Dear Editor,

We are pleased to submit a revised version of the manuscript (acp-2019-1170) "Emission of biogenic volatile organic compounds from warm and oligotrophic seawater at the Eastern Mediterranean" for publication in Atmospheric Chemistry and Physics.

We thank the referee Dr. Silvano Fares and the anonymous reviewer for investing time and effort in reading our manuscript, and for the useful comments which helped us to greatly improve its quality, both scientifically and for clarity. We realized that the various analyses presented in the original version to indicate strong emission of isoprene from the Eastern Mediterranean Sea were not clear or sufficiently complete. Following suggestions by reviewer II on this issue, we reduced the number of tools used to support the strong isoprene emission from the seawater, and demonstrated that our arguments are valid for all measurement periods. The latter was done mainly by adding analysis results to the Supplement to support our arguments for all measurement periods, in an attempt to keep the main text succinct. In addition, we divided the section on the origin apportioning of measured isoprene (section 3.2.1) into several subsections to clarify the logic behind the related analyses.

We seriously considered and addressed all of the reviewers' comments. In the following, we present detailed point-by-point responses to these comments and detail the changes implemented in the revised version. These are followed by the revised marked-up manuscript. We hope that the revised version will be found suitable for publication in Atmospheric Chemistry and Physics.

Sincerely,

Eran Tas

Responses to comments by Dr. Silvano Fares

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 Dr. Fares.

The authors tried to determine sources of BVOCs emitted from a mixed vegetation site 4 km away from the coast of Levantine Basin. They demonstrate relevant biogenic sources frm inland but also from the ocean, and explained different sources of BVOC species with the help of transport models and emission models. I believe this paper helps understanding the complex synamics of Biogenic emission and transport. There are no language flaws and a good amount of references. Showing measured fluxes would have been beneficial to better understand didirectianal BVOC fluxes at the measuring site. A list of minor comments is reported here:

INTRO Lines 113-115: can you explain why an oligotrophic environment is represented by unicellular organisms and plankton?

Answer:

The oligotrophic environment is characterized by limited nutrients. Small cells are basically more effective at nutrient uptake (Fogg, 1986), while unicellular organisms are more efficient at CO_2 fixation (Mazard et al., 2004). This gives rise to both the unicellular and small plankton being better adapted to oligotrophic conditions. In addition, high seawater temperature tends to shift the planktonic community toward an increase in unicellular and small plankton (Mazard et al., 2004;Rasconi et al., 2015).

We provide these explanations in the revised manuscript and have revised the corresponding paragraph as follows: "The Eastern Mediterranean Basin region has been recognized as highly responsive to climate change, and has been aptly named a primary “climate change hotspot” (Giorgi, 2006; IPCC, 2007; Lelieveld et al., 2012). This makes it an attractive site to study the impact of anthropogenic stress and climate change on marine BVOC emissions. In addition, being oligotrophic, there is a predominance of unicellular and small plankton such as cyanobacteria (Krom et al., 2010) that can more efficiently perform CO_2 fixation and utilize nutrients under such conditions, respectively(Fogg, 1986 ;Mazard et al., 2004). Moreover, the high SST tends to further shift the planktonic community toward an increase in unicellular and small plankton (Mazard et al., 2004;Rasconi et al., 2015)." (lines 111-120).

M&M Line 173-195: Although the authors cite other previous papers, since the manuscript is all about detected BVOCs, it is important to provide more details on the calibration procedure.

Answer:

We have added more information on the calibration procedure in Sect. 2.2: " The PTR-ToF-MS was calibrated every 1-2 days for background (zero), and weekly for sensitivity (span), subject to technical limitations (see Table S1). Background (zero) calibration was conducted by sampling ambient air which was passed through a catalytic converter heated to 350°C. Sensitivity calibration was performed using gas standards (Ionicon Analytik GmbH, Austria) containing methanol (0.99±8% ppmv), acetonitrile (0.99±6% ppmv), acetaldehyde (0.95±5% (ppmv), ethanol (1.00±5% ppmv), acrolein (1.01±5% ppmv), acetone (0.98±5% ppmv), isoprene (0.95±5% ppmv), crotonaldehyde (1.01±5% ppmv), 2-butanone (0.99±5% ppmv), benzene (0.99±5% ppmv), toluene (0.99±5% ppmv), o-xylene (1.02±6% ppmv), chlorobenzene (1.01±5% ppmv), α-pinene (1.01±5% ppmv) and 1,2-dichlorobenzene (1.02±5% ppmv) to obtain gas mixtures ranging from 1-10 ppbv. Mixing ratios of compounds for which no gas standard was available were calculated using default reaction rate constants (see Sect. S1)." (lines 191-203).

Line 208: why are you recording slow sensors at 10 Hz?

Answer:

This was a typo. We have revised the text as follows: "These measured data were recorded with a CR10X data logger (Campbell Scientific) at 10-min frequency" (lines 227-229).

Results Lines 271-279: Althogh grouping results and discussion may not be ideal, please insert at least numbers (with SD) while discussing mixing ratios.

