

Reply on RC1

Thank you very much for your valuable comments and suggestions on our manuscript. We appreciate the time and effort you have invested in reviewing our work.

The manuscript, "Surprisingly high levels and activity contributions of oxygenated volatile organic compounds on the southeast of the Tibetan Plateau" based on the VOCs online observation experiment at the South-East Tibetan plateau Station for integrated observation and research of alpine environment in Lulang. It is 101 VOCs species were detected, including 13 OVOCs. The authors analyzed the contribution of OVOCs to VOCs concentration, OH• reactivity and OFP in the southeastern Tibetan Plateau. At the same time, PMF and PAP source analysis methods were combined to explain the maximum possible OVOCs contribution sources. However, there are doubts about the method used by the author to analyze OVOCs species by GS-MS/FID. The concentration of OVOCs obtained by GS-MS/FID method currently has a large uncertainty, so it is impossible to determine whether the conclusion obtained in this paper is correct. Therefore, the publication of this paper cannot be accepted, with deep regret.

Response: Regarding the concern about the method used to analyze OVOCs species by GC-MS/FID, we would like to clarify and provide additional information.

Firstly, the online GC-MS/FID analyzer we used is a mature and commercially available instrument which has been developed and utilized in field campaigns over the years (Wang et al., 2014). Moreover, the use of GC-MS for reporting measured OVOCs is not novel, as similar instruments have been widely utilized in various observations (Geir Legreid et al., 2007a, 2007b; X.P. Lyu et al., 2016; Wu et al., 2020; Yunfeng Li et al., 2021). To ensure the instrument's stability and the accuracy of our data, we implemented stringent quality control and assurance measures throughout the analysis process.

Secondly, regarding the VOCs and OVOCs data collected at the Lulang Observation Station, we have conducted data comparisons with other instruments, such as PTR-MS, used by other research teams for synchronized observations. The consistency of the data is satisfactory, e.g. a correlation coefficient (R) of 0.82 for acetone, further reinforcing the reliability of our measurements.

We hope that these clarifications and additional information address your concerns. Once again, we appreciate your valuable input and look forward to any further suggestions that could enhance our work.

Reference:

Wang, M., Zeng, L., Lu, S., Shao, M., Liu, X., Yu, X., Chen, W., Yuan, B., Zhang, Q., Hu, M., and Zhang, Z.: Development and validation of a cryogen-free automatic gas chromatograph system (GC-MS/FID) for online measurements of volatile organic compounds, *Anal. Methods*, 6, 9424–9434, <https://doi.org/10.1039/c4ay01855a>, 2014.

Geir Legreid, Stefan Reimann, Martin Steinbacher, Johannes Staehelin, Dickon Young, and Konrad Stemmler. Measurements of OVOCs and NMHCs in a Swiss Highway Tunnel for Estimation of Road Transport Emissions, *Environ. Sci. Technol.*, 41, 20, 7060–7066, 2007, <https://doi.org/10.1021/es062309>

Geir Legreid, Jacob Balzani Lo"o"v, Johannes Staehelin, Christoph Hueglin, Matthias Hill, Brigitte Buchmann, Andre S.H. Prevot, Stefan Reimann, Oxygenated volatile organic compounds (OVOCs) at an urban background

site in Zürich (Europe): Seasonal variation and source allocation, *Atmospheric Environment*, 41: 8409–8423, 2007b

X.P. Lyu, N. Chen, H. Guo, W.H. Zhang, N. Wang, Y. Wang, M. Liu, Ambient volatile organic compounds and their effect on ozone production in Wuhan, central China, *Science of The Total Environment*, 541, 200-209, 2016.

Wu, C., Wang, C., Wang, S., Wang, W., Yuan, B., Qi, J., Wang, B., Wang, H., Wang, C., Song, W., Wang, X., Hu, W., Lou, S., Ye, C., Peng, Y., Wang, Z., Huangfu, Y., Xie, Y., Zhu, M., Zheng, J., Wang, X., Jiang, B., Zhang, Z., and Shao, M.: Measurement report: Important contributions of oxygenated compounds to emissions and chemistry of volatile organic compounds in urban air, *Atmos. Chem. Phys.*, 20, 14769–14785, <https://doi.org/10.5194/acp-20-14769-2020>, 2020.

