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 1

In the manuscript 'Heat and continental transport shape the variability of volatile organic compounds in the Eastern Mediterranean: Insights from multi-year observations and regional modelling' submitted to Atmospheric Chemistry and Physics by Grag et al., the authors present conclusions based on a very large dataset spanning over two years of mainly VOC measurements with PTR-ToF-MS at a rural background site in Cyprus, supported by meteorological and air pollution data, as well as modelling with WRF-Chem. The data analysis provided is extensive and detailed, and my main comment is related to the inconsistent grouping of VOCs and I have other small minor comments related to some interpretation of the results and wording.

We sincerely thank the reviewer for the thorough and constructive revision of our manuscript. We appreciate the positive evaluation of the extensive dataset, detailed analysis, and the integration of long-term VOC measurements with meteorological observations and WRF-Chem modelling. We have carefully addressed the comments regarding VOC grouping consistency, as well as all minor comments related to interpretation and wording, which have helped to improve the clarity and robustness of the manuscript.

Major Comments

Comment 1: It appears throughout the manuscript that the 76 "identified" VOCs (even though for many it is simply the chemical composition that has been identified, not a specific VOC) have been grouped in inconsistent ways. I understand that grouping is difficult can be done in various ways depending on what the authors want to discuss, but I would still recommend either unifying the way it is done in the manuscript or alternatively justifying each time why the grouping is done a certain way for each section when presenting results.

We thank the reviewer for this suggestion. We agree that inconsistent grouping could confuse the readers and therefore, we have now adopted a single, unified VOC classification throughout the manuscript based strictly on chemical families:

(1) Oxygenated VOCs (OVOCs),
(2) Aliphatic hydrocarbons,
(3) Aromatic hydrocarbons,
(4) Terpenes,
(5) Nitrogen- and sulfur-containing VOCs.

This framework is now applied consistently across all tables, figures, and text. Source interpretations (biogenic/anthropogenic) are now discussed only narratively. The following changes were incorporated in the revised manuscript:

- Section 3.2 (Lines 320-323): *These VOCs were grouped into five major chemical classes: (i) OVOCs (alcohols, aldehydes, ketones, acids, and other oxygenates); (ii) aliphatic hydrocarbons; (iii) aromatic hydrocarbons; (iv) terpenes; and (v) nitrogen- and sulfur-containing VOCs.*
- Table 1 has been revised by placing isoprene and monoterpenes under the terpenes class rather than the biogenic category.
- In Figure 3, we now justify the separate presentation of OVOCs due to their distinct atmospheric properties.
- The captions of Figures 4 and 5 have also been revised to provide clearer explanations of the applied VOCs classification scheme.
- Other modifications that consider this comment are visible in tracked-changes format of the manuscript.

Comment 2: The abstract and conclusions mention three classes (biogenic, anthropogenic, and secondary/oxygenated) that seem to be the 'main' classification, but it is not really used elsewhere in the manuscript and also, I would argue that is it not a good choice of classification for the following reasons: On the use of 'biogenic' and 'anthropogenic' for compounds: There are several instances in the manuscript where 'biogenic' is used as shorthand for isoprene and monoterpenes and 'anthropogenic' for e.g. aromatics compounds, even though the authors acknowledge themselves in the abstract that monoterpenes have contributions from biogenic and anthropogenic sources, and also mention that aromatic compounds might stem from stress emissions of vegetation. Therefore, this should be made less ambiguous throughout the manuscript, and I recommend the authors to use classification in chemical families for compounds and only discuss sources as 'biogenic/anthropogenic'.

This comment is strongly aligned with comment 1. To address it, we have removed "biogenic compounds" and "anthropogenic compounds" as classification labels and now refer only to chemical families (as discussed in earlier comment). Source attribution is discussed explicitly in the text (e.g., "biogenic sources", "anthropogenic influence", "mixed sources") to avoid ambiguity, especially for monoterpenes and aromatics.

Introduction (Lines 65-85), we have thoroughly revised this paragraph to reduce ambiguity and provide a clearer description of VOC source classifications based on chemical families and known emission pathways.

