

Author's response:

We thank Referees #1 for the careful revision and comments which helped in improving the overall quality of the manuscript.

A point-by-point answer (in regular typeset) to the referees' remarks (in the *italic typeset*) follows, while changes to the manuscript are indicated in blue font.

In the following page and lines references refer to the manuscript version reviewed by anonymous referee #1

Anonymous Referee #1

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This manuscript presents an analysis of the composition and source apportionment of PM₁ filters collected at three sites in Lithuania. For this offline technique, the aqueous extracts from filters were nebulized with Ar for introduction into the HR-ToF-AMS. The use of Ar as the nebulization gas enabled an analysis of the CO⁺/CO₂⁺ fragment ratio and trends in that ratio with season. Positive matrix factorization was also applied on both the offline AMS data set as well as an offline marker data set collected using the same filters. This manuscript provides a good demonstration of the type of data sets that can be generated via this offline AMS technique and the CO⁺/CO₂⁺ analysis provides new insights into the interpretation of AMS data from ambient samples. Thus, I see this paper as appropriate for publication in ACP. However, I have a few concerns, mostly related to sampling artifacts that need to be addressed prior to publication.

- 1) **P2 L9:** *Traffic exhaust OA is listed as a PMF factor from AMS spectra, yet in the experimental it is noted that the contribution is too low to be resolved with PMF and is instead estimated using a CMB approach. I suggest rewording the abstract to clarify this.*

We reworded the abstract as follows: “AMS WSOA spectra were analyzed using positive matrix factorization (PMF), which yielded 4 factors. These factors included biomass burning OA (BBOA), local OA (LOA) contributing significantly only in Vilnius, and two oxygenated OA (OOA) factors, summer OOA (S-OOA) and background OOA (B-OOA) distinguished by their seasonal variability. The contribution of traffic exhaust OA (TEOA) was not resolved by PMF due to both low concentrations and low water solubility. Therefore, the TEOA concentration was estimated using a chemical mass balance approach, based on the concentrations of hopanes, specific markers of traffic emissions.”

Changes in text:

- 2) **P5 L24:** *The nebulizer used was operated at 60°C, how long are the aerosols in this heated region? Was this temperature in the nebulizer also used in the Daellenbach et al. analysis? What effect might this high temperature have on the composition of the organics measured with the AMS compared to online analysis? If this temperature was not used for the Daellenbach analysis, what effect might this have on the factor specific recoveries of this work compared to the results from that previous analysis?*

The nebulizing Ar flow was 0.4 L min⁻¹. Considering the internal diameter (6 mm) and the length of our lines, we can estimate an aerosol residence time in our lines (from nebulization to AMS detection) of ca. 2 s. The aerosol residence time in the 60°C zone is significantly shorter (~100ms). A set of 40 PM₁ filter samples collected in Lithuania (not included within the source apportionment presented in this work) was measured using both the Apex Q nebulizer (Elemental Scientific Inc., Omaha NE 68131 USA) operated at 60°C and using a custom-built nebulizer (Daellenbach et al., 2016). The comparable WSOA/SO₄²⁻ ratio registered using the two systems indicates a negligible loss of volatile organics (Fig. Discussion 1 (Fig. D1)).

We compared organic mass spectral time series and fragments fractional contributions retrieved from the two different nebulization systems. Mass spectra revealed a good correlation for all fragments ($R = 0.94$ on average), similarly the total organic signal showed a correlation of $R = 0.94$ (Fig. D1). Excluding CO₂⁺ and the related fragments (CO⁺, H₂O⁺,

HO⁺, and O⁺, Aiken et al., 2008; Canagaratna et al., 2007), the intensity of which can be affected by the vaporizer history (Fröhlich et al., 2015, Pieber et al., 2016), we observed a good agreement between the normalized AMS mass spectral fingerprints obtained with the two different nebulizers, with 95% of the *i, j* elements not statistically different within 2σ. As stated in the manuscript, here *i, j* represent a generic filter sample and a generic AMS fragment, respectively, while the uncertainty considered here includes blank variability, repeatability, uncertainty related to ion counting statistics and ion-to-ion signal variability at the detector. Overall the new nebulization system revealed a ~7 times higher sensitivity. Given the high correlation and the similarity in the mass spectral fingerprints, we can exclude substantial effects on the recoveries of the different factors.