Yunfeng Li, Rui Gao, Likun Xue, Zhenhai Wu, Xue Yang, Jian Gao, Lihong Ren, Hong Li, Yanqin Ren, Gang Li, Chuanxian Li, Zeliang Yan, Ming Hu, Qingzhu Zhang, Yisheng Xu, Ambient volatile organic compounds at Wudang Mountain in Central China: Characteristics, sources and implications to ozone formation, *Atmospheric Research*, 250, 105359, 2021, <https://doi.org/10.1016/j.atmosres.2020.105359>.

Specific comments

EPA TO15 and TO11A standard methods specify the analysis methods of NMHCs and carbonyl compounds in atmosphere respectively. When GS-MS/FID is used to analyze highly polar carbonyl compounds, there is a large uncertainty. The same adsorption column is used to detect OVOCs and other VOCs species, and the adsorption effect of the column adsorbed other VOCs is not good for polar OVOCs. Meanwhile, humidity and wall effect will make the GC-MS/FID method very susceptible to the detection of OVOCs species. Secondly, GS-MS/FID cannot detect formaldehyde, which accounts for a large proportion of OVOCs in daily detection. And the absence of formaldehyde may lead to the underestimation of the contribution of OVOCs to VOCs concentration and OFP, which has great limitations on the analysis of the nature of OVOCs species. Therefore, the current GC-MS/FID method for detecting OVOCs species is not reliable. The data thus obtained cannot lead to correct conclusions.

Response: Thank you for your further comments and suggestions. We appreciate your feedback and have addressed the points raised below.

Regarding the concerns about the reliability of the GC-MS/FID method for analyzing OVOCs species, we would like to clarify our instrument parameters and method settings. Our GCMS instrument parameters and method settings for this study are based on our previously published article in *Atmos. Chem. Phys.* (23, 10383–10397, 2023; <https://doi.org/10.5194/acp-23-10383-2023>), where we used the same instrument and method.

In our GCMS/FID setup, we employed two different chromatographic columns for separation. The PLOT A1203 chromatographic column (15 m × 0.32 mm inner diameter (i.d.) × 3 μm; J&W Scientific, USA) was used for the separation of 13 C₂-C₅ hydrocarbons, while the moderately polar DB-624 column (60 m × 0.25 mm i.d. × 1.4 μm; J&W Scientific, USA) was used for the separation of other VOCs, including OVOCs. Before the VOCs entered the chromatographic columns for separation, water, CO₂, and O₃ were removed to minimize interference in the analysis.

During the observation period, we performed multi-point calibrations using standard samples, and the linear correlation (R^2) for OVOC species was greater than 0.99 (Figure 1). Additionally, a daily span check was conducted (Figure 2). Although humidity and wall effects can indeed introduce some interference in measurements, our rigorous quality control measures have helped to reduce the uncertainty in OVOC measurements to a certain extent.

Regarding formaldehyde, GCMS method was not quantitative for its analysis. The absence of formaldehyde does indeed lead to an underestimation of the contribution of OVOCs. Typically, the concentration of formaldehyde in the atmospheric environment is slightly higher than that of acetaldehyde. Based on the VOCs data obtained during our measurements at Lulang, we found that the contribution of OVOCs, excluding formaldehyde, to concentration and reactivity is already significant. This does not affect our current conclusions and motivates us to further investigate atmospheric OVOCs in the future.

In the revised manuscript, we will incorporate additional measurement details and engage in a thorough discussion regarding the absence of other oxygenated volatile organic compounds (OVOCs), particularly formaldehyde.

