Response to comments by reviewer #2

We deeply thank the reviewer for the effort invested in reviewing this paper and for its thorough and constructive review. In the following, we present detailed point-by-point responses to the comments by the reviewer.

The authors report BVOC measurements at a site close to the Mediterranean sea. They suggest that a large amount of the BVOCs originate from the sea. This is a result that merrits publication. However, the evidence presented is not very consistent and/or robust in several aspects (see specific comments). The authors use (maybe too) many tools (PMF, Hysplitt, MEGAN, WRF) to substantiate their case, however, for most of these methods insufficient information is given to judge their appropriate application.

The paper needs a substantial revision before publication. I recommend to focus on a careful and clear presentation of the strongest evidence.

Answer:

We realize that the analyses used to support isoprene and DMS from the seawater were not presented clearly enough, and we have therefore revised Sects. 3.2.1 and 3.2.2 to clarify our arguments. In particular, the analyses presented in Sect. 3.2.1 are complex and use several tools. In the absence of available measured VOC flux (see our answer to the next comment), we had to use several independent methods to provide strong supporting evidence for the origin of isoprene from the Mediterranean Sea.

In response to this comment, we excluded the analysis by PMF as well as that of MEGAN v2.1 to support the partitioning of "isoprene+MBO". In addition, to clarify our analysis-based arguments, we divided section 3.2.1 into several subsections. The new subsections and various analyses are integrated in Sect. 3.2.1 as follows: i) "*Potential anthropogenic emission sources of isoprene+MBO*" – ruling out any significant anthropogenic contribution from traffic based on significant differences in diurnal profile for isoprene and MT vs. the diurnal profiles of benzene, toluene, acetonitrile (Figs. S12-S17 in the Supplement) and isoprene vs. CO (Fig. S19 in the Supplement for DOY 225); ii) "*Potential biogenic emission sources of* *isoprene+MBO"* – supporting evidence for dominant emission from a biogenic source based on correlation with temperature, but highlighting the need to partition the isoprene+MBO signal, due to an insufficiently clear association between this signal (i.e., m/z=69) and the measured air temperature; iii) "*Partitioning of isoprene+MBO signal"* – partitioning of the "isoprene+MBO" signal based on m87/m67 fractionation; iv) "*Isoprene origin"* – supporting a dominant biogenic source for the partitioned isoprene (m87/m69 < 2%) based on its correlation with temperature (Fig. 6 in the main text and Figs. S12-S17 in the Supplement), indicating a marine source for isoprene based on analysis of wind direction vs. m87/m69 < 2% (as well as the high day-to-day variation in isoprene mixing ratios as depicted in Fig. 6 in the main text), ruling out a significant contribution of aquaculture farms to the detected isoprene based on HYSPLIT back trajectories (Fig. S20 in the Supplement), and robustness of isoprene mixing ratios to changes in wind direction during each measurement day.

I wonder why the authors did not use the eddy covariance technique to constrain local emissions.

Answer:

We applied the eddy covariance technique to evaluate the flux of CO_2, H_2O and O_3 (CO_2 flux was used to support drought effects on BVOC emission; Fig. S18 in the Supplement). Unfortunately, we could not evaluate VOC fluxes due to technical problems with the high-frequency (10 Hz) recording of the measured data, which was inconsistent. We realize that a statement to this effect was missing in the text, and we have therefore added the following: "Note that due to technical problems, VOC fluxes were not evaluated" (line 175). We also mention the absence of VOC flux evaluation in the caption of Fig. S2 in the Supplement.

Specific comments:

line 78: "... are ESTIMATED to be substantially smaller ..." I guess nobody really knows the marine source strength.

Answer:

We agree, and have changed the sentence accordingly: "Although the emission rates of isoprene into the marine boundary layer (MBL) are estimated to be substantially smaller than terrestrial emissions…" (lines 77-79).

Fig 1: remove the red triangle that separates panel a and b. This is confusing.

Answer:

Done

Table S1: what is meant by poor quality and failed calibration?

Answer:

"Failed calibration" is defined in the revised Supplement as follows: "...data which could not be properly calibrated due to failed calibration" (Supplement lines 32-33). In most cases, failed calibration occurred due to accidental dilution of the calibrated mixture with ambient air. "Poor quality" is defined in the revised manuscript as follows: "…data that corresponded with unrealistic mixing ratios or erroneous recording..." (Supplement lines 34-35). The latter refers to data recording that repeatedly resulted in the same value.

There is no Figure 2.

Answer:

Fixed

Caption of Fig S4 can be improved.

Answer:

The figure caption has been amended (lines 274-277 in the Supplement).

What is the color code?

