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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”

We would like to thank reviewer #3 for the well done review and valuable comments concerning the manuscript. Based on review and the fully addressable concerns of the referee, the authors have revised the manuscript and have made the changes as suggested. The amount of statistical analysis is increased to include correlations, slopes and intercepts between different methods and statistical parameters (median,

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1st and 3rd quartiles) are added to corresponding tables. In addition references are added (Tables 2 and 4, and text) to improve the coverage of the previously published literature discussing field inter-comparison studies. On the following pages is a point-by-point authors' response (AR) to the comments of reviewers, including a descriptions of changes made to the original submission.

Anonymous Referee #3 Received and published: 9 December 2011 The manuscript describes an inter-comparison of several instruments during a yearlong study at the SMEAR-III station about 5 km from Helsinki City center. Aerosol mass, major inorganic ions and OC/EC were measured with a filter-based sampler and a set of semi-continuous instruments, which included a PILS, a real time OC/EC analyzer, FDMS-TEOM and an aetholometer. The material is of interest for the measurement community and the manuscript can be published after revision. The manuscript needs a better statistical analysis of the data and a better coverage of the previously published literature discussing field inter-comparison studies. For example, the multi-year US EPA Supersite program produced numerous papers on field evaluation of semi-continuous instruments, including the ones described in this manuscript, see Solomon et al. for references, which are too many to list here.

Specific comments:

p.6581,I.1 and following: were the ions determined from the same filter as the one used for oc/ec analysis? Please clarify. I understand there was no denuder used in front of the filters. Correction for organic positive artifact using a back-up filter is a fairly common approach and is well characterized (Subramnian et al., 2004). For inorganic ions, however, this is quite unusual. This needs to be clearly stated, because semi-continuous instruments are usually inter-compared with the denuder-filter pack method, which is considered to be the standard for inorganic ion measurements. The back-up filter correction method for OC/EC measurements is based on the generally valid assumption that the filter surface saturates with adsorbed gases after only a few hours of operation (Subramnian et al., 2004). This could be true also for gaseous nitric

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acid and ammonia. However, if the filters are not saturated with these gases during sampling time, the correction using back-up filters becomes highly uncertain. AR: Yes, all chemical analyses of PM₁ samples were made from the same filter. The sentence was clarified to be: A 1 cm² piece was punched for same sample for each analyzing method. The backup filter correction was clarified to the text: In the PM₁ filter collections denuders were not used inline. 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).

p.6583, l.1: please specify the manufacturer and the main operating principle of the semi-continuous OC/EC analyzer. From the given reference it appears to be a Sun-Set Labs semi-continuous analyzer. The given reference (also on p.6579, l.6) is not appropriate for this instrument, because it only describes its characterization. A more appropriate reference would be Turpin et al. (1990), which describes the principle of operation and other details of the instrument, which was a prototype of the commercial instrument. AR: The chapter is rewritten, the manufacturer and operating principle is added to the text, and reference Turpin et al. 1990.

p.6586, l.4: remove “burning” AR: The sentence is reformulated to : Maximum PM_{2.5} concentrations (up to 180 µg m⁻³) were observed during two biomass burning episodes, first in April-May and the second in August, 2006.

p.6587, l.27: I do not see the significance of the observation that the difference between the PILS and the filters for nitrate is similar to the amount observed in the backup filter.

If there is some loss of nitrate from the front filter and some of it is captured on the backup filter, it does not mean that an additionally equal amount will be lost from both of the filters. AR: The sentences are removed from the manuscript.

p.6588, l.7 and following: in addition to the effects of temperature and RH on nitrate loss I would consider the effect of sampling time and filter loading. Longer sampling times could lead to larger artifacts, both positive and negative. The filter loading could increase the pressure drop across the filter and thus facilitate volatilization from the front filter. I suggest that these effects are examined. AR: The artifacts are added and whole chapter is reformulated.

