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.

RC1 (*https://doi.org/10.5194/amt-2021-325-RC1*)

Summary:

The authors introduce a new inlet called the Dual-EESI that combines with a TOF mass spectrometer to alternately measure both gas and particle phases over the span of several minutes. Several flow tube experiments were performed and compared with CIMS measurements to show the proof of concept. They find that the EESI is more sensitive to gas phase compounds than particle phase. Future work will be to develop quantification methods for both phases. Generally, I believe this inlet will be a powerful addition to the EESI technique. But to make that true, I believe the background signal (specifically the signal due to desorption from tubing and EESI walls) needs to be better considered and characterized for sticky or semivolatile compounds (which are a focus of the manuscript). Failure to do so could lead to substantial measurement biases for such compounds. I think this will require major revisions, and perhaps an adjustment to the inlet configuration or sampling method. Once the backgrounds are properly considered, the Dual-EESI will certainly be a valuable inlet and would be appropriate for publication in AMT.

We thank the reviewer for his comments and respond below to his concerns about the performance of the inlet for semi-volatile compounds.

Main comments:

Line 92 and Fig. S5: This figure is used to draw the conclusion that there is essentially no difference in gas-wall interactions across the four tubing types. However, I do not think this experiment was a great way of testing that, because it did not isolate the tubing response. Instead, the measurements are combing the responses resulting from the UV lamps warming up (in the two left hand panels), the residence time distribution of the two flow tubes (especially smearing the decay in the right hand panels), and any wall interactions in the inlet/IMR of the acetate CIMS being used to sample the compounds. Please address the following related to this comment:

-The wall interactions in the acetate CIMS could be negligible if sampling with the Eisele-type IMR at atmospheric pressure, but could be considerable if sampling in a low pressure IMR; please specify.

We used an Eisele-type atmospheric pressure chemical ionization inlet with nitric acid reagent ion in this study as mentioned at line 161. This is now also mentioned in the caption of Figure S5. The new figure caption reads as follows:

"The oxidation product signal was measured by an Eisele-type atmospheric pressure chemical ionization inlet (Nitrate-CIMS) connected after the Dual-EESI inlet at 10 L min^{-1} sampling flow.***"***

-I think what Fig. S5 (especially when turning UV off) does suggest is that these two particular compounds are reaching equilibrium with the wall surfaces of all tubing types on a time scale that is less than the 2-3 min decay time needed to flush out the flow tubes. So while you can't say whether there are differences between tubing types, this essentially shows that the tubing type does not matter for these two compounds when sampling this flow tube setup because the dominant wall effects are elsewhere (and obscured by the lamp warming up or the flow tubes flushing out). My guess is that the tubing wall effects are not dominant because 1) the residence time in that tubing is short, minimizing the adsorption or absorption to the wall relative the compounds that get sampled without first interacting with a wall, and 2) any compounds that desorb from the wall get diluted in the fast (2-10 liter per minute) flow, so concentrations remain relatively low. For comparison, the flow rates used in e.g. Deming et al 2019 and Pagonis et al 2017 were much slower (often 0.3 liters per min) through a meter or more of tubing, leading to much larger wall effects. I suggest you discuss these details in your manuscript in the paragraph at line 92, otherwise please explain if you have a different interpretation. Also, Palm et al. 2019 (https://doi.org/10.5194/amt-12-5829-2019) is another resource that may be helpful for thinking about tubing/inlet wall effects along with the Deming, Pagonis, and Liu papers.

We agree with the reviewer's assessments and interpretations. We used high flows, similar to CIMS, to minimize the residence time in the inlet and thus the adsorption of compounds onto the inlet walls. We moved the part of Figure S5 discussion in experimental section 2.1 to the result section 3.2. The revised text reads as follows:

In Section 2.1, line 89-97:

