

## 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 it is 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 °C, 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<sub>3</sub>, and nitrate radicals (NO<sub>3</sub>) (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
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	
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 (similarly 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 secondary 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.*