Responses to the Reviewers for the Manuscript Submitted to Atmospheric Measurement Techniques entitled "A modular approach to volatile organic compound samplers for tethered balloon and drone platforms" (amt-2024-96)

Note: Reviewer comments are in blue, our responses to the reviewers are in black, and changes to the text are included in red.

Comments to Reviewers:

We would like to thank all reviewers for their time and contributions to improving the manuscript. As requested, major and minor revisions have been made to improve the clarity, introduction, language, analysis, and interpretation. All minor/grammatical revisions were incorporated, and major revisions are discussed in more detail in the comments below.

Reviewer #2

This article describes the conceptual design and deployment of a battery-powered sampler that was used for the collection of volatile organic compounds onto multi-stage solid adsorbent cartridges from a tethered balloon and a drone platform. The sampler was deployed at two sampling locations in Texas and data from these campaigns are presented.

While I appreciate the effort that was put into the study and preparation of the manuscript, in my opinion this work has crucial deficiencies.

There are quite a few other previous tethered balloon and drone VOC sampling systems and deployments that have been reported in the literature. There is relatively little novelty in the particular sampling approach and deployment presented here. Furthermore, I consider the data rather questionable for the reasons described below.

Response: The authors greatly appreciate reviewer 2. They acknowledge there are several UAV (i.e. drone) based sampling systems described within the literature. However, there is a lack of TBS based sampling systems described within the literature. Addressing this knowledge gap is the focus of this manuscript (see research goals 1 and 2 presented in the last paragraph of the introduction). Lastly, additional descriptions regarding QA/QC (i.e., error, accuracy, and precision; see comments/responses below) were also greatly expanded, which markedly improved and strengthened the manuscript.

Specific Comments:

Comment #1: The analytical experiments do not specify the accuracy and precision of the sampling and analysis method.

> **Response #1:** The authors thank the reviewer for their comment. After reviewing the data, the authors estimated a 30% error to reflect the variability in the sampling (e.g., flowrate accuracy) and analysis method (e.g., sampling efficiency, sorbent tube desorption, and instrumental response variability). These error estimates have been added to the text of the manuscript (see below), for example, the flow meter used to calibrate

the sample flow has an error of 2%. Moreover, when sampling using a UAV, potential vertical mixing caused by the UAV propellers introduces an estimated altitude error of ± 5 m (Ventura Diaz and Yoon, 2018; Mckinney et al., 2019). These error estimates were also incorporated into the methods and results sections for clarity (see below).

Lines 157 – 159, "Before each sampling day, a flow calibration was conducted on each sorbent tube to account for potential variability among the tubes and to ensure the flow remained at 0.1 ± 0.002 lpm, as measured using a flowmeter (Model 5200, TSI Inc, MN, USA)."

Lines 200 – 202, "A 30% error was applied to the VOC measurements to reflect the variability in the sampling (e.g., flowrate accuracy) and analysis method (e.g., sampling efficiency, sorbent tube desorption, and instrumental response variability). Specifically, the flow meter used to calibrate the sample flow has an error of 2%.

Lines 117 – 121, "Previous studies have investigated the air velocity distribution around UAVs and found the air flushing time below the UAV is much faster (i.e., seconds) than the VOC sampling timescale (i.e., 10 min), therefore the VOC samples may represent air parcel extending up to ± 5 m surrounding the sampling height (Ventura Diaz and Yoon, 2018; Mckinney et al., 2019). As such, a ± 5 m was applied to the sampling altitudes presented in the text associated with VOC measurements."

Comment #2: The effect of the downwash from the UAV rotors on the actual effective sampling height is not addressed.

Response #2: The error associated with the vertical mixing of the sampled air parcel due to UAV propellers has now been addressed in the response to reviewer Comment #1.

Previous studies have investigated the air velocity distribution around UAVs and found the air flushing time below the UAV is faster (i.e., seconds) than the VOC sampling timescale (i.e., 10 min), therefore the VOC samples represent an air parcel extending up to ± 5 m surrounding the sampling height (Ventura Diaz and Yoon, 2018; Mckinney et al., 2019). The flushing time is likely to be dependent on the size of the UAV, therefore smaller ones may have smaller flush times. The UAV we use is on the same size as the one in (Mckinney et al., 2019), which aligns with the ± 5 m estimation. Furthermore, the models suggest that the area under the UAV body is the least impacted by turbulent flow and therefore the best place to sample VOCs. The following text has been added to the manuscript

Lines 117 – 121, "Previous studies have investigated the air velocity distribution around UAVs and found the air flushing time below the UAV is much faster (i.e., seconds) than the VOC sampling timescale (i.e., 10 min), therefore the VOC samples may represent air parcel extending up to ± 5 m surrounding the sampling height (Ventura Diaz and Yoon, 2018; Mckinney et al., 2019). As such, a ± 5 m was applied to the sampling altitudes presented in the text associated with VOC measurements."