"We tested four different tubing materials—conductive perfluoroalkoxy alkane (PFA), conductive polytetrafluoroethylene (PTFE), stainless steel 306 and coated stainless steel 306—to determine desorption responses of semi-volatile compounds (SVOCs) in the Dual-EESI inlet as shown in Figure S5. Unless specified otherwise, stainless steel 306 tubing coated with functionalized hydrogenated amorphous silicon (SilcoNert 2000, Silcotek GmbH, Germany) was chosen for its rigidness, which allows for stable particle transmission and a lower adsorption rate in comparison to uncoated stainless steel 306 (Pagonis et al., 2017). A pressure sensor is added upstream of the electrospray region because pressure fluctuations > 5 mbar destabilize the electrospray (ES) signal. For high sampling flow applications (> 5 L min^{-1}, Ø = 40 mm, *L* = 0.5 m), it is recommended to use multiple particle filters in parallel to minimize flow impedance (i.e. pressure drop) as characterized in Figure S6. In this study, a single HEPA filter was used and the excess sampling flow rate was maintained at 5 L min^{-1} unless specified.***"***

In Section 3.2, line 219-230:

"Gas-wall interactions are especially important for semi-volatile and intermediate volatility organic compounds (Pagonis et al., 2017; Deming et al., 2019; Liu et al., 2019). We tested four different tubing materials—conductive perfluoroalkoxy alkane (PFA), conductive polytetrafluoroethylene (PTFE), stainless steel 306 and coated stainless steel 306 for desorption responses semi-volatile compounds in the Dual-EESI inlet. Compounds were generated from the OH oxidation of 1,2,4-trimethylbenzene at 30 % RH and 20 ˚C. The oxidation product signals were measured by an Eisele-type atmospheric pressure chemical ionization inlet (Nitrate-CIMS) connected after the Dual-EESI inlet at 10 L min^{-1} sampling flow. Figure S5 shows that, under our sampling configurations, semi-volatile vapors ($C_9H_{12}O_{4-5}$) quickly equilibrates regardless of the tubing materials. This is most likely because the wall losses are dominated by the presence of other surfaces. The rapid equilibration times of ~3 minutes are likely due to the high flow used which ensures a combination of shorter residence time and higher dilution compared to previous studies (Pagonis et al., 2017; Deming et al., 2019; Liu et al., 2019), where gas-wall interactions were more severe and dependent on wall material. A similar behavior is observed for semi-volatile oxidation products of α-pinene + ozone ($C_{10}H_{16}O_3$ and $C_{10}H_{16}O_5$, Figure 4), measured by the Dual-EESI at 5 L min^{-1} sampling flow.***"***

-Lastly, this analysis applies only to the two compounds shown in Fig. S5. It's not clear whether those compounds are particularly 'sticky' or not. Could there be 'stickier' compounds that would interact more with the walls, and then show important differences as a function of tubing type? I'm not asking for a full analysis across a range of C* values, but perhaps you could just state what the estimated C* values are for the two compounds you show? That could help put your measurements in context with the broader measurements in the Pagonis, Deming, Liu, Palm papers.

We focused on semivolatiles measurement here because compounds that are stickier than $C_9H_{12}O_{4\text{-}5}$ might exist mostly in particle phase, leaving the gas-phase concentration below detection limit under the current experimental conditions. As requested, we added the estimated log(c*) values for these two compounds in the caption of Figure S5 as “log(c^*) = 0.06 and -1.97 μg m^{-3}, respectively, calculated from molecular formula according to (Donahue et al, 2011)***”.***

We also noted in the main text result section 3.2 at line 229-230:

“A similar behavior is observed for semi-volatile oxidation products of α-pinene + ozone ($C_{10}H_{16}O_3$ and $C_{10}H_{16}O_5$, Figure 4), measured by the Dual-EESI at 5 L min^{-1} sampling flow.***”***