Answer:

Done. The text which appeared originally on lines 271-279 has been revised as follows: " DMS showed the strongest correlation with the average daytime temperature (r^2=0.27; see Sect. 3.2.2), corresponding to a significant increase in the mixing ratios between early summer (0.072±0.005 ppb, day of year (DOY) 188) and the end of summer (0.19±0.040 ppb, DOY 254), which decreased during the autumn (0.17±0.015 ppb, DOY 255 to 0.066±0.011 ppb, DOY 283). The other BVOCs, except for isoprene+MBO, showed a gradual increase in their average mixing ratios during the summer and early autumn (DOY 198-269; acetone from 3.74±0.767 ppbv to 4.33±0.471 ppbv, acetaldehyde from 1.64±0.595 ppbv to 3.09±0.496 ppbv, MT from 0.089±0.021 ppbv to 0.237±0.120 ppbv, MVK+MACR from 0.125±0.048 ppbv to 0.252±0.070 ppbv), and lower average mixing ratios in the autumn and early winter (DOY 270-286; DMS 0.091±0.026 ppbv, acetone 3.96±1.04 ppbv, acetaldehyde 1.86±0.97 ppbv, MT 0.139±0.064 ppbv, isoprene+MBO 0.182±0.093 ppbv, MVK+MACR 0.153±0.098 ppbv), which can be explained by the correlation with air temperature (Fig. 2). During DOY 257-260, BVOCs showed elevated mixing ratios (daytime averages for DMS, acetone, acetaldehyde, H_2S, MT, isoprene+MBO and MVK+MACR were 0.122±0.016 ppbv, 13.6±3.26 ppbv, 8,138±1.18 ppbv, 0.046±0.021 ppbv, 1.97±0.215 ppbv, 7.68±0.218 ppbv and 0.644±0.084 ppbv, respectively), 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." (lines 290-308).

What does extreme mixing ratios mean? While reading these interesting seasonal variations of BVOCs the reader wonders why you did not show fluxes considering that you have an Eddy Covariance installation at the site and the PTR-TOF-MS allows very fast measurements. Fluxes, when available, may support understanding of BVOC origin, way better than modelling.

Answer:

We have changed "extreme mixing ratios" to "elevated mixing ratios […] as well as irregular diurnal shape, which may be attributed to synoptic-scale induced processes (see Sect. S6)." (lines 303-307). The irregular diurnal shape may be attributed to synoptic-scale induced subsidence and intrusion (see Sect. S6), and therefore, we did not use these measurements for further analyses.

Unfortunately, we encountered technical problems in evaluating flux for the measured VOCs using the rented PTR-ToF-MS (mostly systematic errors in writing the data in 10 Hz frequency, negating the possibility of making cross-correlations). We agree that mentioning eddy covariance measurements without showing BVOC fluxes can be confusing. We therefore address this point in the revised version. To provide a full and proper description of the measurement setup, we retain the information on the eddy covariance in the revised version (used, for instance, to evaluate CO_2 flux; Sect. S3 in the Supplement). Overall, the revised text in Sect. 2.2 reads as follows: "The set of instruments included a platform for eddy covariance measurements of BVOCs, O_3, carbon dioxide (CO_2) and water vapor (H_2O), trace-gas mixing ratios, including O_3, NO_X, SO_2 and CO, and basic meteorological conditions, using an air-conditioned mobile laboratory and two towers (Fig. S2). Note that due to technical problems, VOC fluxes were not evaluated." (lines 171-175). We also mention the lack of VOC flux evaluation in the caption of Fig. S2 in the Supplement.

Lines 379-281: although I understood the sense of this sentence, it may be written more clearly to stress that high mixing ratio corresponding to Isoprene + MBO is a proxy of high isoprene emission.

Answer:

We have removed this section, based on reviewer II's recommendation to focus on the strongest evidence for our analyses.

Line 446: a lifetime of 3.8 hrs does not really support the possibility that isoprene is only emitted during the day. Considering the light dependency of isoprene emission this may be consumed early in the night.

Answer:

We agree and have made it clear that a lifetime of 3.8 h does not rule out isoprene nighttime emission: "Considering the relatively moderate decrease in the measured isoprene during the night (Figs. S12-S17 in the Supplement), this result points to stronger isoprene emissions during daytime, but does not rule out nighttime isoprene emissions" (lines 472-475). Note that pursuant to a comment by reviewer II, we support relatively weak nighttime isoprene production with a simplified kinetic calculation: "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 ~$4.9 \cdot 10^{-5}$ and $1.7 \cdot 10^{-2}$ $\mathrm{ppbv} \cdot \mathrm{s}^{-1}$ (average $5.2 \cdot 10^{-3} \pm 5.6 \cdot 10^{-3}$ $\mathrm{ppbv} \cdot \mathrm{s}^{-1}$) and between $-1.3 \cdot 10^{-3}$ and $1.3 \cdot 10^{-3}$ (average $-1.6 \cdot 10^{-6} \mathrm{ppbv} \cdot \mathrm{s}^{-1}$ $\pm 1.4 \cdot 10^{-5}$ $\mathrm{ppbv} \cdot \mathrm{s}^{-1}$), supporting a much smaller isoprene production rate during the night vs. daytime" (lines 476-482).

Line 499: since you are comparing MEGAN results with previous analysis, you should enter more into detail on what species drive emission, assuming that some of the species present at your measuring site and more inland are described and characterized in some papers for their emission capacity. Perhaps MEGAN adopts a wide plant functional type?

<u>Answer</u>:

MEGAN emissions were driven by emission factors for four specific vegetation species (*Quercus calliprinos* (25%), *Pistacia lentiscus* (20%), *Rhamnus lycioides* (2%), *Pinus halepensis* (<5%); see species composition description on lines 149-155). For two species (*Phillyrea latifolia* (7.5%) and *Cupressus* sp. (5%)), emissions are based on genus level data which are expected to be fairly representative, while for another two (*Sarcopoterium spinosum* (~2%) and *Calicotome villosa* (1%)), the emission factors were calculated based on average emission at the family level (Rosaceae and Fabaceae, respectively), which may lead to larger inaccuracies.

We evaluated the contribution of different species to monoterpene emissions at Ramat Hanadiv and updated the discussion with this information, which compares the ratio between monoterpene emission flux and its mixing ratios with two other *Pinus halepensis* forests: "We used the ratio between MT flux and mixing ratio at the three sites as a basis to address this inquiry. Note that according to the MEGAN v2.1 simulations (see Sect. 2.3), the MT emissions in Ramat Hanadiv were driven by *Quercus calliprinos* (48.1%), *Pistacia lentiscus* (19.8%), *Phillyrea latifolia* (7.12%) and *Cupressus* spp. (6.17%), as well as other species (see Sect. S5), in contrast to the two *Pinus halepensis* plantations, Birya and Yatir. While the fact that MT is not emitted by the same vegetation species should not significantly affect our analysis, we recognize that there may be differences in the MT composition and atmospheric oxidation capacity at the three sites which would influence MT lifetimes and lead to some differences in the flux-to-concentration ratios." (lines 540-549).