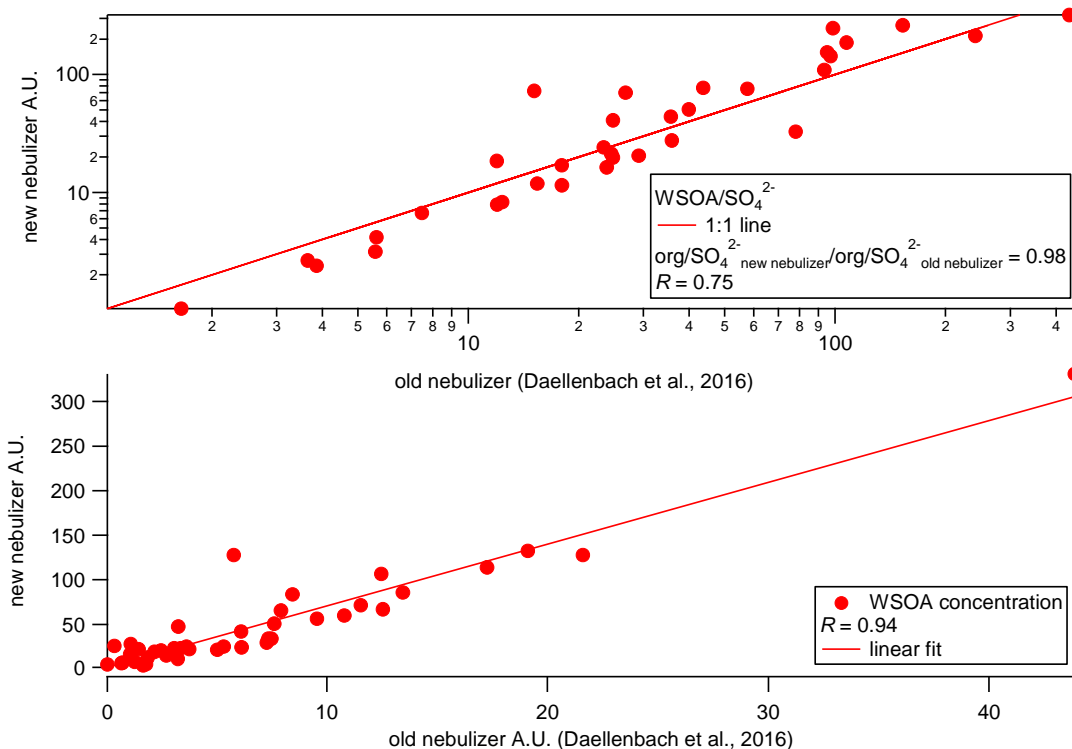


Figure D1. Top: WSOA/SO₄²⁻ ratio registered with a custom-made nebulizer (Daellenbach et al. 2016, here marked as “old nebulizer”) and our nebulization system (“new nebulizer”). Bottom: OA signal comparison.

- 3) **P18 L25:** *PM₁ composition discussed here and shown in Figure 1 shows ions that can be measured with both the AMS and IC (e.g. SO₄, NO₃, etc.). Do the contributions shown in Figure 1 correspond to the IC measurements or AMS? For ions that can be quantified with both techniques, how do the values compare between the AMS and IC?*

Author’s response:

As mentioned at P6, L30-31, the ion concentrations are from IC if not differently specified. For the sake of clarity we added this information in the Figure 1 caption. Following the recommendations of anonymous referees #1 and #2 we added in the revised SI a comparison between offline-AMS and IC:

Offline-AMS comparison with IC and WSOC determination by TOC analyzer

Overall, the comparison between offline-AMS and IC concentrations of NH_4^+ , SO_4^{2-} , and NO_3^- reveals a non-linear relation due to the lower IC detection limits. This is most likely related to the low transmission efficiency of the AMS lens for small particles, particularly predominant for diluted filter extracts.

