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Atmospheric
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Discussions

Interactive comment on "Sources of organic carbon in PM_1 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 #1. The comments are numbered and each of them is followed by a response from the authors.

General comments:

1) The majority of my comments are really just for helping with clarity and flow of the paper, which is perhaps the only minor weakness of this manuscript. In particular, the authors should pay special attention to Figure 6 and its associated text.

RESPONSE: The text has been changed as requested by the Referee in order to improve the clarity and flow. Time-trends for the concentrations of levoglucosan and potassium have been added to Fig. 6. Also the text associated with Fig. 6. has been

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changed as suggested by the Referee.

Specific Comments:

1.Introduction:

2) Page 7808, lines 2-5- I am not exactly sure I understand the point the authors are trying to make with this sentence. Is it that OC from SOA cannot easily be distinguished from regionally transported primary OC? If that is the case then maybe it would be better if part of the sentence read as but also 70% of primary OC may originate from regional transport

RESPONSE: The Referee is right that the sentence was unclear. We did not try to distinguish SOA from primary OC. Our aim was to emphasize the importance of regional transport considering both SOA and primary OC. The sentence has been clarified as suggested by the Referee.

2.Experimental: 2.2.1.Sampling system:

3) Page 7809, line 16- Where the quartz filters pre-baked? This is come practice for organic sampling in order to remove background carbon, but it is not mentioned.

RESPONSE: The Referee is right that quartz filters are typically baked before sampling in order to remove any impurities found on filters as well as gaseous OC adsorbed on filters. In this study we also baked filters before using them in the impactor. A sentence “Prior to the sampling, the quartz filters were cleaned at 550 °C for six hours.” has been added to text.

2.2.2.Chemical analyses:

4) Page 7811, line 9- Since the concentrations for most of the various species measured off the filters using IC are being reported or were not determined because they were below the detection limits, then the actual limit of detections for these various species should also be provided.

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RESPONSE: As suggested by the Referee detection limits have been added to text.

2.3.Online measurements: 2.3.1.Semicontinuous OC/EC analyzer:

5) Page 7821, line 1- How was the blank performed? When I think of collecting a blank for an online aerosol instrument it usually means putting a filter on the inlet to remove particles. Since the blank was done at 3:00 I suspect this was not the case. It is fine for the authors to say that they are referring to whatever they did as an instrumental blank. However, just stating a two-minute sample blank was collected is perhaps not the best way to express this.

RESPONSE: The Referee is right, usually the blank is collected by putting a filter on the inlet to eliminate particles. The two minute blank in the online OC/EC analyzer was not measured this way. The two minute blank was a sample similar to the other samples, however, the collection time was only two minutes instead of 147 minutes used for the “normal” samples. The aim of the two minute sample blank was to take into account the uncertainties related to the operation of the instrument (e.g. switching valves, changing gas flows). The definition of the two minutes blank has been clarified in the text. In this study blanks were also collected by putting a filter on the inlet. Those results were used when the efficiency of the denuder was assessed.

2.3.2.PILS-IC:

6) Page 7813, lines 17-18- Is the time resolution for the PILS-IC system really 15 minutes? Or is it that a new chromatogram is recorded every 15 minutes? The time resolution is actually the time it takes for the sample loops to fill. Did the sample loops really fill in 15 minutes?

RESPONSE: As the Referee stated the actual time-resolution of the PILS-IC was not 15 minutes. The duration of the IC analysis was 15 minutes, however, it took only 7 minutes to fill the IC loop. That means that of 15 minutes time-period 7 minutes sample was analyzed whereas for 8 minutes the sample flow went to waste. Three sentences

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regarding this issue have been added to text

3. Results and discussion: 3.1.PM1 filter measurements: 3.1.1.Annual concentrations:

7) Page 7815, lines 5, 8, 10, 11- Should the units be micrograms C/m3?

RESPONSE: The Referee is right that also units μgC/m3 could be used for OC, EC and WSOC. However, the terms organic, elemental and water-soluble carbon (OC, EC, WSOC) define that only the organic, elemental or water-soluble carbon content of the particles was measured.

3.1.2.Seasonal variation:

8) Page 7816, line 22- What is meant by carbon content of levoglucosan? I believe that Figure 3a is essentially showing the ratio of levoglucosan to OC as a function of temperature. However, saying when the carbon content of levoglucosan was compared to OC would mean to me that the concentration of levoglucosan has been converted to a carbon mass basis using the molecular weight of levoglucosan and carbon and this carbon mass basis levoglucosan was then plotted versus (or compared) to OC.

