

Interactive comment on “Sources of organic carbon in PM₁ in Helsinki urban air” by S. Saarikoski et al.

S. Saarikoski et al.

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Final Author Comments to acpd-2008-0018

We thank for the specific comments of the Referee #3. The comments are numbered and each of them is followed by a response from the authors.

General Comments

1) I would like to draw the attention of authors and readers to a couple of points that have been discussed for decades in the USA and (a bit more recently) in Europe: sampling and analytical artifacts in OC and EC determination. While the community generally recognizes these issues, they are too often by-passed when results are published.

This is the case in this paper as well, although sampling artifacts are not completely

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ignored, but perhaps not enough accurately considered. My first concern regards the use of the back-up filter OC as a measure of the positive artifact. Although it was often used in the past, this "trick" relies on assumptions that are probably not (always) true. Furthermore, the authors' observation of a large amount of nitrate on the back up filters (interpreted as a piece of evidence that nitrate was lost from the front filter and trapped on the back up filter) provides an indication that the amount of OC found on the back up filter was probably not an accurate measure of the positive artifact. Perhaps the authors could tell us why they did not use the fact that the concentrations of OC derived from 24-hr (from filters) and 3-hr (from the on-line OC-EC analyzer equipped with a denuder) integrated measurements were very similar to show that their approach was in fine not so inaccurate.

RESPONSE: The Referee is right that the sampling artifacts were not thoroughly considered in this paper even though they are an important issue within the OC and EC measurements. Regarding positive artifacts the Referee questioned the use of back-up as a measure of positive artifact. We agree with the Referee that based on nitrate most of OC found on back-up filter may be evaporated from the front filter instead of being gaseous organic compounds. However, OC found on back-up filter was only 12±5% (average±stdev) of OC found on the front filter so we did not feel that the issue with artifacts was severe on the OC concentration presented in this paper. The value of 12% roughly equals the uncertainty of our OC measurements. As the Referee stated the comparison of online OC-EC analyzer with the filter measurements indicated that there were no serious artifacts in the filter OC measurements. New sentences about artifacts have been added to text.

2) The second question relates to negative artifacts. How much is the pressure drop below stage 8 of a low pressure Berner impactor operated at 80 L/min? Is the temperature drop within the impactor able to compensate for the pressure drop and suppress volatilization of semi-volatile species? What about losses from the on-line OC-EC analyzer's filter, placed downstream of a denuder, at a temperature that may be several

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10's of degrees larger than ambient? I do not pretend we do have an answer to each of these questions. However, it should perhaps be stated that we are looking in this paper at the sources of the OC collected in the conditions of the experiment, which might well not be exactly the same as ambient particulate OC.

RESPONSE: Even though the impactor we used was part of the low-pressure impactor only upper stages were used and therefore the pressure drop below stage 8 was 2 kPa corresponding to 2% of the total pressure. Because of that we assumed that evaporative losses due to the pressure drop were small. Temperature drop due to adiabatic expansion in the impactor can also be assumed to be small and not affecting the collection of semi-volatile compounds. There can be some evaporation from the online OC-EC filter since it was at higher temperature than ambient and had a denuder prior to it which is known to accelerate evaporation due to the changing of the gas-particle equilibrium. In online OC-EC instrument there were two filters back-to-back, however the second filter may collect only small amount of OC evaporated from the front filter. The performance of semicontinuous OC/EC analyzer and especially the sampling artifacts have been studied in detail by Arhami et al. (2006). A sentence: "Due to the uncertainties in the sampling the sources of the OC were assessed in the conditions of the experiment, which might not be exactly the same as ambient particulate OC" has been added to text.

3) These questions of sampling artifacts plus possible discrepancies in OC/EC determinations linked to the use of different analytical protocols around the world make it quite difficult to compare data obtained in Finland, Japan, France,..., and the USA. Further-more, these references to studies carried out in other countries do not contribute to the authors' goal of determining the sources of OC in Helsinki and make the discussion heavier. All these data might be gathered in a Table and discussed in a dedicated paragraph if needed. The paper would indeed improve by being a bit more concise.

RESPONSE: We understand a point that the Referee raised. However, since the stud-

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ies referred in this paper differed greatly (e.g. different size fractions studied, different sampling/analysis systems) the comparison between studies would be difficult just by gathering the data in a Table. Also, we feel that comparison of our results with the data obtained in other parts of the world is essential for a good paper. Therefore we left the comparison as it was. However, we added two sentences stating the difficulties associated with the comparison of data obtained by using different analytical protocols.