Comment 3: On the use of 'secondary/oxygenated' (this is only done in conclusions, not the abstract): This is also misleading as it is clear that there are primary sources of oxygenated compounds, so it is probably best not to conflate the two.

We agree and have removed the term "secondary/oxygenated", revising the sentences as:

Lines 880-882 (Conclusions): *"OVOCs (acetone, methanol, acetic acid, acetaldehyde) were enhanced during hot, dry periods, indicating amplified primary emissions and secondary formation".*

Lines 36-38 (abstract): *"OVOCs, including acetone, acetaldehyde, methanol, and acetic acid, showed sharp enhancement above 35 ºC, consistent with intensified primary emissions and secondary formation under extreme heat.*

Lines 85-88 (Introduction):*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 4: On lines 283-286, the authors mention six categories, even though five are listed afterwards. Are N- and S-containing compounds two separate categories? Based on Fig. S3, there seem to be lumped

together in the analysis. Then, the 'groups' in Table 1 are a mix of chemical class (aldehyde, aromatics, etc.) and sources (biogenic) and Figure 2 also use a finer grouping of the compound as well as presenting some compounds with high concentrations individually.

We thank the reviewer for pointing out this inconsistency. We have corrected the text to clearly state that the analysis is based on five chemical classes. Nitrogen- and sulfur-containing VOCs are treated as a single combined class in the main analysis and in Figures S3 and 3, where they are grouped together. In Table 1, and S1 however, we retained separate labels for N-containing and S-containing VOCs solely to indicate the elemental origin of these specific example compounds, not to define additional classes. This clarification has now been added to the text to avoid confusion.

We now mention five VOCs classes as shown in lines- 320-323 of the revised manuscript:
"These VOCs were grouped into five major chemical classes: (i) OVOCs (alcohols, aldehydes, ketones, organic acids, and other oxygenated VOCs; (ii) aliphatic hydrocarbons); (iii) aromatic hydrocarbons; (iv) terpenes; and (v) nitrogen- and sulfur-containing VOCs."

In addition, we added the following text as Table 1 footnote:
"For clarity, nitrogen and sulfur containing VOCs class has been separated into distinct classes, N-containing VOC and S-containing VOC in this table to explicitly highlight the nitrogen contribution in acetonitrile and the sulfur contribution in DMS".

Comment 5: On page 10, Table 1 contains 18 selected VOCs, but the Table does not seem to be mentioned in the text, so that it is not clear what the basis for the selection (are those calibrated compounds?). Line 320 mentions the 20 most abundant VOCs in Fig. S3, but those are then again, a different subset of compounds.

We thank the reviewer for this comment. The manuscript has been revised to clearly explain the different selection criteria for Table 1 and Fig. S3. Table 1 presents VOCs that are most frequently reported in previous studies, allowing comparison with existing literature. In contrast, Fig. S3 shows the 20 most abundant VOCs observed in the present study, selected solely based on measured concentrations. Therefore, the two subsets differ because they serve different purposes.

The text has been revised as follows (Lines 318–320): *"A total of 76 VOCs were quantified, and their descriptive statistics for key species (the most studied VOCs in EMME region and European studies) are summarized in Table 1, while the complete list is provided in supplementary Table S1."*

Comment 6: Table 2 use 'terpenes' (so does title of section 3.3.1), which I would recommend using elsewhere in the manuscript too. However, for someone who is not familiar with VOCs, the group separation in Table 2 is not the clearest. Maybe vertical lines would help?

We appreciate this helpful suggestion. The term terpenes is now used consistently throughout the manuscript, in place of BVOCs, wherever it's appropriate. To improve clarity for readers less familiar with VOC classifications, Table 2 has been reformatted by adding vertical separators to better distinguish compound groups. In addition, group labels have been revised for clarity and consistency.

The term "BVOCs" has been replaced with "terpenes" throughout the manuscript. Table 2 has been reformatted with vertical separators between compound groups. The group labels "nitrile" and "aromatics" have been revised to "N-containing VOCs" and "aromatic hydrocarbons", respectively.

Table 2. Seasonal mean mixing ratios (ppbv) of VOCs measured in our study compared with previous regional and European studies.