Answer:

We have added a legend to the figure, as well as for Figs. 4 and 6 in the main text. Each color indicates a specific period of 2-4 sequential days (as summarized in Table 1).

Why are benzene, toluene, and acetonitrile not reported? These compounds should be valuable tracers to constrain traffic emissions (2 highways between the site and the sea!) and biomass burning.

Answer:

In Sect. S3, we have added figures that compare the diurnal profiles of MT and isoprene+MBO with those of benzene, toluene and acetonitrile. In Sect. 3.2.1, we refer the reader to those figures (lines 366-370). Note that as discussed in Sect. S3 (lines 191-192), the correlation of acetonitrile with acetone and acetaldehyde suggests that the former is also emitted from a biogenic source. This was most salient for 13-14 August (see Fig. 1 below).

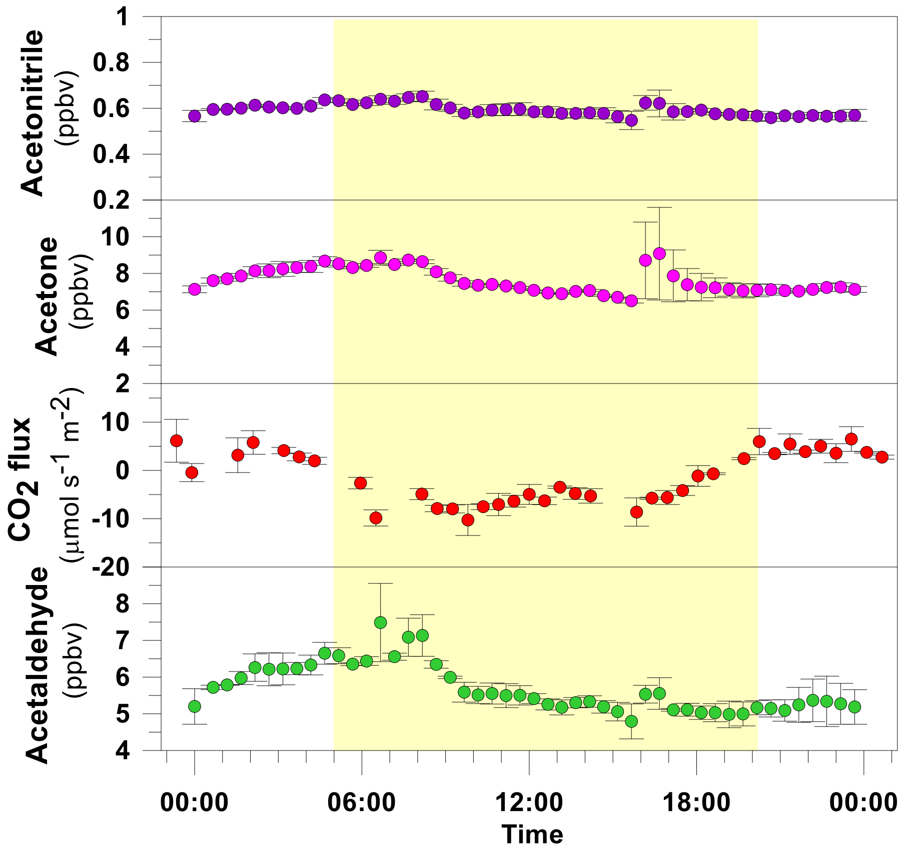

Figure 1. *Average diurnal profiles for acetone, acetonitrile, acetaldehyde and CO_2 fluxes during 13-14 August 2015 (DOY 225-226). Filled circles and vertical bars represent the mean and standard deviation of the mixing ratios, respectively. The anticorrelation between CO_2 and relatively soluble BVOCs suggests limitation of the BVOCs due to the drought effect (see Fig. 4 below and related discussion). The figure suggests a biogenic contribution for acetonitrile, based on its association with acetaldehyde and acetone, and apparent response to midday drought impact.*

The evidence shown in table 1 is insufficient to classify the period September 14-17 as irregular conditions. PAR is less than 20% lower than in the other period in September. All other parameters are similar.

Answer:

We agree and address this point, following additional analyses, as described in the answers to the next two comments.

Lines 277-280: I don't see extreme meteorological conditions and I don't see extreme concentrations in Fig 3.

Answer:

We have revised this according to our response to the next comment as follows: " During DOY 257-260, BVOCs showed elevated mixing ratios […], as well as irregular diurnal shape, which may be attributed to synoptic-scale induced processes (see Sect. S6). We therefore did not use these measurements for further analyses."

The modelling exercise in the supplement is not convincing because there is no reference period. It could be convincing, for example, if much higher boundary layers would be calculated for the second period in September.

