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Atmospheric Chemistry and Physics
Discussions

Interactive comment on "One-year characterization of organic aerosol composition and sources using an extractive electrospray ionization time-of-flight mass spectrometer (EESI-TOF)" *by* Lu Qi et al.

Anonymous Referee #2

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In this work, the authors used a novel offline analytical technique (EESI-TOF) to measure chemical components in organic aerosol. They adapted the online version of this technique to analyze filter extracts, allowing them to analyze filter samples without having to deploy an expensive instrument in the field. The time series of the chemical components are used to perform source apportionment by positive matrix factorization (PMF), a now standard procedure for statistical analyses of large data sets. They report a number of factors, and the interpretation of these factors is carefully discussed. This work is novel and potentially impactful, as this method will allow for widespread use of

a newly developed technique to measure a much larger number of organic compounds than previous techniques. I have one major concern that the authors need to address and a number of minor comments. If this concern can be satisfactorily addressed, I would recommend publication in ACP.

Major comments:

My only major question surrounds the ability to draw meaningful conclusions from the PMF results. In a previous paper, the authors found that the sensitivities of EESI-TOF for individual compounds vary by orders of magnitude and we do not yet have a good understanding of what determines the sensitivity. Here the authors are performing PMF and apportioning the signal of EESI-TOF to various factors, rather than the mass of OA. This is fundamentally different from PMF using AMS because AMS is much more quantitative. One could argue that these results could be biased by compounds to which EESI-TOF is very sensitive. For example, the fact that CSOA is so prominent is because EESI-TOF is very sensitive to tobacco smoke compounds like nicotine, but in reality CSOA is only a minor fraction of actual OA. I would like to see some discussion around this limitation, and how the authors can use these results to convince the readers that the source apportionment is representative. I would also note that the authors present convincing data in previous work that the signals are linear with mass, but that is not necessarily sufficient to avoid the bias described here.

Minor/technical comments:

I understand that using water as a solvent is useful in defining the observed mixture as WSOM. But would there be any utility to using a slightly more organic solvent for extraction such that a larger fraction of the OA can be recovered? The EESI is already using a water/acetonitrile mixture. Seems to me that using the same solvent mix could provide more insights.

A general but minor comment: what is the fraction of OM in PM10 observed here? Would be a good piece of information.

Abstract: In general, the abstract might be too specific, with too much reference into details. I would recommend cutting down on acronyms/abbreviations and focus on the more generalizable points. For example, in line 11 NABEL is not defined, nor is used in the rest of the abstract. This information is not necessary for a casual reader to grasp the main points of the manuscript

Abstract line 5: destroy is not an appropriate word. I recommend replace with "limits" Introduction Line 26: it is customary to include references for climate and health impacts of aerosols.

Introduction Line 31: POA sources and SOA mass do not seem to be parallel to each other. PMF apportions the mass to different sources

Page 3 lines 8-12: these arguments are valid, but filter sampling is also not typically operated in a dense network, because they require intense labor for both sample collection and extraction. Maybe it would be better to argue that since the filter sampling infrastructure is already in place, the marginal cost of additional sample analysis by AMS and/or EESI-TOF is low. Another advantage may be doing retrospective analysis from archived filters.

Page 3 line 23: same comment as above

Page 4 line 14: 14.7 cm diameter is not a standard size; is this correct? Usually 47mm diameter is used

Page 4 line 15: might be useful to add details of the PM10 sampler

Page 4 line 30: why is a temperature of 60C used? Seems rather high. Is it ensure evaporation of water? Is this the temperature required for EESI?

Page 5 line 2: are the mass spectral data averaged over the 5 minutes? Or some time point within those 5 minutes chosen for best representation of the extract?

Page 6 line 5: why is it necessary to use the mass? Isn't it sufficient to use ions (which

represents number of moles)?

Page 6 line 7: typo in "united", maybe "in units of"; same line: x represents the ion, not the composition

Page 6 line 14: unmatched parenthesis

Page 6 line 22: How is WSOC analyzed? Is it on the same Sunset OC-EC analyzer? Or is a different TOC analyzer? The way the first few sentences are written is vague and confusing.

Page 7 line 25: Which anchor profiles are used in this work? I did not really see the details clearly from the rest of the manuscript.

Page 8 line 28: there seems to be a typo here for the factor. The same problem is happening in other parts of the manuscript

Section 3.2.1: this is a very well written section with thoughtful support of interpretation.

Section 3.2.2: this section might be too detailed and only the last paragraph is relevant and interesting. I would recommend shortening the first few paragraphs significantly or move the details to figure captions/supplementary information. I was very distracted by much of the detailed discussion.

Page 11 lines 15-20: might be useful to add a short explanation (in SI) of how mass defect works and the trends in mass defect support structure identification. (e.g. why is the theoretical slope 6e-4?

Page 11 lines 24-29: it is somewhat unusual to see a cigarette smoke factor being so dominant in PMF. Why is this different from previous AMS or molecular marker source apportionment analysis in urban areas? Is it because the EESI-TOF is more selective towards nitrogen-containing compounds? Or is it the size dependence? (PM10 vs PM2.5 or even PM1)

Page 12 Line 19 and Fig 2a: judging from the figure, they do not look correlated (the “dynamic range” is quite narrow for the cellulose measurement.) This line of evidence is relatively weak.

Page 12 Line 23: EESI only suggest formulas consistent with fatty acids, and are not definitively identifying them as fatty acids.

Page 12 Line 26-27: if low solubility of fatty acids for EESI-TOF is invalidating the COA identification, wouldn’t that also refute the identification of plant debris as well? The formulas suggested in the beginning of this discussion are similar to those in COA, and I do not expect their (water) solubility to be significantly higher.

Page 13 lines 24-26: are any of the phenolic products from lignin pyrolysis observed?

Page 13 lines 27 – page 14 line 4: the paragraph focuses on arguing these two factors are observed separately (i.e. resolved by EESI-TOF and PMF), but a discussion of what are the actual difference of the sources would be useful and is currently lacking. What might be responsible for the difference (e.g. fuel type, residential vs wildfire, burning conditions etc.)?

Page 14 line 31: not sure what purpose the equation serves. It does not necessarily show that the dependence is exponential. Might be better to show a log-linear plot (in SI).

Page 15 line 10: I do not see convincing evidence that terpene is necessarily the precursor for SMOA. I am also confused by what do the authors mean by “fragmentation products from terpene oxidation . . . followed by condensation after oxidation of light aromatics via ring-opening”. This needs to be clarified.

Page 16 line 23: the number of filters is 86 here, but 91 earlier. Check for consistency.

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