We thank Reviewer 2 for their comments, which helped improving the quality of our manuscript. A point by point response (in black) to the reviewers' comments (in blue) will follow. Changes in the text are indicated in in *black italics*.

Reviewer 2:

Mass spectrometrical methods are in widespread use to characterize the organic composition of particulate matter. Aerosol mass spectrometers, despite their drawbacks with respect to hard ionization, are often drawn upon for source apportionment studies in combination with PMF. Here, the authors applied a LDI technique for an extensive study of ambient aerosol samples. Measurements and data analysis have been conducted meticulously, also reflecting on uncertainties, and source apportionment results have been compared to AMS data. The work should be published in ACP after some minor revisions.

1) There is not much detail on the experimental setup of the mass spectrometrical experiment. Some hints are given, such as "ion extraction is not orthogonal to the ablation plume", then how is it performed?, or information about mass resolution. In the introduction, the adjustment of laser power is mentioned as one of the advantages of LDI-MS compared to ATOF-MS, but information on the laser power in this experiment is missing save the fact that it is adjustable. Therefore, the authors are encouraged to give more details on the laser/mass spectrometer system.

In response to this question, we added the further information on the laser power and ion extraction to the following paragraphs and adapted the sentence on the comparison between ATOFMS and LDI-MS:

"... Possibly, spiking the filter region with aqueous $AgNO_3$ caused enough of a change to the surface of the filter sample to influence the ionization physics. This could affect the m/z calibration, since ion extraction in our instrument is not orthogonal to the ablation plume but a delayed pulsed extraction. ..."

"…
We recorded the mass spectra of 819 filter samples in an m/z range 65-500 thomsons (Th; 1 Th =1 Da e^{-1}, where e is the elementary charge, ion gate at m/z 60 Th) using a laser-desorption/ionization-ToF MS (Shimadzu Axima Confidence, Shimadzu-Biotech Corp., Kyoto, Japan) equipped with an N_2 laser (wavelength 337 nm, frequency 50 Hz, laser pulse width 3 ns, 130-180 µJ/pulse) in the positive reflectron mode. All the accessible instrumental parameters were kept constant during the whole period of measurements taking place from November 2015 to mid-March 2016. Specifically, the laser intensity was adjustable by means of a rotating wheel of filters with varying transmissivity (0 being blocked and 180 being completely open). We set the wheel parameter to 105 of 180 which would result in an estimated laser energy of ~6-9 µJ/pulse or $2.8\text{-}4.2*10^8$ W/cm^2 with a 3ns pulse and 30µm laser beam diameter. While the laser energy was initially set and kept constant, the aging of the laser during the given time period was also expected to reduce its intensity. We monitored and assessed changes in laser power and other instrumental parameters, as well as possible sources of uncertainty/contamination from sample preparation and intra and inter-day reproducibility, by repeated measurements of a subset of our samples.
..."

"… Similar to the AMS, online single-particle LDI-MS instruments such as the ATOFMS also yield extensive fragmentation. However, such fragmentation can be avoided by measuring offline aerosol samples (filters) using other systems. Samburova et al. (2005a) showed by comparing

measurement with and without matrix addition, that fragmentation was negligible in their instrument (wavelength 337 nm, LDI-MS, Shimadzu/Kratos, Axima CFR). …"

2) The mass resolution is low in this experiment, so it is understandable that the authors did not assign their signals to actual compounds. But I wonder, is there not the possibility to assign at least some prominent peaks relating to past experience or literature data? In this respect, there are many odd mass numbers in the spectra, hinting at the formation of fragment ions. This should be discussed briefly.

As the reviewer points out it is impossible to distinguish the contribution of different ions at the same nominal mass. We agree with the reviewer that it is desirable to assign compounds to the most prominent masses and that the prominent presence of odd masses hints to a rather prominent fraction of signal attributable to fragments. However, it is currently impossible to distinguish odd mass molecular contributors from fragments.

