

## Reply to Reviews

### Referee #1:

This paper presents a new algorithm for the processing of single particle data obtained using an Aerodyne AMS equipped by a light scattering module. This work builds on previous techniques used for the interpretation of data from this instrument and could be very useful in the future for the application to atmospheric science. The approach uses empirical classification rules based on existing mass spectral profiles. Compared to a more general-purpose clustering method (such as k-means), this has a heavily reliance on a priori assumptions on the expected compositions of ambient particles. However, because of the low signal quality of the individual particle data, it can be expected that this will produce much more decisive results and the technique is demonstrated to be open to unexpected particle types. This paper is relevant and suitable for AMT and is largely well written, barring a few issues. I recommend publication, subject to the following comments.

**General: Linear correlation (Pearson's  $r$ ) is not the only metric available for comparing mass spectra and it can be argued that the normalised dot product (also known as uncentred  $r$ ) is more suitable. While the two metrics may produce qualitatively similar results, a particular issue with  $r$  surfaces when considering the applicability of the flowchart on figure 1. Because the exact quantitative value of  $r$  is dependent on the number of zeros (or near zeros) in the mass spectrum in addition to the magnitudes of the signal-containing peaks, the thresholds quoted in figure 1 will not necessarily remain valid if one were to use mass spectra of different sizes to the ones used here (which isn't currently specified). If  $r^2$  is to continue to be used, the authors need to be very specific about the size of the mass spectra they have used in this instance and comment on how the thresholds in figure 1 might change with different sizes. Alternatively, the thresholds could be changed to the corresponding normalised dot product values.**

While we generally agree with the reviewer that the normalized dot product could be a suitable metric to determine the similarity between the measured single particle mass spectra and standard spectra, we do not agree that Pearson's  $R$  is not a suitable metric for this purpose. We have tested the suitability of both Pearson's  $R$  and uncentered  $r$  by calculating these metrics for three pure substances (ammonium nitrate, sulfate and glucose) for a comparison of the respective reference mass spectrum with a randomly chosen single particle mass spectrum of the same pure substance. By adding more and more artificially generated "noise" to all mass spectral lines of the single particle mass spectra, we simulated decreasing signal-to-noise ratio (i.e. decreasing particle size). We found that both metrics (Pearson's  $R$  and uncentered  $r$ ) decreased with decreasing signal-to-noise-ratio similarly (very tight correlation with a slope and regression coefficient of both about 1, see Figure 1), so from this experiment, we cannot conclude that one of both metrics is superior to the other.

