

Interactive comment on “Organic aerosol source apportionment in Zurich using extractive electrospray ionization time-of-flight mass spectrometry (EESI-TOF): Part I, biogenic influences and day/night chemistry in summer” by Giulia Stefenelli et al.

Anonymous Referee #2

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This manuscript presents source apportionment from ambient measurements where an extractive electrospray (EESI) mass spectrometer was deployed alongside an aerosol mass spectrometer (AMS) in an urban setting. The paper demonstrates the capability of the EESI to measure variability in ambient organic aerosol that is consistent with that measured by the AMS, and to also identify additional variability in SOA composition that is not isolated in factor analysis of the AMS data.

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The comparison of the EESI and AMS total signal and the comparison of the factor analysis from each instrument are the strongest results of this manuscript. The authors convincingly demonstrate that the EESI is measuring ambient organic aerosol and that the variability captured by the factor analysis is from different primary and secondary sources. These results (along with the companion wintertime paper) lay important groundwork for establishing how EESI can be used to understand atmospheric aerosol composition and chemistry and will be very useful for future EESI measurements of ambient aerosol.

My main concern with the manuscript is that many of the authors' attributions of EESI signals to particular chemical processes are not strongly supported. For example, at several points the authors attribute components of SOA to either monoterpene, sesquiterpene, or aromatic VOC oxidation products but do not show any data from the co-located PTR-MS to support their arguments. Similarly, the authors simultaneously argue that the SOA being measured is representative of high-NO_x conditions (p 11 ln 30) while also attributing SOA constituents to HOMs produced through low-NO_x autoxidation (p 18 ln 35). At a minimum the authors should report the NO concentrations from the NABEL site to support these arguments. In my opinion this paper is sitting at the borderline between being appropriate for Atmospheric Chemistry and Physics vs Atmospheric Measurement Techniques, and strengthening the connections between observed factors and specific chemical processes would add to the argument that this is in fact an ACP paper.

Specific comments:

P 2 ln 11: Cooking OA should be included in this list of primary OA sources. Several studies have shown substantial contributions of cooking emissions to POA or even total OA. (e.g., Hayes et al., 2013).

P 2 ln 15: Please consider a more recent reference to complement the Heald et al. reference. For example, see Shiravastava et al. 2017.

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P 2 In 26-30 & p 3 In 3: I feel the value of the EESI time response relative to other state-of-the-art techniques is being overstated here. Currently this manuscript does not demonstrate the there is value in the 5-minute EESI data that could not be obtained at the 30-60 min time resolution of a FIGAERO or TAG measurement, and the authors do not acknowledge the time response of the CHARON here. Consider highlighting an event in this study where the OA chemical composition is varying on a 5-minute timescale or reworking this section.

P 2 In 36 & p 3 In 19: Equating the thermal decomposition of the CHARON and the AMS feels very unfair to the CHARON group. I strongly recommend that the authors separate the discussion of fragmentation in these instruments into different sentences that more accurately reflect the extent of thermal decomposition observed by each. Similarly, I encourage the authors to consider softening the claim on p 3 In 19 that there is no thermal decomposition or ionization-induced fragmentation in the EESI. To my knowledge the full extent of the investigation into this is the ~10 standards reported in Lopez-Hilfiker et al. 2019, which only demonstrated that polyols and dicarboxylic acids do not fragment. The components of the SOA measured in the study, especially organonitrates, are likely to be considerably more fragile than those standards and so I am not convinced that there is sufficient evidence to support this claim.

P 5 In 22: The measurement of nicotine as $[M+H]^+$ makes me doubt that other ionization pathways are "almost entirely suppressed". It seems very likely that many amines are sufficiently basic to also be detected through a protonation pathway.

P 12 In 31: As discussed above - authors mention that there were PTR-MS and NO_x measurements at the sampling site but do not show any results. Is there any evidence from those measurements that would support the assignment of EESI SOA factors to NO₃-monoterpene reactions? Or is the attribution solely based on assigned elemental compositions and the diurnal profile?

P 15 In 21: The authors should report a bulk sensitivity to OA during this study, cal-

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culated from the slope of the regression in Fig. 10a and compare it to the bulk SOA EESI sensitivities reported in Lopez-Hilfiker et al. 2019. Much of the discussion in this manuscript is heavily influenced by the fact that the total EESI signal shows decent correlation to AMS OA mass, despite significant variability in compound-to-compound sensitivities (and the inability to measure HOA). Being able to compare the EESI's bulk OA sensitivity to single-compound sensitivities & single-precursor SOA sensitivities would help the reader understand the extent to which the correlation with the AMS measurement may be driven by a handful of high-sensitivity compounds that correlate with total OA. This is especially important because the authors do not show any EESI calibration data.

P 16 In 38: This paragraph is very confusing and I do not follow what readers are supposed to conclude about how extraction in EESI is affecting bulk molecular properties as compared to the AMS.

P 17 In 16: How confidently can you conclude that having a single factor above 50% of EESI signal indicates that the factor is >50% of OA mass? If the EESI is twice as sensitive to SOA as COA, and totally blind to HOA, it seems like an SOA factor could have higher sensitivity than bulk SOA and dominate signal while being a small fraction of OA mass.

P 18 In 29: In this paragraph the claims that ions with an assigned elemental composition correspond to the same molecules measured in other studies need additional support. Based on the number of compounds detected in offline electrospray aerosol measurements overlapping assigned formulas are expected and don't necessarily point to a shared source. Is there evidence in the NO data from the Zurich site that HOM formation could have been occurring? Can this be reconciled with the claim discussed above that the chemistry forming the regional SOA is high-NO_x?

Figure 10: In panel B the regression lines are thin, hidden behind the markers, and quite dark and monochromatic (to this reader's eyes). Consider some combination of

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enlarging the figure, bringing the regression lines to the front, and making the colors easier to differentiate.

Minor comments:

P 5 In 13: Please state the resolution achieved in this study instead of the nominal ToFwerk maximum.

P 5 In 29: Was it the heated capillary or the electrospray capillary that clogged? Please clarify. Also please clarify what is meant by “dirty solution”.

P 5 In 33 & p 19 In 19: clarify that “signal stability within $\pm 7.3\%$ ” is a relative standard deviation and not the range of signal intensity observed.

P 6 In 7: In point #3 do you mean to say “subtracted from the ambient spectrum”?

P 11 In 5: Close parentheses on the reference.

P 11 In 9: Report nicotine as C₁₀H₁₄N₂ to stay consistent with the omission of “Na+” from other assigned elemental compositions.

P 12 In 3: This sentence is either missing a clause or the word “that” should be removed.

P 14 In 1: Section 3.2.5 could be moved to SI. Good additional proof of the robustness of the factor analysis, but quite long and of less general interest than the rest of the manuscript.

P 18 In 36 & p 19 In 2, possibly others: elemental compositions with “0” instead of “O”.

References:

Hayes, P. L., et al. (2013), Organic aerosol composition and sources in Pasadena, California during the 2010CalNex campaign, *J. Geophys. Res. Atmos.*, 118, 9233–9257, doi:10.1002/jgrd.50530.

Shrivastava, M., et al. (2017), Recent advances in understanding secondary organic
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aerosol: Implications for global climate forcing, *Reviews of Geophysics*, 55(2), 505-559.

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