Nevertheless, considering internally mixed nebulized particles, the composition of the particles is not supposed to change with the solution concentration, as also confirmed by dilution tests conducted on our filter extracts (Fig. D2).

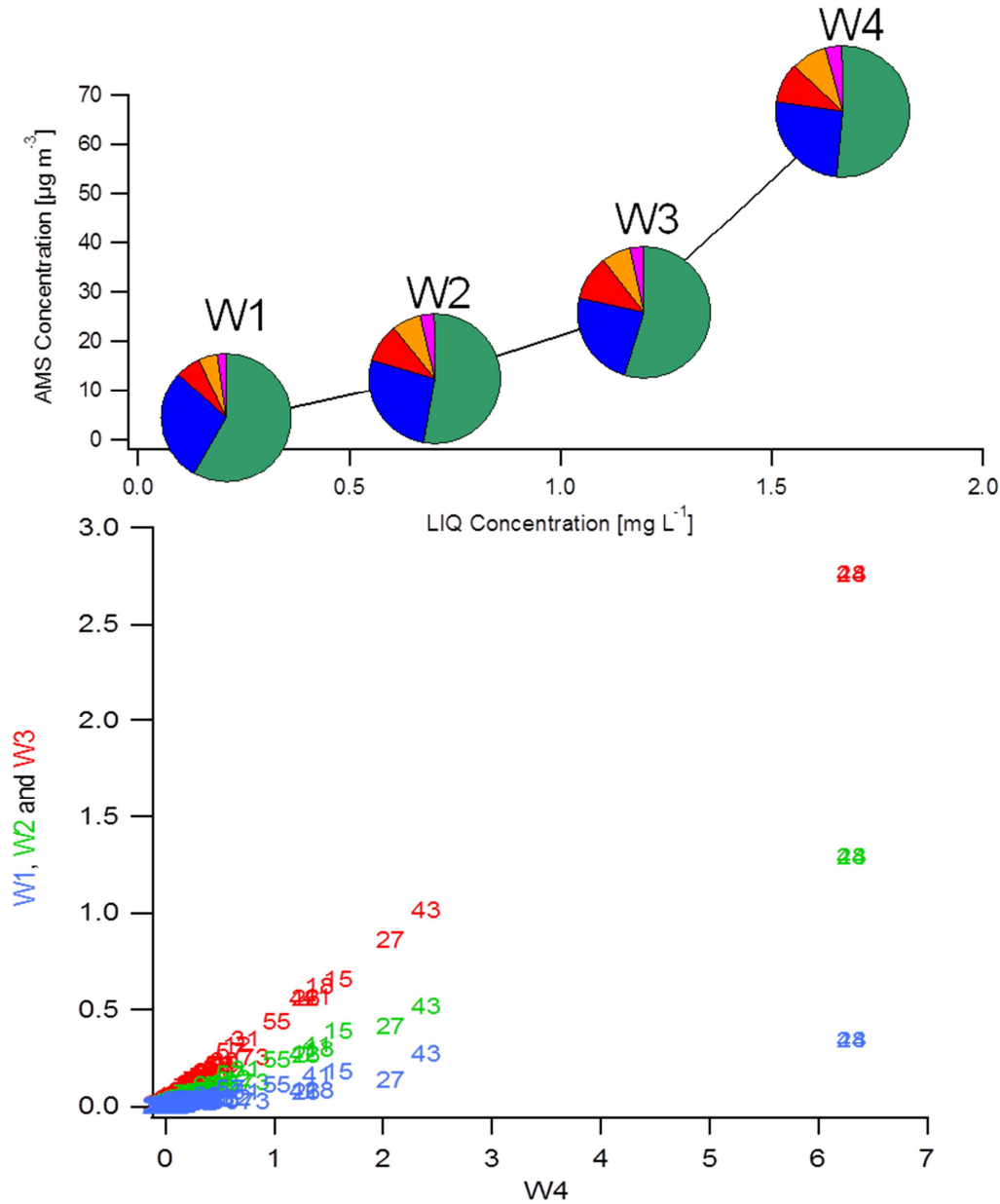


Figure D2. Dilution tests: NR PM composition and comparison of mass spectra registered at different dilutions.