Answer:

In comparing the boundary layer height (BLH) with the corresponding BLH for the second period in September, as well as for the whole month, we realized that BLH for DOY 257-260 was not significantly smaller than average, except for DOY 257 for which the radiation was lower than for DOY 258-260 (see Fig. S22 in the Supplement).

In addition to the elevated mixing ratios during DOY 257-260, the diurnal profiles of the BVOCs for this period differed from other periods by not showing any clear increase during the day, and starting to continuously decrease from about 0800–0900 h, except for DMS, where the decrease started earlier (see Fig. 3 below and Fig. S7 in the Supplement). Our new analysis indicates subsidence of air from the upper troposphere which is typical for the studied area during the summer, leading to a significant change in the mixing ratios (e.g., of O_3) within the boundary layer, via air exchange with the upper troposphere along with the subsidence (e.g., (Tyrlis and Lelieveld, 2013;Zanis et al., 2014;Li et al., 2018). Such subsidence can frequently lead to shallowing of the BLH. As evidenced by our model simulations, DOY 257-260 were characterized by notably early (~0900 h) shallowing of the BLH (see Fig. 2 below), strongly supporting the occurrence of subsidence for DOY 257-260.

The fact that anthropogenic trace gases also showed a similar diurnal profile, but with an earlier decrease in mixing ratios during the morning (Fig. S7 in the Supplement) suggests that the anthropogenic trace gases were also significantly diluted by the subsidence which was apparently accompanied by intrusion. We attribute the delayed and more moderate decrease for BVOCs compared to anthropogenic VOCs to an increase in emission in response to increasing temperature and radiation intensity for the former. Our analysis is insufficient to conclusively explain the elevated BVOC mixing ratios and irregular diurnal profile during DOY 257-260. Nevertheless, we exclude this period from the rest of the analyses (except in Fig. 2 in the main text) as in the original version of the manuscript, due to the irregular diurnal profile. We have revised our explanations of the elevated mixing ratios and irregular diurnal shape for this period, according to the above (see Sect. S4).

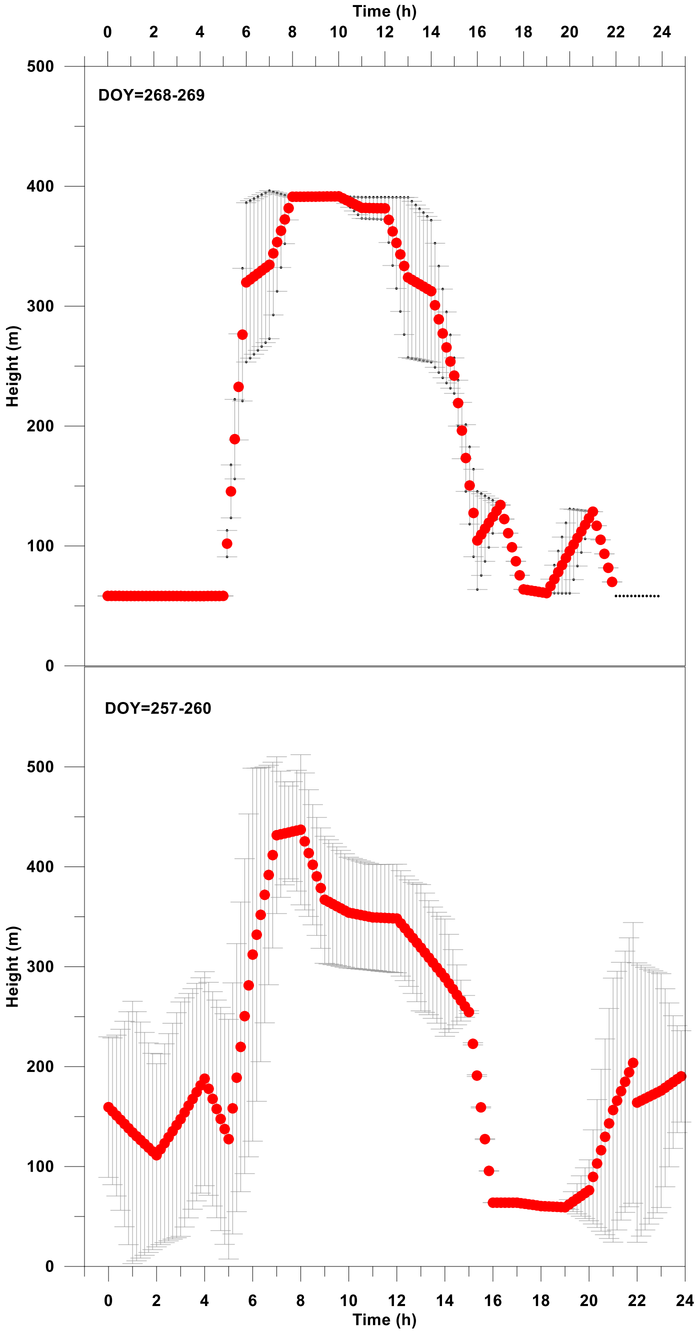

Fig. 2. Average diurnal profile of the boundary layer height (BLH) during DOY 268-269 (upper panel) and DOY 257-260 (lower panel). Gray vertical error bars represent standard deviation.