Location	Measurement	Study Reference	Year, Season	Terpenes		Aromatic Hydrocarbons			Oxygenated VOCs							N-containing VOC
				Isoprene	Mono-terpenes	Benzene	Toluene	Xylenes	Methanol	Ethanol	Acetic Acid	Acetaldehyde	Acetone	MVK+ Methacrolein	MEK	Acetonitrile
CAO, Cyprus (Background)	PTR-ToF-MS	This study	Spring 2022-24	0.12	0.20	0.14	0.06	0.03	3.22	0.47	0.84	0.97	2.03	0.06	0.35	0.10
			Summer 2022-24	0.18	0.39	1.30	0.07	0.03	3.92	0.35	1.00	0.61	2.90	0.09	0.28	0.13
			Autumn 2022-24	0.06	0.23	0.12	0.06	0.02	2.22	0.23	0.52	0.42	1.90	0.04	0.24	0.12
			Winter 2022-24	0.03	0.22	0.15	0.09	0.04	1.14	0.33	0.27	0.39	1.05	0.03	0.29	0.08
CAO, Cyprus (Background)	PTR-MS, GC-MS	Debevec et al., 2017	Winter, 2015	0.05	0.24	0.12	0.05	0.02	2.93			0.41	1.15	0.03	0.22	0.12
Ineia, Cyprus (Background)	PTR-MS	Derstroff et al., 2017	Summer, 2014	0.06	0.11	0.02	0.01	0.02	2.90		0.95	0.32	2.25	0.03	0.11	0.11
Zurich, Switzerland (Urban background)	GC-MS	Legreid et al., 2007	Spring 2005	0.08		0.41	1.46	0.97	2.18	6.87			1.66	0.04	0.24	
			Summer 2005	0.16		0.23	1.43	0.83	3.18	3.94		0.80	2.12	0.12	0.20	
			Autumn 2005	0.08		0.48	1.70	1.10	1.11	7.61		0.45	1.24	0.04	0.17	
			Winter 2005	0.06		0.75	1.25	0.91	1.21	7.53		0.82	1.17	0.05	0.22	
Athens, Greece (urban)	PTR-MS	Kaltsonoudis et al., 2016	Summer 2012	0.73	0.92	0.22	0.81	0.67		1.52	2.17		4.28	0.35	0.50	0.20
			Winter 2013	1.05	0.43	1.00	2.34	1.69		1.80	2.11		2.24	0.41	0.59	0.16
Cape Corsica, France (urban)	PTR-MS	Michoud et al., 2017	Summer 2013	0.19	0.41	0.03	0.08			0.18			3.43	0.06	0.48	
Oak Mediterranean Forest, France	PTR-MS	Kalogridis et al., 2014	Spring 2012	1.19	0.06	0.07	0.05		2.28			0.38	1.28	0.21		
Oak Mediterranean Forest, Spain	PTR-ToF-MS	Seco et al., 2011	Summer	0.15-0.75	0.13-1.42	0.04-0.09	0.08-0.47		4.14-6.05	1.15-2.87	1.32-2.94	0.54-1.26	2.26-3.83	0.17-0.54		0.16-0.22
			Winter	0.02-0.07	0.005-0.067	0.11-0.19	0.06-0.41		1.28-2.70	0.47-2.08	0.39-1.43	0.23-0.66	0.79-1.55	0.01-0.05		0.08-0.10
Barcelona, Spain (urban background)	PTR-ToF-MS	In't Veld et al., 2024	Spring 2022	0.04	0.05	0.14	0.47		3.50			0.92	1.93	0.09	0.22	0.41
			Summer 2022	0.18	0.19	0.08	0.80		3.73			0.31	2.50	0.17	0.24	0.29
Montseny, Spain (rural background)			Spring 2022	0.05	0.02	0.13	0.22		1.46			0.48	1.02	0.05	0.19	0.10
			Summer 2022	0.30	0.45	0.04	0.09		3.89			0.84	2.76	0.55	0.30	0.12
Oak Mediterranean Forest, Spain	PTR-MS	Yáñez-Serrano et al., 2021	Summer 2019	0.42	0.15	0.04	0.13		4.60			0.77	2.08	0.30	0.29	0.12
			Autumn 2019	0.09	0.09	0.04	0.21		1.60			0.30	1.37	0.08	0.27	0.06