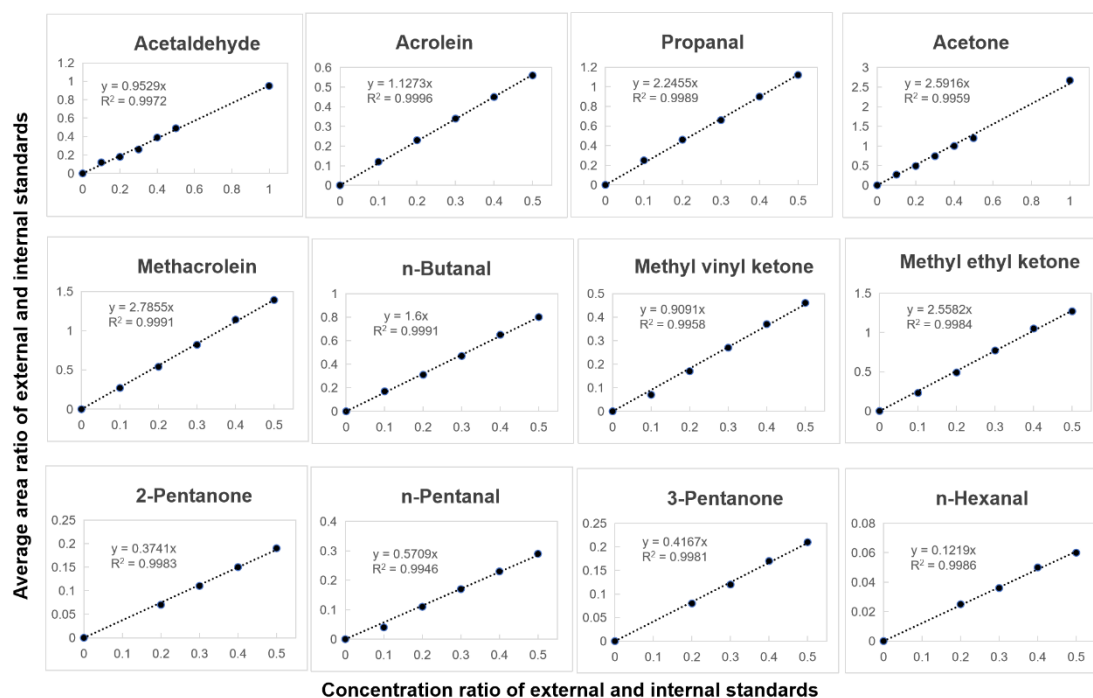


Figure 1. Multi-point calibration results of OVOCs

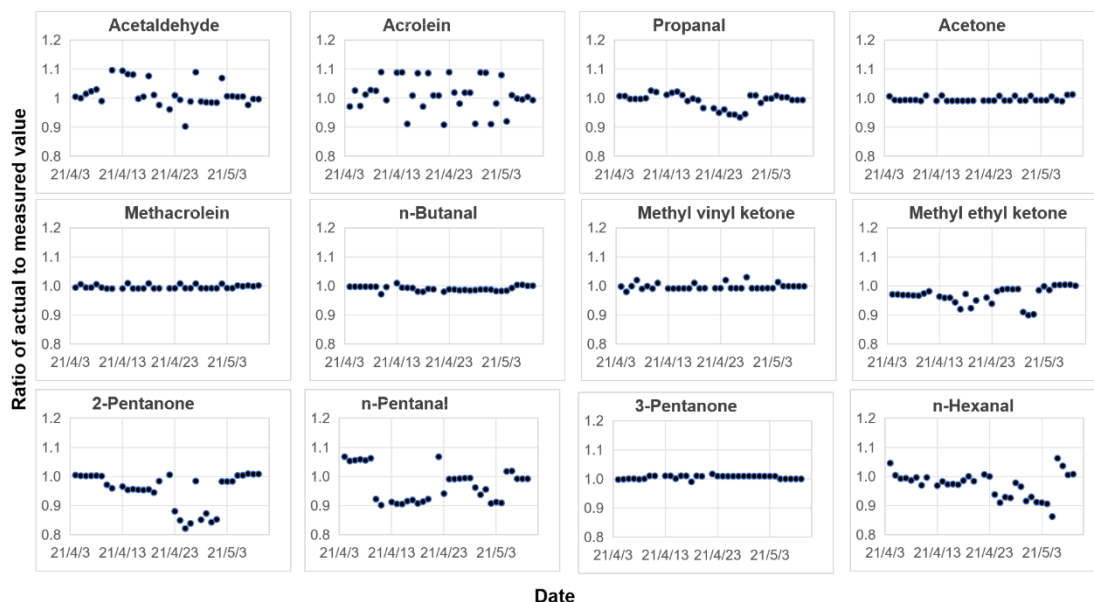


Figure 2 Time-series variations in daily span check results

In lines 72-76, when describing the situation around the observation site, the author mainly introduced the sites tens of kilometers away. This description does not seem to highlight the point, nor does it play a significant role in understanding the origin of OVOCs species at the Lulang. It is suggested that the author consider the description here and make changes.

Response: The observation site is located in the forested regions over an area of 2.46 million hectares, accounting for 53% of the total land area and with a forest coverage rate is 46%. Other than the limited pollutants' emissions of the 318 national highway running through it, the most nearby anthropogenic emission source might be the nearby towns and cities. Our original intention in introducing these distant populated areas was to emphasize the remoteness and sparsity of the Qinghai-Tibet Plateau, as well as to suggest that anthropogenic emissions from these regions, although distant, may contribute to the background VOCs concentrations. Additionally, we included this description to provide a broader understanding of this lesser-known area, aiming to familiarize readers with its unique characteristics. We will rewrite and add some information in the revised manuscript.

Lines 160-173 describe the dominant species in no obvious order or logic, but the conclusion of the paragraph in line 173 states that OVOCs and alkenes have an important effect on the air of Lulang. It is suggested that OVOCs and other VOCs species should be explained in two parts based on the conclusion.