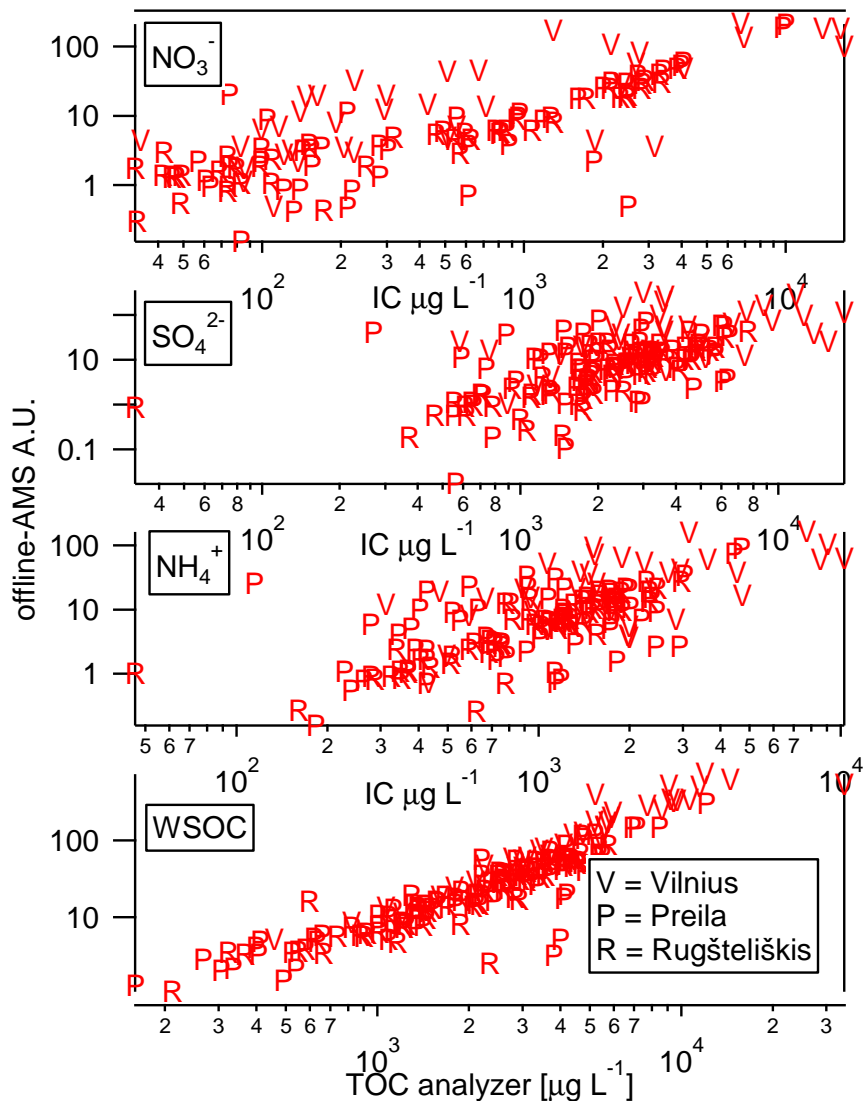


Figure D3. Offline-AMS comparison with different techniques with IC and WSOC measurements by TOC analyzer.

Figure D2 and D3 were added to the SI as Fig. S16 and S17:

The following paragraph was added to Fig. S16 caption:

This low particle transmission efficiency for diluted solutions results in a high scattering at low concentration. Additional scattering is observed in the relation between offline-AMS and IC SO_4^{2-} . This is related to the presence of refractory sulfate salts (e.g. Na_2SO_4 , ammonium sulfate) which are detectable by IC, but not with the AMS, consistent with lower slope obtained between offline-AMS and IC SO_4^{2-} , compared to the other species.

These species are likely formed during nebulization, e.g.



For these reasons we only reported inorganic ion concentrations from IC.