Comment 7: Then, Figure 5 shows the temperature dependence of 16 compounds. The authors could maybe have used the selected compounds of Table 1 for consistency. I understand that using groups of compounds might be less appropriate here for discussion. These same 16 compounds are then used in the following figures. I was wondering if each or some of these compounds are used as proxy for/represent a whole group of compounds. This could be stated explicitly and the selection of compounds to focus on argued more precisely.

We thank the reviewer for this insightful comment. We have clarified that the 16 compounds shown in Fig. 5 were selected as representatives of major VOC chemical families and are well-suited for examining temperature-dependent behaviour. Table 1 includes 18 compounds, of which 16 are used consistently in Figs. 4, 5, and 8, while acrolein and glyoxal are included only for descriptive statistics due to their relevance and widespread study. These two compounds were excluded from the temperature-dependence analysis because of their distinct physicochemical behaviour and secondary formation pathways. The selected 16 VOCs are used as indicators of their respective chemical groups rather than being chosen based on abundance.

Text has been added (Lines 476-477): *"The VOCs selected in this figure serve as representative indicators for their respective chemical families."*

Comment 8: On top of that, I understand that for modelling purpose the grouping and classification has to be done according to the compounds in the model (section 3.7).

This is indeed the case. For the modelling component, the grouping and classification of VOCs necessarily follow the compound structure and chemical mechanism implemented in the model. Recognizing the concerns raised, we have ensured that Section 3.7 strictly adheres to the model-specific compound groupings and have clarified this alignment in the revised manuscript to avoid any ambiguity.

The caption of Figure 9 has been revised to reflect this model-specific classification as: *"The selection, grouping, and classification of VOCs presented in this figure follow the compound categories available within the chemical mechanism of the model to ensure consistency between observations and simulations."*

Comment 9: All this to say that I would recommend using a consistent grouping of compounds throughout the manuscript, which will automatically improve the presentation of the results and the discussion and make it easier to follow for the reader. It will also make the wording of the conclusions clearer, in my opinion. For instance, the authors could use the groups and (representative) compounds from the model and add additional groups from Figure 3. Alternatively, the authors could focus on selected VOCs (Table 1), explaining their decision either because they are the most abundant (or most abundant within their class), or they are the ones for which calibration is available, or they represent a group of compounds or a source (e.g. marine, traffic), or any other clearly-defined reason. I understand the difficulty of presenting clearly such a large dataset and that many people are involved in the data analysis, however, I believe that the manuscript would benefit from streamlining the presentation of the results to tell a consistent story rather than stick together various pieces.

We sincerely thank the reviewer for this comprehensive and constructive comment, which adds further insights to the previous comments regarding the use of consistent grouping. In response, we have reorganized the presentation of the VOC dataset to ensure a uniform grouping strategy throughout the text, tables, figures, and conclusions. The revised manuscript now primarily follows a chemical-family-based compound classification, while incorporating the additional compound groups presented in Figure 3 where relevant.

In line with the responses and actions on the previous comments, the manuscript has been revised to apply a consistent chemical-family-based grouping of VOCs. Compound selection criteria are now explicitly stated, and representative species are harmonized across tables and figure captions.

More specific comments:

Comment 1: Lines 140-143: The authors mention automatization of the blank measurements and calibration once a day. Can the authors comment if these daily measurements have shifted throughout the measurement period, depending on when the instrument was started? Are they distributed more or less equally, or might they influence diurnal patterns? Have some specific hours less data than others due to that?

The automated blank and calibration sequence was intentionally designed to shift in time throughout the measurement period. Specifically, the sequence consisted of 20 minutes of blank measurement followed by 40 minutes of diluted calibration gas and was repeated every 23 hours. As a result, the non-measurement period occurred approximately 1 hour earlier each day, progressively moving through all hours of the day over the course of the campaign. This approach ensured that no specific time of day was systematically underrepresented in the dataset and that the calibration and blank measurements did not bias the observed diurnal patterns.