Response: We have rewritten the paragraph to ensure a logical flow of information and better align with the conclusion stated in Line 173. Here is a revised version:

"Figure 2 presents the 50 species with the highest mixing ratios, along with their corresponding VOC- K_{OH} , OFP, and SOAP values. These 50 species collectively accounted for 98.5% of the TVOCs. Among them, acetaldehyde and acetone emerged as significant contributors, with mixing ratios of 1.96 ± 1.71 and 1.87 ± 0.69 ppb, respectively. These two species alone accounted for 16.7% and 16.0% of the TVOCs. Acetaldehyde, due to its high reactivity, made the largest contribution to VOC- K_{OH} and the OFP.

In contrast, ethane and acetylene, despite having mixing ratios of 1.46 and 0.52 ppb, respectively, and ranking third and fourth among the 50 species, contributed relatively little to VOC-k_{OH} and the OFP due to their lower reactivity. Other species, such as alpha-pinene, also stood out. Although its mixing ratio was 0.10 ± 0.03 ppb, ranking 25th, it made significant contributions to VOC-k_{OH} (5th, 6.2%) and the OFP (12th, 2.8%).

Additionally, alpha-pinene's contribution to the SOAP was second only to aromatics. Isoprene, despite its low mixing ratio of 0.02 ± 0.01 ppb and accounting for only 0.2% of the TVOCs, made a notable contribution of 1.5% to VOC-k_{OH} due to its high reactivity with k_{OH}. MACR and MVK, secondary products of isoprene, with a combined mixing ratio of 0.13 ppb, were also significant, contributing 4.0% to VOC-k_{OH} and 4.3% to the OFP.

Overall, the analysis reveals that OVOCs and alkenes, including acetaldehyde, acetone, alpha-pinene, and isoprene, play a crucial role in shaping the air quality at Lulang. Their combined effects on VOC-k_{OH}, OFP, and SOAP underscore their importance in the region's atmospheric chemistry."