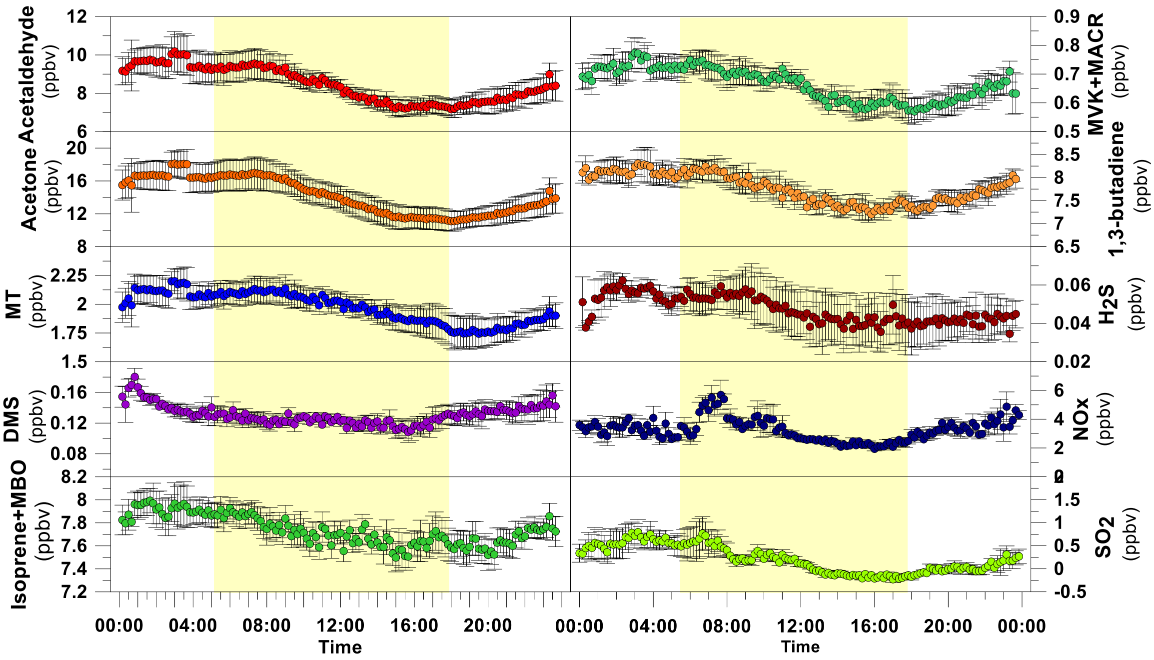

Fig. 3. *Daily average diurnal profile for selected VOCs which were dominated by biogenic sources (monoterpenes (MT), isoprene+2-methyl-3-buten-2-ol (MBO), dimethyl sulfide (DMS), acetone, acetaldehyde and the sum of methyl vinyl ketone and methacrolein (MVK+MACR)) and anthropogenic sources (1,3-butadiene, H_2S, NO_X and SO_2) for 14-17 September 2015. Filled circles and vertical bars represent mean mixing ratios and their standard deviation, respectively.*

Lines 281-283: Please explain why the shape suggests a biogenic source. Also, it would be useful to see the data for DMS and other BVOCs to show their difference!

Answer:

This is now explained in the text as follows: "The diurnal profile of isoprene+MBO suggests a predominantly biogenic source due to a clear daytime increase and a correlation with temperature for most of the periods (Fig. 4, Figs. S3-S9). However, its day-to-day mixing ratios showed higher variability (Fig. 2), which was quite different from both DMS and the other BVOCs. The origin of the BVOCs is explored in the next section" (lines 309-313). Note that isoprene+MBO differed from DMS and other BVOCs in the day-to-day variation, as is evident in Fig. 2 (above), and supported by calculations (see Table 1 below).