Lines 169 to 173 have been revised as*: "The instrument was automatically switched to measure VOC-free air for 20 minutes after every 23 hours, followed by 40 minutes of calibration using a certified gas standard (Apel-Riemer Environmental, USA) containing major VOCs diluted to ~20 ppbv. This 23-h cycle caused the non-measurement period to shift by approximately 1 h each day, ensuring that no specific time of day was systematically underrepresented and that diurnal patterns were not biased."*

Comment 2: Sections 2.1 and 2.3: I would include the information regarding the location of the meteorological measurements in section 2.1 and give it a clear label that then can be used in section 2.3 to make it even clearer that the meteorological data is taken from that location, while air pollutants are co-located at the CAO-AMX site (within 20m).

Thanks for this comment. Section 2.1 and 2.3 has been revised as:

"Meteorological data were recorded at a temporal resolution of 5 minutes from a dedicated station located in the village of Xyliatos, approximately 2.85 km from the primary observational site at the CAO-AMX."

Section 2.3 has been revised thoroughly as shown in the track changes format.

Comment 3: Section 2.5: There is a small clarification needed when it comes to the description of the emissions. The authors mention EDGAR-HTAP and MEGAN, but then in the outer model domain mention that EDGAR was used. Is it meant for both anthropogenic and biogenic sources or is it still specifically for anthropogenic emissions (similary to EDGAR-HTAP)

We appreciate the reviewer's observation and therefore, we now specify that EDGAR refers exclusively to anthropogenic emissions, while biogenic emissions are consistently simulated using MEGAN across all domains.

Lines 259:260: *"The EDGAR emission inventory is used for anthropogenic emissions, and MEGAN for biogenic emissions".*

Comment 4: Line 239: the authors mention 'xylene (XYL), representing xylene and more reactive aromatic species'. There are three xylene isomers, so I would suggest writing 'xylene (XYL), representing xylenes (or 'xylene isomers') and more reactive aromatic species' and use 'xylenes' when appropriate and not referring to the modelled species in WRF-Chem. In addition, xylenes have the same mass as ethylbenzene and I'm not sure if it shows up with the same m/z.

The description of XYL has been updated to: *"xylene (XYL) represents xylenes (xylene isomers) and other reactive aromatic species."*

Comment 5: Lines 299-301: The authors write that organic acids 'mainly arise from biogenic emissions, anthropogenic emissions and secondary photochemical oxidation of VOCs' and it made me wonder what other sources there might be.

We appreciate the reviewer's observation. Our intention was to refer specifically to three well-established source categories: (1) direct biogenic emissions, (2) direct anthropogenic emissions, and (3) secondary formation through photochemical oxidation of VOCs. To avoid implying unspecified additional sources, we have removed the word "mainly" and revised the sentence for clarity.

Lines 339-341: *"Organic acids, dominated by acetic acid (median: 0.68 ppbv) and formic acid (median: 0.42 ppbv), contributed 13% of total VOCs. Their contributions likely arise from a combination of direct biogenic and anthropogenic emissions, as well as secondary formation, which could not be quantitatively distinguished".*

Comment 6: Lines 466-467: The authors suggest that a 'probable cause' for increased methanol levels could be 'increased fire activity with average temperature beyond 38°C'.

We have indicated that elevated methanol levels are primarily attributable to biogenic sources, such as plant metabolism and microbial activity, hypothesizing that forest fire emissions can additionally contribute under high-temperature conditions. We have improved the clarity on this occasion by presenting the fire activity as a potential, secondary source rather than the primary cause.

Lines 536-538: *"Elevated methanol levels at high temperature are primarily consistent with biogenic sources, such as plant metabolism and microbial activity, although emissions from forest fires may also contribute under high-temperature conditions. (Paton-Walsh et al., 2008; Yokelson et al., 1999; Dorokhov et al., 2018)".*

Comment 7: Section 3.5: While this is an 'Inter-species relationship' section, when the authors write for example that 'isoprene, monoterpenes, and MVK correlate strongly [...] indicating secondry photochemical formation and biogenic influence during high radiation periods', this seems to mean implicitly that this is the case for isoprene, so compounds correlating with it follow a similar pattern. However, the correlation matrix contains such correlations with environmental conditions, including solar radiation, so the authors could use that information as well to support their statements.