- 4) **P19 L14-20:** The nitrate concentration shows clear seasonality with larger contributions in the winter and the sulfate concentration looks relatively constant

throughout the year. However, in Figure 1, the ammonium concentration appears to also be relatively constant throughout the year. Is this correct? If so, can the authors comment on potential counter ions for NO_3^- ?

Author's response:

Considering the NH_4^+ , SO_4^{2-} and NO_3^- concentrations in $\mu\text{Eq m}^{-3}$, the agreement between (NH_4^+) and ($\text{SO}_4^{2-} + \text{NO}_3^-$) is high, with an average ($\text{SO}_4^{2-} + \text{NO}_3^-$)/ NH_4^+ ratio of 0.99 over the year and 1.02 during winter. The Pearson correlation coefficient R between ($\text{SO}_4^{2-} + \text{NO}_3^-$) and NH_4^+ was 0.92 considering the whole year and 0.84 considering only winter. Therefore, the role of other counter ions is negligible.

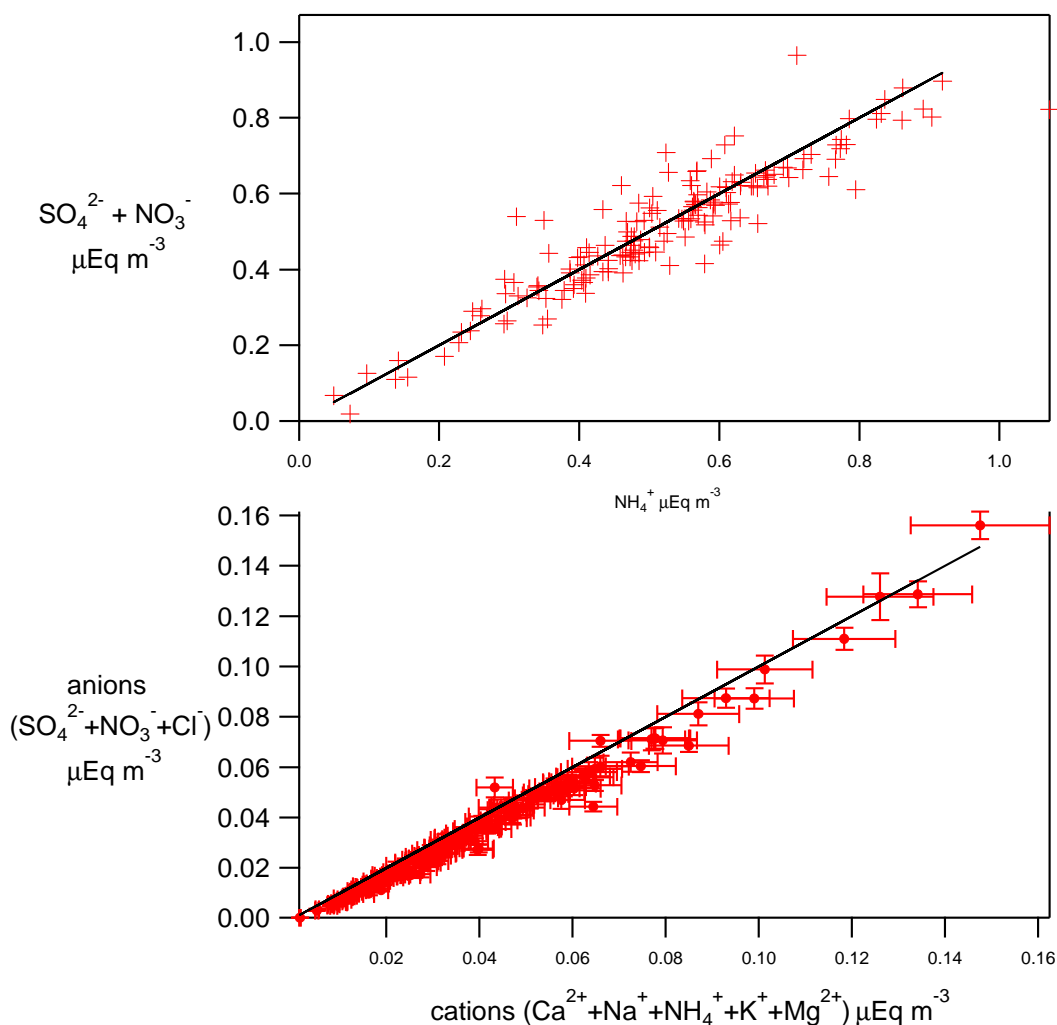


Figure D4. NH_4^+ correlation with $\text{SO}_4^{2-} + \text{NO}_3^-$. Data in $\mu\text{Eq m}^{-3}$ (top); ion balance (bottom).