<u>References:</u>

Fry, J. C.: Oligotrophs. In Microbiology of extreme environments, edited by C. Edwards, Open University Press., 1990.

Platt, T., Rao, D. V. S. and Irwin, B.: Photosynthesis of picoplankton in the oligotrophic ocean, Nature, 301(5902), 702–704, doi:10.1038/301702a0, 1983.

Fogg, G. E.: Picoplankton, Proc R Soc Lond,, B, :l-30 1986

Mazard, S. L., Fuller, N. J., Orcutt, K. M., Bridle, O., and Scanlan, D. J.: PCR analysis of the distribution of unicellular cyanobacterial diazotrophs in the Arabian Sea, Appl Environ Microb, 70, 7355-7364, 10.1128/Aem.70.12.7355-7364.2004, 2004.

Rasconi, S., Gall, A., Winter, K., and Kainz, M. J.: Increasing Water Temperature Triggers Dominance of Small Freshwater Plankton, Plos One, 10, ARTN e014044910.1371/journal.pone.0140449, 2015.

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).

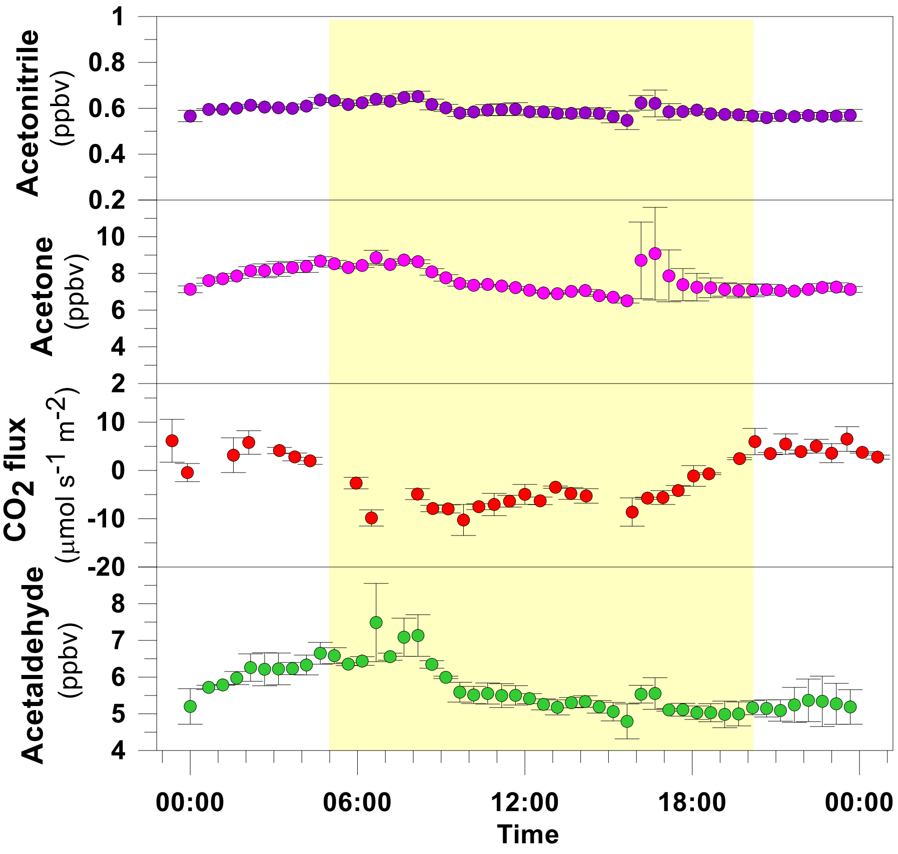


Figure 1. *Average diurnal profiles for acetone, acetonitrile, acetaldehyde and CO_2 fluxes during 13-14 August 2015 (DOY 225-226). Filled circles and vertical bars represent the mean and standard deviation of the mixing ratios, respectively. The anticorrelation between CO_2 and relatively soluble BVOCs 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." (lines 302-308).

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. S6).

