

Interactive comment on “Organic aerosol source apportionment in Zurich using an extractive electrospray ionization time-of-flight mass spectrometry (EESI-TOF): Part II, biomass burning influences in winter” by L. Qi et al.

Anonymous Referee #3

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The paper by Qi et al. is a comprehensive study of wintertime organic aerosol composition and sources, using factorization of mass spectra obtained from two online instruments; one that uses aerosol volatilization + EI (AMS) and one based on extractive electrospray ionization (EESI-MS). This I believe is the first study that reports on field measurements of the EESI-MS and highlights its potential for organic aerosol source apportionment, given its soft ionization and lack of thermal fragmentation. The results are quite interesting, indicating that a large fraction of OA in wintertime in Zurich is derived from fresh and aged biomass burning (this picture is different than what

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AMS-based factors suggest since the contribution of BB to AMS-OOA factor cannot be separated from other sources of OOA). The paper is overall well-written (although I still have some editorial suggestions below). There are a lot of figures in the main text (and SI), but given the extent of the presented data, maybe there's no way around it. I recommend publishing the paper after following comments are addressed.

Technical comments: P1, L19: “This suggests the EESI-TOF apportionment can be approximately taken at face value, despite ion-by-ion differences in relative sensitivity.” Perhaps this is too strong of a statement since this environment is under major influence of BB (and little HOA) and not a mix of very different sources as can be common in other environments, especially in the summer.

P6, L3: why were the ions smaller than 135 amu small? Was tuning changed on purpose to increase transmission of larger ions? Or is there something different in the mass spec design compared to that of a typical CIMS/AMS?

P6, L8: Just out of curiosity, how stable was the background?

P8, L2: why were different factors constrained for AMS and EESI-ToF?

P10, L1-2: If OOA1 has some of the C_xH_y fragments, shouldn't that be the more volatile OOA factor?

P15, L3: It's surprising that the SOAEESI factor is less oxidized than the oxidized BB factors. At least in the AMS-based PMF factors, the SOA (OOA) factors are quite more oxidized than the BBOA factor. Do the EESI data suggest that AMS OOA factors may contain the aged BB emissions too? Could the authors elaborate on this. After reading the paper, I realize the authors address this in Section 3.5. It will be good to include a sentence in P15 indicating that this surprising result is going to be further examined.

P17, L27-28: If the slopes of the mass defect vs. m/z points for both less and more aged BB is similar, how can one trust interpreting the slopes to understand types of functional groups added to the molecules included in the other factors?

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Section 3.5: I believe this section should be discussed earlier. As I was reading the paper, I kept thinking what if differences in sensitivity of the EESI to different molecules is playing a role in determining the identified factors, so it is reassuring if one reads this section before getting deep into the EESI-based PMF factors. Perhaps the first paragraph of this section that's not discussing the PMF factors yet can be moved to earlier parts of the paper.

P18, L7-9: What's the explanation for a lower sensitivity of EESI for the times levoglucosan was low? Based on the AMS factors, the initial period is not dominated by HOA that EESI is blind to.

Editorial comments: Some correlation coefficients were presented as R, some as R². Please use one consistently. Quality of some figures was not good when viewed at 100% and the legends/axis labels were blurry.

P 1, L15: "...was derived..."

P1, L21: consider changing "...utilize a..." to "...utilization of a..."

P2, L14: delete "of" in "...fragments typical SOA molecules".

P6, L2: change "The total number fitting of 1125 ions..." to "The total number of 1125 fitted ions..."

P6, L9: delete "the" to read "...were removed from further analysis."

P6, L19: "An HR-ToF-AMS..."

P6, L21: "spent"

P14, L4/5: it should be NOAAAMS (not NSOAAMS). Related to this, the discussion on NOAAAMS and the EESI-based factor is provided after this sentence, not before.

Fig. 6b- unit for precipitation is not included.

P14, L12: "period 1" should be move to "...study, period 1, occurs..."

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P15, L25: I believe you mean EESI-CHON fragments correlate better NSOA_EESI. I don't think AMS_CHON fragments are displayed.

Fig. 12b. Green color for more aged secondary BB factor is too hard to see against the white background.

P18, L10: consider replacing "big events" to some other phrase

Fig. 13b: intercept of the black line appears to have two negative signs in front

P18, L31: change "primarily" to "primary"

P18, L34: replace "WB-related" by "BB-related"?

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