In absence of vast literature databases with the same instrument, we prefer to refrain from interpreting the fingerprints further than by comparing to reference samples since we fear to over-interpret the data. Earlier work confirms the prevalence of the same peaks for 1 site present in our dataset but cannot attribute these peaks to specific compounds (Zurich, Kaserne, Samburova et al., 2005).

As reviewer 2 mentions, the prominent presence of odd masses might hint to a rather prominent fraction of signal attributable to fragments as reviewer 2 mentioned. However, it is currently impossible to distinguish odd mass molecular contributors from fragments. According to Samburova et al. (2005a), fragmentation in this type of instrument is negligible. The mass spectral signatures acquired in this study are similar to the ones in Samburova et al. (2005a) and the lower laser energy applied in this study is lower than in the former study. This suggests that also during our measurements fragmentation was not a prominent process. We mention the possible influence of fragmentation now also in the main text:

"…

The operational mass resolution, m/Δm, based on the measurements conducted on one sample tray per month and the accuracy of both calibration steps are shown in Fig. 1b and 1c, respectively. The operational resolution of the instrument was only determined for the silver mono- (resolution 1100), di- (1700), and trimer (2100) as we are confident of the absence of interfering ions for these peaks. In comparison to the LDI-MS, the HR-ToF AMS in V-mode (and W-mode) has a resolution of ca. 2'000 (4'000) at m/z 100 Th and an m/z calibration accuracy < 20 ppm (< 10 ppm, DeCarlo et al., 2006). With this accuracy and resolution, neither distinguishing different ions at the same nominal mass nor estimating properties such as O/C and H/C for a nominal mass following Stark et al. (2016) was possible for the quartz-filter-LDI-MS measurements. Instead, the spectra were integrated to UMR sticks. The presence of considerable signal at odd masses might indicate that significant fragmentation occurs during desorption and ionization of the organic matter in the LDI-MS (Fig. 1a, 3, 4). However, Samburova et al. (2005a) suggest that fragmentation in this instrument is negligible. The mass spectral signatures acquired in this study are similar to the ones in Samburova et al. (2005a) and the lower laser energy applied in this study is lower than in the formed study. This suggests that also during our measurements fragmentation was not a prominent process. Overall, the extent of fragmentation remains unclear.

…"

3) Figure 3 reveals, if there are a lot of signals resulting from a sample, a big unresolved hump is visible (as can be seen from the wood burning in comparison to the clean, well

structured spectrum from tunnel weekend). Can this be improved/targeted by reducing the laser power, or will this lead to a severe and unacceptable loss in sensitivity?

For such separations, we suggest to extract PM with different solvents in order to get a better idea on their properties in future work. Samburova et al. (2005) observed such humps also in water-soluble PM for 1 of the sites present also in this study (Zurich, Kaserne).

4) What is the gain in spiking with silver nitrate? In the end, you have to calibrate the spectra without showing peaks from silver ions with an independent calibration procedure, as is mentioned in the manuscript. Why then not apply the second procedure, for which obviously no spiking is necessary, in general and omit the silver nitrate solution?

Both reviewers mentioned a similar point. We have taken this feedback as an opportunity to better clarify our two-step calibration procedure, as detailed more fully in the following (the same response has been written to both reviewers):

The m/z calibration parameters in our LDI-MS measurements were highly variable between different samples. Therefore, to determine unit mass resolution integration regions it was necessary to perform an m/z calibration on every single sample.

In other mass spectrometers, some peaks are always observed, independent of the sample, and can therefore be used for an m/z calibration and/or to assess the performance of an initial m/z calibration: E.g. in the Aerodyne AMS the ions N_2^+, CO_2^+, W^+, etc. are present under most conditions. As another example, In chemical ionization mass spectrometry m/z calibration is typically performed using the known chemical reagent ions. For a reliable m/z calibration such known anchor ions are crucial. In many complex mixtures as for ambient aerosol, the signal observed at any nominal mass is composed of ions from numerous organic compounds and peaks are broad. Therefore, the exact mass of such a peak is unknown hindering an accurate m/z calibration.