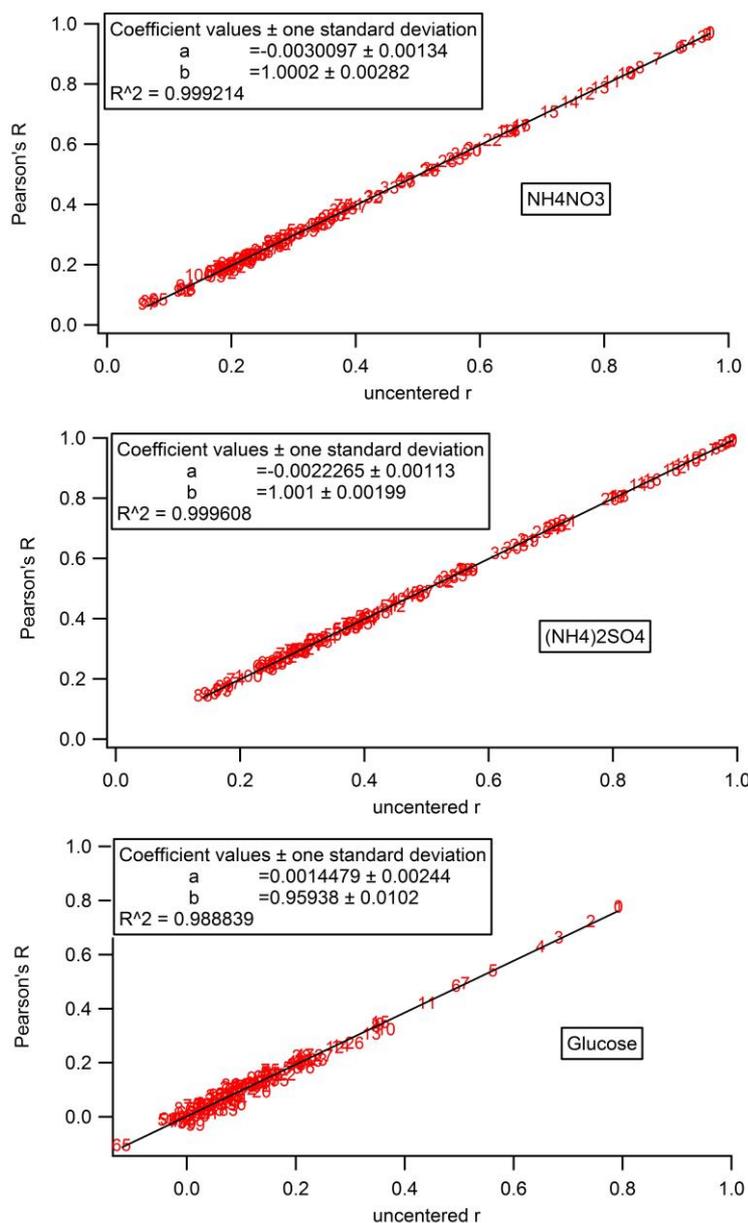


Figure 1: Pearson's R versus uncentered r for the correlation of single particle mass spectra of three substances (ammonium nitrate, ammonium sulfate, and glucose) with their respective reference mass spectrum. The numbers represent the amount of white noise added to the single particle mass spectrum (0: original mass spectrum; the larger the number, the more noise was added).

This means that in both cases, at some point noise is overwhelming any signal; and in both cases, a rather arbitrary threshold for detection needs to be chosen. I.e. in any case, this threshold is determined by the fact that mass spectral signatures can only be identified with enough confidence at a certain signal-to-noise-ratio. Therefore, we do not think that the use of uncentered r instead of Pearson's  $R^2$  values would change the fact that smaller particles' mass spectra are harder to identify than larger particles' mass spectra, because of the smaller ion counts. The thresholds for positive detection still remain valid. We do agree, however, that more work on the detection limits for different substances is needed. This was already stated several times within the manuscript (e.g., p. 5667, line 15; p. 5678, line 13), and will be addressed in future work.

**Page 5658, line 14: As it stands, the comment about AP240 thresholding is unlikely to make any sense to someone not already familiar with the operation of the TOF-AMS. This needs expanding or referencing.**

We agree and added an according reference:

“On-board AP240 thresholding (Kimmel et al., 2006) was used during all measurements with a threshold of 4–5 bits.”

The according reference is:

J.R. Kimmel, P.F. DeCarlo, D.R. Worsnop, and J.L. Jimenez. Quantitative Time-of-flight Mass Spectrometry of Aerosols Using a Digitally Thresholded Analog-to-Digital Converter. Annual Conference of the American Society for Mass Spectrometry, Seattle, 2006. Available online at [http://cires.colorado.edu/jimenez-group/ToFAMSResources/ToFManual/Docs/Kimmel\\_ASMS\\_2006.pdf](http://cires.colorado.edu/jimenez-group/ToFAMSResources/ToFManual/Docs/Kimmel_ASMS_2006.pdf) (last access: 19.08.2013, 15:00).

**Page 5660: Many studies of particulate engine emissions (including the cited Canagaratna et al.) focus on diesel rather than gasoline emissions, as they are arguably the more atmospherically significant. While I accept that the choice of particle generator used here will depend on availability, the authors should discuss the anticipated differences between gasoline and diesel emissions and whether this would be expected to affect the analysis presented here.**

While there are differences to anticipate in the overall emissions of diesel and gasoline engines (e.g., the large content of soot in diesel emissions), the fraction of these emissions which can be measured by the AMS is limited in principle to unburned fuel (diesel or gasoline) and lubricating oil (see Canagaratna et al., 2004; Schneider et al., 2006). Both diesel and gasoline consist largely of alkanes and cycloalkanes, but with different lengths of the carbon chains. The anticipated differences between the mass spectra of these chemically very similar substances obtained with the AMS are expected to be very minor compared to the overall uncertainties associated with the fragmentation patterns observed for different single particles.