Figure D4 was added to Fig. S11.

- 5) **P20 L 28-31:** The background-OOA factor appears to correlate with NH_4^+ much better at Preila and Vilnius than Rugsteliskes (Figure S11). Are there any potential reasons for the lower apparent correlation at Rugsteliskes? How much uncertainty is there in the NH_4^+ measurement? What is the significance of a correlation of B-OOA with NH_4^+ ?

Author's response:

The B-OOA factor correlation with NH_4^+ is significant at all stations: $R = 0.82$ ($R^2 = 0.67$) for Vilnius, 0.87 ($R^2 = 0.76$) for Preila, and 0.71 ($R^2 = 0.50$) for Rūgštelėškis. The correlation of B-OOA with a secondary inorganic component such as NH_4^+ could suggest the secondary origin of B-OOA, as also inferred by the comparison with the marker-source apportionment (section 4.4.2). The repeatability of NH_4^+ IC measurements was 10%, while according to our error estimate (Section 3.1.3), the average relative uncertainty on the B-OOA factor for Rūgštelėškis was 12%. We estimated that up to half of the total unexplained variability in the relationship between NH_4^+ and B-OOA in Rūgštelėškis can be due to the abovementioned errors, while in Preila and Vilnius the B-OOA vs NH_4^+ , most of the unexplained variability can be attributed to the errors. For Rūgštelėškis the remaining unexplained variability (27%) may be related to variability in the precursor composition and/or in the air masses photochemical age.

This information was added to Fig. S11 caption.

- 6) **Section 2.1 and P21 L1-17:** *Were the High-Volume samplers located in temperature controlled rooms? If not, what effect could higher summer temperatures have on the composition of the organic compared to the winter samples? Could the S-OOA factor be complicated by collection differences caused by the loss (on the filter) of more volatile organic molecules during summer months?*

Author's response:

High volume were equipped with temperature control systems maintaining the filter storage temperature always below 25°C, which is lower or comparable to the maximum daily temperature during summer (Fig. 3b). This should prevent large negative artifacts involving the most volatile fraction.

We added this information in P4, L16:

In order to prevent large negative filter artifacts, the high-volume samplers were equipped with temperature control systems maintaining the filter storage temperature always below 25°C, which is lower or comparable to the maximum daily temperature during summer.

- 7) **P2 L6:** *the $\text{CO}_2^+:\text{CO}^+$ ratios reported in section 4.5 are greater than 1. The less than sign should be switched.*

Corrected as suggested

- 8) **P10 L22-23:** *a verb such as "was used" is missing.*

Corrected as "was constrained"

- 9) **P22 L3:** *I suggest some mention directing the reader to Figure 5 be made in the text as the time series for the factors are discussed in this section but no mention of Figure 5 is made.*

We introduced a reference to Figure 5 at P22 L3

- 10) **P25 L13:** *"Using the ratio (1.88) calculated from offline-AMS". Suggest adding $\text{OM}/\text{OC}_{\text{BBOA}}$ ratio to communicate what ratio is being used in the calculation here.*

Corrected as suggested

- 11) **P30 L 25-26:** suggest rephrasing, the double negative “unlikely return uncertain CO+ values” is confusing.

Rephrased as: “should return accurate CO+”

- 12) **P45 Figure 2 and P46 Figure 4:** Suggest either writing out the factor names in the labels (background-OOA instead of B-OOA etc.) or giving the names and labels in the caption.

Factor names and labels added in Figure 2 and Figure 4 captions.