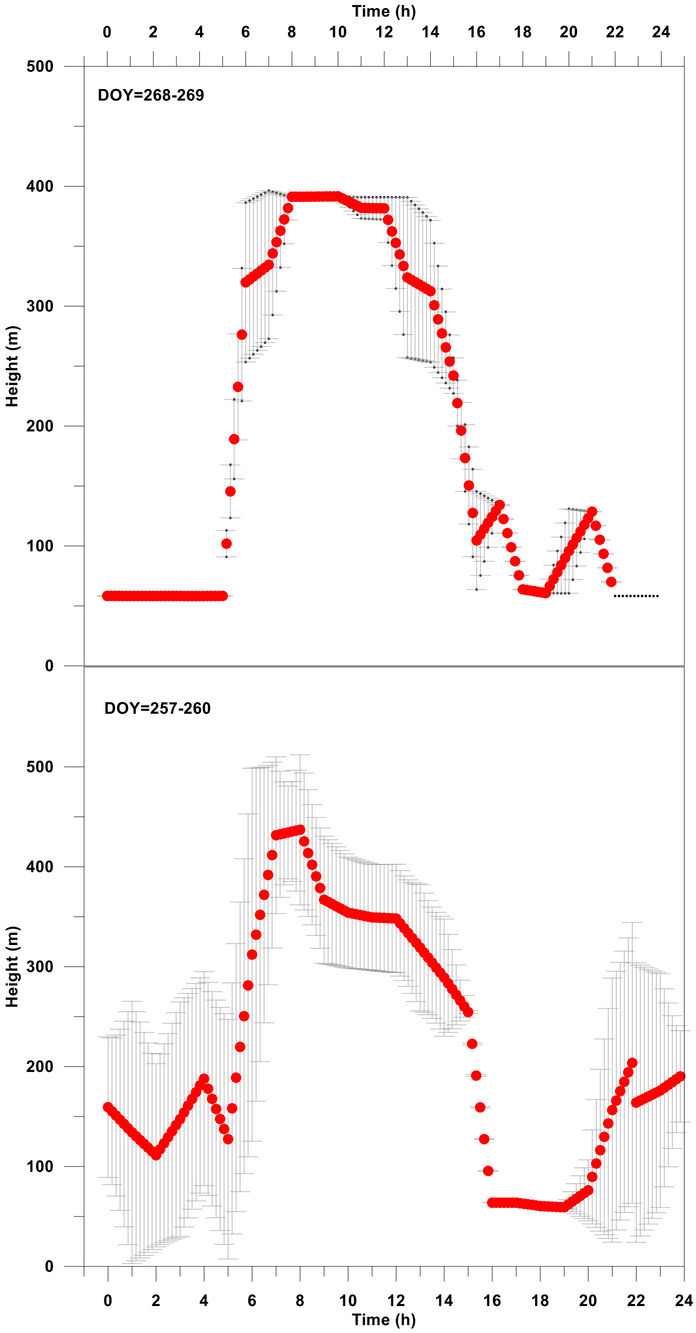


Fig. 2. Average diurnal profile of the boundary layer height (BLH) during DOY 268-269 (upper panel) and DOY 257-260 (lower panel). Gray vertical error bars represent standard deviation.

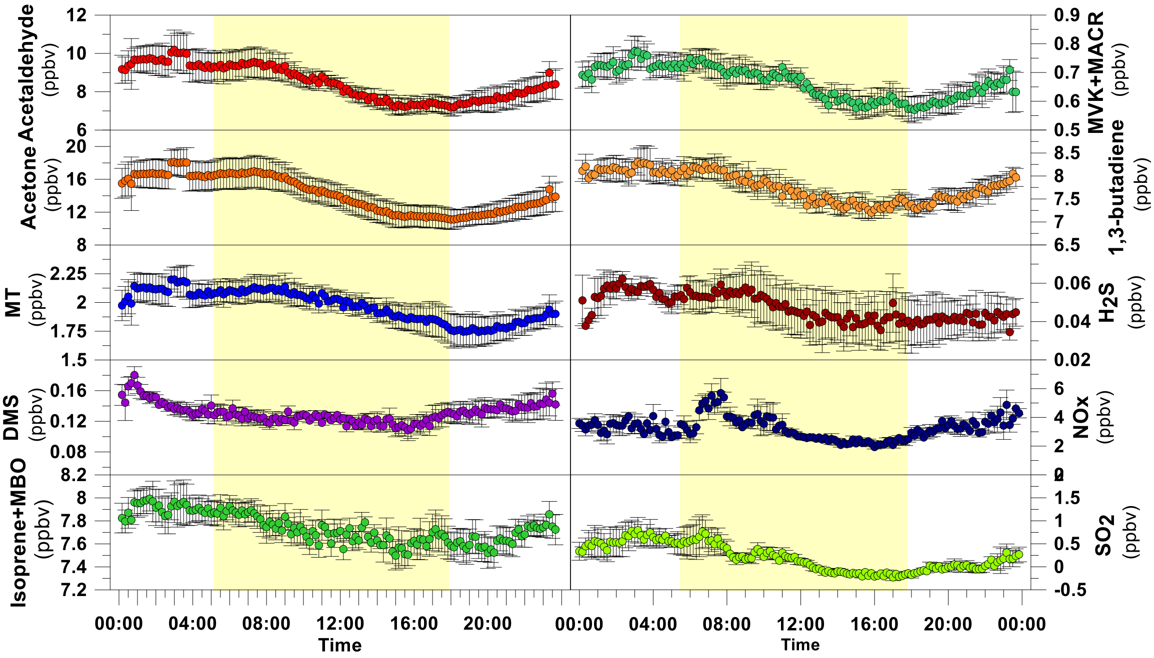


Fig. 3. *Daily average diurnal profile for selected VOCs which were dominated by biogenic sources (monoterpenes (MT), isoprene+2-methyl-3-buten-2-ol (MBO), dimethyl sulfide (DMS), acetone, acetaldehyde and the sum of methyl vinyl ketone and methacrolein (MVK+MACR)) and anthropogenic sources (1,3-butadiene, 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.

