Author's Response to Referee Comments

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Manuscript Title: Heat and continental transport shape the variability of volatile organic compounds in the Eastern Mediterranean: Insights from multi-year observations and regional modeling

Review format: Reviewer comments appear in **black**, authors' responses in **blue**, and changes made to the manuscript appear in **red** italics.

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Referee 2

This manuscript "Heat and continental transport shape the variability of volatile organic compounds in the Eastern Mediterranean: Insights from multi-year observations and regional modelling" presents VOCs data measured by PTR-ToF-MS between 2022 and 2024 at a rural background site in Cyprus experiencing heat waves. A detailed discussion is presented on the oxygenated VOCs, the dominant class of VOCs at this site. Long-term time series of OVOCs are relatively rare, yet the authors provided valuable insights by presenting both seasonal and diurnal patterns of these compounds alongside other chemical classes, and by clearly summarizing the contributions from biogenic, anthropogenic, and secondary emissions. In addition, the contribution of the clustered air masses to VOC mixture at this site is presented, including the seasonal variations. Nevertheless, the modelled VOCs by WRF-Chem model simulation overestimate measured VOCs highlighting the limitations of this model under those meteorological conditions. The manuscript deserves publication given the unique dataset acquired and the additional insights it provides. However, several points outlined below require further clarification and detail-

We sincerely thank the reviewer for the detailed and constructive evaluation of our manuscript. We appreciate the positive assessment of the unique multi-year VOC dataset from the rural Cyprus background site and the value of our analysis on seasonal and diurnal patterns, OVOC dominance, source contributions, and air mass influences. The reviewer's suggestions have helped us improve the clarity and completeness of the manuscript, and we have addressed them carefully in the revised version.

Specific comments

Comment 1: L361: Is there an explanation for why concentrations in summer 2022 (Fig. S4), show a less pronounced seasonal pattern in comparison to 2023 and 2024 in summer? The higher VOC concentrations observed in spring 2024 in comparison to the other spring campaigns are also linked to ambient temperature?

We thank the reviewer for the comment. Summer 2022 experienced lower temperatures, leading to weaker seasonality. Spring 2024 had unusually warm conditions that enhanced primary emissions, evaporation, and secondary production. This explanation has been added.

We have added this in manuscript lines (Lines 413-421) as*: "The less pronounced seasonal enhancement observed in summer 2022 compared to 2023 and 2024 is likely due to comparatively lower ambient temperature (of about 1-3 ºC on average), resulting in reduced temperature-driven emissions. In contrast, summer 2024 was characterized by exceptional heat, including record-breaking temperatures (>45ºC) across Cyprus, which strongly intensified direct VOCs emissions and secondary production. June 2024 was the warmest June on record in Cyprus, with 43 of 52 stations registering record maximum temperatures; during the 14–15 June heatwave, maximum temperature reached 45.3 °C, resulting in two heat-related deaths and widespread wildfire impacts (Department of Meteorology, Cyprus, 2024)".*

Comment 2: L437-440: What is the CO diurnal pattern? As CO is mostly influenced by combustion and traffic-related emissions, it could help to give further explanations for the morning and evening peaks.

We thank the reviewer for this insightful comment. In the revised manuscript, we explain the CO diurnal pattern, attributing the early-morning minimum and afternoon-late evening maximum to boundary-layer dynamics and regional transport rather than local traffic emissions, supported by weak correlations with aromatic VOCs and moderate winter-autumn correlations with benzene.

Added text Lines 647-656*: "At the rural Cyprus background site, CO shows a diurnal cycle with an early-morning minimum and an afternoon-late evening maximum, which may be driven by boundary-layer dilution after sunrise and subsequent accumulation under regionally influenced air masses. The generally weak correlation between CO and aromatic VOCs suggests that CO variability is primarily controlled by regional transport and its longer atmospheric lifetime, rather than local traffic emissions. Seasonally, CO exhibits moderate correlations with benzene in autumn (r ≈ 0.4) and winter (r ≈ 0.5), likely reflecting enhanced regional combustion sources, reduced boundary-layer heights, and slower photochemical removal during colder months. Correlations are weak in spring and summer due to stronger photochemical processing and deeper boundary layers. CO shows no correlation with toluene or xylene in any season, consistent with their shorter lifetimes and the absence of fresh local emissions at this background site."*

Comment 3: L460: I'm wondering why ethanol does not show a temperature dependence as it is the case for methanol and acetone. In general, I'm surprised to see in the hierarchical clustering (Fig. 6) that ethanol is not closely related to methanol or acetone.