Specific Comments:

4) Page 7807, line 19-24: there are also studies showing that biomass combustion particles are much less harmful than traffic particles because the fraction of non soluble particles is much larger in the latter. Listening at experts, it seems that adverse health effects are not directly linked to the mass of PM inhaled.

RESPONSE: Yes, the Referee is right that the solubility of particles seems to be more related to adverse health effects than the PM mass. That's why we removed a phrase: "on the mass basis" from the text.

5) Page 7812, line 22: was the efficiency of the denuder tested only once? It might well depend on the OC mix, which is season dependent. As the denuder breakthrough + blank contributes significantly to the amount of TC collected every 3 hours, this question is critical.

RESPONSE: The efficiency of the denuder was tested twice. In this paper only the results from the first test were presented since the results from the second test were very similar to those from the first (difference less than 10%). However, the reason for the similar results might be that both the tests were conducted in summer. The Referee is absolutely right that the efficiency of the denuder can depend on season as well as the composition of OC. We have to study the efficiency of denuder carefully in the future. The effect of sampling artifacts on the performance of a semicontinuous OC/EC analyzer has been studied in detail in Los Angeles by Arhami et al. (2006).

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6) Page 7815, line 23: of course sulfate was the most abundant ion, since nitrate was not considered.

RESPONSE: The mention that sulfate was the most abundant ion measured has been removed.

7) Page 7816, line 6 and Fig. 1: is that really a seasonal variation or a drop that occurred beginning of October 2006, and another time in December 2006. Can these sharp changes be explained by e.g. meteorological conditions ?

RESPONSE: Sharp changes in the ratio of WSOC to OC cannot be explained by measured meteorological parameters (T, RH or wind speed and direction) since they changed smoothly compared to the steep change in the WSOC to OC ratio. A sentence: "The measured meteorological parameters (T, RH, wind speed and direction) could not explain the change in the WSOC/OC ratio." has been added to text.

8) Page 7817, line 4: the observation that Oxalate/OC is steady for $T < 0^{\circ}\text{C}$ does not appear clearly on Fig. 3b.

RESPONSE: The Referee is right that the Ox/OC ratio is not steady $< 0^{\circ}\text{C}$ since the ratio fluctuates greatly even though it does not decrease with decreasing temperature as was the case $> 0^{\circ}\text{C}$. Because of that phrase "was steady" has been changed to "did not correlate with temperature".

9) Page 7819, line 7-8: the contribution of SOA is never properly "measured".

RESPONSE: The Referee is right, "measured" has been changed to "determined"

10) Page 7823, line 6: please clarify: "There can be a seasonal trend also for the biomass combustion particles in LRT".

RESPONSE: PMF suggested that some particles transported to Helsinki (LRT factor) originated from biomass combustion. That was indicated by a high loading of potassium in LRT. There was a clear seasonal variation for the biomass combustion factor,

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shown by the concentration of levoglucosan, that was supposed to originate from local/regional sources. Similarly it can be assumed that there was also a seasonal trend for biomass combustion particles transported to Helsinki since the seasonal variation seems to depend on temperature. The whole section discussing the loss of levoglucosan from the particles has been changed as suggested by the Referee #1. Therefore the sentence: "There can be a seasonal trend also for the biomass combustion particles in LRT" has been removed from the manuscript.

11) Page 7828, line 1-3: are there also significant emissions of biogenic VOCs during winter ?

RESPONSE: According to the study of Hakola et al. (2003) the concentrations of monoterpenes can be unexpectedly high in winter. In Central Finland the concentration of monoterpenes was 97 pptv in winter whereas the concentration equal to 250 pptv was measured in summer. Winter concentrations were explained by small emissions from Picea Abies but also much longer lifetimes of monoterpenes in winter than in summer.

Hakola, H. et al. (2003). Seasonal variation of VOC concentrations above a boreal coniferous forest. Atmos. Environ. 37:1623-1634.

12) Figure 4, left panel: what are units on Y-axis, % ?

RESPONSE: There are no units on the y-axis since the y-axis is relative contribution (0-1) which means the contribution of a given factor to the total concentration of the compound.

Interactive comment on Atmos. Chem. Phys. Discuss., 8, 7805, 2008.

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