Atmospheric Measurement Techniques Discussions

Interactive comment on "Monitoring of inorganic ions, carbonaceous matter and mass in ambient aerosol particles with online and offline methods" *by* H. Timonen et al.

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AMTD MS No.: amt-2011-48: Title "High time-resolution chemical characterization of the water-soluble fraction of ambient aerosols with PILS-TOC-IC and AMS"

Firstly, we thank the referee #2 for the positive assessment and helpful comments. 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 (AR: Authors' Response) in the following.

Anonymous Referee #2 Received and published: 8 December 2011 The manuscript by

Timonen et al. presents an impressive data set with online and offline measurements of several aerosol species. It also presents data regarding the important question of what the instruments measure which is crucial for all aerosol measurements. I would however like to have seen a more elaborating discussion regarding how these measurements should be handled in the future.

Minor comments: R2: P 5, L3: positive artefacts. The positive artefacts in filter sampling regarding organics are known, but can it be directly translated to inorganics. I would like some referencein the matter. AR: The backup correction was clarified and a reference was added: Concentrations measured for the back-up filters were subtracted from those of the front filters by assuming that they were only adsorbed gas-phase components of the sample air (positive artifacts) and the adsorption was equal in the front and back-up filters. Correction for organic positive artifact using a back-up filter is a fairly common approach and is well characterized (Subramanian et al., 2004). For inorganic ions, however, this approach is less used. But it is known, that nitrate and ammonium appears in fine particles mainly in the form of semi-volatile ammonium nitrate and it may evaporate from the front filter during sampling causing negative artifact or gaseous nitric acid might react with alkaline particles in filter causing a positive artifact (Schaap et al., 2002).

P6, L23: Clearify. If the IC gets 0.1 ml/min it would get 1.5 ml in 15 minutes. What is the larger 1 ml loop used for. AR: In ion chromatography small loops (50-200μl) are typically used to gain optimal separation. In PILS collections, the sample is so dilute, that a larger loop volume needs to be used in order to collect larger masses of analytes and thus to get sufficient signals in analysis. Additionally, when the loop volume is filled only in a slightly shorter time than what an analysis run takes, the collected samples represent more continuously the ambient analyte concentrations than "snap shot" samples of a few minute collection. The text in question was modified as follows: Due to 15-min analysis run times in PILS-IC system, 1000 μl loops were used to collect representative samples (collected ion masses were sufficiently large

and dataset was semi-continuous) for subsequent IC analyzes.

P7, L16: The reference Viidanoja et al. (2002) is not the original reference to pyrolysis during thermal analyses of atmospheric carbon. I would suggest Johnson et al 1979 or 1981. AR: Following reference was added as suggested: Johnson, R.L. and Huntzicker, J.J. (1979). Analysis of volatilizable and elemental carbon in ambient aerosols. In Proceedings, Carbonaceous Particles in the Atmosphere, Novakov, T., Ed. National Science Foundation & Lawrence Berkeley Laboratory, Berkeley, CA, pp. 10-13.

P7, L25: Inadequate method description: How is the RT-OCEC measuring optical EC. Is it like a PSAP but without the reference filter? Does it involves any MAC (mass absorption coefficient) or corrections for filter scattering?

AR: Following explanation was added to text: In addition to thermal EC and OC measurements, the RT-OCEC measures optical EC with one minute timeresolution using the laser light transmission values measured before and after the analysis cycle. A predetermined calibration factor, based on numerous ambient measurements, is used to convert laser attenuation to EC mass on the filter.

P8, L22 and table 1: No r-values found in the table. Add the r-values since they contain crusial information regarding the data. AR: The r -values, slopes and intercepts are added to the table

P10, L19: The explanation regarding that the difference is caused by evaporation is not elaborated. AR: The sentence was reformulated: The difference can be due to the different cutoff sizes (PM1 and PM2.5) and possibly also due the evaporation of semivolatile compounds from the PM1 filter during collection.

P14, L5: The sentence is too general. I suggest adding "According to this method.." to the sentence. AR: The sentence was removed.

P14, L13: Since the result is based upon interfering gases are effectively removed from the aerosol. How have the denuder efficiency been tested? AR: The explanation how

denuder efficiency was tested was added to the text: The efficiency of the denuder was tested by adding a polytetrafluoroethylene (PTFE) filter to the sampling line prior to the denuder to remove particles and measuring OC and EC concentrations for 24 hours using a similar procedure to the normal measurements.

P16, L25: add "the" prior to "degree". AR: Word "the" was added.

P 20, L 2: are nitrate and ammonium (or 9.1 and 41 %) supposed to be reversed? AR: You are right. The sentence is corrected: Sulfate measured from the filters was 18% higher than that from the PILS-IC whereas nitrate and ammonium were 41 and 9.1 % lower when compared to the PILS results.

Figures: The axis, markers and labels are not consistent AR: The axis, markers and labels are thoroughly reviewed.

Fig 1-3, 5: X-axis label should be with the name of the month. The repeated year makes it harder to read. Extra for figure 1 is that the 1st in every month is implied. AR: The labels are changed for fig. 1-3 to be the name of the month and the full dates are added to figure captions.

Fig2-3: Line to the last data point is missing, probably because two months of missing data. AR: Yes, unfortunately PILS had technical difficulties and therefore we don't have results for that period (December 2006-january 2007). The line is left out to indicate that.

Fig 8-10: X-axis. There are of different lengths and sometimes with, and sometimes without minor unit markers. AR: The minor unit markers are removed and scales of x-axis are now similar.

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