We agree that this is an interesting observation. The weaker temperature dependence of ethanol reflects its more mixed source profile. Unlike methanol and acetone, which are strongly driven by temperature-dependent biogenic and photochemical production, ethanol receives significant contributions from anthropogenic sources that are less temperature sensitive. This variability also explains why ethanol does not cluster closely with methanol or acetone in Fig. 6, as its temporal behavior is influenced by a broader range of non-biogenic sources.

We have added this discussion in the manuscript (lines 544-549): *"Ethanol also shows temperature dependence, but it is weaker compared to methanol likely reflects its mixed source profile at the study site. While methanol is largely controlled by temperature-driven biogenic emissions and photochemistry, ethanol receives significant contributions from non-biogenic sources (e.g., solvent use, vehicular exhaust, long-range transport, and agriculture), which are less temperature sensitive. As shown in Fig. 5, ethanol levels increase markedly only above 38 ºC, suggesting additional evaporative emissions from anthropogenic sources."*

Comment 4: L565: "The dominant clusters originated from Northwest Asia (C4, 34.3%) and Europe (C3, 33.6%), jointly accounting for more than two-thirds of air mass transport." By looking at the wind rose (Fig. 2d), N-W and S-W are the most dominant wind directions while N-E winds don't seem to be predominant. Fig. 7 showed that the C4 is coming from N-E. Could you explain, for example, why C1 and C2 do not account for a greater proportion to the air mass contribution?

Although the wind rose indicates dominant surface winds from the NW and SW sectors, the back-trajectory clusters represent synoptic-scale transport patterns over several days, which do not necessarily align with near-surface winds at the receptor site. C3 and C4 correspond to persistent, large-scale European and Northwest Asian flows, which occur more frequently compared to the shorter, more locally influenced trajectory pathways represented by C1 and C2. As a result, C3 and C4 collectively contribute more than two-thirds of the long-range air mass transport, despite the dominance of NW-SW winds in the local wind climatology.

Added clarification in L709-712: *"Despite dominant local northwesterly winds (Fig. 2d), air mass back trajectories analyses indicate that the site is influence by long-range transport from Europe and Northwest*

Asia (C3-C4 clusters), Fig. 7, followed by Marine and North Africa regions. ,with little contribution from slow moving trajectories associated with local emissions (C0)".

Comment 5: Section 3.7 on WRF-Chem model simulation. I understand the importance of being able to simulate VOCs mixing ratio. Nevertheless, I felt that this section did not do justice to this dataset, as only good adequations are shown between modeled and measured for isoprene (despite the model can capture the seasonal variations for the other VOCs). It is important to highlight the limitations and the need to improve the model but the authors should give more details on how to improve future estimations, especially as such heat waves even might occur more frequently in the future.
We have expanded the discussion on pathways for improving future VOC estimates, explicitly linking our recommendations to published findings:

Added Lines- 796-806: "Biogenic emission (isoprene and monoterpenes) parameterisations require improved representation of high-temperature and water-stress responses (Sindelarova et al., 2014). In particular, heat-stress emission factors and land-atmosphere coupling should be targeted in future work, consistent with studies showing that drought stress algorithms improve the capability of MEGAN isoprene emission estimates (Wang et al., 2022). Photochemical reaction pathways, chemical ageing and deposition processes that show sensitivity to heat wave atmospheric states can be investigated to more properly quantify atmospheric removal in WRF-CHEM (Knote and Jimenez, 2015; Knote et al., 2015). In addition, wildfire and anthropogenic VOC emissions should be produced using high spatiotemporal (hourly, 1x1 km) resolution to capture the impact of applying diurnal variability and vertical distribution to fire emissions, along with VOC speciation that better reflects regional source profiles."

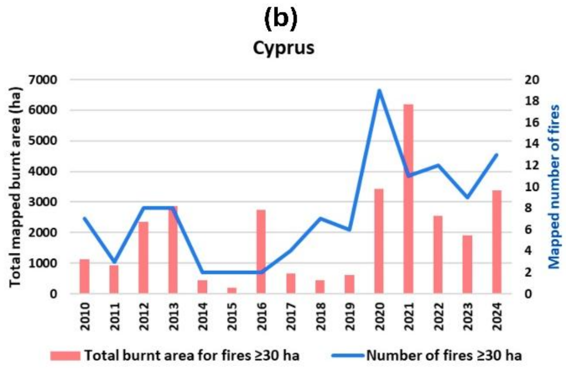
Finally, based on the reviewer's important point about increasing heat wave frequency, we have added discussion emphasizing that these model improvements are critical for reliable prediction of air quality during extreme events under future climate scenarios:

Lines- 855-858: "As the frequency and intensity of heatwaves are projected to increase under future climate scenarios (Zittis et al., 2021; Lelieveld et al., 2016), the non-linear response of VOC emissions to temperature stress must be better parameterized to prevent significant underestimations of SOA and ozone formation."

