Atmos. Chem. Phys. Discuss., 8, S10676–S10688, 2009
www.atmos-chem-phys-discuss.net/8/S10676/2009/

Atmospheric Chemistry and Physics Discussions

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

M. Dall’Osto et al.

Received and published: 23 January 2009

Interactive comment on “Real time chemical characterization of local and regional nitrate aerosols” by M. Dall’Osto et al.

We thank the reviewers for their careful review of our manuscript. We have addressed each comment below in italics.

Anonymous Referee #1

Real time chemical characterization of local and regional nitrate aerosols M. Dall’Osto et al.

This paper presents an interesting analysis of a dataset containing high time resolution data (sub hourly) for the nitrate composition of fine particles in background air in London, as collected during a field campaign by two co-located ’real time’

particle mass spectrometers, the TSI ATOFMS and Aerodyne C-ToF-AMS. By combining the true single-particle compositional capabilities of the ATOFMS with other information (such as size distributions, temporal trends, and air mass back trajectories), the authors distinguish two broad categories of nitrate-containing particles: locally-derived, particularly during night-time; and from long-range transport.

The manuscript is clearly presented and fluently written. The context and motivation of the work are clear. The analysis of the data is comprehensive and sound, and the results interesting. The manuscript should be accepted for publication in ACP.

We thank the reviewer for his/her comments and appreciation of the synergy of the two different mass spectrometers.

Minor typographical points:

(1) There are a number of instances where there is a missing space between ’m/z’ and the associated positive or negative value, for example, p19465 (line 2), p19466 (lines 2-10), p19468 (lines 23-27), p19469 (lines 2-6).

This has been corrected.

(2) There are a few instances of inappropriate hyphenation of a word between two lines,for example p19459 (sulphate and despite), p19468 (nitrate), p19469 (nitrate). This latter issue was presumably not under the control of the authors.

Not under the control of the authors.

Anonymous Referee #2

In this manuscript Dall’Osto and co-authors 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.

We thanks the reviewer for appreciating the analysis of the two complementary aerosol mass spectrometers. We will address the concerns below.

General Comments:

(1) 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.

This point is already addressed in the first paragraph of page 19465, which includes the statement: “the particle names consequently refer more to the origins of the core particles upon which the nitrate condenses than necessarily to the source of the nitrate ion itself”.

(2) 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 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.

The following text has been added.

The AMS was run under standard operating conditions and calibrated using 350 nm monodisperse ammonium nitrate particles, selected using a DMA. Based on the fact that the recorded composition was always a mixture of nitrate, sulphate and organics, a collection efficiency of around 0.5 was expected, based on the characterisation work of Matthew et al. (2008). This was validated by deriving a total particulate volume concentration (assuming the component densities reported by Cross et al., 2008) and comparing with a volume concentration derived from a differential mobility particle sizer (DMPS, Williams et al., 2000), assuming spherical particles and only including particles up to 600 nm in mobility diameter (this is to eliminate particles of an aerodynamic size too great to be effectively measured using the AMS). When compared, the AMS-derived volume concentration is either in good agreement or slightly less than the DMPS-derived equivalent. Given that a certain fraction of the submicron particulate volume (such as elemental carbon) is not detected by the AMS, this is the expected behaviour. A collection efficiency greater than 0.5 would result in periods where the MS-derived volume concentration would exceed that of the DMPS.

(3) 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.

Art-2a does not generate artificial results, but it reflects what the ATOFMS sees. It is a method that has been used for several years and has been validated (Song et al, 1999). The average of about 1 particle per cluster per hour is not a problem as the 306 clusters have very different abundances. For example cluster number 1 represented 43567 particles, whilst cluster 306 is composed of only 2 particle mass spectra. The first 30 ART-2a clusters describe 90% of the ATOFMS particle mass spectra (153 595), and the first 60 clusters describe 95% of the population. More than 150 of the remaining 306 clusters comprise less than 30 mass spectra each and they are simply describing mass spectra with a very high level of noise/signal. Local nitrate was composed of 2 ART-2a clusters (number 2 and 6), regional nitrate was composed of 3 clusters (number 4, 9 and 15). The similarity of the clusters that were merged was very high, mainly due to little difference in the intensities of peaks. The obtained local and regional nitrate particle types are different in 3 aspects. First, the size of the particles describing the 2 is very different, as discussed in the paper (about 300 nm and 600 nm for local and regional, respectively.). Second, the ATOFMS particle mass spectra are different. Although we agree with the reviewer that the mass spectra of the local and regional nitrate are similar, the positive mass spectra are quite different (at least in ATOFMS terminology). The regional nitrate particle type has strong elemental carbon peaks that are not present in the local nitrate type. Third, the temporal trends of the two particle types are different. The first week of the REPARTEE-I (4th-10th October) shows a very clear temporal trend for the local nitrate, whilst there are none of the regional particle type at all. We agree with the reviewer that during the period of 14th-20th October the temporal trends of the local and regional nitrate particle types are similar. However, they are not identical and the difference is supported by independent AMS measurements (Figure 8 for example demonstrates the qualitatively different diurnal variations of the local and regional nitrate particle types).

(4) 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.

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper

The latter possibility summarized very clearly by the reviewer is what we believe is happening. We think (as Figure 8 obtained by a different instrument such as the AMS demonstrates) that the nitrate that evaporates from the LRT nitrate during the day can condense on the large reservoir of the local nitrate core particles. We believe that the local nitrate core particles are simply represented by the aerosol found within the London local area. The core of the local nitrate is indeed there all the time but somehow it is not seen as a special ATOFMS cluster. One possibility is that the core of the regional nitrate is an heavily aged particle type with a general signature of ammonium, sulphate, nitrate, organic and elemental carbon. It could be possible that the local nitrate is not that aged, and it has got different types of cores, including several less aged local aerosols emitted locally within London. Detailed Comments:

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

OK

(6) P19461 L 24-26: Can you provide an estimate of the particle losses in this inlet line?