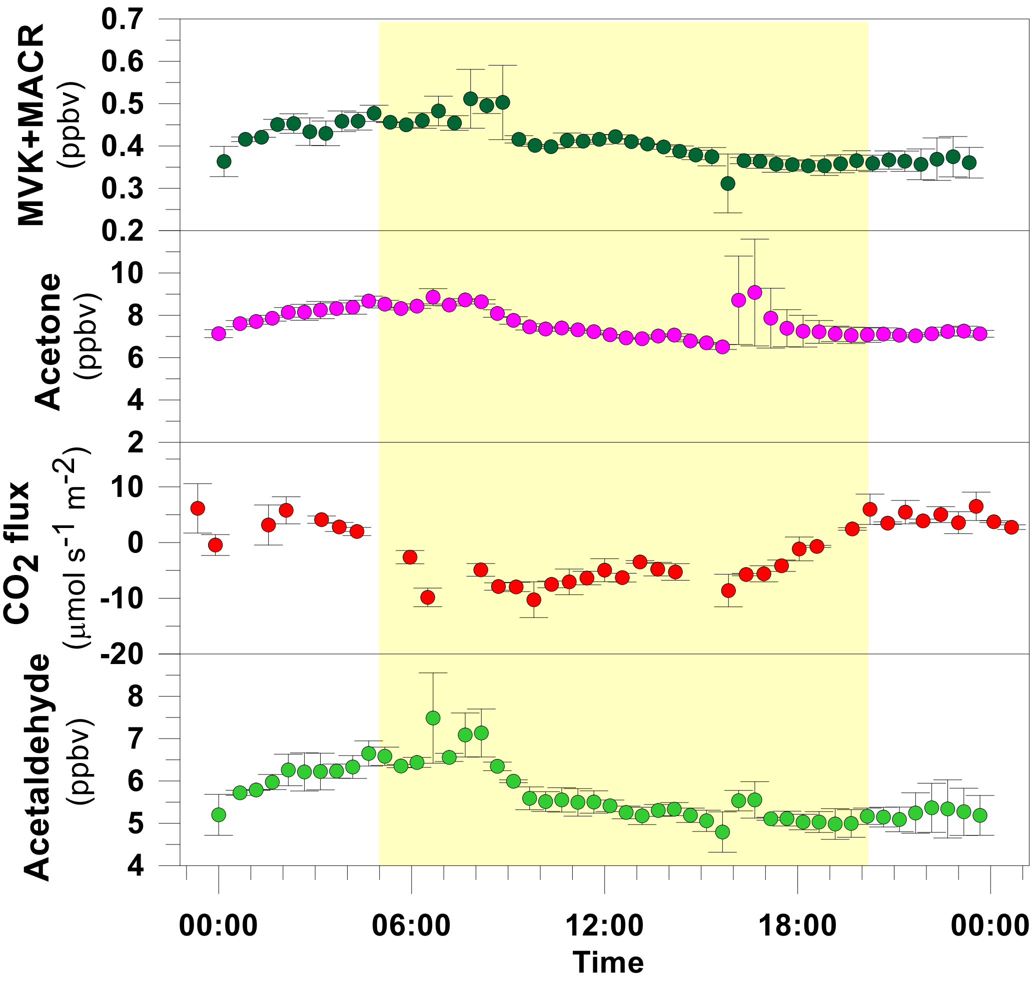


Fig. 4. *Average diurnal profiles for acetone, acetonitrile, acetaldehyde and CO_2 flux during 13-14 August 2015 (DOY 225-226). Filled circles and vertical bars represent the mean and standard deviation of the mixing ratios, respectively. Yellow shaded area represents daytime. The anticorrelation between 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.

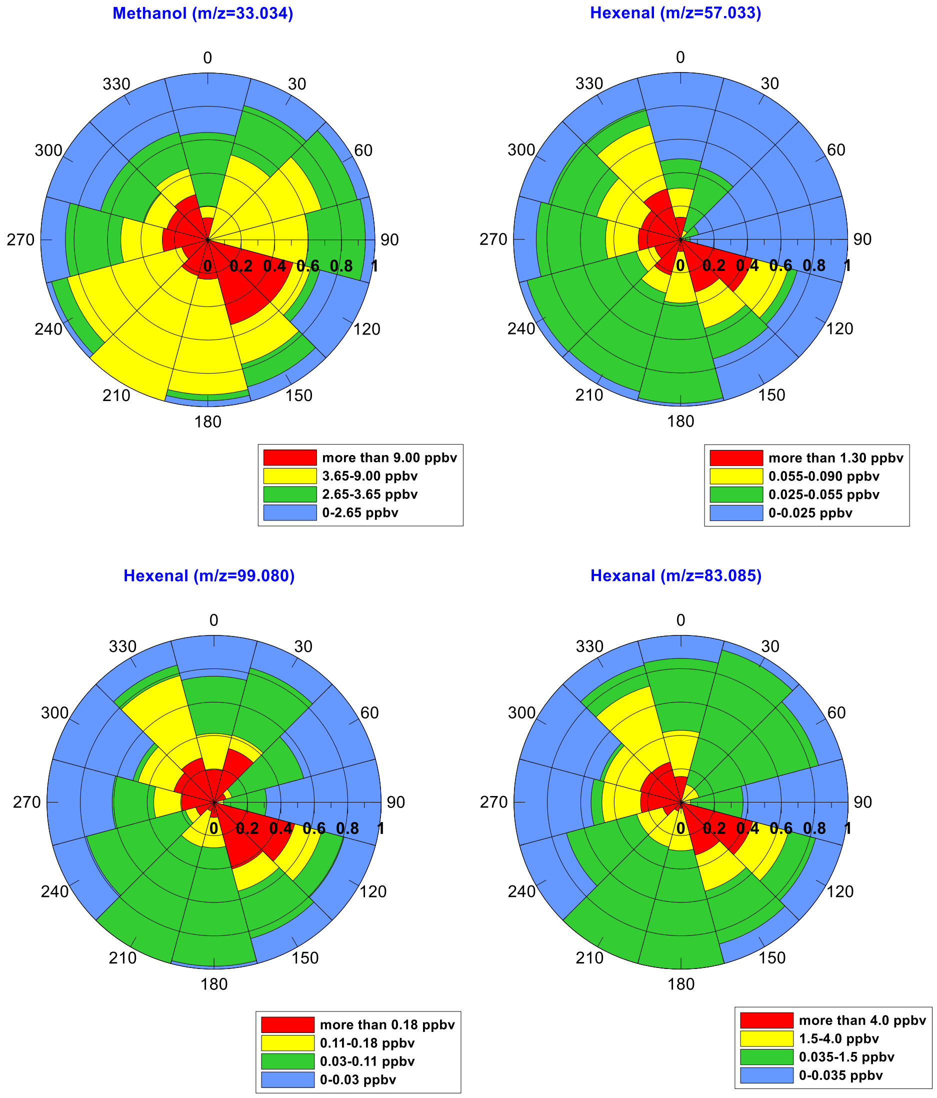


Fig. 5. *Methanol, hexanal and hexenal mixing ratios as a function of the contribution from each wind sector. The radial dimension represents the fraction of time for each wind sector during which the mixing ratios were within a certain range, as specified in the color key.*