Note also that acetaldehyde and acetone, and to a lesser extent MVK+MACR, showed somewhat less typical biogenic diurnal shapes compared to the other BVOCs during some of the measurement periods. This can be explained by the former species' higher solubility compared to the other BVOCs that we investigated, making them significantly more susceptible to drought effects via stomatal activity, as compared to non-soluble BVOCs (Niinemets et al., 2004;Niinemets et al., 2014). This is demonstrated, for instance, for 13-14 August (see Fig. S11 in the Supplement). The figure indicates an increase in the downward CO_2 flux after sunrise, until ~0930 h, then a moderate decrease in this flux until ~1500 h which can be attributed to a drought-induced midday depression in the photosynthetic rate. This apparent midday depression was followed by an additional peak in the downward CO_2 flux at around 1600 h. Acetaldehyde and acetone showed a decrease in mixing ratios between ~0900 and 1600 h along with the decrease in the downward flux of CO_2, and peaked again at ~1600 h, suggesting a strong limitation of their emission due to the drought conditions. MVK+MACR did not show a peak at ~1600 h, and it was less clearly affected by the midday depression compared to acetaldehyde and acetone.

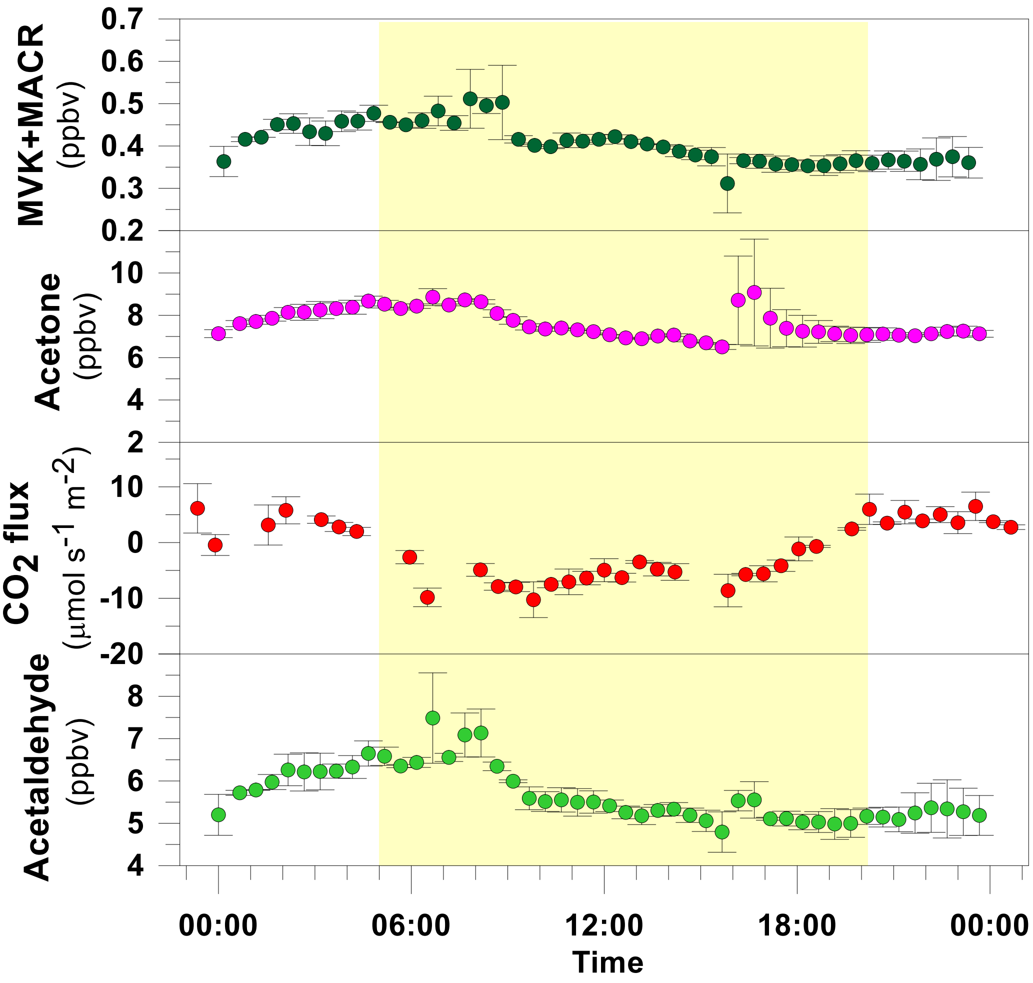

Fig. 4. *Average diurnal profiles for acetone, acetonitrile, acetaldehyde and CO_2 flux during 13-14 August 2015 (DOY 225-226). Filled circles and vertical bars represent the mean and standard deviation of the mixing ratios, respectively. Yellow shaded area represents daytime. The anticorrelation between CO_2 and soluble BVOCs, during the daytime, suggests limitation of the BVOCs emission due to the drought effect. In particular, elevated mixing ratios of acetaldehyde and acetone between ~0700 and 0900 h, and between ~1600 and 1700 h, and lower mixing ratios in between, are in line with the trends of CO_2, suggesting a midday depression in photosynthesis as well as in the emission of the four relatively soluble VOCs in response to a drought effect (see (Niinemets et al., 2014;Niinemets et al., 2004)).*

Line 303: would be good to see hexenal and hexanal in Fig 4, even if these compounds are not calibrated!

