

## Author response to referee # 2 / editor:

We thank the reviewers and editor for their critical reading and important input. In the following we address the questions point by point (reviewer comments in italic, our replies in normal font, changes in the manuscript marked in blue).

*In general this paper is a very interesting and detailed extension of the utility of the AMS factor analysis methods.*

*The main issue that I have with it is the treatment of sampling artifact which will result from varying collection efficiencies due to volatility and solubility. I think that more information should be shown to demonstrate that the techniques is OK to go off on its own. The comparison of log-log data shows very large point to point differences in the calculated/measured masses of OA between both techniques. The non-appearance of the OOA2 factor in the offline solution (it looks like very oxidized OA offline) might suggest that a volatility artifact sneaks through to the final results.*

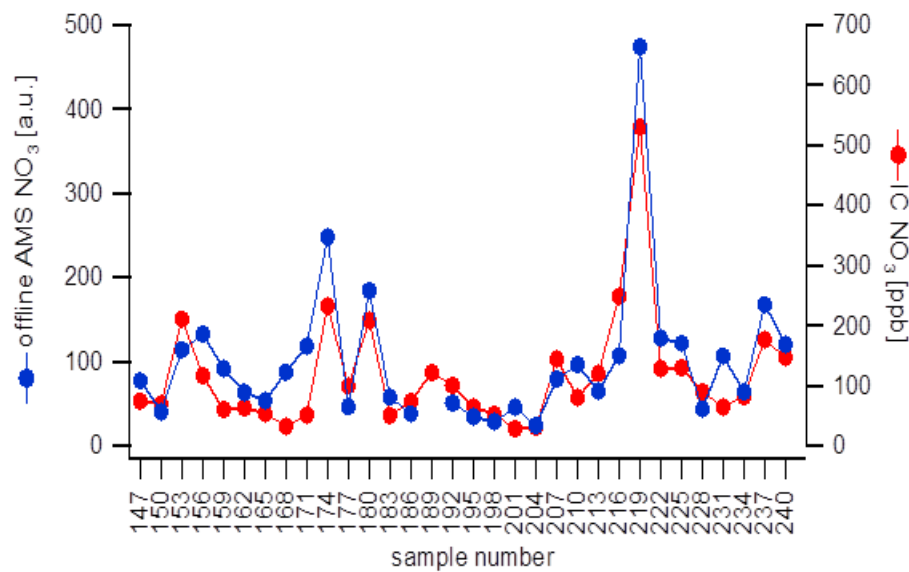
*One of the main purposes of this manuscript is the statistical analysis of biases between the newly developed offline AMS and different reference techniques. To that purpose the time series of different PMF factors from offline AMS and online ACSM are compared in order to obtain recoveries of the specific factors. These recoveries involve biases and uncertainties from among others filter sampling, water-solubility of different compounds, and PMF (also using different chemical and time resolutions). Thus we indeed attempt to assess also a possible volatility bias.*

*Comments in addition to reviewer one. More confidence in potential artifacts caused by variations in the filter sample collection and nebulization could be provided by studying the sampling method using OA components of known solubilities and testing the procedure to see if the predicted behavior is observed.*

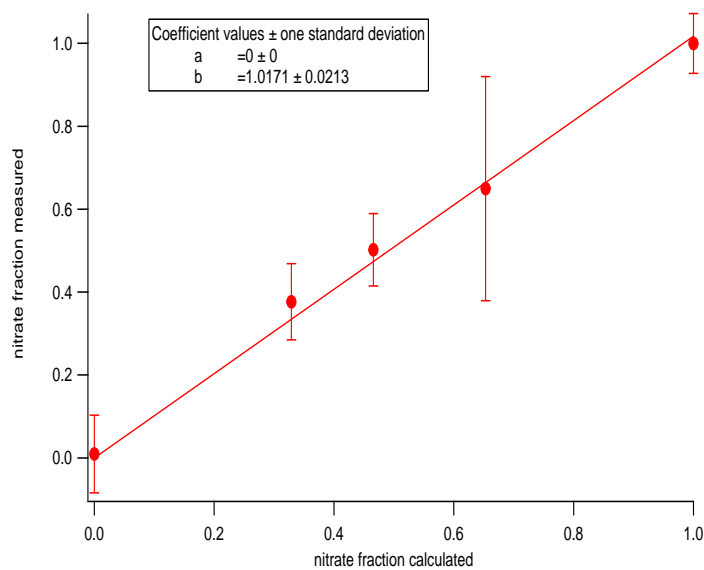
We acknowledge the artifacts related to offline sample collection and storage (Viana et al., 2006; Jacobson et al., 2000) and issues related to compounds water solubility and volatilization during extraction and nebulization. We believe that the most direct approach to assess biases between offline and online measurements due to the aforementioned issues is to compare PMF results performed on real world offline samples and concomitant online measurements. In particular, the methodology we have adopted offers the assessment of the collection and recoveries of a complex mixture of genuine particulate phase compounds present in a complex matrix. The partitioning (collection and nebulization), and solubility (extraction) of these compounds is dependent on the particle morphology (e.g. adsorption of hydrocarbons and PAHs on soot) and particle composition and levels (amount of absorptive mass). Therefore, analyzing isolated single compounds with known solubility may not represent the actual behavior of the atmospheric components.