Line 186: There are a few issues with this discussion of the camphor background percentage here. First, the 1.2-1.5% camphor signal measured at the end of the combined FP-PP-FP cycle is not the appropriate gas phase background to subtract from the amount of camphor sampled at the end of each TP mode. Again, I will suggest that you consider the framework presented in Palm et al. 2019 (https://doi.org/10.5194/amt-12-5829-2019). The total signal at the end of TP is the sum of the signal from compounds that are sampled directly without wall interaction plus the amount of background signal from compounds that had interacted with a surface (which depends on how much and how long a compound was sampled) and then desorbed to be sampled. That background signal is dynamic and depends on the sampling history. A more appropriate gas phase background to subtract would be that measured immediately after switching from TP to FP (after the residence time of the tubing has cleared). The concentration measured at that time will be a close approximation of the amount of background signal generated at the end of TP. For camphor in Fig. 2, it looks like the background signal could be ~10% or more of the total signal. For stickier compounds, this value could be even higher, for example it looks like ~30% of the signal for $C9H12O8$ in Fig. S18. By waiting to the end of the FP-PP-FP cycle, the background signal decays due to desorption from tubing and EESI wall surfaces while sampling clean (scrubbed) air, and is no longer relevant to the end of the prior TP. However, even the background measured shortly after switching from TP to FP is not completely accurate, because you are simultaneously changing the sources of background by switching the tubing the air is sampled through. During TP, the background can come from both the blue tubing and the EESI inner surfaces (including tubing between the blue tubing and the EESI). But when sampling FP, you cut out the background coming from the blue tubing and only sample that from the EESI (assuming the background from the walls downstream of the carbon denuder is negligible). Now, if the background coming from the blue tubing is negligible compared to the background coming from inside the EESI, then this doesn’t matter and your background measurements will be close enough. But if the blue tubing is a substantial source of signal, this could be a major problem for sampling some sticky or semivolatile gases through this inlet. This could be tested by sampling a sticky compound and then injecting clean air for several seconds either upstream or downstream of the blue tubing to see if there is a difference (which would be due to background signal in the blue tubing). To summarize this lengthy comment, please carefully consider (and be explicit about) your background determination and subtraction methods, determine if the current inlet configuration and sampling method is sufficient, and make adjustments if necessary to reduce/remove these biases.

We agree that measurement of the background is non-trivial. The two main considerations are the differences between sampling pathways when switching from TP to FP and desorption kinetics. Regarding the first issue, our analysis of the tubing material effect above suggests that the sampling tube-vapor interaction is likely minor, and that the background is dominated by surface-vapor interactions at the mass spectrometer inlet. The use of charcoal denuder in the green channel in Figure 1 (PP and FP) should not affect particle-related backgrounds, and also eliminates the effects of upstream sampling differences between pathways (e.g., desorption from HEPA filter). Therefore, the FP and PP channels should be applicable for TP background measurements. The appropriate background-correction strategy is an area of active debate in the literature, with studies such as Palm et al. (2019) preferring a fast zero-method (i.e. FP_1). We note that Palm et al., (2019) used an improved, coaxial ion-molecule reaction ionization region, which reduced vapor-wall interactions and shortened the signal rise time compared to more conventional IMR designs. In the present system, our sampling scheme follows FP_0-TP-FP_1-PP-FP_2, where FP_0 is the FP_2 from the previous sample

cycle. We show that the rise time from FP_0 to TP is very short compared to what has been reported for IMR-CIMS, indicating that vapor-wall interaction is minor. The background rapidly decays during FP_1 and remains relatively stable during FP_2. We also show that there is no appreciable change in FP_2 values (and where $FP_0 \approx FP_2$), when the sampling channels are being alternated during measurements. For these reasons, we prefer to use FP_2 as our background. We clarify our sampling schemes, the difference between two FP periods (FP_1 and FP_2), and our choice of background 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.***"***

Line 335: I believe this Dual-EESI inlet will be very valuable for being able to sample gases and particles at the same time. It's not clear to me, though, that it will be as useful for deducing SVOC volatilities. I believe that to be an extremely difficult task for any instrument or combination of instruments, just given measurement uncertainties for both gas and particle measurements. This may be too much to ask for this paper, but I'm wondering of you could provide an estimate of how large the error bars will be on a calculation of the C* value for a given compound? E.g. you could make assumptions about the relative sensitivities and measurement uncertainties for a compound in the gas vs. particle phase, and propagate the measurement uncertainties through to estimate the uncertainty on partitioning fraction or C*. My guess is the uncertainties in C* will be an order of magnitude or so, and will only be able to be estimated for the 2-3 or so order of magnitude range where semivolatile compounds are measurable in both phases above detection limit simultaneously. In the end, maybe it is enough to be able to say whether or not a compound is semivolatile. Any thoughts you have about the utility of the Dual-EESI in this respect would be useful to add to the manuscript, though again this is not to take away from the other very useful aspects of the Dual-EESI.

We agree with the reviewer's assessment and have incorporated into our conclusion.