Hexenal and hexanal can provide an indication of green leaf volatile (GLV) emissions following wounding. Considering that this aspect is not central to our study, we included it in the Supplement (see Sect. S7). A source analysis similar to that presented in the original Fig. 3 was also performed for hexanal (m/z=83.085), hexenal (m/z=57.033 and m/z=99.080) and methanol (m/z=33.034), and the reader is referred to this analysis from the main text (lines 328-331). Note that hexenal is also detected at m/z=43.018 and m/z=81.070 (Brilli et al., 2011; Pang, 2015), but we did not include these fragments in the hexenal mixing ratio calculations because m/z=43.018 can be affected by 1-hexyl acetate and other GLV fragments (m/z=43.018), while m/z=81.080 can be affected by MTs. Hexanal is also detected at m/z=83.085 and m/z=101.096, but we used only m/z=83.085 to evaluate its mixing ratios, because the latter contributes about 99% to the mixing ratios, represented by the three peaks. Fig. 5 below indicates elevated emission of GLVs, but a comparison of this figure with Fig. 3 in the main text suggests that there was no obviously higher excess of these GLVs from the southeast, compared to the other wounding BVOCs.

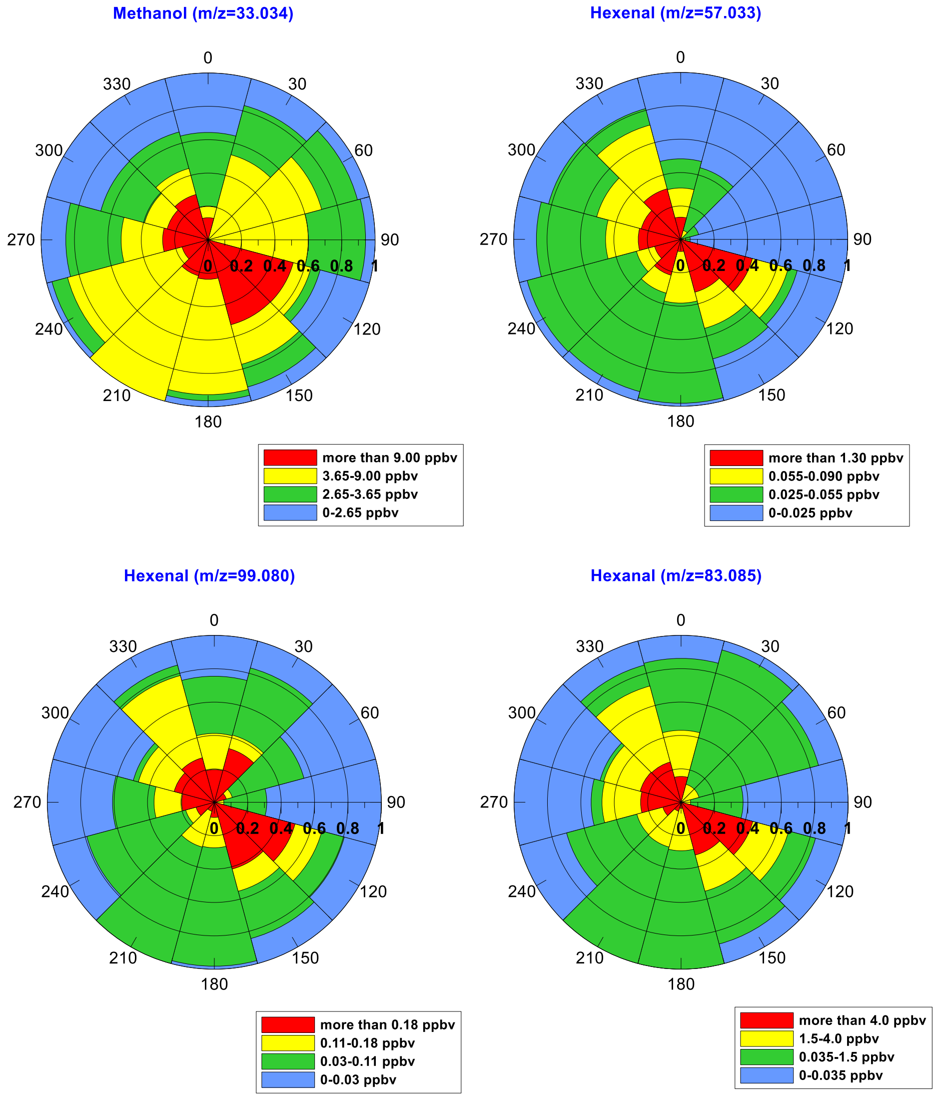

Fig. 5. *Methanol, hexanal and hexenal mixing ratios as a function of the contribution from each wind sector. The radial dimension represents the fraction of time for each wind sector during which the mixing ratios were within a certain range, as specified in the color key.*

309-312: the fact that MEGAN does not predict local isoprene emissions is no convincing argument. Surely not all species (including invasive species) are included in the MEGAN model.

