Review of Lopez-Hilfiker et al. (2019)

This manuscript presents results from a newly developed extractive electrospray (EESI) ion source for real-time analysis of organic molecules in aerosol particles. The results are impressive, and the EESI source will be useful for future studies in this area. However, significant clarification is needed before publication, in particular to convince the reader that the performance shown is typical of this source across a wide range of analytes and situations.

Major points

Improved detection limits (DL) is noted throughout the manuscript as a major advance (if not the main one) for this new instrument configuration. However, only a couple general statements are provided regarding DLs (e.g., p13 ln 18-21) without sufficient details to fully understand this key aspect (see additional comment below). I would have expected a subsection in section 3 to be dedicated to showing DLs for a range of elemental formulae or compounds such as those shown in some of the dense example spectra. Also, dependency on sampling time or sampling history, solvent type, compound or m/z and other important aspects that may affect DLs as would be typical in an instrumental characterization paper like this one. Perhaps a mass spectrum of DLs would be appropriate (probably requiring assignment of an approximate fixed sensitivity).

Both mass flux and Hz are used throughout the plots in the paper for signal metrics in various places. Can the authors explain this choice (using one vs the other)? Is it preferred to reflect the mass weighting of the ion signals when showing multiple compounds such as the mass spectra, while not needed for showing single ions? Or if there is not uniform reasoning behind this, perhaps consider using a consistent metric throughout?

Title: the title refers to the EESI-TOF instrument, but the paper is all about the EESI source with no new information or modifications for the TOF mass spectrometer. A TOF does not seem strictly needed either, and EESI has been used before with other mass analyzers. I strongly suggest that the title is updated to reflect this, to something like "An extractive electrospray (EESI) ion source for online mass spectrometric measurements…"

P1 ln 13: DLs without the relevant sampling time are meaningless, please state

P6 ln 3-7: Again, it is unclear what the relevant sampling period for the stated numbers are, please clarify. Strictly speaking, the amount of sample should be stated as well, but given the similarity of the discussed instruments they are probably comparable.

P6 ln 11-14: This statement about "EESI" is unclear whether it refers to previous work or this paper. Probably previous work since it comes before the final paragraph stating what is presented in this paper? If so, provide references?

P7 ln 4-5: It is stated that 1 um Teflon filters are used for blanks. Often for online aerosol instruments, hepa filters with small pressure drops under extended aerosol exposure are used for blanking. Can the authors comment on any issues with pressure differences associated with switching between filter/no-filter during extended sampling with a clean filter and as the filter loads up with aerosol since substantial pressure changes (~20 mbar) might substantially alter the spray. It is noted later (P12 ln 2-3) that only a 2% change in the [NaI]Na+ ion was observed during filter switching during sampling of ~30 ug/m3 of a-pinene ozonolysis SOA, however from that it is not clear how well this type of filtering works under extended operation of polluted air. Did the authors operate with this type of filter for the proof-of-concept tests described in Section 4? It would also seem that using a teflon, low surface area, filter could have less potential artifacts from adsorption/desorption of sticky gases, than HEPA filters with large surface areas composed of glass or plastics. Thus, providing more information/experience on this aspect could be of substantial value for future uses of this source.

P7 ln 7: the gas-phase denuder seems quite small for this application. What is its capacity? Has breakthrough been tested? How often does it need to be replaced, as a function of sampled concentration?

P7 ln 18: "We find that maximum ion transmission is achieved by maximizing the flow rate into the mass spectrometer, which for our pumping configuration is nominally 1 L min-1". It is unclear to me if the authors are simply stating here that sensitivity simply increases with an increasing ion flux into the mass spectrometer, or if there is an additional benefit of the higher flow. I would also be curious to what extent this effect can be separated from the evaporation process changing with flow, and if this was characterized as part of this work.

P 8 ln 6: this statement is too vague. Please provide more information about the estimated temperature or range of temperatures, and the method of estimation.

P 8 ln 19: is this 1 L min-1 STP, or at some reduced pressure going into the MS?

P10 ln 15: how was this binding energy quantified?

P12, ln 24: "In the absence of fragmentation or decomposition, which has not been observed for any system presented herein". It is unclear how the authors reach this conclusion, it is not supported by the data presented. While it is indeed encouraging that the pure compounds measured by EESI-ToF in this manuscript did not decompose during analysis (although none of them are particularly unstable), this certainly cannot be shown for the various types of SOA analyzed, since its compositions is not known otherwise. The similarity of the EESI and FIGAERO results, which are known to be affected by decomposition (Lopez-Hilfiker et al., 2016, cited in the manuscript, also Stark et al., ES&T 2017), suggest that the EESI might also have some degree of decomposition or fragmentation.

More importantly, this study does not present any indirect evidence that the chemical compositions identified by EESI are indeed consistent with no fragmentation. E.g. in the CHARON instrumental manuscript (Mueller et al 2017) a comparison of O:C ratios for bulk (AMS) and CHARON was performed, showing - as expected - a lower O:C in the CHARON consistent with some fragmentation/elimination of oxygenated fragments. Such a comparison for the EESI-ToF for one of the simpler SOA cases would increase confidence that the effects of decomposition and fragmentation are low. In the absence of such supporting evidence, I would strongly qualify the above statement

P13 ln 20-21: Detection limits need associated averaging time information to be meaningful. ~5s, like in Fig. 2?

P13 ln 21-23: Are these comparisons of detection limits of other instruments for similar averaging time?

P 14 ln 29: The authors describe the EESI-ToF sensitivity to benzene SOA as an outlier compared to the other five SOA systems studied. Looking at Fig. 4 the benzene SOA sensitivity is within the variability of EESI-ToF citric acid sensitivity, and the factor of ~20 difference in bulk SOA sensitivity (RRFs 0.05 to 1) is similar to the factor of ~30 spread observed for single compounds. There is also a consistent trend in EESI-ToF sensitivity of SOA produced from the homologous series of benzene, toluene, and trimethylbenzene. Additional clarification is needed to justify considering benzene SOA an outlier and excluding it from the calculation of the variability in EESI-ToF SOA sensitivity.

P15 ln 8-10: Molecular identification would clearly be a major difficulty in doing do this as well. I.e. even if you could just order any compound you wanted, it would be difficult to determine if the isomer detected was the one calibrated for.

P15/L15 - P16/L9: This section on comparison of EESI-ToF vs FIGAERO/I-CIMS raw signal seems a bit underdeveloped and potentially susceptible to misinterpretations. The Hz signals of many compounds are compared between the two instruments which show good correlations overall and among ions series on a log-log basis. It is stated that I-CIMS reaction rates are collision-limited which in conjunction with adduct binding energies dictate sensitivity, which can be operationally estimated by exploring declustering potential (a.k.a. voltage scanning). Based on the good agreement, it is concluded that therefore the EESI-ToF spectra likely reflect the actual distribution of compounds in particles. However, it has been shown that the relative sensitivities for I- can vary widely; therefore there seems to be a large unsubstantiated logical leap here. I worry that readers will interpret the statement that I-CIMS is collision-limited and seemingly glossed over additional factors controlling sensitivity as meaning that the uncalibrated I-CIMS spectrum essentially reflects the relative distributions of compounds in particles.

Why wasn't the voltage scanning sensitivity estimation method used here? This could help close this gap, providing a more direct look at response factor variability for the EESI for a wide range

of atmospheric SOA surrogate compounds? It is especially surprising that this step wasn't taken, given the authors' development of that method. Without calibration or knowing the general instrument sensitivity and declustering settings, it would seem that the slopes don't have much meaning. That said, the good correlation certainly is interesting, useful and promising that the current analysis suggests that similar empirical sensitivities may be derivable/parameterized for the EESI-ToF.

P 15 ln 23: How representative are the 12 m/z's presented in Fig. 5 of the 100+ shown for the same chemical system in Fig. 9? Namely what fraction of the aerosol signal is attributable to these twelve m/z's? Was the FIGAERO comparison extended to other m/z's?

P16, L27-28: How is this known? Analysis of the SMPS distributions? Is the 20 nm seed particle mode separable from the a-pinene ozonolysis nucleation mode? Ensuring that a substantial fraction of the seed is coated seems pretty important to this demonstration. If this is problematic, and nucleation was unavoidable, why weren't larger seed particles used? 20 nm (and growing to 70 nm) seems surprisingly small for this test (and not representative of the size particles in the atmosphere where most of the mass resides).

P17 Section 3.4 (Water vapor dependence): This is a nice analysis. Have the authors considered whether some of the compounds with substantial H_2O-dependence effects may be dominated by semi-volatile gases breaking through the denuder? Possibly looking at the humidity-dependence of signals that are enhanced during the filter blanks would help understand that possibility.

P17 ln 19: it would be informative if the authors reported the relative mass fluxes of water from the ESI and from the sample flow (at let's say 50% RH).

P 19 ln 1: Kumbhani et al. report using a 100 μm ID capillary, while this EESI-ToF uses a 50 μm ID capillary. Authors should revise their statement that the Kumbhani et al. capillary has a 5x smaller ID than the EESI-ToF capillary, and revise the subsequent discussion.

P 19 ln 8: please provide a range of expected sizes for the electrospray droplets.

P21 ln 29: Add FIGAERO-CIMS to list of instruments that show thermal decomposition? (see comment above)

P23 ln 7: Change "...for most precursors." to "...for most precursors TESTED."

Figure 5 and discussion: Comparison of several apparent slopes in Fig. 5a with the bars in Fig. 5b seems to not match the relative slopes relationships. E.g. C914H14O7 looks steeper than C914H14O4 and C1016H14O4 but the opposite in Fig. 5b (0.4 vs 0.55 and 0.6). Is this simply due to non-log linear fits being calculated where the regression is highly weighted toward the largest signal data? If that is the case, perhaps also reporting the average ratio (could easily be

added to the same bar plot). Other options may be a log-log fit or other regression fitting methods that don't emphasize the high value data points. The point here is that at least inspection of a log-log plot shows that the relative trends shown in Fig. 5b and discussed in the text may not be robust for each ion but rather reflect just a few of the high-signal points for each ion. On the other hand, if the lower signal points are noisier and closer to DLs, then perhaps it is fine weight those more strongly. Finally, the type of fit (ODR?) and if it was constrained through zero should be reported.

Figure 5 and discussion: It would be useful if the authors reported what fraction of the aerosol signal the sum of all the select ions represents. Most of it? Similarly, it would be useful to show the EESI-ToF and I-CIMS aerosol mass spectra (possibly on a log-scale).

Figure 8b: Please include the particle volume distribution geometric standard deviation on Figure 8b to give a sense of the overlap of sizes, since this experiment was not conducted with monodisperse particles.

Other points

P1, ln 18: Would suggest replacing "SOA compounds" with "identified SOA components" or similar

P3, ln 23-31: Need references for many of these statements.

P 4 ln 8: My understanding is that instruments like the ATOFMS and PALMS have much more fragmentation of organic molecules than the AMS. The laser ablation instruments often turn organics into C1+, C2+, and ammonium into NO+. However, as worded this section gives the opposite impression.

P5, ln 10-11: Text states: "Further, there remain fundamental limits to the detection of highly oxidized compounds, as well accretion products for which there is currently no satisfactory online detection technique." It's not clear what is meant by "fundamental limits" which is vague in this context. Please clarify. Also add "as" between "well" and "accretion".

P9, ln 29: This is perhaps a typo? I have not seen water at 25 C to have more than 18.2 MOhms resistance.

P10 ln 28: this sentence is missing a verb

P15 ln 6: a reference to the CIMS strategy described is needed

P16, ln 12-13: Add reference for this statement about matrix effects and ion suppression being common in ESI.

P20 ln 17-18: Remove unneeded "of" and "as" which make the sentence grammatically problematic.

P20 ln12-13 / Fig 9a/b: Please state how mass concentration was determined from SMPS measurements as shown in Fig. 9a/b.