

Response to the comments of anonymous referee #1

We thank the referee for the valuable comments which have greatly helped us improve the manuscript. Please find below our responses (in black) after the referee comments (in blue). The changes in the revised manuscript are written in *italic*.

General comments

The measurement campaign was very short (January 25 – February 5), so the authors should add a short discussion on the significance and representativeness of their results.

We agree with the comment that the period of the measurement campaign is short. However, the Zurich-Kaserne site has been extensively characterized in previous studies using AMS and ACSM. The general similarity of the AMS results obtained in the current study to previous publications gives us high confidence that the results obtained here are typical of wintertime conditions at the site (with the exception of the special events clearly separated by the $EVENT_{EESI}$ and $EVENT_{AMS}$ factors).

We add a short note in section 2.1 (P4, L27-31), “*Although the measurement period is relatively short (12 days), the similarity of the AMS results obtained in the current study to previous AMS and ACSM measurements at the same site (Lanz et al., 2007, Canonaco et al., 2013, Richard et al., 2011, Daellenbach et al., 2016) give us high confidence that the sampled aerosol is representative of typical wintertime conditions. Exceptions to this are resolved by the source apportionment into unique event-driven factors, as discussed in the results section.*”

Also a short note should be added on why PMF was done separately for AMS and EESI-TOF data, and if the authors expect results to differ for a combined approach (if possible at all).

A combined AMS/EESI-TOF PMF analysis is potentially of high interest and may facilitate quantitative interpretation of EESI-TOF data. However, such combined analyses are highly complex, requiring careful balancing of the explained variability within the two component datasets (Slowik et al., 2010; Crippa et al., 2013). In addition, such combined analyses tend to decrease the ability of the component datasets to retrieve factors resolvable by only a single instrument (such as HOA_{AMS} , or factors driven by chemical signatures observable only by the EESI-TOF). As a result, we focus here on exploring the ability of the novel EESI-TOF measurements to improve factor separation and design the source apportionment analysis to maximize this potential.

As requested, we address this in the manuscript (section 2.3) (P8, L8-9) as follows:

“Execution of PMF analysis on separated AMS and EESI-TOF datasets minimizes the complexity of the analysis, while maximizing the factor resolution ability of the EESI-TOF.”

Conclusions are a bit meager, and some effort could be taken in better describing the (atmospheric) implications of the results.

The following text has been added to the conclusion (P21, L1-4), “*Comparisons of bulk measurements, as well as of individual factors or groups of factors between the EESI-TOF and AMS indicate good agreement, but with the differences in elemental ratios. This suggests that, despite significant uncertainties in the relative response*

factors of individual ions measured by the EESI-TOF, responses at the level of the PMF factors are relatively similar, with the main differences resulting from the high sensitivity to levoglucosan in the EESI. Furthermore, source apportionment of EESI-TOF provides more classification of SOA factors, separating EESI biomass burning factors as more/ less aged instead of primary / secondary, identifying organic nitrogen containing factors as primary-dominated nitrogen factor / organonitrate-containing secondary factor, which are not possible for AMS PMF.”

A few important references are given as “in prep.” (also see specific comments below) – if these references are not available soon the authors should consider removing them and adding more information to the present manuscript.

We agree with the comment. In this manuscript, we presented four “in prep” references, and we modified as bellow:

1. “Lopez-Hilfiker et al., in prep”, now the paper is public on AMTD, so it is cited as “Lopez-Hilfiker et al., 2019”.
2. “Stefenelli et al. in prep”, the paper is now online in ACPD, so it is cited as “Stefenelli et al., 2019”.
3. “Bertrand et al., in prep”, the paper has been submitted, so here we change it to “submitted”.
4. “Lu et al., in prep”, status is unchanged.

Specific comments

P. 5, l. 9: What is “most”? Since the paper about the instrument is not available yet, this statement has to be made more quantitative/explicit. Which gas phase species are removed, based on what properties? The denuder only “reduces the gas phase background” – so what is left?

The referenced paper is now available from Atmospheric Measurement Techniques (<http://doi.org/10.5194/amt-2019-4>), and the reference has been updated. As a result, we have not otherwise modified the current paper but summarize here for reference.

The denuder has not been fully characterized on a compound-by-compound basis, but removes most gas-phase organics with high efficiency (e.g. pinonic acid, 99.6%).

Otherwise, the main source of background (i.e. non-particle-derived) signal is the working solution. This includes a variety of ions related to the NaI dopant and its clusters with acetonitrile and/or water. However, impurities in the working solution also generate detectable background signal. Finally, particles can pass through the denuder but then deposit on a surface rather than be extracted in the spray. Semi-volatile material desorbing from such deposited particles constitutes an additional source of background.