Comment #3: It appears that sampling tubes do not seem to have shutoff valves on the inlet side but are always open to the outside air during the flight, which allows them to passively sample VOCs during the entire deployment. These types of adsorbent tubes have been found to have passive uptake rates of approximately 0.5 ml/min in typical deployments at the surface (e.g. [*Mowrer et al.*, 1996; *Walgraeve et al.*, 2011; *Markes*, 2021]). This sampling rate might be higher under the highly turbulent conditions during the flight deployment. This will add substantial additional sampling VOCs during times when there is no active (pumped) sampling. For instance, if a deployment would be 2 hours from the time of installation to the removal, this would add on the order or 60 ml of sampling to the 1 l of sampling at the deployment altitude. VOCs might be higher at the surface than aloft, so one will never know exactly now much of the analysis results actually reflects the VOCs mole fraction at the balloon sampling height.

Response #3: The authors agree the sorbent tubes can be used in both active (i.e., pumped) and passive sampling, thus the authors collected several passive samples on TBS and UAV flights to characterize any sampling artefacts resulting from passive sampling. These sampling blank tubes (e.g., passive) were analyzed in the same manner as the sample tubes (e.g., active) and revealed collection of minimal masses of the measured VOCs from passive sampling (e.g., < 5% of the mass collected on the active sampled tubes). During the QA/QC process, the authors also blank corrected their VOC samples for potential passive sampling during flights (as described above), travel, and storage prior to chemical analysis. Therefore, the VOC values presented in the manuscript represent the most conservative values and are designed not to overestimate the VOC amount collected. For additional information the following text was added.

Lines 198 – 200, "Following chemical analysis, the samples underwent a blank correction to account for artefacts from passive sampling, travel, storage prior to analysis, and potential laboratory contamination."

Comment #4: The manuscript does not clearly state that samples are collected sequentially. The profiling data do not truly represent vertical profiles as intended in this sampling, but also need to consider that atmospheric VOCs may change rather rapidly in plumes in an urban or suburban environment. This temporal aspect of the sampling is not recognized in the manuscript.

Response #4: The authors have added details to the manuscript to clarify that the samples were collected sequentially during the test flights and the sample flights. Evidence of the samples being collected sequentially is also provided in Figures 2 & 3, which show a timeseries of the meteorological, ozone, VOC, and aerosol data. The specific text addressing this comment is below. Additionally, a note describing the temporal offsets during descending legs of the flights as it relates to VOC measurements was also provided (see below).

Lines 214 – 215, “During sampling, each sorbent tube was used once, while the process (i.e. powering the pump and opening and closing a unique combination of values) was repeated sequentially until all samples were collected.”

Lines 236 – 238, “Sequential VOC samples were collected on three of the August 4th flights, including a morning flight (Flight #2, Sample 1), a midday flight (Flight #3, Samples 2 and 3) and a late afternoon flight (Flight #6, Samples 4, 5, and 6).”

Lines 216 – 217, “Note, these sequential samples provide VOCs measurements along a vertical TBS or UAV flight, where VOCs measurement are offset temporally during the descent leg of the flight.”

Comment #5: It has long been known [*Goldan et al.*, 1995] [*Pollmann et al.*, 2005] that unsaturated VOCs, in particular biogenic VOCs such as isoprene, undergo rearrangement and loss during atmospheric sampling with prefocusing techniques from reaction with ozone in ambient air. A series of approaches have been researched and used by researchers over the years to mitigate this artifact [*Helmig*, 1997]. It does not appear that the sampler had any sort of scrubber for selective removal of ozone in the sampling flow path. It is therefore questionable if and what fraction of the actually present VOCs were captured by the sampling protocol.

Response #5: Similar to a number of UAV systems described in the literature (Chen et al., 2018; Mckinney et al., 2019; Batista et al., 2019; Asher et al., 2021; Li et al., 2021; Leitner et al., 2023; Zhai et al., 2025), this system did not incorporate an ozone scrubber prior to the sorbent tube. This potential issue has been acknowledged in the manuscript (see conclusions and future considerations). However, it is important to note that while VOCs may have large reactivity coefficients with the hydroxyl radical, for example isoprene’s $k_{OH} \approx 100 \times 10^{-12}$ cm^{-3} mol^{-1} s^{-1}, they can have smaller reactivity coefficients with ozone, $k_{O3} \approx 1 \times 10^{-12}$ cm^{-3} mol^{-1} s^{-1} (Atkinson and Arey, 2003). Based on the estimated lifetime of isoprene with the hydroxyl radical (1 -2 hours; (Atkinson, 2000)) and the two order of magnitude difference in the reactivity coefficients, the isoprene ozone half-life is estimated to be significantly longer (e.g., hours to days) than the active sampling period (10 minutes).