This assumption was validated by comparing the measured ensemble mass spectrum obtained from the gasoline engine exhaust measurement to literature mass spectra of diesel engine exhaust (Canagaratna et al., 2004; Schneider et al., 2006): Pearson's  $R^2$  values were found to be 0.96 and 0.92, respectively. No obvious differences were observed between the different mass spectra.

This discussion was now also incorporated into the manuscript (page 5660, line 23):

“Although only mass spectra of gasoline engine exhaust, but not of diesel exhaust particles were acquired, the obtained single particle mass spectra can be considered to be representative of both types of engine exhaust particles: The average ensemble mass spectrum of the organic fraction measured during this source measurement was compared to ensemble mass spectra obtained from diesel exhaust measurements (Canagaratna et al., 2004; Schneider et al., 2006), and found to agree very well (values of the squared Pearson's correlation coefficient  $R^2$  were 0.96 and 0.92, respectively).”

Canagaratna, M. R., et al. (2004). "Chase Studies of Particulate Emissions from in-use New York City Vehicles." *Aerosol Science and Technology* 38(6): 555-573.

Schneider, J., et al. (2006). "Mass spectrometric analysis and aerodynamic properties of various types of combustion-related aerosol particles." *International Journal of Mass Spectrometry* 258(1-3): 37-49.

**Page 5661, line 7: Is the increased bounce of larger particles due to the higher fraction of dust and sea salt?**

Not necessarily. As stated in the cited reference (Hinds, 1999), generally particles show an increase of bouncing upon impaction with growing size, as rebound energy outcomes adhesive forces with growing size (Hinds, 1999; pp. 146-147). But of course also other particle properties, as phase or composition (like for dust or sea salt) can lead to an increase of bounce.

Hinds, W. C. (1999). *Aerosol technology: properties, behavior, and measurement of airborne particles*. 2<sup>nd</sup> edition. New York, John Wiley & Sons, Inc.

**Page 5662, line 24: The use of glucose as a proxy for biomass and biomass burning OA needs further validation. To wit, glucose has different H:C and O:C ratios compared to species such as levoglucosan. A comparison of a glucose mass spectrum with those of biomass and biomass burning obtained from the AMS library would address this.**

Although the sum formulas and O:C ratios of glucose (C<sub>6</sub>H<sub>12</sub>O<sub>6</sub>) and levoglucosan (C<sub>6</sub>H<sub>10</sub>O<sub>5</sub>) are slightly different, the molecular structure of both substances is very similar. Moreover, mass spectra of glucose and levoglucosan (both from Schneider et al., 2011) were compared to each other and to the mass spectrum of glycogen (Schneider et al., 2011; a polymer made up of glucose-monomers, similar to cellulose) and to the average mass spectrum of biomass burning organic aerosol derived via Positive Matrix Factorization from various ambient measurements (Ng et al., 2010). (All these mass spectra are from AMS ensemble measurements and available via the AMS mass spectral database, <http://cires.colorado.edu/jimenez-group/AMSsd/>) In all cases, agreement was reasonable: Pearson's R<sup>2</sup> (uncentered r) for the correlation of glucose and levoglucosan was 0.86 (0.93); comparison of glucose and levoglucosan to glycogen yielded values of Pearson's R<sup>2</sup> (uncentered r) of 0.70 (0.85) and 0.72 (0.84), respectively; comparison to BBOA average mass spectrum yielded Pearson's R<sup>2</sup> (uncentered r) of 0.50 (0.72) and 0.62 (0.79), respectively.

This discussion has, as requested by the reviewer, now also been incorporated in the manuscript (page 5663, line 2):

“This was validated by a comparison of the ensemble mass spectrum of glucose with those of levoglucosan (R<sup>2</sup> of 0.86), glycogen (R<sup>2</sup> of 0.70) (all from Schneider et al., 2011) and the average mass spectrum of biomass burning organic aerosol obtained via positive matrix factorization from different datasets (R<sup>2</sup> of 0.50) (Ng et al., 2010).”

Schneider, J., et al. (2011). "Mass-spectrometric identification of primary biological particle markers and application to pristine submicron aerosol measurements in Amazonia." *Atmos. Chem. Phys.* 11(22): 11415-11429.

Ng, N. L., et al. (2010). "Organic aerosol components observed in Northern Hemispheric datasets from Aerosol Mass Spectrometry." *Atmos. Chem. Phys.* 10(10): 4625-4641.