Answer: We agree and have changed the text in this section as follows: "The MEGAN v2.1 simulations indicated that the known plant species in the nature park should not be a significant source of isoprene. It is possible that other local plants, such as invasive species, contributed to the observed isoprene concentration, but this would require a large area covered by high-isoprene-emitting species to result in the observed isoprene concentration at this site." (lines 336-340).

Later in this section we mention that: "The elevated mixing ratios of isoprene+MBO from the west may be primarily attributed to the emission of isoprene from marine organisms, as discussed in Sect. 3.2.1." (lines 348-350). The discussion in Sect. 3.2.1 indicates that the Mediterranean Sea is the dominant isoprene source, but in the revised version, we emphasize the potential role of other sources on the coastline: "Yet, while it is likely that the Mediterranean Sea is the dominant isoprene source, rather than the aquaculture farms or the nature park, additional measurements on the coastline are required to quantify the contribution of other isoprene sources." (lines 458-461).

315: I cannot follow all details of the kinetic analysis in the supplement, but I doubt that this can rule out the possibility of local emissions. I do not understand why the authors do not process their data with the eddy covariance technique. This would give a clear answer on whether there are local emissions or not.

Answer:

We provide a more detailed explanation of the kinetic analysis (see Sect. S4 in the Supplement). We have also revised the original text on line 315 as follows: "However, kinetic analysis indicated that the isoprene emission from the memorial garden is much too small to account for the observed MVK+MACR associated with transported air masses from the memorial garden (see Sect. S4)." (lines 345-348).

324: I do not agree that this has been demonstrated...

Answer:

We have added a table to the Supplement that supports this (Table S3; see Table 1 below) and refer the reader to this table (lines 360-363).

Table 1. *Coefficients of variation for the daily mean mixing ratios of the investigated VOCs*

VOC	**Standard deviation of the daily mean mixing ratios** (ppbv)	**Coefficient of variation**
Isoprene	2.914	1.138
Acetaldehyde	1.539	0.549
Acetone	1.339	0.321
Monoterpene	0.227	0.908
MVK+MACR	0.130	0.650
DMS	0.014	0.323

327: Figure S12: it would be informative to see how the scatter plot looks like for other VOCs.

Answer:

In the revised Supplement (Fig. S10), we now include a scatter plot of the other BVOCs vs. temperature (see Fig. 6 below). The figure suggests that a correlation between isoprene and temperature may be masked by the high day-to-day variations in isoprene+MBO. The text has been changed accordingly: "These day-to-day variations apparently masked the seasonal correlation of isoprene with temperature (see Fig. S10)." (lines 363-364)