In matrix assisted LDI-MS matrix molecules or matrix fragment ions have been used previously. However, the native matrix of our samples was highly variable, so that no ions provided suitable anchors for calibration. Therefore, we chose to spike our samples with $AgNO_3$. In the absence of such anchor ions an m/z calibration, even to integer accuracy, is not feasible.

Indeed, as mentioned in the reviewer's comment, we observed differences between the average spectrum containing $AgNO_3$ and the average spectrum without $AgNO_3$ which we related to changing ionization conditions. Hence, we did not report atmospheric data for $AgNO_3$-spiked samples. Rather, we used the $AgNO_3$-spiked spectra to obtain a first calibration (based on Ag^+ anchor ions), used the first calibrate to define prominent, filter-specific anchor ions, then calibrated the unspiked spectra using these anchor ions. This procedure is explained in Section 2.2.2 Data treatment of the revised manuscript (unchanged from original) and was essential to enabling an objective calibration to be performed. Because only prominent peaks were used in the second calibration step, the possibility of an influence of $AgNO_3$ on these samples is minimal.

Although we had mentioned these issues in the submitted manuscript, we have clarified them further following both reviewers' comments. We adapted the respective part of the manuscript to:

"…

The m/z calibration parameters were highly variable between different samples. Therefore, to determine unit mass resolution integration regions it was necessary to perform an m/z calibration on every single sample. However, unlike in the Aerodyne AMS (N_2^+, O_2^+, W^+), there are no dominant

anchor ions present in these spectra that could be used for an m/z calibration. In absence of such ions, we performed a two-step calibration procedure. Each sample was spiked with silver nitrate ($AgNO_3$*, Sigma Aldrich, >99.8%) as an internal standard (approach illustrated in Fig. 1). In order to avoid the suppression of the sample signal, the internal standard (aqueous solution 500 ppt to 20 ppm) was only placed (as a droplet) on a small part of the sample. The 499 spectra from all positions on the measurement grid were separated and defined as (1) silver-spiked (lower panel in Fig. 1a), (2) silver-free (upper panel in Fig. 1a), and (3) intermediate-silver. Intermediate-silver cases were defined using the signal intensity in the regions of the mass spectrum where silver was expected, in comparison to adjacent silver-free regions of the spectrum, and were discarded. To calculate the first calibration, we calibrated the average silver-spiked spectrum of each filter sample, using the peaks of the silver monomer (m/z 107, 109 Th), dimer (m/z 214, 216, 218 Th), and trimer (m/z 321, 323, 325, 327 Th). We found that this calibration of silver-spiked was not directly applicable to the average silver-free mass spectrum. Possibly, spiking the filter region with aqueous *$AgNO_3$* caused enough of a change to the surface of the filter sample to influence the ionization physics. This could affect the m/z calibration, since the delayed-pulse ion extraction in our instrument is not orthogonal to the ablation plume but nearly parallel. Therefore, a second calibration was obtained for the averaged silver-free spectra using prominent non-silver peaks present in both spectra. Such a two-step calibration is necessary to achieve accurate m/z calibrations of the silver-free spectra.*
…"

5) What is the difference between WSOM and WSOC?

WSOC refers to the water-soluble organic carbon concentration only considering the carbon mass, i.e. number carbon atoms multiplied with the mass weight of carbon per m^3. WSOM considers also all other atoms present in the organic molecules (e.g., oxygen, hydrogen, nitrogen, sulfur) by determining a ratio organic matter per organic carbon (OM/OC).

We completed the manuscript with this information:

"*… This involved the analysis of the water-soluble organic matter (WSOM) by a high resolution time-of-flight AMS.* …"

"*…* OC_{Sunset} *was determined using the Sunset OC/EC analyzer and* $(WSOM/WSOC)_{oAMS}$ *through WSOM measurements (described in Section 2.1, WSOC being water-soluble organic carbon).* …"

6) Page 2, line 2: Omit the impact with EI, call it just electron ionization.