Line 360-361: ***"***Using the Na^+-adduct formation for gas- and particle-phase species measurements, the Dual-EESI simplifies the gas and particle-phase composition analysis.***"***

Line 364-366: ***"***We also compare the relative sensitivity of gaseous versus particulate species, which as shown in Fig. 7 are linearly related but with considerable spread. This introduces approximately a factor of 11 uncertainty in using the particle-phase calibration to estimate gas-phase concentrations. This factor of 11 likewise dominates the uncertainty in estimating the partitioning coefficient for SVOC (0.3 μg m^{-3} ≤ c^* ≤ 300 μg m^{-3} under typical ambient conditions (C_{OA}~10 μg m^{-3}).***"***

Line 346: The correlation of R^2 = 0.115 in Fig. S25 is quite low, so it does not seem to justify your conclusion here that higher gas relative to particle phase detection is correlated with diffusivity in air. Perhaps the estimation of diffusivity based on molecular formula (without knowledge of structure) leads to uncertainties that are too high in the diffusivity estimation? Anyway, I would suggest it would be fine to leave Fig. S25 out.

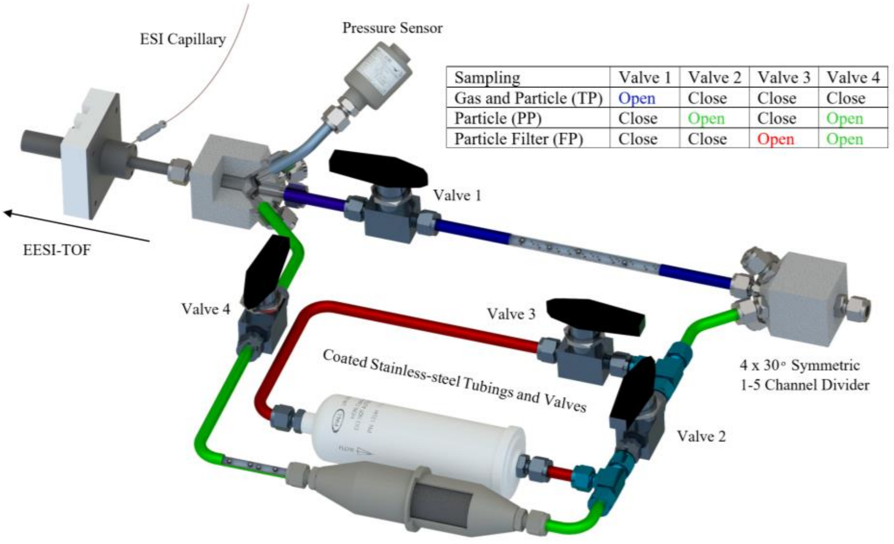
We agree that the low R^2 value could be due to the high uncertainty of parameterization used to estimated molecular diffusivity without structural information. We have revised our discussion of Figure S25 **accordingly and we** ***have revised our discussion of Figure S25 as follows.***

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.***"***

Technical comments:

Fig. 1: The legend is difficult to understand. I would suggest labelling the valves and identifying which ones are open or closed for each sampling method, rather than which sampling lines are open or closed. For instance, one of the valves on the green line has to be closed during particle filter mode. Also, particle filter mode is labeled as background in the legend, please make them the same to be consistent.

We updated the Fig. 1 as requested for the labelling of the valves and background as shown below.



Sampling	Valve 1	Valve 2	Valve 3	Valve 4
Gas and Particle (TP)	Open	Close	Close	Close
Particle (PP)	Close	Open	Close	Open
Particle Filter (FP)	Close	Close	Open	Open

Fig. S6: This figure didn't copy correctly.

We re-rendered Figure S6.

Line 168: Here also, be consistent with the labelling of each mode, i.e., use TP, PP, and FP instead of gas a particle, particle, and background measurement.

We changed the labelling of each mode by using TP, PP and FP instead of gas and particle, particle and background measurement.

Line 171: Isn't EESI not expected to happen in the FP mode, when the particles have been filtered out prior to sampling?

We clarified the ionization setting 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 308: missing ")" at the end of "(right panel of Figure 5".

We added the missing ")".

Fig. S12: The inlet should be labeled "Dual-Phase-EESI-Inlet" instead of ESI.

We updated Fig. S12 using Dual-Phase-EESI-Inlet label as shown below.