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)

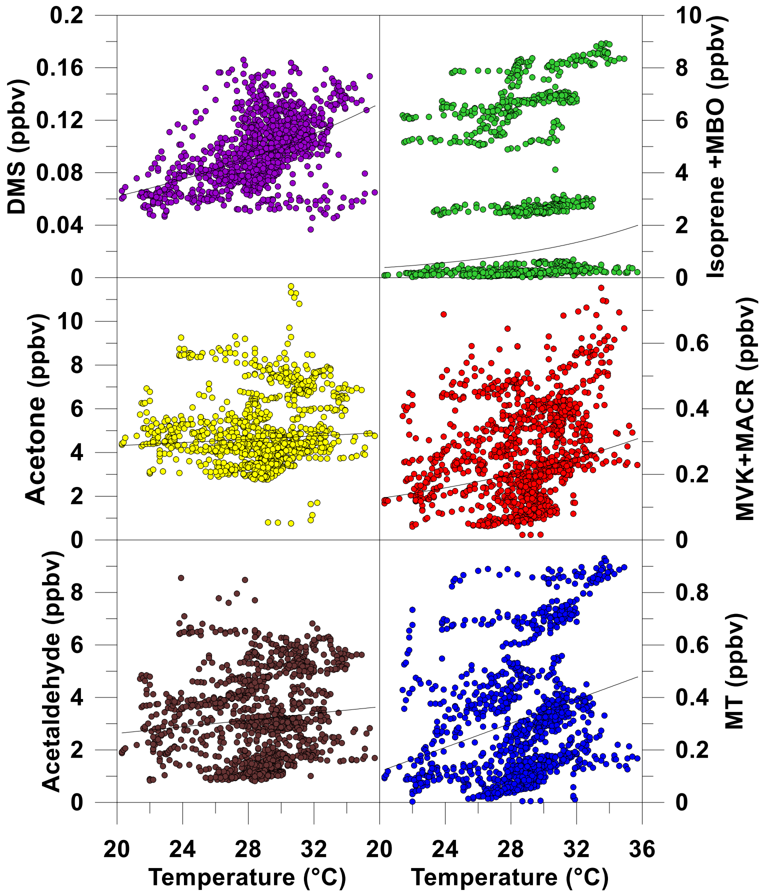


Fig. 6. *BVOC mixing ratios versus temperature. Filled circles represent mixing ratios; exponential fit lines are in black.*

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

<u>Answer</u>:

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 ~$4.9 \cdot 10^{-5}$ and $1.7 \cdot 10^{-2}\,\mathrm{ppbv \cdot s^{-1}}$ (average $5.2 \cdot 10^{-3} \pm 5.6 \cdot 10^{-3}\,\mathrm{ppbv \cdot s^{-1}}$) and between $-1.3 \cdot 10^{-3}$ and $1.3 \cdot 10^{-3}$ (average $-1.6 \cdot 10^{-6}\mathrm{ppbv \cdot s^{-1}} \pm 1.4 \cdot 10^{-5}\,\mathrm{ppbv \cdot s^{-1}}$), 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).

References:

Fry, J. C.: Oligotrophs. In Microbiology of extreme environments, edited by C. Edwards, Open University Press., 1990.

Platt, T., Rao, D. V. S. and Irwin, B.: Photosynthesis of picoplankton in the oligotrophic ocean, Nature, 301(5902), 702–704, doi:10.1038/301702a0, 1983.

Ganor, E., Foner, H. A., Bingemer, H. G., Udisti, R., and Setter, I.: Biogenic sulphate generation in the Mediterranean Sea and its contribution to the sulphate anomaly in the aerosol over Israel and the Eastern Mediterranean, Atmos Environ, 34, 3453-3462, Doi 10.1016/S1352-2310(00)00077-7, 2000.

Li, Q., Gabay, M., Rubin, Y., Fredj, E., and Tas, E.: Measurement-based investigation of ozone deposition to vegetation under the effects of coastal and photochemical air pollution in the Eastern Mediterranean, Sci Total Environ, 645, 1579-1597, 10.1016/j.scitotenv.2018.07.037, 2018.

Niinemets, U., Loreto, F., and Reichstein, M.: Physiological and physicochemical controls on foliar volatile organic compound emissions, Trends Plant Sci, 9, 180-186, 10.1016/j.tplants.2004.02.006, 2004.

Niinemets, U., Fares, S., Harley, P., and Jardine, K. J.: Bidirectional exchange of biogenic volatiles with vegetation: emission sources, reactions, breakdown and deposition, Plant Cell Environ, 37, 1790-1809, 10.1111/pce.12322, 2014.

Tyrlis, E., and Lelieveld, J.: Climatology and Dynamics of the Summer Etesian Winds over the Eastern Mediterranean, J Atmos Sci, 70, 3374-3396, 10.1175/Jas-D-13-035.1, 2013.

Vlasenko, A., Slowik, J. G., Bottenheim, J. W., Brickell, P. C., Chang, R. Y. W., Macdonald, A. M., Shantz, N. C., Sjostedt, S. J., Wiebe, H. A., Leaitch, W. R., and Abbatt, J. P. D.: Measurements of VOCs by proton transfer reaction mass spectrometry at a rural Ontario site: Sources and correlation to aerosol composition, J Geophys Res-Atmos, 114, Artn D2130510.1029/2009jd012025, 2009.