Comment 6: Wildfires have been mentioned a few times, but it would be an asset to this manuscript if further details could be provided, as the wildfires that occurred in 2022 and 2023 could potentially have been captured at this monitoring site. Did the authors see a typical VOC signature from those wildfires?
Indeed, it is valuable to include the wildfire data of Cyprus in our study. We added a few sentences supporting our results in section 4.3.2.
Lines 603-613 have been added in the section 4.3.2 as- *Wildfire activity may also exhibit pronounced variability and likely influenced the observed VOC composition at the CAO-AMX site (Fig. S6). From 2022-2024, the regional fire activity began in spring; however, its timing and intensity differed substantially. In 2022, the burned area increased rapidly in early summer, exceeding ~1800 ha in June (EEFIS, 2025). In 2023, fire activity was comparatively weaker during spring and early summer, with the largest burned areas occurring later in the season (August-September, 900 and 700 ha respectively). In contrast, 2024 was characterized by an earlier onset of wildfires, with fires occurring from April onwards and peak burned areas of >700 ha in May and ~2250 ha in June. As a result, springtime fire influence was strongest in 2024 compared to 2022 and 2023 (EEFIS, 2025). These spring and summer wildfire episodes, particularly in 2024, are expected to have enhanced biomass-burning-related VOCs at the site. Fire-influenced air masses typically exhibit elevated concentrations of acetonitrile, methanol, and other OVOCs.*

(a)

Year	No. of fires	Burned Area (ha) in Cyprus		
		Total	Forest & wooded	Agricultural & others
2018	131	1136	997	139
2019	99	733	494	239
2020	108	1305	1002	303
2021	111	6612	4791	1821
2022	131	**685/2650**	433	252
2023	19	2010	1270	740
2024	28	**3529**	1542	1987



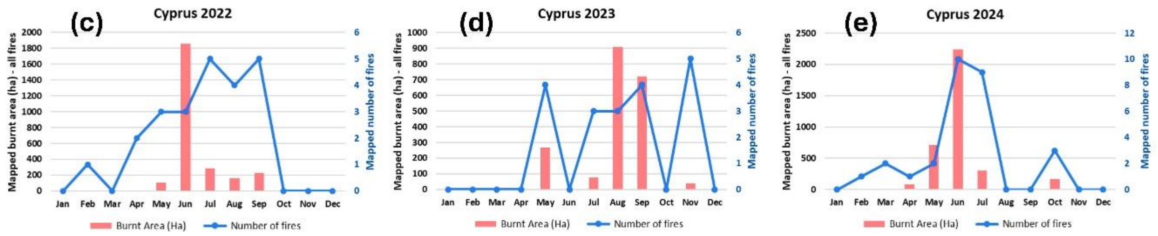


Figure S6. Interannual and seasonal variability of wildfire activity and burned area in Cyprus. (a) Annual statistics of wildfire occurrence and burned area in Cyprus from 2018 to 2024, including total burned area and its partitioning into forested/wooded and agricultural/other land-cover types. (b) Interannual variability (2010-2024) in total burned area and number of large fires (≥30 ha). (c-e) Monthly distribution of burned area and number of fires for 2022, 2023, and 2024, respectively.

Technical corrections

Comment 1: L53-54 "these compounds are frequently classified into the broader categories of oxygenated VOCs (OVOCs), biogenic VOCs (BVOCs), and anthropogenic VOCs (AVOCs), each of the species with distinct sources, reactivities, and atmospheric lifetimes" I found a bit misleading to classify OVOCs as their own category as they can be emitted both from biogenic and anthropogenic sources as well.

We thank the reviewer for pointing this out. We agree that classifying OVOCs as a separate category alongside BVOCs and AVOCs can be misleading, as OVOCs are a chemical class rather than a source-based category and can originate from both biogenic and anthropogenic emissions.

