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Atmospheric
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Discussions

Interactive comment on "Real time chemical characterization of local and regional nitrate aerosols" *by* M. Dall'Osto et al.

Anonymous Referee #2

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In this manuscript Dall'Osto and coauthors present co-located measurements of ambient aerosol particles using two different aerosol mass spectrometers - an ATOFMS and a C-ToF-AMS - at an urban site in central London. The focus of the data analysis presented in this paper is on nitrate-containing aerosol particles. From their data the authors extract information on two different kinds of nitrate-containing particles which they call 'local nitrate' and 'regional (LRT) nitrate', assuming that the first type is locally produced while the second type is transported to the site mainly from continental Europe.

The present manuscript is an excellent example for the added value of measuring ambient aerosol with complementary aerosol mass spectrometers like a single particle laser ablation instrument (ATOFMS, which generates more qualitative information, however on a single-particle level) and a thermal evaporation electron impact aerosol ensemble mass spectrometer (C-ToF-AMS, which does not generate single particle information, but provides quantitative information on particle ensembles): The ATOFMS data were used to identify particle types while the AMS was used to quantitatively investigate the aerosol for times where the different particle types are present. However, as discussed below, this approach needs a very careful analysis in order to avoid generating artifacts. In addition I suggest a more careful handling of the results as also detailed below.

Since I believe that the approach of using such complementary datasets to extract additional information from ambient aerosol measurements has a great potential, I suggest publication of this manuscript in ACP, however only after the following - partially serious - concerns have been addressed. In general the paper is clearly written with only very little typographical errors and a clear structure. No significant improvement is needed here.

General Comments:

As shown in the paper ammonium nitrate generally evaporates from and condenses onto the aerosol particles depending on ambient conditions. Therefore one can assume that both, the nitrate on the ’regional’ as well as on the ’local’ particles did condense locally onto the particles on which it was detected; the main difference of both particle types is probably the ’core’ particles onto which the nitrate condensed. Therefore it is questionable whether it is adequate to talk about ’local’ and ’regional’ nitrate or ’local’ and ’regional’ nitrate aerosols. It would be more adequate to talk about nitrate condensing onto local and onto regional aerosol.

Unfortunately no information is given about the AMS data processing. Generally in AMS data processing a correction factor for incomplete collection efficiency has to be applied to the data. This CE factor is typically 0.5 for internally mixed ambient aerosol particles. However, for particles containing a large fraction of ammonium nitrate - as

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it is apparently here the case - this factor has been observed to vary significantly over time, sometimes even reaching 1 for particles consisting mostly of ammonium nitrate. If this effect is not considered in the data processing large systematic errors (up to 100%) can be introduced into the AMS mass concentrations, generating temporal behavior in the data that does not reflect the actual ambient conditions.

I am wondering whether the method of data processing for the ATOFMS data can generate results instead of reflecting the actual ambient conditions. Here 153 595 single particle mass spectra were clustered into 306 clusters using ART-2a. This results in an average of about 1 particle per cluster and hour and thus the temporal trends of the individual clusters might have large statistical uncertainty. Since the mass spectra of the resulting two nitrate clusters look very similar it is conceivable that the major criteria for assignment of the ART-2a clusters into one of these two classes is based on the temporal trends of the individual clusters. Therefore it is not surprising that the resulting classes show different temporal trends. Can you comment on how you make sure to avoid that such differences in temporal behavior of the two nitrate types are not artificially generated by this manual merging process? This question arose mainly from the fact that both particle classes show large abundance during the second pollution event (October 14-19). Apparently there is no clear separation between the two particle classes causing particles from the LRT-nitrate class ’leaking’ into the ’local nitrate’ class. Otherwise it is not clear to me why during this event of increased particle loading due to regional transport also the ’local nitrate’ class shows ˜10 times larger abundance compared to the background values. Or is there a large reservoir of ’local nitrate’ core particles that can be ’activated’ by nitrate that has been evaporated from the ’LRT nitrate’ particles condensing onto them? If this is the case this ’local nitrate core’ particle type should be there all the time and should be a large fraction of the total aerosol.

Detailed Comments:

P19461, L4: "C-Tof_AMS" –> "C-ToF-AMS" (as at the other locations in the text)

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L 24-26: Can you provide an estimate of the particle losses in this inlet line?

