Response to Referee #1 Report

Overview: The authors have appropriately responded to all reviewer comments.

Thank you for taking the time to review the revised manuscript and to make further suggestions. We have made point-by-point responses below in blue, with the corresponding updates to the manuscript text indicated in green/quoted.

Comment 1: A remaining point is that some of the responses are not reflected in the updated manuscript - the information that monoterpene fragmentation was accounted for and that the authors do not expect toluene and benzene peaks to be impacted by it; and why 5 Hz was chosen as a measurement frequency.

Previous comments and responses on monoterpene fragmentation:

l. 153: Are the authors sure that there is no fragment of monoterpenes on the toluene (and potentially also benzene) mass in the PTR? See Kari et al. (2018)

With the soft ionization conditions used during NAAMES, there is no significant monoterpene fragmentation to m/z 93 (used to quantify toluene) or 79 (used to quantify benzene). There is still fragmentation to m/z 81 (~50 %) and m/z 95 (minor), but this is corrected.

l. 540 ff: Are these really benzene/toluene? Please consider fragmentation as discussed by Kari et al. (2018).

See response to l. 153.

We have now added to the manuscript:

"**Table 1** lists the compounds examined in this study, which include methanol (detected as $CH_4O{\cdot}H^+$ at *m/z* 33.033), acetonitrile ($C_2H_3N{\cdot}H^+$, 42.034), acetaldehyde ($C_2H_4O{\cdot}H^+$, 45.033), methanethiol ($CH_4S{\cdot}H^+$, 49.011), acetone ($C_3H_6O{\cdot}H^+$, 59.049), dimethyl sulfide ($C_2H_6S{\cdot}H^+$, 63.026), methylethyl ketone ($C_4H_8O{\cdot}H^+$, 73.065), dimethyl sulfoxide ($C_2H_6SO{\cdot}H^+$, 79.021), benzene ($C_6H_6{\cdot}H^+$, 79.054), toluene ($C_7H_8{\cdot}H^+$, 93.070), C8 aromatics ($C_8H_{10}{\cdot}H^+$, 107.086), C9 aromatics ($C_9H_{12}{\cdot}H^+$, 121.101), and monoterpenes ($C_{10}H_{16}{\cdot}H^+$, 137.132) (Pagonis et al., 2019). The mass used to measure isoprene ($C_5H_8{\cdot}H^+$, 69.070) was affected by contamination issues and we therefore omit this compound. The monoterpene signal was corrected for fragmentation to *m/z* 81.070 (~ 50 %) and 95.086 (minor); fragmentation to *m/z* 93.070 and 79.054 was insignificant due to the soft ionization conditions. Acetone and MEK are detected with their isomeric aldehydes (propanal; n-butanal + 2-methylpropanal). However, observations during the Atmospheric Tomography Mission (ATom) over the North Atlantic show the ketones to be dominant in this environment, with aldehyde:ketone ratios of 0.02-0.05 (propanal:acetone) and 0.16-0.23 (n-butanal:MEK; 2-methylpropanal was not detected) (Thompson et al., 2022; Apel et al., 2021; Wofsy et al., 2021). Furthermore, n-butanal is strongly fragmented (> 50 %) by the first-generation PTR-ToF-MS ion funnel deployed during NAAMES and was primarily detected at *m/z* 55.054 rather than 73.065. We therefore presume the NAAMES measurements of Σ(acetone + propanal) and Σ(MEK + n-butanal + 2-methylpropanal) to be dominated by acetone and MEK for the discussion that follows. The remaining masses above are assumed here to be dominated by the individual species listed."

Previous comment and response on the reason for 5 Hz measurements:

l. 110: Why were the measurements not conducted at 10 Hz?

Eddy covariance was not the original objective of the NAAMES study, and 5 Hz measurements were performed for a combination of practical reasons (e.g., file size, data load) and based on the measurement PI's prior scientific experience.

We have now added to the manuscript:

"The NAAMES measurements were conducted at 5 Hz sampling frequency (selected as a compromise between response time, file size, and data load) with an estimated accuracy of 10 % + 5 ppt."

Comment 2: Regarding the 5Hz/10Hz question: I assume that the 5Hz resolution helped the signal/noise ratio? Would averaging to an even lower time resolution work for this dataset (considering that you saw most fluxes at less than 1 Hz time resolution) and give an even better signal/noise ratio in concentration measurements and thus the resulting fluxes, so that the USN would be reduced?

It is a fair question. Averaging to 5 Hz (or potentially to 1 Hz) reduces USN accordingly. However, the flux calculation itself also reduces the influence of USN, since in principle noise that is not correlated with the wind fluctuations is to some extent filtered out. And then there is the tradeoff that at lower measurement frequencies one starts to miss the high-frequency flux contributions, introducing another type of error that will depend on the specific surface and meteorological conditions.

A quantitative examination of these specific effects, and their interactions, is beyond the scope of what we can accomplish here. We have added the following statement acknowledging that this is still an open question:

"Future work could extend these findings by exploring the extent to which different measurement frequencies may mitigate USN impacts, and the resulting trade-offs with high-frequency flux attenuation."

Comment 3: The comment on line 287 where I asked whether method iii) is the same that is called "noise covariance method" in Wolfe et al. (2015) was probably not clearly phrased, but I was confused regarding the naming of the methods and whether they are the same (because the phrase "noise covariance method" does not appear in this study's text), not doubting that the paper was correctly cited. Please use the name used in the original paper where it is appropriate so that readers do not struggle to find out which method from the reference was used.

The supplement of Wolfe et al. (2015) (Section S2.3 and Figure S16) discusses two error methods, the "white noise error" (steps 1-4 in Section S2.3 and y-axis in Figure S16) and the "standard error of the covariance" (equation 6 and x-axis of Figure S16). Our Method iii refers to the latter. We describe it as "the $\overline{w's'}$ standard error" while Wolfe et al. describe it as either "the <w'x'> Standard Error" (in Figure S16) or "standard error of the covariance" (on page S6). So we feel the naming is consistent as is.

References

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