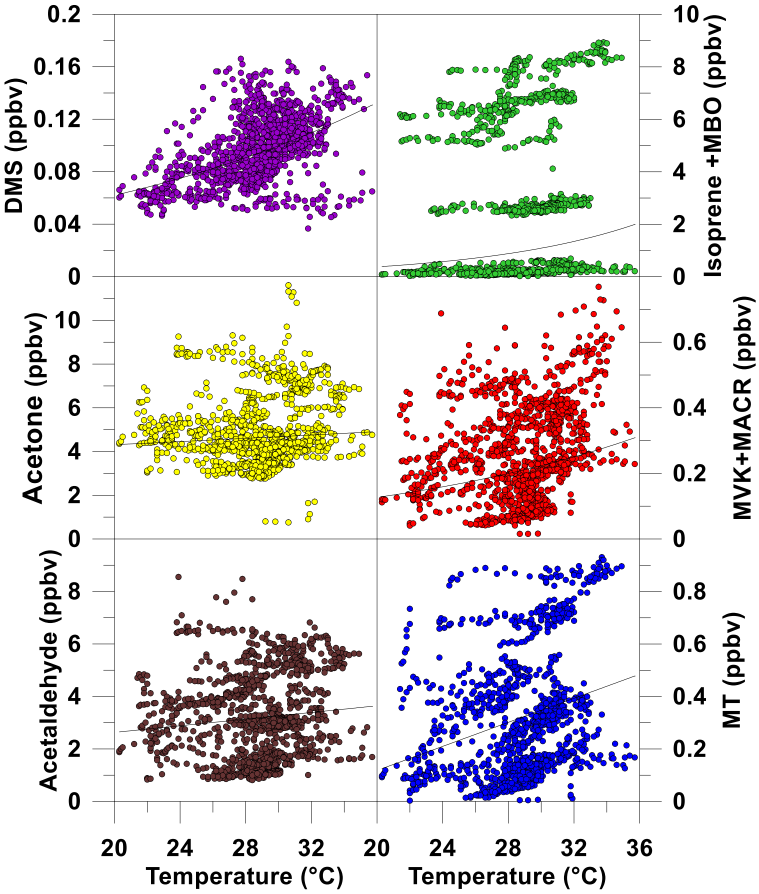

Fig. 6*. BVOC mixing ratios versus temperature. Filled circles represent mixing ratios; exponential fit lines are in black.*

328: Figure S10 shows data for one day. This is insufficient to make general claims.

Answer:

We have added a series of figures (Figs. S12–S17) to the Supplement which clearly demonstrate that the diurnal profiles of MT and isoprene were significantly different from those of benzene, toluene and acetonitrile, which were used as proxies for transportation emissions. Note that as discussed in Sect. S3 (lines 191-192), a correlation of acetonitrile with acetone and acetaldehyde suggests that acetonitrile is probably also emitted from a biogenic source. This was most clear for 13-14 August (see Fig. 1 above).

334: Fig 5 caption: There is no "regression" you just show a scatter plot temp vs iso+MBO

Answer:

The figure caption has been amended accordingly.

369-370: Given the fact that you measured at high E/N (140 Td) I am not so sure that such high fractions of MBO are expected at 87 Th. Maybe you can prove this by showing calibration measurements.

Answer:

We do not expect that an E/N of 140 Td will almost completely fragment MBO. For example, Vlasenko et al. (2009) reported 1:3 MBO fragmentation at 135 Td. However, the reviewer makes the excellent and important point that high m87/m69 ratios are not possible if only MBO is an expected contributor to m87. This comment helped us realize that there was excess MBO signal from nonfragmenting $C_5H_{10}O$ isomers, mostly at night, that correlated better with anthropogenic sources. Thus, we have changed the label for the MBO measured at m87 MBO*, where "*" stands for methyl propyl ketone (MPK), pentanal, and other $C_5H_{10}O$ isomers. We have also updated the discussion accordingly. MBO contributions from m87 are expected in homogeneous coniferous ecosystems, but isomeric contributors are expected to m87 in other environments, in particular those with anthropogenic influences. Although MPK emissions have previously been reported from tobacco plants, the wind-sector analysis of nighttime influences on the m87 (m87/m69 > 0.3) signal indicates that the MBO excess was indeed mostly from an anthropogenic source.

445-447: I think that it would be interesting to estimate daytime isoprene production from these lifetime values.

Answer:

Daytime and nighttime isoprene production mixing ratios were calculated, assuming a lifetime of 37 min and 3.8 h during the daytime and at night, respectively. We have added a discussion of this analysis to Sect. 3.2.1: "A rough estimation of isoprene production rate can be calculated by subtracting the isoprene loss rate, evaluated from its calculated lifetime, from its measured mixing ratios. These simplified calculations indicate a daytime and nighttime isoprene production rate ranging between $\sim 4.9 \cdot 10^{-5}$ and $1.7 \cdot 10^{-2}\ \text{ppbv} \cdot \text{s}^{-1}$ (average $5.2 \cdot 10^{-3} \pm 5.6 \cdot 10^{-3}\ \text{ppbv} \cdot \text{s}^{-1}$) and between $-1.3 \cdot 10^{-3}$ and $1.3 \cdot 10^{-3}$ (average $-1.6 \cdot 10^{-6}\text{ppbv} \cdot \text{s}^{-1} \pm 1.4 \cdot 10^{-5}\ \text{ppbv} \cdot \text{s}^{-1}$), supporting a much smaller isoprene production rate during the night vs. daytime" (lines 476-482).

475-478: what was the sea surface temperature in 1995 as compared to 2015?

Answer:

According to Ganor et al. (2000), the sea surface temperature on August 15 and 16 when the DMS samplings were performed was 28.6°C, while between August 10 and 20, it reached up to 30.1°C-30.7°C. Accordingly, we revised the original text on lines 475-478 as follows: "Interestingly, the mixing ratios measured in this study are lower by about 1-2 orders of magnitude than those measured in the same region during August 1995 (Ganor et al., 2000). This could be attributed to a change in the marine biota as a consequence of seawater warming, considering that reported SST during mid-August 2015 (IOLR, 2015) was higher than the SST reported by Ganor et al. (2000) by up to 1.5–2.1°C" (lines 512-517).

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