P. 5, l. 12: This might be discussed in the instrument paper, however, as this is not available, a short discussion should be included here: Are artefacts due to extraction to be expected, depending on solvent?

As noted in the previous comment, the instrument paper is now available and this issue is discussed in detail there. Briefly, the principal artifacts deriving from the use of the water, acetonitrile solvent are the potential for clusters of analyte ions with acetonitrile. These are weakly-bound clusters, and their prevalence depends strongly on voltage settings (i.e. collision energy) in the ion transfer optics. Formation of these clusters was found to be negligible at the settings used in the current study. We have clarified this as follows (P5, L25-26):

“Depending on voltage settings in the ion transfer optics (i.e. collision energy), clusters with acetonitrile can potentially be detected, however these clusters were observed to be negligible during the current study.”

P. 5, l. 15: This implies heating afterwards. Please clarify.

This is discussed in detail in the instrument paper and clarified in the manuscript as follows (P5, L20-22):

“The droplets then enter the mass spectrometer through a capillary heated to 250 C, however, the very short residence time in this capillary means that the effective temperature experienced by the analyte is much lower and no thermal decomposition is observed.”

P. 5, l. 26 – 32: Have the authors tried to relate the mass flux to ambient concentrations? Please discuss this. Do the authors expect a simple calibration with levoglucosan to be able to cover “instrument flow rate, EESI extraction/ionization efficiency, declustering probability, and ion transmission”?

The reviewer raises two issues here: (1) assessment of the EESI-TOF mass flux in terms of reference measurements, and (2) utility of the levoglucosan calibration. These points are discussed separately below.

The comparison of EESI-TOF mass flux and ambient OA concentrations is the subject of section 3.5 and Fig. 13. Fig. 13a presents the correlation 0.94 between the EESI-TOF mass flux and ambient concentrations. Figures 13c and 13d respectively show the O:C and H:C atomic ratios for the EESI-TOF as a function of those for the AMS. The EESI-TOF and AMS O:C ratios are correlated ($R=0.62$), however, the O:C ratios estimated by the EESI-TOF are systematically higher than those measured by the AMS. For H:C ratios, we do not observe a correlation. The EESI-TOF values are scattered around approximately 1.56, independent of the AMS H:C ratios which vary between 1.11 and 1.44. The cause for this discrepancy is not yet understood but may be related to differences in ion relative sensitivity.

As this is already a major section of the manuscript, we assume that the reviewer’s question was triggered by the sequence of discussion in the original manuscript rather than a general inadequacy in section 3.5. As a result, we have added the following statement to the initial discussion of EESI-TOF mass flux identified by the reviewer:

“A comparison of the EESI-TOF mass flux to the AMS signal in terms of total signal or mass, bulk properties, and source apportionment results in section 3.5.”

Regarding the second point, here it is important to distinguish between factors affecting the EESI-TOF sensitivity that are ion-dependent, and those which act uniformly across all ions. We use the levoglucosan calibration only to assess the stability of the instrument with respect to the second category (e.g. flow rate, effects of geometric overlap between aerosol and spray droplets on extraction efficiency, effective primary ion concentrations). Ion-specific considerations (extraction/ionization efficiency and ion transmission) cannot be characterized through this simple calibration. However, these are expected to be fundamental properties of the detected ions (in combination with specific instrument settings which are unchanged throughout the study (e.g. voltages in the ion optics), and although unknown are thus assumed to remain constant.

The statement on levoglucosan calibration has been revised for clarity as follows (P6, L7-8):

“EESI-TOF stability and linearity with mass were confirmed by periodic measurement of nebulized levoglucosan aerosol with quantification of the mass concentration with an SMPS.”

P. 6, l. 11 -13: Please include (e.g in the supplementary) more details on error calculations (show data periods chosen, values etc.) This can be very useful for readers / future users.

The original error matrix includes mass spectra from both direct ambient sampling and filter blank processed with Tofware. Then filter periods were interpolated to yield an estimated background spectrum during ambient measurements. We describe and add more clear detail in the main text as following (P6, L19-24):

“The corresponding error matrix σ_{ij} , which has the same dimensions as the data matrix, follows the model of Allan et al. (2003), which calculation includes the uncertainty deriving from electronic noise, ion-to-ion variability at the detector and ion counting statistics. The error estimates in this case incorporate the uncertainties related to both the ambient measurements (δ_i) (direct ambient sampling period) and the background (β_{ij}) (filter blank measuring period, both are processed with Tofware), which are combined in quadrature according to Eq. 2:”.

P. 8, l. 1-2: Why were exactly these factors constrained in the AMS PMF? Please clarify. Does that introduction of subjectivity distort your solution?

