Response to reviewers for the paper "Absorption of VOCs by polymer tubing: implications for indoor air and use as a simple gas-phase volatility separation technique" Melissa A. Morris , Demetrios Pagonis , Douglas A. Day , Joost A. de Gouw , Paul J. Ziemann , and Jose L. Jimenez

We thank the reviewers for their comments on our paper. To guide the review process we have copied the reviewer comments in black text. Our responses are in regular blue font. We have responded to all the referee comments and made alterations to our paper **in bold text**. All line numbers refer to the originally submitted manuscript.

Anonymous Referee #2

Overview:

R2.0. The manuscript describes a new measurement technique to separate gas-phase organic compounds by volatility using different types of sampling tubing. This is an innovative approach that can be leveraged by the broader atmospheric research community to address major research challenges related to, for example, gas and aerosol chemistry of volatile organics in complex mixtures. It is also incredibly valuable that the research group publishes all the models they have developed on their website that is open access to everyone. The introduction is very clear and nicely places the work in context with prior literature. The figures are publication quality and clearly demonstrate major findings from the systematic testing of partitioning delays of different tubing material across a range of compound volatilities. However, the paper seems to end prematurely without demonstrating the use of the gas volatility separator technique in a real measurement application with a mixture of organics. How would one leverage this technique to develop plots of the relative contribution of different volatility classes in the original sample? That still isn't entirely clear. I also think the manuscript could be strengthened by focusing the tables and figures in the main manuscript on the most critical findings and leaving some of the details for the SI. It was a little challenging to pull the main points out of all the details. I recommend the paper for publication after some (mostly) minor revisions that address the concerns summarized here and described below.

Major comments:

R2.1 One of the key findings is the tubing categorization as slow vs fast vs adsorption only. Figure 2 is a nice illustration of the differences between the tubing types for the range of compound volatilities studied. Figure 3 is more challenging to read. Particularly 3b. There are too many lines with too many different colors and dashes. If the main point is just to illustrate that the SLM does not work for polypropylene, I think it would be more effective to show the time-series example for 1 of the ketones (not 2) and then also provide a more quantitative metric for the model prediction for all the compounds in a table next to the graph. What was your metric for deciding when the SML model worked or it didn't? You provide all the details about the fit parameters for the model but no clear quantitative description to evaluate how well the models did at predicting the measurements. Even just a simple linear regression comparing modeled vs measured values at each time point could possibly work to draw a more objective line between a "good fit" and a "poor fit."

For figure 3, we think that it is important to show both C_{10} and C_{12} ketones for the single vs multiple layer model in panel (b), as it illustrates some key features of the model and the data. However, we understand that having so many traces in one graph can be confusing. We have revised the graph to make 4 instead of
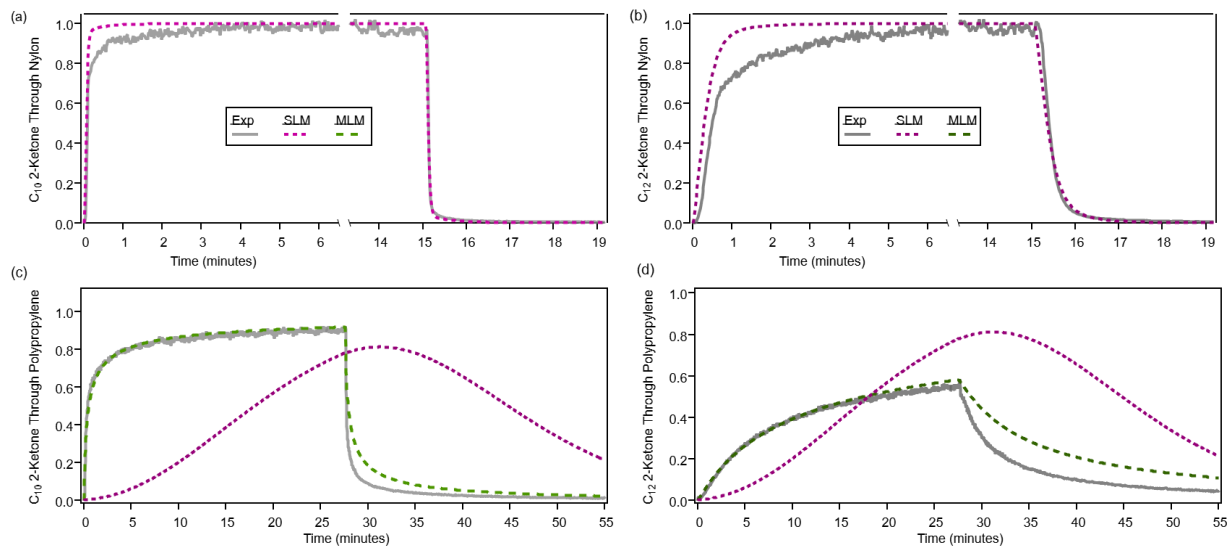
Please also see the response to R1.2(c), where we have made changes to the manuscript to be more quantitative with our model fitting metrics.

R2.2 Section 3.1.3 doesn't appear to be providing critical information about the key results. The only figures cited are in the SI, not in the main text. Perhaps this entire section could be moved to the SI? It reads as a minor technical point.

We believe that this short section adds value in the main manuscript. It explains why the model fits are still imperfect with the multilayer model, and points the reader to the literature that would need to be explored if a better fitting model was desired.

R2.3a Section 3.2. It was surprising to read that the absorption delay times are often larger than the desorption delay times for the slow-diffusion materials. This point appears to be glossed over fairly quickly, but could the authors describe the implications of this for using the GVS technique to classify volatility distributions from an ambient measurement?