Nevertheless, we show in Figure 1 that compounds as volatile as  $\text{NH}_4\text{NO}_3$  are measured reliably by the offline AMS setup. On the one hand, we show that the signal seen in the AMS

matches very well the reference concentrations from IC, for concentrations as low as 50 ppb. On the other hand, tests conducted at Aerodyne (Xu et al., in prep.) show that the offline methodology is also capable to faithfully reproduce the composition in the liquid phase/extracts (here in particular for nitrate in presence of sulfate, Figure 2). Moreover, the methodology adopted here comparing online and offline source apportionments account for biases and errors due to offline positive and negative sampling artifacts, instrumental differences (see the ACSM discussion below) and differences related to PMF analysis of data with different time and instrumental resolution. While we cannot isolate the impact of each of these uncertainties, we determine factor dependent recovery parameters, displayed as probability density functions, which allows an uncertainty assessment. As we mentioned in the conclusion, this inter-comparison exercise should be performed on other datasets as well to better constrain these parameters.

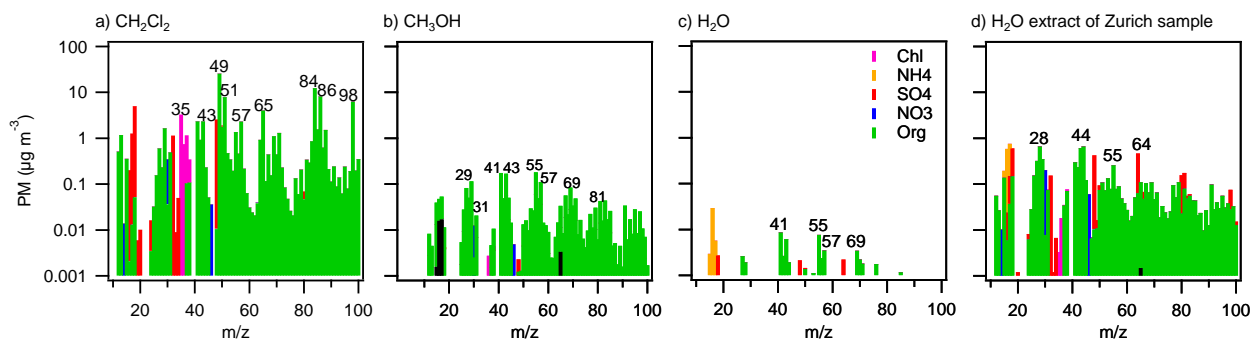


**Figure 1:** Comparison of nitrate signal in offline AMS and ion chromatography.



**Figure 2:** Comparison of the nitrate fraction measured by AMS compared to the calculated nitrate fraction in a  $\text{NH}_4\text{NO}_3/(\text{NH}_4)_2\text{SO}_4$  mixture (Xu et al., in prep.)

*Have the authors tested the OA remaining on the filters by extraction using another solvent? Some sort of mass balance recovery could be made.*



**Figure 3:** AMS spectra generated by atomizing the solvents tested here (a- $\text{CH}_2\text{Cl}_2$ , b- $\text{CH}_3\text{OH}$  and c- $\text{H}_2\text{O}$ ). For comparison, an  $\text{H}_2\text{O}$  extract of Zurich-april2011 sample is also shown.