First, we correct a small mistake in the original manuscript, where it was stated that both traffic and cooking factors were constrained in the AMS PMF analysis whereas in fact only traffic was constrained.

With regards to the proposed introduction of subjectivity, we note that it is well-established that factor constraints select specific solutions (i.e., the selection environmentally reasonable subset) from a large set of solutions of approximately equal mathematical quality. These solutions may not be operationally accessible during analysis in the absence of factor constraints (or other rotational control allowing multidimensional exploration; note that rotation via the global f_{peak} parameter is insufficient). As a result, the solution returned by unconstrained PMF analysis is itself subject to distortion, as its selection by the model from among other solutions of similar quality is effectively arbitrary. Factor constraints address this problem and have been shown to significantly improve PMF model performance by minimizing such arbitrary distortions (Canonaco et al., 2013, Elser et al., 2016).

In the current study, the α -value for HOA was selected according to the correlations between the time series of HOA with the traffic species NO_x (P10, L9-10).

P. 11, l. 16 – 18: How do the diel patterns of the nicotine and COA factors compare? Could it be that they are similar due the influence of restaurant opening times, with people gathering outside the restaurants to smoke?

This is a good point and likely contributes to the necessity for constraining the CS-OA_{EESI} to obtain a clear separation. We have added diurnal plots of the EESI-TOF factors to the supplement (Fig. S6). The following statement has been added to the manuscript (P12, L9-13):

“The difficulty in separating these factors, despite their expected chemical differences, is likely due to strong temporal correlation between cooking and cigarette-smoking emissions due to the proximity of local restaurants (Fig. S6, the diurnal patterns of nicotine and COA_{EESI} factors), where people gather outside to smoke during mealtimes. We therefore attempted to obtain a clean cigarette smoking signature from the dataset to serve as an anchor profile with which to constrain this source.”

P. 12, l. 6-7: As Figure 2b shows, C₈H₁₂O₆ has a very prominent signal in the LABB spectra. The authors speculate that this ion represents hydroperoxides from the oxidation of phenolic compounds by OH radicals during daytime. Biomass burning seems to be mostly going on during evening/night times – how come daytime oxidation of compounds primarily emitted at night would have such a bit signal?

Here, we made a mistake. This was an early interpretation, but forgot to revise in the text. Oxidation typically leads to a large set chemically related compounds because all these reactive pathways branch in complex ways. In contrast, strong isolated peaks (e.g. levoglucosan) are more likely to result from a specific emissions source and/or process (e.g., because cellulose is a polymer, its pyrolysis leads to a relatively small number of discrete major products including levoglucosan). Although we are unsure of the compound(s) comprising C₈H₁₂O₆, it is very likely to be primary and not an oxidation product, since it is observed as an isolated peak with high relative intensity.

The incorrect interpretation is deleted in the text.

P. 12, l. 14-15: Already mention here what this “different” thing is

This statement related to the lack of correlation observed between primary/less aged AMS vs. EESI-TOF wood burning factors at the start of campaign, and has been clarified as follows (P13, L8-11):

“Fig. S8 compares the BBOA_{AMS} factor (Fig. 2a) with LABB1_{EESI}, LABB2_{EESI}, and the sum of LABB1_{EESI} + LABB2_{EESI}, with R 0.59, 0.79, and 0.82, respectively. The correlation is generally good except during the first part of the campaign (25 January to 27 January) which as discussed later relates to the complexity of wood burning classification between the EESI-TOF and AMS.”

P. 12, l. 23 – 25: January 27 – 29 was a weekend, and a quick google search revealed that the Zurich game festival (<http://www.ludicious.ch/ludicious-2017/>) was taking place then, which would mean a lot around Zurich Kaserne, eating, smoking: :Also LABB2 is high then, despite higher temperatures. How do the authors explain this?

Thanks for the significant information. The following statement is added to the manuscript (P14, L3-5):

“The Zurich game festival was taking place at the weekend (the event is apparently held in a building on the SW side of the courtyard), though no human activities in the immediate vicinity of the sampling inlet were evident by inspection of the on-site camera.”

LABB2 is the more event-driven WB and as such is likely not connected to regular (approximately temperature-driven) domestic heating but rather the activities of the large number of people nearby participating in this event. Probably some local wood burning is associated with this.

P. 15, l. 31 – 33: How sure can the authors be that the molecular formulae they measure correspond to the mentioned compounds? Please add a short discussion on this uncertainty.

We agree that this section requires clarification. In particular, the implication that the EESI-TOF identifies specific molecules is misleading, as the instrument can provide only a molecular formula. In some cases, e.g. $C_6H_{10}O_5$, we know that at a minimum several chemically similar isomers are present (i.e., not only levoglucosan but other sugars such as mannosan and galactosan). We have modified both the labels and caption of Fig. 10, as well as the accompanying text, to clarify this point.