**Page 5665, line 23: The discussion of uncertainty here does not make a distinction between accuracy and precision (i.e. systematic vs. random errors), which I think is warranted. While all effects should be considered for the reporting of a single datum, when obtaining certain comparative statistics, only precision needs to be considered, which as far as I can tell, consists only of the ‘MS-retrieval’ component. The authors should make the distinction between the two types of error clearer.**

In order to make this distinction clearer we added:

“This uncertainty [ $\Delta_{MS-retrieval}$ ] is dominated by counting statistics, i.e. random, while both  $\Delta_{scaling}$  and  $\Delta_{RIE}$  are systematic errors.”

Some more discussion on which errors to use under which conditions could be added, but we think that this depends very much on the specific situation, and therefore should be decided individually, with the information provided in mind.

**Page 5667, line 1: The caveat should be added that oleic acid only appears hydrocarbon-like under unit mass resolution (UMR) analysis. Subjected to higher resolution analysis, there is a clear distinction in that it contains oxygen-containing peaks such as C<sub>2</sub>H<sub>3</sub>O<sup>+</sup>.**

We changed the sentence accordingly to include the information on UMR:

“This is due to the fact that both oleic acid and engine exhaust unit mass resolution spectra exhibit typical patterns of hydrocarbon-like organic aerosol ( $R^2$  for correlation of reference mass spectra is 0.76), so a distinction between these two species is difficult.”

**Page 5669, line 6: It is not very informative to state that the Gaussian fits are not perfect without showing an example, but moreover, there is nothing to say that the data should conform to a Gaussian distribution anyway (the distribution for a single component is more likely to follow a Poisson distribution), so it begs the question why it was even used in the first place. If Gaussian fitting is found to be problematic (as seems to be the case), then the authors should really consider using a different fitting function or report a more robust statistic, such as the median.**

We do not state that the Gaussian fits are not perfect, but rather that the distribution of ratios itself is not symmetrical. This is simply due to the nature of these ratios: They can take on indefinitely large positive values, but the smallest value is always 0 (it is not possible for one of the species to have negative ion numbers). Using the median would yield similar results, since the maximum obtained from the Gaussian fit always approximately equals the maximum of the distribution. We use the Gaussian fit here instead of the median to also have a direct measure of the width of the scattered distribution of the ratios (this width is represented by the standard deviation of the Gaussian fit, see next comment). Furthermore, we think a Gaussian fit is appropriate, since the distribution represents in principle the product of the distribution of e.g. the ratio of nitrate to sulfate within a large number of single particles, and the distribution of ionization efficiencies for the individual particles. Both these distributions do not represent “rare” events (as typical for Poisson distributions), but should follow a normal distribution, meaning their product also should be normally distributed.

**Page 5569, line 28: How is the standard deviation obtained from the Gaussian fits? Is this the fitting uncertainty or the width of the distribution?**

The standard deviation is obtained from the width of the distribution. The fitting uncertainty, on the other hand, is included within the uncertainty range of the averages given in Table 2 (see also Table 2, footnote c). In order to make this clear, we changed the text to:

“While the standard deviation obtained from the width of the Gaussian fit is smallest,…”

**Page 5674, line 24 (also later on page 5679): The statement about unambiguity isn't strictly correct because the algorithm itself contains a lot of operator-lead decisions in its design, so while the results are more decisive, it still not truly objective. If the authors want to claim it to be completely unambiguous, they would need to demonstrate its effectiveness against an independent data source.**

We agree with the reviewer's point and have reworded slightly at various locations:

Page 5657, line 6: “The algorithm yields well-defined results, which are comparable between different datasets,…”

Page 5674, line 24: “From single particle analysis with the algorithm presented here, much more definite results are obtained.”

Page 5678, line 26: “It was also possible to differentiate between hydrocarbon-like organic aerosol of different sources (cooking- and traffic-related emissions).”