We corrected the manuscript.

"… Instruments equipped with electron ionization (EI), such as the aerosol mass spectrometer (AMS, Canagaratna et al., 2007) and aerosol chemical speciation monitor (ACSM, both Aerodyne Research, Inc., Ng et al., 2011a; Fröhlich et al., 2013) provide quantitative online measurements of OA (Jimenez et al., 2016). …"

7) Please use "such as" instead of "like" in elaborating insertions.

We corrected the respective parts of the manuscript.

"… Although the importance of matrix effects is evident, studies with a single-particle LDI-MS (ATOFMS, laser wavelength 266 nm) have achieved good correlations of major aerosol components with well-established reference measurements such as elemental carbon (EC, Sunset Analyzer, Sunset Laboratory Inc.), OA (AMS), NH_4 *(AMS),* SO_4 *(AMS),* NO_3 *(AMS), and K (collected*

with a particle-into-liquid sampler, PILS), suggesting that underlying matrix effects did not dominate measurement reproducibility (Healy et al., 2013). …"

"…Similar to the AMS, online single-particle LDI-MS instruments such as the ATOFMS also yield extensive fragmentation.. However, such fragmentation can be avoided by measuring offline aerosol samples (filters) using other systems. …"

"… The correlation with eBC_{tr} *suggests that traffic2 is related to primary emissions from the combustion process. Based on the lack of correlation between traffic1 and* eBC_{tr}*, traffic1 might also be influenced by other processes, such as e.g. secondary production. Additionally, tailpipe exhaust cannot be distinguished from other traffic related emissions in the tunnel samples and might also contribute to traffic1. …"*

"… The north-south gradient in the BB/K^+ *ratios might be caused by imperfections of the separation of the burning conditions by PMF, but other effects such as the age of the stove population and the used technology could contribute as well. …"*

8) Page 8, line 28: Please do not use Thompson as unit of m/z differences. Maybe Dalton or stay with m/z.

We prefer to use Thomson as a unit for m/z for the case that some ions have more than one charge. We now include a statement on the unit of m/z that we use in this manuscript, including a description on how Thomson (Th) relate to Dalton (Th=Da e^{-1}). Additionally, we also added the unit of m/z throughout the manuscript wherever it was missing.

"… *We recorded the mass spectra of 819 filter samples in an m/z range 65-500 thomsons (Th; 1 Th =1 Da* e^{-1}*, where e is the elementary charge, ion gate at m/z 60 Th) using a laser-desorption/ionization-ToF MS (Shimadzu Axima Confidence, Shimadzu-Biotech Corp., Kyoto, Japan) equipped with an N2 laser (wavelength 337 nm, frequency 50 Hz, laser pulse width 3 ns, 130-180 μJ/pulse) in the positive reflectron mode.* …"

"… In general, the mass spectra from winter-time were characterized by higher contributions from higher-molecular-weight fragments compared to summer. For the winter sample from San Vittore, a large "hump" was present, on top of which signals appeared with high intensities and a highly regular pattern of m/z differences of 14 Th. …"

9) Page 13, line 6: In the first sentence of the conclusion, I would not call it a novel method, rather the utilization of a known method in use since approx. 2000 with some new developed novel aspects.

We changed the manuscript according to the reviewer's suggestion.

"… In this study, we advanced a known method for the chemical characterization of particulate matter collected on quartz-fiber filters by LDI-MS and applied the method to 819 samples. …"

References:

Samburova, V.,Szidat, Hueglin, C., Fisseha, R., Baltensperger, U., Zenobi, R., and Kalberer, M.: Seasonal variation of high-molecular-weight compounds in the water-soluble fraction of organic urban aerosols, J. Geo. Res., 110, D23, doi:10.1029/2005jd005910, 2005.

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