Figure labels now highlight the molecular formula, for example: “ $C_6H_{10}O_5$ ” (~ levoglucosan).

The revised Fig. 10 caption is as follows:

“Fig. 10. Apportionment of selected ions by EESI-TOF PMF. (a) Time series of the mass flux ($ag\ s^{-1}$) and (b) mean fraction apportioned to each factor. Each ion is associated with a compound of interest having this molecular formula, however, the relative isomeric abundance of this compound cannot be confirmed by the EESI-TOF.”

Revised discussion (P16, L31):

“Here we investigate the apportionment of eight ions associated with compounds of interest: $C_6H_{10}O_5$ (approximately assigned to levoglucosan), $C_7H_7NO_4$ (methyl-nitrocatechol), $C_9H_{10}O_5$ (syringic acid), $C_8H_8O_4$ (vanillic acid), $C_8H_6O_4$ (phthalic acid), $C_5H_6O_4$ (glutaconic acid), $C_7H_8O_4$ (tetrahydroxy toluene) and $C_7H_{10}O_5$ (pentahydroxy toluene). Note that because the EESI-TOF can provide only a molecular formula, we cannot establish for certain the identity of a compound or assess the relative isomeric abundances. For example, $C_6H_{10}O_5$ is likely to consist not only of levoglucosan, but also other sugars such as mannosan and galactosan. The named compounds are thus provided for reference, but their identification should not be considered as conclusive and the ions cannot be assumed to be isomerically pure. Nevertheless, as these assignments are based on molecular

investigations of wood burning-related emissions they are likely to be qualitatively correct and provide a useful framework for interpreting molecular aspects of the source apportionment results.”

Technical corrections

P. 2, l. 19 – 21: Sentence structure

This sentence was modified in response to a comment by Reviewer #3, and now reads as follows (P2, L18-20):

*“This suggests the EESI-TOF apportionment **in the current study** can be approximately taken at face value, despite ion-by-ion differences in relative sensitivity.”*

P. 3, l. 16: Family?

Done. We change to **GC-family (P3, L16)**.

P. 3, l. 23: It would be beneficial if this paper was available once this manuscript is online

Done. The instrument paper “An Extractive Electrospray Ionization Time-of-Flight Mass Spectrometer (EESI-TOF) for online measurement of atmospheric aerosol particles” now is public on Atmospheric Measurement Techniques Discussions (**AMTD, <http://doi.org/10.5194/amt-2019-45>**).

P. 4, l. 24: I suggest removing this reference unless the paper is available at the time of publication of this one.

We believe there is small typo here, and the reviewer refers to a reference at P.4. l. 14. This paper is now available at ACPD, and the reference has been updated.

P. 6, l. 1: Number fitting?

Done (P6, L9-10). *“**The total number of 1125 fitted ions** (including 882 Na⁺ adducts, one H⁺ adduct, and 242 unknown ions) between m/z 135 and 400 were identified.”*

P. 6, l. 6: Servo and MS? Specify

The revised text reads (P6, L11-14):

*“Data were pre-averaged to 1 min time resolution, and high resolution peak fitting was performed. Individual 1-min spectra were classified as either ambient measurements, background sampling (through the particle filter), **or transitional measurements immediately after switching between ambient/background sampling. Transitional measurements were excluded from further analysis.**”*

P. 7, l. 20: Minimizes

Done (P7, L29). “Equation (3) is solved using a least squares algorithm that iteratively **minimizes** the quantity Q (Eq. 4),...”

P. 17, l. 7: separately?

We have revised the text for clarity (P18, L12-19):

The factor dendrogram identifies several groups of EESI-TOF PMF factors consistent with the interpretations provided above: (1) more aged biomass burning factors (MABB_LOWEESI, MABB_TRANSEESI and MABB_HIGHEESI), (2) less aged biomass burning factors (LABB1EESI and LABB2EESI), and (3) the cooking-related OA and cigarette smoking OA factors. The more aged and less aged biomass burning factor groups are themselves likewise grouped. This clustering is consistent with our interpretation of these factors, as discussed in the previous section. Ions are clustered to different groups using the standardized values. In each factor, there are distinguished molecules (lists of the specific ions (standardized value above 1.5) for each factor is shown in Table S2). The other two resolved groups, one group including SOA1 and EVENT factor, one group containing SOA2 and NSOA factor, apparently don't retrieve the common ions, which make less sense for the current study.”

Fig. 2, 6: Add arrows/lines to clarify the corresponding stick labels

Done. The arrows are added to the figures.

Fig. 10: The figure looks squished

Done. The shape of the figure is changed.