p.6588, l.9: Please clarify: how was the ammonium loss determined: from the back-up filter or from the comparison with the PILS? AR: The sentence is removed as unnecessary.

p.6588, l.11: How does ammonium loss compare to that of nitrate? Ammonium nitrate is the main component that is subject to losses of nitrate and I would expect that ammonia and nitrate losses should be equimolar. If they are not, it could be an indication of a problem with the back-up correction method due to uncertainty in the amount of adsorbed gases on the filter, as discussed above. AR: In PM1 samples the amount of ammonia in backup filter was very small (only 1%) of total concentration measured for the front filter, whereas for nitrate the concentration in backup filter was 42% of the amount measured in the front filter. It is likely that part of the losses can be explained by evaporation of ammonium nitrate from filter, but due to large difference in numbers, the amount of nitrate found in backup filter can not be explained only due to evaporation of ammonium nitrate. The chapter concerning nitrate and ammonium was clarified: The average PM1 filter to PILS-IC ratio for nitrate had large variation from 0.34 to 1.0 (Fig. 2), suggesting that the percentage of nitrate evaporated from the filter varied possibly due to the chemical composition or meteorological conditions like temperature or humidity. In addition, long sampling times (24-72 h) could lead to larger artifacts (both positive and negative) and the filter loading could increase the pressure drop across

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the filter and thus facilitate volatilization from the front filter (Hering and Cass, 1999, Subramanian et al., 2004, Arp et al., 2007 and references therein). For ammonium the results of PILS and PM1 agreed well. On average PM1 filters gave slightly smaller concentrations for ammonium than the PILS-IC (Figs. 1 and 2). For ammonium the PM1 filter to PILS-IC ratio was larger during the cold period and smaller in summer (Jun-Aug, Fig. 2).

p.6589,l.11: it should be noted that while the temperature is increased in the PILS, the RH is also increased. In fact, it operates in super-saturated conditions, leading to water condensation on the particles. It is well known that the partial pressure of ammonium nitrate at high relative humidity is significantly reduced (see the Seinfeld and Pandis book, for example). Thus, I would not expect large evaporative losses in such humid conditions. Given the potential problems with the unusual filter sampling approach used in the study, I would think the filter is more likely to be blamed for the discrepancies. AR: The sentence in line 11. page 6589 refers to work done by Sorooshian et al, 2006. They observed that the collection efficiency has been shown to be lower for ammonium (88 %). The sentence is clarified: Sorooshian et al. (2006) observed that the average collection efficiency for all species from a variety of aerosols exceeded 96% except for ammonium (88%) when compared to simultaneous measurements with a differential mobility analyzer (DMA). Ammonium has been theoretically shown to be the most vulnerable to volatilization in PILS with greater losses caused by increasing droplet pH and temperature (Sorooshian et al., 2006).

p.6590,l.9: I suggest removing this sentence, because the processes occurring in the filter do not have any connection with what is happening in the PILS. AR: The sentence is removed as suggested.

p.6591,l.21: how were the blanks and denuder breakthrough measured? AR: 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.

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A value of $0.52 \pm 0.10 \mu\text{gC m}^{-3}$ was measured for the denuder breakthrough. The explanation was added also to the text.

p.6592, l.10 and following: When discussing the mass closure, it would be very useful to provide an estimate of its sensitivity to the value of OM/OC factor. A wide range of values (1 to 2.5) was reported for this factor (see, for example, Pang et al., 2006). Given the large fraction of OC observed in this study, I think the assumed value could have a significant effect on the mass closure. AR: Yes, the OM/OC -ratio will definitely have an effect to mass closure. We have been using typically value 1.6 based on recommendations by Turpin and Lim, 2001. But depending on source, the value will likely range between 1.2 and 2.5. If we are using lowest likely value 1.2, the contribution of POM would be 20 % to total measured mass, and if using OM/OC -ratio 2.5 the contribution would be approximately 40 % to total measured mass. The 1.6 OC multiplier used here is likely conservative, and its value is also seasonally dependent; refinement of the multiplier is under study and will likely be considered in future applications, but it is currently beyond the scope of this study.