P19462, L17: Here you claim that "the ATOFMS can provide quantitative information on the particle number as a function of composition". According to the existing literature this is not completely true. For particle types with non-spherical shape the focusing in the aerodynamic lens might be less efficient as for spherical particles, resulting in lower detection efficiency. In addition some particle types have higher or lower detection efficiencies due to the presence or absence of easy-to-ionize particle components, which can for example for pure ammonium sulfate particles result in the complete absence of these particles in the data. As long as these effects are not quantitatively known the statement above is not true.

L22: The C-ToF-AMS used in this study is not the "High-Resolution Time-of-Flight Aerosol Mass Spectrometer" as stated here. Also the statement in line 28 on this page ("... for high-resolution mass analysis") is not true.

P19463, L12: Please provide the manufacturer of the Partisol Sampler as you did for the other instruments.

Last paragraph: Add information on the AMS data processing, especially on calibrations, quality assurance measures and corrections (see also general comment).

P19464, L19-23: In Figure 1 it is hard to see, which bar corresponds to which day since the mark and the dates are between the bars. Apparently the date is written at the beginning of the bars. Then the two periods of elevated mass concentrations are observed one day earlier than written in the text.

P19465, L19-22: While generally the correlation between AMS mass concentration and ATOFMS count rate is very good in Figure 2 the AMS observed large nitrate peaks on the nights of the 11. and the 14., which are much smaller in the ATOFMS data. What is the cause for these two temporally very constrained differences? Could this be associated with variations in the AMS collection efficiency for nitrate particles?

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L23-27: If the ’LRT nitrate’ and ’local nitrate’ particle types are really different in origin (local and transport) it does not really make sense why during the transport episodes the local particle type also shows the larges concentrations. Can you comment on this?

P19466, L14: There is no ammonium shown in Figure 4

L16-18: Did the averaging over several events (nights) broaden the size distributions of the individual nights?

L22: Figure 5 and the text to this figure would be easier to understand if "a" and "b" would be added to the individual panels as in the other figures.

L23-26: If the ATOFMS size distributions are only meant to provide qualitative information, why are they then scaled using the APS data - isn’t this scaling procedure meant to provide quantitative data?

L27: What does this mean, that the particles are "formed locally within London"? Are these freshly generated particles? Nucleated particles (how long would they need to grow to 200 nm, would they still be within London after this time)? Primary particles (would they be in this size range)? The same applies to P19471, L16.

L28 - P19467, L1: If the ’local nitrate’ particle type is generated by nitrate condensing onto "locally emitted particles", there must be a ’local nitrate core’ particle type which should peak during the day or during maximum emission times (rush-hour?). Since the ’local nitrate’ type is very abundant during the second transport event there should be a large reservoir of such a ’local nitrate core’ particle type all the times, which would be ’activated’ to nitrate particles during this episode. So this particle type should be the dominating particle type for the non-pollution times.

P19470, L18-20: Here it is assumed that the change in the ratio of LRT and local nitrate is caused by a subsequent evaporation of ammonium nitrate from ’LRT nitrate’ particles and condensation onto ’local nitrate’ particles. Why should this progressive transport

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from one nitrate particle type to the other one happen? The residence time of the LRT particles in the London area is much shorter than a day, so I don't see any chance why there should be a 'transport process' of nitrate from one particle type to the other one over a period of several days. In addition - as mentioned before - this explanation would need the assumption of a large reservoir of 'local nitrate core' particles, which has nowhere been mentioned in the text.

P19471, L15 and 21: Also here the behavior of "nitrate aerosols" and "type(s) of nitrate" are discussed. Since the nitrate has condensed locally onto the particles which may be from local or remote sources it does not seem to be adequate to talk about local or transported nitrate.

L15-25: Here different particle sizes of the different types of nitrate are compared. It is unclear how these sizes were determined. While the 200 nm of the 'local nitrate' particles (L15) are determined by ATOFMS the 600 nm of the 'LRT nitrate' (L21) is from AMS measurements. The ATOFMS size distributions (Figure 5) show a minimum at this particle size for this particle type. According to the ATOFMS size distribution data shown in Figure 5 only very minor differences are observed in the size distributions of the two particle types. In order to determine whether they are significant information on the uncertainty (e.g. numbers of particles within each size bin of the ATOFMS data) would be needed.

Interactive comment on Atmos. Chem. Phys. Discuss., 8, 19457, 2008.

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