Comment #6: Calibrating the adsorbent sampling with diluted liquid solutions is far from ideal as it does not reflect the actual air sampling. Utilization of certified VOC compressed gas standards is a much more widely used and accepted way for calibration in atmospheric VOCs monitoring.

Response #6: The authors agree with the reviewer that compressed gas standards are also used to calibrate VOC instrumentation and are likely considered the gold standard for atmospheric VOC monitoring, particularly for online gas phase instrumentation such as a PTR-MS. Moreover, our group operates a PTR-MS that is calibrated using certified gas standards and we recognize that acquiring these types of standards can be difficult to obtain with lead times taking at least 6 – 12 months (as there is a limited number of

vendors that supply custom VOC blends, such as Apel-Riemer Environmental Inc). However, more importantly these types of certified gas standards are for a select few VOCs and often are designed for instruments such as the PTR-MS. This means that they often are missing VOCs typically not measured using PTR-MS or the Aerodyne Vocus. These types of calibration gases also require a dilution system or approach that provides different concentrations to the instrument. Otherwise, they are calibrating at one single concentration, whereas we deployed a minimum of 5 calibration concentrations using certified liquid standard solutions with dynamic linear ranges varying with individual VOC sensitivity.

In this study, sampling is specifically designed to be portable to assess a wide range of VOCs. Certified liquid standard solutions for calibration or internal standards are a necessity for any TD-GC/MS system (Mckinney et al., 2019). Moreover, utilizing diluted liquid solutions to calibrate sorbent tubes is also a well-established and accepted calibration approach for offline analysis. Liquid standard solutions have been used for sorbent tube analysis in several studies, including (Ribes et al., 2007; Gallego et al., 2010; Gallego et al., 2012; Schieweck et al., 2018; Schieweck et al., 2021; Hellén et al., 2024). In addition, the US EPA TO-17 method for the analysis of VOCs from active sampling onto adsorbent tubes enables both gas and liquid standards to be used for calibration purposes.

Comment #7: I could not find the Dieu Hein , 2019, reference (line 55) in the references list.

Response #7: The Dieu Hein reference was added to the list of references. The sentence was also reworded as

Lines 65 – 68, "A review of vertical sampling technologies for VOCs highlighted the limitations of available chemically sensitive sensors for aerial platforms and noted the UAV's potential to carry payloads consisting of multiple sensors and provide high spatiotemporally resolved data (Dieu Hien et al., 2019)."

Comment #8: The sampling only captures a subset of VOCs present in the atmosphere, probably well below half of the total VOC ppbC. This needs to be realized. The term 'Total VOC concentration' (line 286) is not quite accurate in this context.

Response #8: The authors thank the reviewer for the comment and apologize for any confusion caused by the terminology. The intent was not to refer to the total VOCs present in the atmosphere at a given time but rather the VOCs included in our list of target analytes. Where applicable, the terminology has been changed to "select VOCs" or "VOC mixing ratio". To clarify this further and provide appropriate context, the following sentence has been added to section 3.3,

Lines 326 – 327, "It is important to emphasize that the analytes quantified in this study represent only a select subset of the total VOCs present in the atmosphere."

Comment #9: Results are presented in ppb, which is a mole fraction unit. Calling this a concentration (e.g. line 288) is not correct.

> **Response #9:** VOC mixing ratios are typically presented as ppbv. This has been corrected throughout the manuscript including the specific line 288 given by the reviewer.

Comment #10: The url that is provided for the data availability statement only leads to the archive portal, but not to the particular data that were generated in the study.

> **Response #10:** The link for the TBS data was updated and text describing data availability was provided for the UAV measurements. Note: The data generated in the study were part of two TRACER field campaigns and were funded by different agencies (see below)
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> Lines 415 – 418, "TBS VOC data from select flights are presented here and can be found through the ARM Data Discovery portal, along with all ARM data used in this study (https://iop.archive.arm.gov/arm-iop/2022/hou/tracer-ozone/usenko-tbsvoc/?ticket=ST-25071-YsBQmA--n2APXsJidpMOvKzmbtQ-prod-cas-fwapp-5cdbdb454-dn9sh Last access date: 7 January 2025). The UAV VOC data is available upon request from the TCEQ."

Comment #11: Information provided in Table S2 is not clear. What does the product number refer to? What are the numbers in columns 4 and 5? Significant figures are inconsistent.

> **Response #11:** The product numbers in the table refer to the vendor product number. For clarity, the vendor name was added to the Table S2 caption (Sigma Aldrich). The table was also adjusted to center the lower and upper limit of the calibration range (i.e., columns 4 and 5) under the table header. The significant figures were also modified and limited to two.

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