Zanis, P., Hadjinicolaou, P., Pozzer, A., Tyrlis, E., Dafka, S., Mihalopoulos, N., and Lelieveld, J.: Summertime free-tropospheric ozone pool over the eastern Mediterranean/Middle East, Atmos Chem Phys, 14, 115-132, 10.5194/acp-14-115-2014, 2014.

Emission of biogenic volatile organic compounds from warm and oligotrophic seawater at the Eastern Mediterranean

Chen Dayan[1], Erick Fredj[2*], Pawel K. Misztal[3], Maor Gabay[1], Alex B. Guenther[4], Eran Tas[1*]

[1]Hebrew University of Jerusalem, Rehovot, Israel (chenescohen@gmail.com), [2]Lev Academic Center, Jerusalem, Israel, [3]The University of Texas at Austin, Austin, ~~Texas~~TX, USA, [4]University of ~~Irvine~~ California, Irvine, ~~California~~CA, USA, [5]~~University of California at Berkeley, Berkeley, California, USA~~

* Correspondence to:

Eran Tas, The Department of Soil and Water Sciences, The Robert H. Smith Faculty of Agriculture, Food and Environment, Hebrew University of Jerusalem, Rehovot, Israel. eran.tas@mail.huji.ac.il,

Erick Fredj, Department of Computer Science, Jerusalem College of Technology, Jerusalem, Israel, erick.fredj@gmail.com

Abstract

Biogenic volatile organic compounds (BVOCs) from terrestrial vegetation and marine organisms contribute to photochemical pollution and affect the radiation budget, cloud properties and precipitation via secondary organic aerosol formation. Their emission from both marine and terrestrial ecosystems is substantially affected by climate change in ways that are currently not well characterized. The Eastern Mediterranean Sea was identified as a climate change "hot spot", making it a natural laboratory for investigating the impact of climate change on BVOC emission from both terrestrial and marine vegetation. We quantified the mixing ratios of a suite of volatile organic compounds (VOCs), including isoprene, dimethyl sulfide (DMS), acetone, acetaldehyde and monoterpenes, at a mixed vegetation site ~4 km from the southeastern tip of the Levantine Basin, where the sea surface temperature (SST) maximizes and ultra-oligotrophic conditions prevail. The measurements were performed between July and October 2015, using a proton transfer reaction time-of-flight mass spectrometer (PTR-ToF-MS). The analyses were supported by the Model of Emissions of Gases and Aerosols from Nature (MEGAN v2.1). For isoprene and DMS mixing ratios, we identified a dominant contribution from the seawater. Our analyses further suggest a major contribution, at least for monoterpenes, from the seawater. Our results indicate that the Levantine Basin greatly contributes to isoprene emission, corresponding with mixing ratios of up to ~9 ppbv several kilometers inland from the sea shore. This highlights the need to update air-quality and climate models to account for the impact of SST on marine isoprene emission. The DMS mixing ratios were one to two orders of magnitude lower than those measured in 1995 in the same area, suggesting a dramatic decrease in emission due to changes in the species composition induced by the rise in SST.

1. **Introduction**

Biogenic volatile organic compounds (BVOCs) emitted from terrestrial vegetation and marine organisms significantly affect air pollution and health via increasing regional photochemical O_3 pollution (Curci et al., 2009), enhancing local O_3 removal via chemical reaction (Calfapietra et al., 2013) and serving as precursors for secondary organic aerosol (SOA) formation (Griffin et al., 1999; Lang-Yona et al., 2010; Ren et al., 2017). Considering the large global emission rate of BVOCs, mostly from terrestrial vegetation (700–1000 TgC year^{-1}; Laothawornkitkul et al., 2009), biogenic SOA formation further impacts the radiation budget, precipitation, and climate (Chiemchaisri et al., 2001; Wuebbles et al., 1989). BVOC oxidation likewise increases CO_2 levels, as a direct product, and methane concentrations, by reducing the oxidation capacity (Penuelas et al., 2010).

Only a relatively minor fraction of all BVOCs (>10,000) are known to have sufficient reactivity and emissions to play an important role in the climate and photochemistry (Guenther, 2002). Here, we focus on some of the important emitted reactive BVOCs, including 2-methyl-1,3-butadiene (isoprene), dimethyl sulfide (DMS), and some oxygenated VOCs~~ (OVOCs)~~. Emission of isoprene from vegetation has received a lot of attention in recent years, because this compound has the highest global emission rates among all reactive BVOCs from vegetative sources (Guenther, 2002), and due to its high photochemical reactivity and contribution to SOA amounts, estimated to be at least 27-48% of total global SOA formation (Carlton et al., 2009; Meskhidze and Nenes, 2007). It is also well recognized that isoprene is emitted from seawater~~, too~~ as well (Bonsang et al., 1992; Goldstein and Galbally, 2007; Kameyama et al., 2014; Liakakou et al., 2007; Matsunaga et al., 2002), by marine organisms, including phytoplankton, seaweeds and microorganisms (Alvarez et al., 2009;

Broadgate et al., 2004; Kameyama et al., 2014; Kuzma et al., 1995). Although the emission rates of isoprene into the marine boundary layer (MBL) are estimated to be substantially smaller than terrestrial emissions, 0.1~~–~~-1.9 TgC year^{-1} (Arnold et al., 2009; Palmer and Shaw, 2005) vs. 400-750 TgC year^{-1} (Arneth et al., 2008; Guenther et al., 2006, 2012), they play an important role in SOA formation (Hu et al., 2013) and photochemistry (Liakakou et al., 2007) in the marine environment, particularly in more remote areas (Ayers et al., 1997; Carslaw et al., 2000).

~~Dimethyl sulfide (~~DMS~~)~~ is another important source for SOA formation and for atmospheric sulfur. The DMS emission rate is much higher from seawater than from terrestrial vegetation, because the marine environment contains different types of phytoplankton, algae, and microbial activity (Gage et al., 1997; Stefels et al., 2007; Vogt and Liss, 2009). DMS emission in the MBL is estimated at 15-34.4 Tg year^{-1} (Kettle and Andreae, 2000; Lana et al., 2011), the largest natural source of sulfur in the atmosphere (Andreae, 1990; Simo, 2001), accounting for nearly half the total sulfur emission to the atmosphere (Dani and Loreto, 2017).