RESPONSE: The Referee is right that in Figure 3a the carbon content of levoglucosan was compared to OC. The carbon content of levoglucosan was calculated by dividing the concentration of levoglucosan by its molecular weight (162.14) and multiplying it by the molecular weight of carbon associated with the levoglucosan (72.06). The reason for this conversion was that now we were able to plot the fraction of organic carbon originated from levoglucosan as a function of temperature since OC and levoglucosan were both on carbon mass basis. However, by plotting directly the ratio of levoglucosan concentration to OC versus temperature would have resulted in a very similar trend to that presented in Fig. 3a. Figure caption 3 has been clarified.

3.1.4.Characterization of sources:

9) Page 7822, lines 20-26- This section seems to be suggesting that there was no change in the potassium concentration from season to season whereas the levoglu-

cosan concentration changed leading to the trend in the levoglucosan/potassium ration shown in Figure 6. Did the potassium concentration really not change? It would be very useful to the reader if the time series of potassium and levoglucosan were both added to Figure 6.

RESPONSE: There was a sentence in manuscript that says: “By comparing levoglucosan to potassium, the concentration of levoglucosan decreased more shaply than that of potassium.” The concentration of potassium indeed decreased from winter to summer, however, the decrease was not as significant as that observed for levoglucosan resulting in a trend for the ratio of levoglucosan to potassium. That can be seen from the time series of levoglucosan and potassium concentrations added to Figure 6a as suggested by the Referee.

10) Page 7822 starting at line 20 to Page 7823 ending at line 8- I find this section a bit confusing. The authors at first seem to suggest the trend seen in Figure 6 is due to levoglucosan being photochemically oxidized. However, right after that the authors say the PMF analysis indicates that it is due to loss of levoglucosan during transport. The authors need to work on this section. Perhaps showing the trend and then directly stating the reason for this trend would be the best approach.

RESPONSE: Our data showed that levoglucosan was lost from particles for some reason. We found two explanations. The less sharp decrease of potassium concentration than that of levoglucosan from winter to summer suggested that the loss of levoglucosan was related to radiation. However, by looking at the PMF results there was no seasonal variation for long-range transport (LRT) with which 35% of potassium was associated. In contrast, biomass combustion factor had 39% of potassium and that factor showed a clear seasonal trend. By assuming that potassium and levoglucosan both originated solely from biomass combustion we concluded that levoglucosan had disappeared from the LRT particles. However, since two explanations were quite contradictory, and we did not find any difference between winter and summer LRT composition by the PMF, we excluded the part concerning the loss of levoglucosan related to

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transport (PMF results) from the manuscript. We also followed the suggestions from the Referee and started the discussion by showing the trend first.

3.2.Online measurements:

11) Page 7824, lines 16-21- I am not totally sure I understand what the authors are saying here about the OC concentration peaking in the daytime. Generally the OC should peak in the morning. What could potentially peak in the afternoon would be the ratio of the WSOC (or SOA) to OC.

RESPONSE: The Referee probably assumes that OC concentration peaks in the morning because of large emissions from traffic combined with the weak mixing due to the low boundary layer. That can be the situation in some cases, however, there are some studies in which the OC concentrations have been found to be relatively independent of traffic (e.g. Jeong et al., 2004). OC has been found to peak in daytime due to SOA formation (e.g. Plaza et al., 2006; Polidori et al., 2006; Takegawa et al., 2006) since the majority of OC can be from SOA. Typically only the hydrocarbon-like organic aerosol (HOA) peaks during the morning rush hour whereas oxygenated organic aerosol (OOA) shows a slight increase in the afternoon (Zhang et al., 2005). Unfortunately we did not have an instrument to measure WSOC online so we could not be sure if there was the SOA formation in Helsinki in the daytime.

Jeong, et al. (2004). Measurement of real-time PM2.5 mass, sulfate, and carbonaceous aerosols at multiple monitoring sites. ATmos. Envion. 38:5247–5256.

Zhang et al. (2005) Hydrocarbon-like and oxygenated organic aerosols in Pittsburgh: insight into sources and processes of organic aerosols. Atmos. Chem. Phys. 5:3289–3311.

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