As discussed in section 3.1.3 and our previous response to R2.2, the material-VOC interactions show some more complex behaviors that are not perfectly captured by the model. As also discussed in response to comment R1.8 (and the text added to the manuscript quoted there), it is important for users of this method to perform their own calibrations with the tubing system and species of interest.

In our field application mentioned above (response to R1.4b) we used a Vocus PTRMS to sample the output of the tubing, which allows a clearer interpretation of the data.

R2.3b How long does slow-diffusion tubing need to be conditioned before reaching equilibrium?

The timescale to reach equilibration when sampling through the slow-diffusion tubing depends on the

flow rate, the geometry of the tubing, and the volatility of the compounds sampled. In our work, at a nominal flow rate of 2 LPM, slow-diffusion tubing reached equilibrium with highly volatile species in 1 second or less, while other species took up to 25 minutes to reach equilibrium. As this is apparent from the time series shown in the figures, we have not modified the manuscript in response to this point.

R2.3c Why would there be more variability in absorption delays than desorption delays?

See response to R2.3a.

R2.4 Does it make sense for Section 3.2 to be its own section? I think the description of key findings in Figure 5 would be more clear if they were discussed in the same section instead of separated between sections 3.2 and 3.3.1 and 3.3.2.

We prefer to keep the sections as they are. The logic for their separation is clear, as 3.2 refers to materials used to sample gases only, while 3.3 discusses materials used to sample gases and particles simultaneously. This concerns two mostly separate research communities, and thus we think the presentation of the material in this order is quite practical.

R2.5 Figure 8b is the most important figure of the entire paper and it is buried at the end. I think it would be more effective to move this before some of the technical details about humidity effects on desorption of metal tubing or contaminant peaks in conductive tubing (new vs aged).

We also like Fig. 8b a lot, but we do not think it is "buried." It needs to be discussed after the conductive silicone tubing has been discussed. It makes most sense to us to discuss the silicone tubing artifacts in the same section as all other aspects of that tubing. Also, the section discussing the stainless tubings is conceptually similar to the preceding sections, and more different from the final section on the GVS. Thus we prefer to keep the current order of the sections, with Figure 8b at the end, as it relies on information shared throughout the manuscript.

R2.6 The abstract states, "we demonstrate how to use a combination of slow- and fast-diffusion tubing to separate a mixture of VOCs into volatility classes," but the paper actually stops just short of actually demonstrating that. Can you take the data shown in Figure 8a and develop a synthesized volatility distribution of the starting mixture from that data? Figure 8b shows the distribution being transmitted through each of the different tubes, but the demonstration is missing that final step of actually reverse-engineering the original volatility distribution. I think it would have been even more compelling to demonstrate how this would work with two different mixtures composed of contrasting contributions from SVOC/IVOC compounds.

We understand the reviewer's point. However, it would be circular to use the data for the ketones to determine the properties of the GVS, and then use the GVS to retrieve the volatility distribution of the ketones. We do not have the system set up at present to conduct more experiments with other mixtures, which in any case would be a substantial amount of work, perhaps enough for its own separate manuscript. Instead, we have changed the sentence in the abstract to read:

"We demonstrate a system combining several slow- and fast-diffusion tubings that can be used to separate a mixture of VOCs into volatility classes."

Technical comments:
R2.7 Lines 252-255: It wasn't entirely clear what the authors meant by "short times" and "long times" in this description. Do you mean earlier in the absorption phase and later in the absorption phase of the sampling cycle?

We have reworded this text to clarify this point. Lines 250-256 originally read:

"The desorption of the fast diffusion materials proceeded at a changing rate, initially being faster than the corresponding absorption rate, and later being slower than the corresponding absorption rate (as shown in Fig. S7). This meant that, at short times, compounds diffused out of the polymer faster than they went in, and at long times, compounds diffused out of the polymer slower than they went in. The behavior at long times is expected; to enter the polymer, compounds just partition to the surface, but to exit the polymer, compounds must diffuse back to the surface before re-partitioning into the gas phase, therefore taking longer to exit than enter. The behavior at short times was a surprise."

and have been replaced with:

"The desorption of the fast diffusion materials proceeded at a changing rate, initially being faster than the corresponding absorption rate, and later being slower than the corresponding absorption rate (as shown in Fig. S7). This meant that, early in the absorption period, compounds diffused out of the polymer faster than they went in, and later in the absorption period, compounds diffused out of the polymer slower than they went in. The behavior at later times is expected; to enter the polymer, compounds just partition to the surface, but to exit the polymer, compounds must diffuse back to the surface before re-partitioning into the gas phase, therefore taking longer to exit than enter. The behavior early in the absorption period was a surprise."

R2.8 Line 260: unclear what is meant by having to "split the difference" to model the whole time series.

Lines 259-261 originally read:

"We noticed this anomaly in our data while modeling; the multilayer model could reproduce either the absorption period or the desorption period for a material very well, but had to split the difference between the two periods to model the whole time series (as shown in Fig. S8)."

and have been replaced with the following text to clarify this point:

"We noticed this anomaly in our data while modeling. When the model was asked to optimize the fit parameters to just the absorption period of the data, the resulting desorption period had high model error (as shown in Fig. S8). The inverse was true when the model was asked to optimize the fit parameters to just the desorption period. When the model was asked to optimize the fit parameters to the whole time series, they fell in between the absorption-only and desorption-only fit

parameters, and provided an adequate but not perfect fit to both periods."

R2.9 Lines 329-331: I think this sentence is supposed to be the final sentence of the preceding paragraph. Otherwise it is unclear what "these" materials refers to.

Lines 328 and 329 have become one paragraph.

R2.10 Line 355: typo in the sentence, "We believe this due to the…"

Line 355 has been revised to read "We believe this **is** due to the…"

In addition to the changes listed above, we have made some additional small changes for clarity, described at the end of the response to reviewer #1.