In lines 174-185, in the comparison between this experiment and other background sites or ordinary sites, the comparison logic is rather confused, and I can't see what the author wants to highlight at last. It is suggested that the author clarify the description logic, rearrange the content, and summarize the corresponding conclusion.

Response: To clarify the description and rearrange the content, we have revised the paragraph as follows:

"The mean TVOC mixing ratio observed in this study was compared with previous observations in mountain sites Table S1 presents a comparison of the levels of major alkane, alkene, acetylene, and aromatic species reported in the literature with those determined in the present study. Our comparison results suggest high altitude and low temperature might account for relatively low TVOC observed in this study. Specifically, our observation was slightly lower than that previous measurement conducted at Mt. Wudang in Hubei Province during May to June 2018 (12.17 ± 3.66 ppb; Li et al., 2021). Furthermore, the average mixing ratio of 52 C₄–C₁₂ compounds observed at Lulang was lower than the values reported for Mt. Tai in June 2006 (6.95 ± 5.71 ppb; Mao et al., 2009) and Gongga Mountain in Sichuan Province for the period January 2008 to December 2011 (8.75 ± 5.76 ppb; Zhang et al., 2014b). However, it is evident that the levels observed in this study were close to those reported at the Menyuan atmospheric background station (Zhao et al., 2020) and the Waliguan World Meteorological Organization Global Atmosphere Watch (GAW) station (Xue et al., 2013), both located on the northeast of the Tibetan Plateau. The overall TVOC mixing ratio in these observations roughly follows the rule of "high temperature and more abundant VOCs". As our colleagues extended PTR-MS measurement in May, BVOC mixing ratio almost doubled as compared with PRT-MS observation in April during our campaign period.

TVOC mixing ratios in these maintain sites were approximately 10 times higher than those reported for the Antarctic and Arctic regions (Hellen et al., 2012; Pernov et al., 2021), while substantially lower than those determined at the regional background site, such as Lin'an regional GAW station in the Yangtze River Delta, rural stations in Tengyue in southwest China (Tang et al., 2009), and Xianghe on the North China Plain (Yang et al., 2020).

In summary, our observation site features a typical atmosphere of subalpine coniferous forest climate with slightly anthropogenic emission perturbation"

In lines 303-315, after completing the fitting of photochemical aging parameters, the author only analyzed acetaldehyde and acetone, and did not mention other species. It is suggested that the author supplement the reasons why these two species were discussed separately, or supplement the analysis of other species.

Response: The reason we focused our analysis on acetaldehyde and acetone is that they are among the most abundant and widely distributed species in the atmosphere, making them highly representative. Their high abundance and diversity of sources, including both anthropogenic and natural origins, make them key compounds in atmospheric chemistry.

While other OVOCs may have lower relative abundances, their sources, as our modeling suggests, are more limited and primarily natural. Given the scope and focus of our study, we chose to prioritize the analysis of acetaldehyde and acetone, which are not only more abundant but also play a crucial role in atmospheric photochemical processes.

We agree that a more comprehensive analysis of other OVOCs would provide additional insights. In the revised manuscript, we will emphasize the rationale behind selecting these two species, while highlighting other photochemical tracers, such as MVK.

Technical comments

In Line 16 of the article, ";" in (TVOCs; average level of 11.7 ± 4.4 ppb) looks some strange. It is suggested that the author to change.

Response: The revised sentence will read: "The 13 OVOCs detected accounted for 49% of the total VOCs (TVOCs), with an average level of 11.7 ± 4.4 ppb."

There are some formatting problems in the illustrations of the article, such as the English font in the figures does not seem to use the New Roman font, and the scale lines of the picture frame sometimes face inward and sometimes face out, so it is suggested that the author should unify to make the graphics more beautiful. Secondly, the vertical axis label fonts of sub-figure 1 in Figure 4 overlap, so it is suggested that the author modify them.

Response: accepted.

In the reference part of the article, the subscript format of "O₃" should also be set. It is suggested that the author check and refer to all literatures and unify the format.

Response: accepted.