We have revised the text to clarify it. (Lines 85-88) as- Oxygenated VOCs (OVOCs) including alcohols, aldehydes, ketones, and organic acids constitute a chemical class with both biogenic and anthropogenic origins, but they are also predominantly formed secondarily via the oxidation of primary VOCs by hydroxyl radicals (OH), O_3, and nitrate radicals (NO_3) (Huang et al., 2020; Mellouki et al., 2015; Wang et al., 2022b).

Comment 2: L141: What is the concentration of the certified gas standard? How do you calibrate the VOCs that are not included in the gas standard?

We thank the reviewer for the comment. The certified gas standard used for calibration contains major VOCs at approximately 20 ppbv each. For VOCs not included in the gas standard, the quantification was performed using the transmission curve of the PTR-ToF-MS, increasing the uncertainty to 50%.

The concentration of certified gas is mentioned in Lines 169-172.

Comment 3: L210-211: "atmospheric research-hemispheric transport of air pollution (EDGAR-HTAP) version 2 emission inventory. while BVOCs were simulated online": Should be "(EDGAR-HTAP; version 2 emission inventory)? And a comma instead of a period.

The sentence has been revised to correct the punctuation and clarify the reference.
In Line 245: (EDGAR-HTAP) version 2 emission inventory has been converted into (EDGAR-HTAP; version 2) emission inventory.

Comment 4: L213, L629: wrong format for the citation.
Thanks for noting this.
The citation format has been corrected as per the journal format.

Comment 5: In Table SI, the units for the measured VOCs should be indicated.
We thank the reviewer for the comment.
The units for all measured VOCs have been added to Table S1 for clarity.

Comment 6: L229: add a subscript for NO_2.
Thanks for noting it.
The subscript is now added in line 255 and NO2 has been shown as NO_2.

Comment 7: L297-298: "Elevated levels during summer (Fig. 2b) suggest increased biogenic activity and enhanced photochemical production". Fig 2b refers to the seasonal variations of RH, should it be 2a? Additionally, the elevated levels during summer could be linked to solvent evaporation and/or fuel evaporation.
We appreciate the reviewer's observation. The figure reference has been corrected as Fig. 3b, which presents the seasonal variations of VOCs concentrations. Additionally, we have revised the text to acknowledge that elevated summertime VOC levels may also result from increased solvent use and fuel evaporation, in addition to biogenic activity and enhanced photochemical production.
Lines 389-391: Elevated levels of most VOCs during summer (Fig. 3b) suggest the influence of increased biogenic activity and enhanced photochemical production, as well as contributions from solvent use and fuel evaporation.

Comment 8: L393-394: It would be useful to indicate the concentrations for the monoterpenes. By looking at Table 2, it is not clear if the row containing CAO, Cyprus; Winter 2022-24 belongs to this study (likely) or to Debevec et al (2017).
We thank the reviewer for this comment. The row for Cyprus, CAO, Winter 2022–2024 in Table 2 corresponds to our study, and this has now been clarified in the table. In addition, the concentrations of monoterpenes have been explicitly indicated in the main text for clarity.
Table 2 has been updated to clarify that the row for Cyprus, CAO, Winter 2022–2024 refers to the present study. Line 458-460 shows monoterpene concentration now as- *"Monoterpenes, while also of biogenic origin mainly, demonstrated a more even seasonal distribution, with 38% of levels occurring in summer (0.39 ppbv) and 19-22% across other seasons (0.20-0.23 ppbv)".*

Comment 9: L434, 459: It should be Mediterranean Sea.
Corrected as "Mediterranean Sea"

Comment 10: L511: It would be great to indicate the MVK/isoprene ratios for future comparisons.
We thank the reviewer for this helpful suggestion. In the revised manuscript, we now explicitly report and discuss the MVK/Isoprene ratios for daytime and nighttime conditions.
Lines 594-599 were added and shown MVK/Isoprene ratio- *"Also, the elevated nighttime MVK/Isoprene ratio (0.96) indicates substantial isoprene oxidation, consistent with an aged air mass that has undergone prolonged exposure to OH radicals. This further supports enhanced oxidation of biogenic precursors (Guo et al., 2012). In contrast, the lower daytime ratio (0.62) suggests comparatively fresher isoprene*

emissions, reflecting active daytime production of isoprene and limited conversion to MVK, which requires time to form through photochemical processes (Apel et al., 2002).”

Comment 11: Figure 6; on the y and x axis, label "Cluster" is indicated but it is not clear to me what it means.

We have explained it in figure caption as *“Here, cluster denotes the air-mass trajectory group identified by the HYSPLIT back-trajectory analysis (Fig. 7)”*