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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.

Anonymous Referee #3

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The manuscript describes an inter-comparison of several instruments during a year-long 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,l.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 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.

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.

p.6586, l.4: remove “burning”

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

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of the filters.

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.

p.6588,l.9: Please clarify: how was the ammonium loss determined: from the back-up filter or from the comparison with the PILS?

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.

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 know 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.

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.

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

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

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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.

p.6593, l.3 and following: What PM2.5 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 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.

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.

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.

p.6594, l.16-17: replace "that particular" with "each"

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.

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.

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 non-normal probability distributions.

References

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Interactive Comment