A following clarification was added to the text: Also the used multiplier to convert carbon to particulate organic matter will have an effect to the results of mass closure. The OM/OC -ratio depends on source and age of aerosols and can ranges typically from 1.2 to 2.5 (Turpin and Lim, 2001, Saarnio et al. 2010, Jimenez et al. 2011). An estimated value 1.6 was used based on previous studies and recommendation by Turpin and Lim, 2001.

p.6593, l.3 and following: What PM_{2.5} mass was used for this classification, the sum of measured components? Please clarify. Overall, I would suggest removing this section, because it is not very informative and could be misleading. There were at least two bio-mass burning events that had a significant impact on aerosol concentrations, accounting for most of the observations with high concentration. Thus, the bins with high concentration are probably mostly influenced by these biomass burning events and are not necessarily representative of high aerosol concentration events originating due to

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other processes. In any case, a better description should be given for this classification (how many observations per bin, how many of them are influenced by biomass burning, etc.). Figure 7 is very difficult to read in the stacked format. Diurnal pattern would be easier to judge, if individual components are given separately. AR: The section is removed as it is not very informative.

p.6593, l.25: it should be noted that such diurnal behavior of aerosol nitrate was observed by many studies in ammonia-limited conditions, not just the two cited studies, while in ammonia-rich conditions the diurnal profile is different. AR: The chapter was reformulated to include the variation in ammonia conditions: Of the ions only nitrate had a diurnal trend with a peak concentration in the morning between 6 and 9. Diurnal cycles of nitrate depend on available atmospheric ammonia concentrations of the specific location (Seinfeld and Pandis, 2006). Similar behavior for nitrate has been observed in previous studies e.g. by Hennigan et al., (2008) and Poulain et al., (2011).

p.6594, l.7: The second part of this sentence is not clear. Did you mean: “: : that may also contribute slightly to the decrease in nitrate concentrations”? In any case I do not agree that “slightly” is the right word here. Ammonium nitrate equilibrium constant is very sensitive temperature and its strong partitioning to the gas phase during warm periods has been well documented in the literature. AR: Yes, you are right. The sentence was reformulated as following: Concurrently with increased mixing layer height the ambient temperature is increasing, that may decrease nitrate concentrations by transferring of particle-phase nitrate into the gas-phase.

p.6594, l.16-17: replace “that particular” with “each” AR: Corrected as suggested by referee.

p.6594, l.16 and following: Were biomass burning events excluded from calculations of seasonal, weekly and diurnal averages? While the study period is long for a field study, it is still fairly short to draw conclusions about seasonal changes in aerosol concentration. A few strong pollution events, such as biomass burning could significantly bias the

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analysis. I strongly recommend that a more rigorous statistical analysis is performed on the data. AR: Yes, they were excluded. During 2006 we had large biomass burning episode in may and august. That is one of the reasons why we choose one month to represent each season. A sentence was added to the manuscript: The values measured during biomass burning episodes (may and august, 2006) were excluded from the data, when seasonal and diurnal trends were studied.

p.6592, l.23: I do not think this study has shown that volatility of the measured compound has an effect on PILS measurements. All this study has demonstrated is a comparison between the PILS and a filter-based method. The only conclusion one can draw is that the two methods disagree and it is more probable that the differences are due to the problems with the filter, not the PILS. This sentence needs to be either removed or reformulated to adequately describe the results of the study. AR: The sentence is removed as proposed.

Table 2: I would suggest using descriptive statistics (mean, median, 1st and 3rd quadrilles) instead of simple mean and standard deviation, which could easily be biased by a few high or low values and, in general, are not very informative for nonnormalprobability distributions. AR: The statistics (mean, median, 1st and 3rd quadrilles) are added to tables.

Interactive comment on Atmos. Meas. Tech. Discuss., 4, 6577, 2011.

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