We agree that interpretations regarding biogenic influence and secondary photochemical formation should be supported not only by inter-VOC correlations but also by relationships between VOCs and relevant environmental parameters.

Accordingly, we have revised Section 3.5 to explicitly incorporate correlations between key VOCs (including isoprene, monoterpenes, and MVK) and meteorological variables such as solar radiation and temperature, which are already included in the correlation matrix. This strengthens the evidence for biogenic influence and enhanced photochemical processing during high-radiation periods.

Lines 627-631: *Isoprene strongly correlate with MVK ($r = 0.75$), indicating secondary photochemical formation and biogenic influence during high radiation periods. Isoprene is also positively associated with temperature, and solar radiation ($r=0.5$) indicating that variability in isoprene and MVK is driven by photochemical processing. On the contrary, monoterpenes shows weak correlation at both interspecies level, and with meteorological parameters, showing its mixed sources from both biogenic and anthropogenic origins.*

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 temerature 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 ($r \approx 0.4$) and winter ($r \approx 0.5$), 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

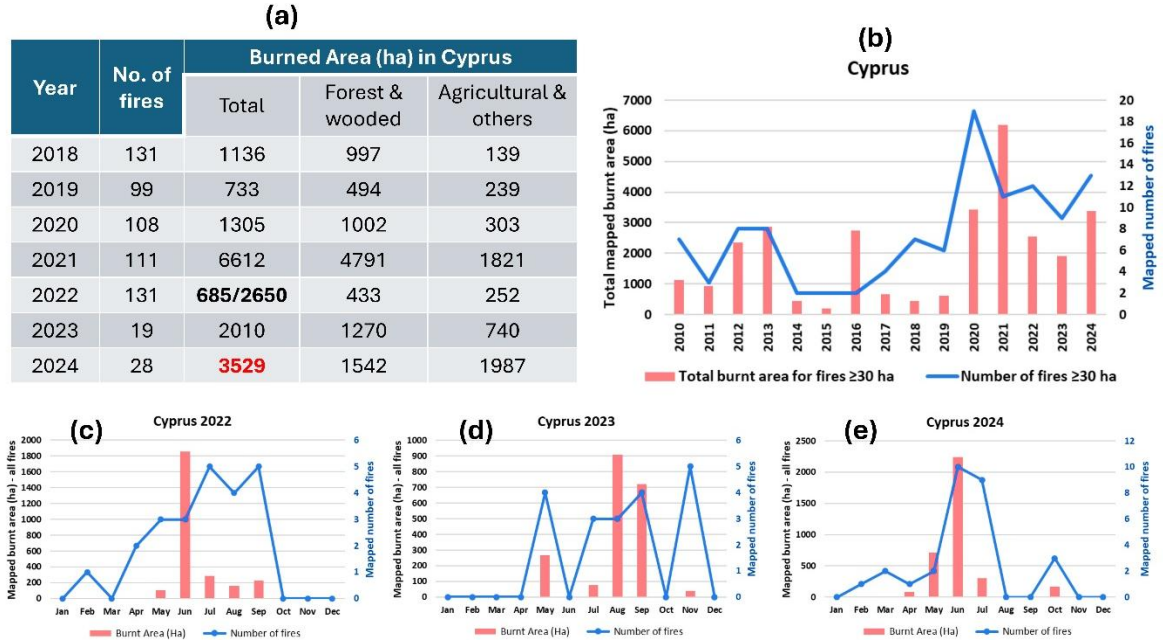

Figure S6. Interannual and seasonal variability of wildfire activity and burned area in Cyprus. (a) Annual statistics of wildfire occurrence and burned area in Cyprus from 2018 to 2024, including total burned area and its partitioning into forested/wooded and agricultural/other land-cover types. (b) 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)”*