**Page 5676, line 16 (also later on page 5679): I'm not sure I follow the argument about the boundary layer affecting nitrate concentration or mixing state. While a suppressed boundary layer can increase the number concentration of continuously-emitted primary particulates through reduced dilution, this will not apply to pre-existing particles or secondary species like nitrate. If there is an increase in nitrate-containing particles at night, this will be because there are a larger number of particles for the nitrate to condense onto, but this will occur independently of the mass concentration of particulate nitrate. The phenomenon of particles growing into the detection regime of the instrument sounds plausible, however.**

The reviewer is absolutely right in that the number concentration of pre-existing particles of the type “OOA and inorganics” likely will not be affected by the reduced boundary layer height. However, all substances (particles and gases) which are emitted in the boundary layer undergo reduced dilution at a lower boundary layer height, so also HNO<sub>3</sub> precursor gases (NO<sub>2</sub>, N<sub>2</sub>O<sub>5</sub>) leading to nitrate condensation can concentrate, leading to an increased condensation onto pre-existing particles. We do agree, however, that particles of the type of “OOA + inorganics” are not likely to increase in number due to the boundary layer height, and therefore reformulated the according sentences to make this clearer (changes highlighted):

“From ensemble mode measurements, also a night-time increase of nitrate mass concentration was found. The increase of nitrate mass per particle detected by the single particle measurements gives direct evidence of nitrate partitioning to the particle phase, caused by the lower temperature during the night and less dilution of the emitted nitrate precursor gases due to reduced boundary layer height. Additionally, the number concentration of “OOA and inorganics” particles measured in single particle mode increases during night-time (Fig. 6a). This might have two reasons: First, it could be an indication for the additional influence of the lowering of the boundary layer height, if the number of particles for nitrate to condense onto would increase and only the nitrate content would be measured in single particle mode.

Second, as nitrate condenses onto pre-existing particles, small particles which up to then were below the detection limit of the light scattering probe can grow to sizes where they are detected, increasing the number of detected particles.”

“From the single particle measurements, it was also found that number concentration of particles classified as “OOA and inorganics” increases during night-time, which likely has two causes: the increase of gaseous precursors due to the decrease of boundary layer height, leading to a larger number of particles in which (only) nitrate is detected, and/or hitherto smaller particles growing into the detectable size range of the LSP-AMS.”

**Page 5678, line 3: Remove comma after ‘both’.**

Changed, thank you.

**Figures 4 and 5: Why are these in black and white? They would be much clearer in colour.**

We have changed Figure 4. However, using the same color coding throughout the paper, Figure 5 remains in black and white, because only species are shown that have been printed in black or grey throughout the paper.

**Figure 6: Unless they would cause any major problems, I would have like to have seen the error bars included for sulphate and organics.**

We have now included the error bars also for sulphate and organics in Figure 6. To make this possible without too much confusing the reader’s eye, we have used a lighter color for the error bars than for the data points.

### **Referee #2:**

The publication presents new classification algorithm for single particle analysis with aerosol mass spectrometer with light scattering probe (LSP). Using LS and ensemble mass analysis parallel, the LS gives extra information on particle phase that is not reached straight for instance with MS or pToF modes, because of limitations of single particle detection and hence in the fragmentation table used in the IGOR analysis tool. LS modes straight information from the case of nitrate partitioning into particle phase during the night time mentioned in the publication gives new important information on aerosol particle chemistry and aging process. Single particle analysis at laboratory experiments with different mixtures and ambient measurements were deal diversely. The used methods, calculations, results and other relevant information were represented technically well, understandably and in fluent language. For the future the used instrument hopefully will be integrated to HR-TOF mass spectrometer to achieve more sensitive and higher resolution data to produce elemental information of mass peaks from single particles.

**Divide of organics into OOA and HOA according to percentage of organic content was interesting. It would be interesting to see the PMF method derived factors from ensemble data from the same device compared to different groups found from single**

## **particle classification (mass spectrum, single peaks, time series or diurnal cycles) from ambient data.**

Generally, a comparison of time series of ensemble mass concentrations and single particle number concentrations is not straightforward, due to e.g. varying particle size distributions or different measurement size ranges. Therefore, all comparisons of time series have to be taken with care. Comparisons of mass spectra, however, seem reasonable independent of such caveats.

