, 2006. Saarikoski, S., Timonen, H., Saarnio, K., Aurela, M., Järvi, L., Keronen, P., Kerminen, V.-M. and Hillamo, R.: Sources of organic carbon in fine particulate matter in northern European urban air, *Atmos. Chem. Phys.*, 8, 6281-6295, 2008. Saarnio, K., Aurela, M., Timonen, H., Saarikoski, S., Teinilä, K., Mäkelä, T., Sofiev, M., Koskinen, J., Aalto, P. P., Kulmala, M., Kukkonen, J. and Hillamo, R.: Chemical composition of fine particles in fresh smoke plumes from boreal wild-land fires in Europe, *Sci. Total Environ.*, 408, 2527-2542,

2010.

line 26: "the ion concentrations" should be "the ion concentrations were"

AR: The change has been made according to the suggestion

page 1786, line 17: AMS total mass is higher than the TEOM mass in Figure 2 (top). Despite the uncertainty of the measurements, AMS measures only non-refractory material and therefore the total mass calculated by the AMS would be expected to be lower than the total mass provided by the TEOM. How do the authors explain this?

AR: You are right, TEOM should show larger values for total mass than AMS. The difference in this study is caused by the fact that the TEOM results are not corrected for the evaporation. According the previous studies the TEOM results should be multiplied with multiplier ranging from 1.3-1.4 to correct for the evaporation of semivolatile compounds. Multiplier is dependent on chemical composition of aerosols, and therefore depending e.g. on location and season. We decided to use the uncorrected data. Data is used only to observe the trends and correlations, and it is only indicative and not used in the calculations. A sentence was added in the section 2.6 TEOM "The results of TEOM are not corrected for evaporation of semivolatile aerosol compounds."

Figs 3 and onwards: it would be necessary to add regression equations and R2 values for all the plots. In their current form, interpretation by the reader is highly impaired.

AR: The correlation coefficients and equations of fitted curves (including the slope and intercepts) have been added after each legend. The correlations are given also in text.

page 1787, line 4: what kind of samples were those described as "rest"? What were the main aerosol sources? And the r2 value obtained?

AR: Firstly the third subset was renamed to be "other samples" to better describe the situation. During the measurement period, we had two clear sources, traffic and biomass burning episode. Subset three "other samples" includes all the samples that did not fit on the previous two subsets i.e. they have other sources than the biomass

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burning episode and traffic. The fitted curves and corresponding equations have been added to the figures and an explanation about the third subset has been added to the text.

page 1787, line 2: how is it possible that the correlation for all samples between WSPOM and POM results in  $R^2=0.88$ , and once the dataset is divided into 3 subsets the highest  $R^2$  value is 0.85? If all the other  $R^2$  values are weaker, this cannot be possible.

AR: You are right. A mistake was made with the recording of the values. The correlation between WSPOM and POM is  $=0.66$ . The correlations for the subsets are: 1)  $r=0.85$ , 2)  $r=0.66$  and 3)  $r=0.31$ . The values were corrected to the text.

line 3: the absence of correlation between WSPOM and POM during traffic periods could be interpreted as the influence of traffic emissions from traffic (and therefore no WSPOM)

AR: You are right. A following sentence was added to the text: "The different slope for traffic sources is probably explained by the fact that traffic emissions are more local, fresh and water-insoluble, when compared to aged water-soluble long-range transported aerosols. Also it is likely that traffic emissions are partly primary particles due to incomplete combustion of fuel in engines."

line 18: are these subsets the same as those described above? If so, simply state "the same subsets". The use of the term "similarly" is confusing here.

AR: The change has been made as suggested.

Fig 4: please add  $R^2$  values and equations. In addition to the dispersion of the data ( $r^2$  values), it would be interesting to highlight in the text the slopes of the regression lines, for example: for the forest fires the slope is  $XX (>1)$  indicating primary WSPOM emissions with increasing CO, whereas during traffic episodes the slope is  $YY$  (close to zero) meaning that there is no WSPOM emission. The same for the "rest" episodes.

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AR: The equations for fitted curves have been added to the figures, as well as the most important ones have been also included to the text (chapters 3.2 and 3.3) as you suggested.

line 24: how can oxalate be a major component if it contributes with only 1-3%? Please clarify or re-write.

AR: The sentence was re-written: "Oxalate is a water-soluble acid, contributing typically 1-3 % of the fine mode WSPOM."

page 1788, line 23: "the WSPOM/POM ratio was found to have a similar temporal pattern..." I do not really see this pattern. I think the authors overly-interpret the data here. This should be removed from the abstract as well.

AR: To clarify the interpretation the figure 7 has been replaced with the another, that is more clearly showing the WSPOM/POM -ratio as a function of day temperature during 12-16. Also we have clarified in the text that there may be many reasons for this observation (emissions, mixing, aerosol aging) and temperature is not explaining the mechanism.

page 1789, line 3: please inverse the order of 18:00 and 6:00

AR: The change has been made as suggested.

line 6: "had a correlation" should probably be " had a certain correlation", the correlation is not that good.

AR: The change has been made as suggested.

line 7: "typically below 50%..." I don't see this either. Please support this statement with the mean ratios + std dev for <12\_C and 12-18\_C, or else remove it. If the ratios do not confirm the statement, the authors could simply write that they observed a "certain" correlation and that the order of magnitude is similar to that published previously by Jaffrezo.

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AR: The change has been made as you suggested. The whole section was rewritten.

line 19: please add (BVOCs) after the definition of the term.

AR: The change has been made as suggested.

page 1790, lines 1-15: this is the main ogoal of the paper, and I believe the authors succeed in it. However, they should avoid over interpretation of the data regarding the sources of WSPOM; the dataset is probably too small for this purpose.

AR: We have carefully read and re-written the parts of article containing interpretations.

line 26, "SOA formation also" should be "SOA formation might also"; this hypothesis is not fully confirmed by the data.

AR: The change has been made as suggested.

Lines 2-5: this last sentence should be removed, the data do not prove it.

AR: The change has been made as suggested.

line 6: "system provide" should be "sysmet may proide"

AR: The change has been made as suggested.

line 11: "observations were valuable" should be "observations may be valuable"

AR: The change has been made as suggested.

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Interactive comment on Atmos. Meas. Tech. Discuss., 3, 1775, 2010.

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