

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.

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Firstly, we thank the reviewer#1 for the positive assessment and helpful comments. Below, we provide a point by point response to the raised questions. For clarity, we first list the referee comment, and then our response (Authors' Response) in the following.

Reviewer #1: This paper presents data from a roughly 1 month study in Finland in which a variety of online instruments were deployed to measure aerosol composition. The authors present a unique approach to running some of the instruments and the data appear of high quality. The results are not highly novel, but are of general scientific interest, however, I wonder if a more detailed analysis could have been undertaken.

The following are examples: Many of the comparisons between measurements only give correlations, why not include other regression results (slope, intercepts).

AR: The equations of fitted curves (including the slope and intercepts) have been added on the pictures after each legend to clarify the interpretation.

The slopes for WSPOM vs Oxalate and POM seem surprisingly similar for biomass burning and non-biomass burning plumes, if true maybe discuss further?

AR: The slopes have been added to the figures to clarify the interpretation. In figure 3 (WSPOM vs POM) the slope of fitted curve for biomass burning plume is 0.74, for traffic 0.16 and for the rest of the samples the slope is 0.52. Similarity of the slopes might be caused by the fact that biomass burning for domestic heating is likely one of the PM sources in springtime in Finland. But since we don't know the source of so called "other" samples, it is difficult to speculate anything. For oxalate only the results measured during the biomass burning episode are above quantification limit ($0.1 \mu\text{g m}^{-3}$). The rest of the samples (concentration below $0.1 \mu\text{g m}^{-3}$) have been added to the plot to show the "normal" concentration level, but must be noticed that the error of these results can be substantially larger than for the results above quantification level, therefore we cannot really speculate anything about the slopes of these samples. The slopes and interpretation has been added also to the text.

Why is the slope for traffic sources so different (it's due to primary OA)?

AR: The slope is probably different due to primary OA emitted by traffic and also the age of aerosols (Traffic emissions are fresh from surrounding roads vs. long-range transported biomass burning emissions). The following sentence was added to the chapter 3.2 to explain the difference: "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."

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Average diurnal profiles of WSPOM and other secondary compounds and T might also be of interest.

AR: The diurnal profiles of WSPOM and other secondary compounds have been thoroughly examined. We were not able to find any real trends. At first the long range transported episode dominates, hiding the diurnal changes. After the episode, some trends like peak in the WSPOM in afternoon can be found, but the dataset is too short to draw any conclusions. Therefore we had to leave that out from the manuscript.

A positive correlation between the WSPOM to POM ratio and T is thought to indicate biogenic VOCs were involved in SOA formation because higher T leads to higher biogenic emissions. But why would higher biogenic emissions produce higher ratios? Is the idea that biogenic SOA is adding to the regional organic aerosol, some of which is not biogenic, hence the ratio increases? Higher ratios may just indicate more chemically aged aerosol; could that be linked to T?

AR: We believe that the observation on the trend in the WSPOM/POM -ratio as a function of maximum daytime temperature is real. Increased biogenic emissions and subsequent SOA formation is suggested to be one possible candidate for that, because the trajectories during our experiments came mainly from the western and northern Scandinavia with only minor anthropogenic sources. However, we cannot rule out other reasons. We added chemical aging in the list of the other possible variables.

Minor points.

The background is somewhat incomplete and more references could be added.

AR: More references have been added to introduction to expand the background information. Also more references have been added to other chapters to make the background more consistent.

Page 1776, Line 10, change completed with compared ?

AR: The change has been made according to the suggestion.

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Page 1784, Line 15, should it read: filter placed on the oscillating element?

AR: The change has been made according to the suggestion.

Page 1784, line 22, change smokes to smoke (also other places in the paper)

AR: The change has been made according to the suggestion.

Page 1785, line 7, be specific, what secondary ions?

AR: The list of secondary ions was added to clarify the sentence: “However, high concentrations of secondary ions (sulphate, nitrate and ammonium) in inorganic aerosol composition suggested that biomass burning emissions were mixed with other anthropogenic sources during the transport.”

Any comment on why the ratio (slope in Fig 3) for WSOPM/POM seems similar for forest fire and other, even though very different sources.

AR: The slopes have been added to the figures to clarify the interpretation in figure 3. For WSPOM vs POM the slope of fitted curve for biomass burning plume is 0.74, for traffic 0.16 and for the other samples the slope is 0.52. Similarity of the slopes might be caused by the fact that biomass burning for domestic heating and saunas is likely one of the PM sources in springtime in Finland. But since we don't know the source of so called “other“ samples, it is difficult to speculate anything.

Page 1787, line 21 states: This suggests that primary WSPOM is produced in biomass burning. (This point is also made in the Abstract). In a biomass burning plume, is a correlation between a species and CO sufficient to prove that the species is of primary and not secondary origin. It might be possible for a secondary species to also be correlated, at least to some extent. Maybe this could be tested. For example, K⁺ is clearly primary, maybe NO₃⁻ is mainly secondary? Is the K⁺ - CO correlation better or worse than WSPOM or NO₃⁻ vs CO? Later the correlation between WSPOM and oxalate is noted for smoke, since it is stated that WSPOM is primary does this mean oxalate is also primary? It would be interesting to compare oxalate – CO correlations. The

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point is that more thought should be given to the meaning of correlations with CO in the biomass burning plumes.

AR: Firstly, the testing is a very good idea, but unfortunately the correlations are both weak, so the conclusion cannot be drawn based on that test. But, as you suggest, we compared the correlations of oxalate and CO. There was a strong correlation between oxalate and CO ($r=0.83$) for samples collected during the forest fire, indicating that primary WSPOM and oxalate are likely produced in the biomass burning. A following clarification was added to the chapter 3.4. “The oxalate concentrations during the forest fire episode were clearly correlated with WSPOM (Figure 5, $r=0.82$, slope 27). Also, a strong correlation was observed between oxalate and CO ($r =0.83$) during the biomass burning episode, suggesting that oxalate was produced in the biomass burning process or it was formed subsequently after the burning by secondary formation. Oxalate concentration was not correlated with the concentrations of secondary inorganic ions (sulphate, ammonium or nitrate), suggesting that the source regions of the oxalate and inorganic secondary ions are different.

Fig 6, identify WSPOM/POM and T on the plot.

AR: The change has been made according to the suggestion.

Fig 3, 4, 5, and 7, in some of these plots it would be helpful to give linear regression data (eg, r) on the plots.

AR: The equations of fitted curves (including the slope and intercepts) have been added to each figure.

In table 1, some other online WSPOM papers that could be included: Hennigan, et al., Correlations between water-soluble organic aerosol and water vapor: A synergistic effect from biogenic emissions?, *Environ. Sci. Tech.*, 42, 9079-9085, 2008.

Hennigan, et al., On the volatility and production mechanisms of newly formed nitrate and water soluble organic aerosol in Mexico City, *Atm. Chem. Phys.*, 8, 3761-3768,

2008.

Weber, et al., A study of secondary organic aerosol formation in the anthropogen influenced southeastern United States, J. Geophys. Res., 112, D13302, doi:10.1029/2007JD008408, 2007

AR: References added as suggested.

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

AMTD

3, C830–C835, 2010

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