Three different solvents were tested covering a wide range of polarity. These include high purity dichloromethane (98%,  $\text{CH}_2\text{Cl}_2$ ), methanol (98%,  $\text{CH}_3\text{OH}$ ) and ultrapure water ( $\text{H}_2\text{O}$ ,  $\text{TOC} < 5$  ppb). Figure 3 presents, in logarithmic scale, AMS spectra generated by atomizing these solvents. The atomization of pure dichloromethane results in high OA concentrations ( $\sim 100 \mu\text{g m}^{-3}$ ) with m/z ratios assigned to the solvent (e.g. m/z 35|37:  $\text{Cl}^+$ , m/z 49|51:  $\text{CH}_2\text{Cl}^+$  and m/z 84|86:  $\text{CH}_2\text{Cl}_2^+$ ) and to hydrophobic contaminations (e.g. m/z 27, 29, 41, 43, 55, 57). Likewise, in the case of methanol, the resulting mass spectra are dominated by similar organic contaminations ( $\sim 2 \mu\text{g m}^{-3}$ ). The origin of these contaminations remains currently unidentified; their levels can nevertheless exceed the OA mass ( $1\text{-}40 \mu\text{g m}^{-3}$ ) produced by atomizing water extracts of ambient samples. Without eliminating these contaminations and the remaining solvent, it is difficult to use these solvents. In contrast, very low signal is recorded in the case of pure water atomization, with average OA concentrations of  $0.15 \pm 0.6 \mu\text{g m}^{-3}$ , making it possible to use this solvent as an aerosol extraction agent.

Additionally, using water as solvent has the advantage that the extracted carbon mass can be calculated by scaling to routinely measured quantities (i.e. WSOC), while such measurements are not frequently performed or well characterized for organic solvents. In the absence of such reference measurements, estimations of ambient OA mass using the offline AMS method become much more uncertain.

*Is the non-appearance of the OOA2 factor from the offline in comparison with the online solution an indication that collection efficiency artefacts are appearing in the data?*

Also referring to:

*The non-appearance of the OOA2 factor in the offline solution (it looks like very oxidized OA offline) might suggest that a volatility artifact sneaks through to the final results.*

The Figure captions of the Figures 10 – 12 were not precise. We changed the captions so that it is clear that OOA is the sum of OOA1 and OOA2.

The source apportionment results on the offline AMS and online ACSM data show 2 separated OOAs (OOA1 and OOA2). In both datasets OOA1 has a higher f44 than OOA2. As mentioned in the manuscript, the separation of the OOA1 and OOA2 is based on different features of the datasets. The separation for the online data is based on the diurnals (traditional OOA1/OOA2 separation) and for the offline data based on the seasonality. The less oxygenated OOA2 found offline is dominant in summer and the more oxygenated OOA1 in winter. For this reason, only the sum of OOA1 and OOA2 is considered in the determination of  $R_k$ . Further assessments of the differences in the OOA separation on offline AMS data is above the scope of this article and will be addressed in future publications.

The spectrum of the less oxygenated OOA factor (OOA2) is less oxygenated for the online than for the offline dataset. Fröhlich et al. (2015) performed an ACSM inter-comparison and assessed the degree of oxygenation of the organic aerosol using the fraction at m/z 44, f44 (mainly  $\text{CO}_2^+$ ). Among the 13 Q-ACSMs (same type of instrument as used for the reference online ACSM measurements in Zurich) the lowest value for f44 was 0.085 and the highest 0.185. Fröhlich et al., 2015 also show that the source apportionment results in terms of attributed concentrations are not affected, only the factor profiles. Thus comparing f44 of measurements or of PMF factor profiles from different instruments is rather difficult. Therefore, we think that one cannot conclude that semi-volatile organics are lost based on a different f44 in OOA factors, as besides of the reason mentioned above some of this discrepancy comes from instrumental differences.

*The statement on line 14 page 8612 that the “technique can capture a large part of the organic fraction” is all very well, but can it capture OA without temperature and humidity dependent biases which will affect the final data and be interpreted as real changes in volatile to oxidised fractions measured by the offline technique. I do not think the paper covers this issue well enough.*

We agree that the offline AMS PMF results alone have biases in the time series which are assessed with the factor-specific recoveries ( $R_k$ , Figure 10 in the manuscript). When correcting the offline PMF results with  $R_k$  (Figure 11 in the manuscript), the biases are corrected. As for the uncertainties (e.g. due to differences in the sampling temperature/RH, varying absorption/evaporation artifacts), they are reflected in the probability density functions in Figure 10 in the manuscript.

## Reference:

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