More information on particle losses (which are minor) in the particle inlet can be found in Dall’Osto et al (2008).

(7) 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.

We agree with the referee, “quantitative” has been changed to “semi-quantitative”

(8) P19462 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.

Corrected

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

Added

(10) P19463 Last paragraph: Add information on the AMS data processing, especially on calibrations, quality assurance measures and corrections (see also general comment).

OK, see point 2 above.

(11) 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.

The date is written at the beginning of the bars, and the elevated mass concentrations are referred to PM2.5. The two periods are 10th-11th of October and 14th-20th of October. Pg 19464 line 20 has been modified accordingly.

(12) 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?

The fact that the correlation is not good on the nights of the 11th and the 14th (where the ATOFMS appears to underestimate the nitrate aerosol) is a problem that is under investigation. The comparison between the AMS and the ATOFMS requires a great deal of time and this REPARTEE-I dataset is providing excellent insight into the properties of the two instruments. The differences in the trends of the nights of the 11th and the 14th seems to be reflected in other particle types that the ATOFMS found and it will be the basis of another paper. Just as a brief summary for the reviewer (and the readers) it seems that the periods in Figure 2 where the AMS and the ATOFMS are not correlating well are due to two different particle types (amine-rich and nitrate with a stronger EC component).

(13) 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?

We believe that part of the nitrate evaporating from the regional nitrate condenses not only on its original core (LRT nitrate core) during night time but also on aerosol available within London, creating more local nitrate. Figure 8 and second and third paras of page 19470 explain it further. However, further studies need to be carried out in order to fully understand the mechanisms involved in the interaction between the two different types of nitrate.

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

This is corrected

(15) P19466 L16-18: Did the averaging over several events (nights) broaden the size distributions of the individual nights?

The AMS mass loadings of the nights with high concentrations of local nitrate (first week of the field study, Figure 2) were too low to give reliable size distributions of

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper

the nitrate aerosol mass loading. However (see for example Figure 8), trends for four different nights affected by both local and regional nitrate can be seen. The averaging processes may have broadened the distributions slightly.

(16) P19466 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.

Figure 5 has been changed

(17) P19466 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?

We prefer to consider them semi-quantitative, as the error limits associated with the size distributions are not yet fully understood.

(18) P19466 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.

Local nitrate aerosol is the component of nitrate that is formed locally in London, and not transported regionally from Continental Europe. The local nitrate was found to spike during night time and we believe this nitrate is condensed on aerosol available within London and not transported regionally. This nitrate aerosol is freshly generated, but it is not a homogeneous nucleation process. Instead, it is nitrate condensing from the gas phase to the aerosol available in the urban area.

(19) 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.

We believe that the local nitrate core is the aerosol available within the urban area. Whilst we do see a clear trend for the regional nitrate core (Figure 6), we do not see any local nitrate core. The reasons could be multiple, including a dimension limitation (too small to be seen by the ATOFMS), with a chemical composition difficult to detect by the ATOFMS, or a non-unique local nitrate core (different types of aerosol, regardless its chemical composition, could be the local nitrate core).

(20) 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 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.

We have described the data, and demonstrate that such a transfer process is feasible. There are facets of processes occurring that remain, as yet, not fully explained. This is one such facet.

(21) 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.

We think we have addressed this point already.

(22) P19471 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.

The particle size distributions measured by the same instrument (AMS) are compared. The first type of nitrate is characterised by small particles, peaking in the smallest detectable ATOFMS size at 200 nm. This is a particle number distribution determined by the ATOFMS. Then we state that the AMS supports the ATOFMS finding, by showing half of the nitrate aerosol loading (detected during the same time period) distributed in particle sizes smaller than 350 nm. This is an aerosol mass loading size distribution, and is compared with the larger mode (peaking in the accumulation mode at about 600 nm) and seen by the AMS. We agree the particle number size distributions are not hugely different, but when considering the volume size distributions the differences increase. This is one reason why we prefer to treat such ATOFMS particle number size distributions as only semi-quantitative. However, when considering the quantitative aerosol mass loading size distributions obtained by the AMS (Fig 4) the difference is clear. The text has been modified to make this clearer.

REFERENCES ADDED

Cross, E. S., J. G. Slowik, P. Davidovits, J. D. Allan, D. R. Worsnop, J. T. Jayne, D. K. Lewis, M. Canagaratna and T. B. Onasch (2007). "Laboratory and ambient particle density determinations using light scattering in conjunction with aerosol mass spectrometry." Aerosol Science And Technology 41(4): 343-359.

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper

Dall'Osto, M., Harrison, R. M., Coe, H., and Williams, P.: Real-time observation of secondary aerosol formation during a fog event in London, Atmos. Chem. Phys. Discuss., 8, 20019-20050, 2008.

Matthew, B. M., A. M. Middlebrook and T. B. Onasch (2008). "Collection efficiencies in an Aerodyne Aerosol Mass Spectrometer as a function of particle phase for laboratory generated aerosols." Aerosol Science And Technology 42(11): 884-898.

Williams, P. I., M. W. Gallagher, T. W. Choularton, H. Coe, K. N. Bower and G. McFiggans (2000). "Aerosol development and interaction in an urban plume." Aerosol Science And Technology 32(2): 120-126.

NEW FIGURE 5 A revised version of Figure 5 has been prepared

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

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper