We thank the reviewers for their comments. The original comments are in normal font type. Our point-by-point responses are shown below in ***bold italic***. Manuscript changes are shown in blue.

RC2 (*https://doi.org/10.5194/amt-2021-325-RC2*)

This manuscript presents a novel mass spectrometric technique for studying gas- and particle-phase organic compounds with a single electrospray (ESI) ion source. The instrument operates by alternately sampling form three distinct channels: a direct inlet, an inlet where gas-phase compounds are denuded, and an inlet where particles are filtered, and gas-phase compounds are denuded. These three channels allow the authors to separate ESI background, from gas- and particle-phase signal by difference.

The technique works, is useful for studying the atmosphere, and is appropriate for AMT. My suggested revisions are below.

My main criticism is that this is a SESI + EESI instrument, and not a dual-EESI. These acronyms each correspond to distinct ionization pathways, and each have extensive literature describing the factors that affect their sensitivity. I think the authors will be best served by connecting their technique with the existing literature by calling this “dual ESI”, “S/EESI”, or anything that conveys that the method aims to separate EESI signal from SESI signal.

The novelty of this work is that the authors are bringing together two established techniques (SESI+EESI) in a single ion source. There are already SESI techniques for studying organic gases in the atmosphere that go beyond “technically possible”, and the authors cite one example (Zhao et al 2017). That work already demonstrated linear SESI response for organics in the atmosphere, and even characterized the strong humidity dependence of SESI sensitivity.

Overall, I feel that there are significant details missing from this paper, covered in the additional comments below. The most critical area in need of discussion is the slow response time of the instrument to the gas-phase analytes, and how this response time affects the background subtraction. The authors largely avoid addressing this by sticking to raw time series instead of showing background-subtracted data, and since the background subtraction is central to the technique more detail is needed.

In secondary electrospray ionization (SESI), ions generated by electrospray ionization are used to charge the analytes in the gas-phase. In the design used by Zhao et al. (2017), the electrospray is generated at ambient pressure, charged ions are generated after droplets pass through the evaporation region, and the ionization of neutral analytes occurs at reduced pressure in a cross-flow ion-molecule reactor. In our design, the gas and/or particle analytes intersect with an unheated electrospray at ambient pressure before entering the heated ion capillary of the mass spectrometer. Therefore, we expect that the droplet-vapor interaction is more dominant than gas-phase charge transfer, making the technique more EESI than SESI for gas-phase detection. The higher ionization efficiency of gases vs. particles follows the size dependence ionization efficiency of particles determined by Lee et al., 2021, where smaller particles (including gases) have higher ionization efficiency due to their higher collision efficiency with the charged droplets. We have added the following clarifications in the revised manuscript at line 171-179:

In the EESI scheme, when particles intersect with the charged ES droplets, they can be extracted into the aqueous phase and subsequently ionized via Coulomb fissions of these ES charged droplets. The gas molecules can be ionized by gas-phase ions formed during charged ES droplet evaporation, which is termed secondary electrospray ionization (SESI) (Wu et al., 2000). This approach was used in the design of Zhao et al. (2017), where charged ions were generated first before mixing with neutral analyte gasses inside a cross-flow ion-molecule reaction tube. According to the settings of our Dual-EESI inlet, which does not use a heated sheath flow to air ES droplet evaporation, analytes intersect with the ES droplets at ambient pressure. Therefore, EESI (i.e. analyte-droplet interaction) is expected to dominate in TP and

PP channels, though SESI (i.e. ion-vapor interaction) may still occur in all channels including FP where gas desorption from the tubing wall coexists.

Line 70: What was the ESI working solution? Looks like AcN:Water and NaI dopant, and I'm guessing the solvent ratio is 1:1, but this needs to be added to methods

We added the description of the ESI operational condition at line 98-106:

*"*Throughout the whole experiment, acetonitrile/H_2O (50/50 v/v) doped with 100 ppm NaI was used as the ES working solution. A potential difference of around 2.6-2.9 kV relative to the MS interface was applied to the ES solution, and an air pressure difference of 300 to 600 mbar was applied to the ES solution bottle reservoir, delivering 2.7 – 5.4 µl min^{-1} of ES solution via a polyimide fused silica capillary (o.d.: 369 µm and i.d.: 75 µm, BGB Analytik, Switzerland). The ES droplets intersected with the sample analytes before entering the heated TOF-capillary kept at 275 ˚C (<1 ms residence time), undergoing a Coulomb explosion as the ES droplets evaporated. The ions generated from organic molecules were detected predominantly (> 95 % relative abundance) as sodiated adducts ($[M+Na]^+$) in the positive ionization mode by the TOF. The raw mass spectra (1 Hz) were post-averaged every 10 seconds using Tofware (version 2.5.13). All measured analyte signals were normalized by the most abundant electrospray ion (i.e. $[NaI+Na]^+$) to account for the variation of the electrospray signal (± 5 %).*"*

Line 166: $[M+H]^+$ ions for PTR-MS

We changed "M^{+1}" to "$[M+H]^+$" as requested.

Line 177: EESI only occurs if there are soluble particles present to be intercepted by the ESI drops. So in the FP channel, only ESI is occurring, since there are no gas- or particle phase analytes. In the PP channel signal is due to both ESI and EESI. In the TP channel signal is ESI + EESI + SESI

ESI is usually meant as the infusion electrospray solution, this is not the case for our ES configuration. Thus, we clarified the ionization scheme at line 171-179:

*"*In the EESI scheme, when particles intersect with the charged ES droplets, they can be extracted into the aqueous phase and subsequently ionized via Coulomb fissions of these ES charged droplets. The gas molecules can be ionized by gas-phase ions formed during charged ES droplet evaporation, which is termed secondary electrospray ionization (SESI) (Wu et al., 2000). This approach was used in the design of Zhao et al. (2017), where charged ions were generated first before mixing with neutral analyte gasses inside a cross-flow ion-molecule reaction tube. According to the settings of our Dual-EESI inlet, which does not use a heated sheath flow to air ES droplet evaporation, analytes intersect with the ES droplets at ambient pressure. Therefore, EESI (i.e. analyte-droplet interaction) is expected to dominate in TP and PP channels, though SESI (i.e. ion-vapor interaction) may still occur in all channels including FP where gas desorption from the tubing wall coexists.*"*

Line 185: The FP measurements surrounding the TP measurement are very uneven, due to the slow response time of the camphor gas. The subtraction of FP from TP is critical for determining gas-phase signal later in the paper, and so the authors must discuss how they defined average FP signal for slow-responding gases.

The average of the FP signal is defined as the average signal during the second FP measurement window, FP_2 in the TP-FP_1-PP-FP_2 cycle. We demonstrated in Figure S13 that the FP signal of camphor does not vary by more than few % within the background/sampling measurement period ratio of 0.1 – 1 as discussed in line 190-193. Slow responding gases such as semivolatiles were addressed in Figures S5 and S18 where $C_9H_{12}O_{4-5}$ require 4 minutes to reach it previous background level. We have clarified our choice of background measurement in the revised text:

In Section 3.1, line 182-184:

"Each complete sampling cycle proceeds as follows: FP_0-TP-FP_1-PP-FP_2, where FP_0 is the FP_2 measurement from the previous measurement cycle. Both camphor and levoglucosan with concentrations of approximately 500 pptv and 10 µg m^{-3} respectively, were measured during TP measurements (blue shade). During the combined FP_1-PP-FP_2 period in Figure 2a, the camphor signal decreased by a factor of 50.***"***

In Section 3.1, Line 194-207:

"The background signals of the Dual-EESI vary by less than a factor of 2 for all the tested sampling sequences and are reproducible during FP_1 and FP_2 measurements. Similarly, for semivolatile compounds generated from precursor oxidation (Figure 4 and Figure S18), the average signal measured during FP_1 and FP_2 periods are lower than 15% and 10% of the TP signals, respectively. Averaged FP_2 measurements remain consistent for different sampling durations (Figure S13), indicating that background buildup is negligible. The rise time from FP_0 (i.e. FP_2 of the previous cycle) to TP as shown in Figure 2 is very short (< 1 min) compared to that observed using ion-molecule reaction (IMR) CIMS (Palm et al., 2019), where it was required to carry out fast zero measurements to account for vapor-wall interactions. For the Dual-EESI inlet, such effects are likely minor given the fast rise time and consistency of FP_2. Therefore, we use FP_2 as our background measurement. This is similar to the background treatment of single-phase EESI (Lopez-Hilfiker et al., 2019), which follows a FP_0-PP-FP_1 sampling scheme and uses the average of FP_0 and FP_1 as the background, where FP_0 is the FP_1 measurement of the previous cycle. As a result, the Dual-EESI is able to provide quasi-simultaneous gas- and particle-phase measurements for standard compounds with measurement cycle periods as low as 5 minutes, including background correction. This capability was further tested below using environmentally relevant complex mixtures of gases and particles.***"***

Fig 3: Should y-axis read "Relative Signal" instead of "Relative Gas Concentration"?

Both figures are relative signal from EESI where the signals were generated by ionization of either gas-only or particle-only analytes. Thus, we labelled y-axis as "Relative Gas Concentration" and "Relative Particle Concentration" for clarity.

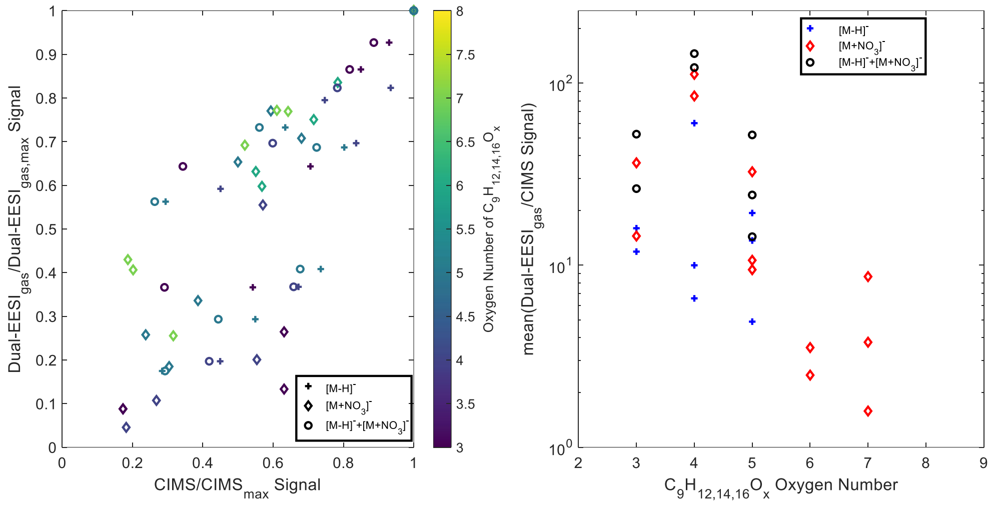
Fig 3: There is clear and consistent structure to the residuals of gas-phase (SESI) sensitivity, and the authors must address this. I do not agree that this is a linear response for gas-phase analytes.

While we agree with the reviewer that residuals seem to have a structure in Figure 3, the point does not deviate strongly from linearity with errors less than 20% (and $R^2 = 0.94$). In addition, we have little statistics to support a non-linear relationship. For example, the comparisons between the Dual-EESI and Nitrate-CIMS in Figure 6 indicate a linear relationship.

Fig 6: I am unable to follow the significance of including the deprotonation ionization pathway from the nitrate CIMS. Are these data points all from a single experiment? Or did the authors run separate experiments with difference conditions in the Nitrate CIMS IMR? If it's all one experiment, then some acids are being detected as both [M+NO3]- and [M-H]- by the nitrate CIMS (e.g. C9H12O5, C9H14O5, and C9H16O5). Those two nitrate CIMS peaks would correspond to a single SESI peak [M+Na]+; so the authors should be summing the two nitrate CIMS signals in order to plot against the SESI signal, and not plotting the nitrate CIMS ionization mechanisms separately. There is no discussion in the text to help the reader understand the significance of the two ionization schemes, and the authors must add clarification.

All data points were taken from a single experiment where the precursor concentrations were varied. The $[M+NO_3]^-$ and $[M\text{-}H]^-$ ions were observed in the same Nitrate-CIMS spectra. Following the reviewer's suggestion, we added the sum of the $[M+NO_3]^-$ and $[M\text{-}H]^-$ ion intensities in the figure when the same compound undergoes two ionization pathways. Since linearity is observed between

$[M+NO_3]^-$ or $[M-H]^-$ ions of Nitrate-CIMS to $[M+Na]^+$ ions of the Dual-EESI, combined linearity is also expected for sum of the $[M+NO_3]^-$ and $[M-H]^-$ ions from CIMS as shown in the updated figure below.



We updated the caption that the two ionization pathways of Nitrate-CIMS for the same compound may not have the same sensitivities.

Updated caption for Figure 6: *"*Comparison between the Dual-EESI and Nitrate-CIMS for a series of TMB oxidation products in the gas phase. Since some analytes detected in Nitrate-CIMS might have two ionization pathways via deprotonation or nitration, for each analyte M, we compared $[M-H]^-$, $[M+NO_3]^-$ and $[M-H]^-$+ $[M+NO_3]^-$ from Nitrate-CIMS to the $[M+Na]^+$ of the Dual-EESI. Please note that summation of detected ions in CIMS was only implemented for ions which can be detected in both $[M-H]^-$ and $[M+NO_3]^-$ of the same compound, where their respective sensitivities in Nitrate-CIMS may differ. (a) Normalized signal of the Dual-EESI and the Nitrate-CIMS to their respective maxima where the color scale indicates the oxygen number. (b) Averaged intensity ratio between the Dual-EESI in the gas phase and Nitrate-CIMS for TMB products with different oxygen numbers ($C_9H_{12,14,16}O_{3-8}$).*"*

Modified line 324-326: *"*Figure 6a shows that Na^+-adduct formation in the Dual-EESI in the gas phase is linear with respect to the two different ionization pathways of the Nitrate CIMS, where some analytes undergo two different ionization pathways (Riva et al., 2019).*"*

Line 335: There is no discussion of how the saturation concentration for Figure 7 is calculated. Is it based on the attributed molecular formula? What conclusion am I supposed to draw from the C* trend?

The original figure caption cited Donahue et al. (2011) for the calculation of saturation concentration; we now clarify that this is based on molecular formulae. Using this calculation, we demonstrated that saturation concentration cannot explain the relative gas-to-particle sensitivity response of the Dual-EESI. This is now stated in the manuscript at line 344-348:

*"*The spread in Figure 7 indicates that the saturation vapor concentration alone is insufficient to describe the differences in gas vs. particle relative response factors for the Dual-EESI. Other factors such as diffusivity may also contribute, the unclear correlation ($R^2 = 0.115$) between the gas/particle sensitivity ratio and binary diffusivity values estimated using only molecular formulae (Fuller et al., 1996) could be caused by the lacking knowledge of analyte structures.*"*

Figure 7: are those actually arbitrary units? Or is that signal? The authors confidently discuss signal ratios, so I think this is signal, but that's not clear.

We removed (A.U.) and updated Figure 7 label axis for clarity.

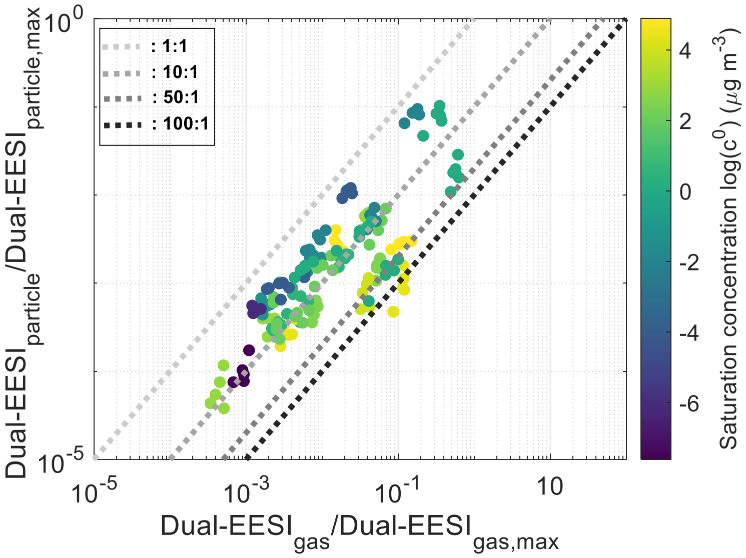


Figure S6 did not render legibly in my pdf

We re-rendered Figure S6.