A comparison of HOA diurnal cycles is already shown exemplarily in Figure 5. We have added to Figure 5 now a panel with the comparison of HOA mass spectra from single particle and ensemble mode measurements, and added some further information on HOA as well as OOA comparisons of time series and mass spectra in the text:

“The derived mass spectrum of ensemble HOA compares well with the average mass spectrum of all “cooking” and “traffic” particles (Pearson’s  $R^2$  of 0.80) (Fig. 5b). Comparison of the mass spectra furthermore reveals that in the average single particle mass spectrum, more signal at higher  $m/z$  is found. This most likely is due to the fact that in single particle analysis, especially the larger HOA-type particles are measured. For the smaller particles, since the overall signal intensity is lower, AP240 thresholding (see Section 2.1) is more likely to affect the signal intensity at larger  $m/z$ , as their signal intensity more often will be below the given threshold and truncated. For larger particles, signal intensity at higher  $m/z$  is often still large enough to not be influenced by the thresholding. This influence of on-board thresholding should be investigated in more detail in future work. Also the time series of ensemble and single particle HOA agree reasonably well ( $R^2$  of 0.65), despite differences in measurement techniques (e.g. mass vs. number concentration, different measurement size ranges).”

“The average mass spectrum of the organic content of all single particle mass spectra classified as “OOA and inorganics” shows no obvious differences to the OOA mass spectrum derived via positive matrix factorization from ensemble measurements (Pearson’s  $R^2$  of 0.98). Despite differences in measurement techniques (see above), also the time series agree reasonably well ( $R^2$  of 0.68).”

## **Volume measured by AMS and compared to a mobility particle analyzers (DMPS or SMPS) one could be interesting to be shown or mentioned for understanding the overall wellness of the used TOF-AMS ensemble mass data in ambient measurements.**

We did not include this kind of information here because a thorough intercomparison to various co-located instruments was already presented in (Freutel et al., 2013). We therefore added only a summary of the most relevant information, and refer the reader for more detailed information to the cited paper:

“As presented in (Freutel et al., 2013), both total mass concentration time series, and average ensemble volume size distributions measured by the AMS agree within about 10 -20 % with respective measurements of co-located instruments.”

Freutel, F., et al. (2013). "Aerosol particle measurements at three stationary sites in the megacity of Paris during summer 2009: meteorology and air mass origin dominate aerosol particle composition and size distribution." *Atmos. Chem. Phys.* 13(2): 933-959.

**Figure 1 is confusing and needs background information from the text, before the reader is able to follow it. Simplification of the figure in this kind of paragraphs might be useful for the reader point-of-view in the future publications.**

The reviewer is right, Figure 1 is hard to understand without the information from the text. However, we have a dilemma here: We wanted to show somewhere in the paper just how exactly the algorithm does work. So Figure 1 is not really a simplified way of showing how the algorithm does work, but rather a detailed flow chart to enable the reader to reproduce the algorithm on his or her own. A more simplified scheme to illustrate just how the algorithm basically works was therefore already additionally shown in Figure 2 of the manuscript. Instead of simplifying Figure 1, which would remove important information on the working principle of the algorithm, we therefore decided to rather make to the reader more clear the scope of the different figures. Furthermore, we decided to switch the order of Figures 1 and 2, in order to refer the reader first to the simplified way of how the algorithm works. The flowchart of (former) Figure 1 really is best to understand in conjunction with the according text, and we added an according notice to the figure legend:

Figure 2 (formerly Figure 1) legend now reads: “Figure 2. Schematics of the developed classification algorithm. SO<sub>4</sub>: sulphate; NO<sub>3</sub>: nitrate; Org: organics; MS: mass spectrum; &&: logical AND. For further information on the different steps, refer to Section 3.1.1.”

The text in Section 3.1.1 was changed to:

“To demonstrate the working principle of the developed classification algorithm, an exemplary application of the algorithm on one single particle mass spectrum containing OOA, nitrate and sulphate is shown in Figure 1. A detailed flow chart depicting the individual steps performed by the algorithm is presented in Figure 2.”

**Furthermore, a detailed examination of all steps in the analysis procedure led to some additional corrections:**

- Diurnal cycles were corrected to refer to local time (CEST).
- An improved version of the algorithm yielded 8 particles of OOA+K+inorganics instead of 11. The remaining 3 particles are classified as OOA and inorganics. The corresponding diurnal cycles of OOA+inorganics and references in the text were corrected accordingly.
- We found a small error in the procedure for the calculation of the saving efficiency, which is now fixed. All corresponding figures were corrected accordingly.

All those changes are only very slight and do not affect any of the statements made in the manuscript.