Oxygenated VOCs, including aldehydes, alcohols, ketones and carboxylic acids, can induce tropospheric O_3 formation via alkylperoxy formation (Monks et al., 2015; Müller and Brasseur, 1999; Singh, 2004) and act as OH precursors, particularly in the upper troposphere (Lary and Shallcross, 2000; Singh et al., 1995; Wennberg et al., 1998). Similar~~ly~~ to isoprene and DMS, ~~OVOCs~~ oxygenated VOCs serve as precursors to SOA formation (Blando and Turpin, 2000).

Emission of BVOCs from both terrestrial and marine sources is fundamentally influenced by climate changes. For instance, most BVOC emissions from terrestrial vegetation tend to increase exponentially with temperature ~~(T)~~ (Goldstein et al., 2004; Guenther et al., 1995; Monson et al., 1992; Niinemets et al., 2004; Tingey et al., 1990), while drought can negate the effect of temperature on the emission rate from vegetation (Holopainen and Gershenzon, 2010; Llusia et al., 2015; Peñuelas and Staudt, 2010; Schade et al., 1999). ~~Seawater~~ Increases in seawater acidification and sea surface temperature (SST) ~~increases~~ significantly affect BVOCs in various ways, including by altering the biodiversity, spatial and temporal distribution and physiological activity of marine organisms, influences that are currently not well characterized (Beaugrand et al., 2008, 2010; Bijma et al., 2013; Bopp et al., 2013; Dani and Loreto, 2017). Accordingly, the effect of climate change on BVOC emissions into the MBL is largely unknown (Boyce et al., 2010; Dani and Loreto, 2017).

The Eastern Mediterranean Basin region has been recognized as ~~a~~ highly responsive ~~region~~ to climate change, and has been aptly named a primary “climate change hotspot” (Giorgi, 2006; IPCC, 2007; Lelieveld et al., 2012). ~~making~~This makes it an attractive site to study the impact of anthropogenic stress and climate change on marine BVOC emissions. In addition, being~~Being~~ ~~both warm and~~ oligotrophic, ~~it~~ there is a pre~~-~~dominance of unicellular and small plankton such as cyanobacteria (Krom et al., 2010~~; Rasconi et al., 2015~~)~~,~~ that can ~~,~~more efficiently perform CO$_2$ fixation and utilize nutrients under such conditions, respectively (Fogg, 1986~~)–~~; ~~(~~Mazard et al., 2004). Moreover, the high SST tends to further shift the planktonic community toward an increase in unicellular and small plankton (Mazard et al., 2004; Rasconi et al., 2015). ~~making~~ ~~it an attractive site to study the impact of anthropogenic stress and climate change on marine BVOC emissions.~~

At the southeastern tip of the Mediterranean Basin is the Levantine Basin, which is ultra-oligotrophic and the warmest region in the Mediterranean Sea (Shaltout and Omstedt, 2014; Azov, 1986; Krom et al., 2010; Psarra et al., 2000; Sisma-Ventura et al., 2017; Yacobi et al., 1995), particularly in its northern section (Efrati et al., 2013; Koç et al., 2010). This region has experienced a significant increase in SST during the last decade (+0.12±0.07–°C year^{-1} (Ozer et al., 2016), with temperatures exceeding 30°C 2 km from the coastline in 2015 (IOLR, 2015).

Most of the surface BVOC measurements at the Eastern Mediterranean are from Finokalia, Crete (Kouvarakis and Mihalopoulos, 2002; Liakakou et al., 2007). To the best of our knowledge, only a few measurements of BVOCs have been performed in the Levantine Basin, including BVOC emissions in Cyprus (e.g., Debevec et al., 2017; Derstroff et al., 2017) and DMS measurements in Israel (Ganor et al., 2000).

This study includes the first measurements of a suite of BVOCs near the Levantine Basin coast. The measurements were performed in a mixed-Mediterranean vegetation shrubbery, with the main objective of studying the contribution of both seawater and local vegetation to the concentrations of key BVOCs, including isoprene, DMS, acetone, acetaldehyde and monoterpenes (MTs). A special focus was given to the effect of meteorological conditions on the contribution of each source to the measured concentrations.

2. Methods

2.1 *Measurement site*

Field measurements were performed in Ramat Hanadiv Nature Park (33°33'19.87"N, 32°56'50.25"E). The measurement site is situated at the edge of the park’s memorial garden. This site is located about 3.6 km from the Mediterranean shore, 120 m above sea level. The characteristics of the park have been detailed by Li et al. (2018) and are ~~briefly~~ shown in Fig. 1. The nature park consists of mixed natural Mediterranean vegetation: *Quercus calliprinos* (~25%), *Pistacia lentiscus* (~20%), the sclerophyll *Phillyrea latifolia* (broad-leaved phillyrea) (~7.5%), invasive species (~10%), *Cupressus* (5%), *Sarcopoterium spinosum* (~2%), *Rhamnus lycioides* (~2%) and *Calicotome villosa* (~1%). The park's western part features a few scattered *Pinus halepensis* (<5%) combined with planted pine (*Pinus halepensis* and *Pinus brutia*) and cypress (Massada et al., 2012). During the measurements, the average canopy height was ~4.5 m, the leaf area index was ~1.3 and the vegetation cover fraction was ~0.5. The site is exposed to various anthropogenic contributions: two highways are located 1.5 km and 2.5 km west of the measurement site, a power plant ("Hadera") is at a distance of 11 km south of the site, and a major industrial zone (Haifa) is 30 km to the north. Aquaculture farms totaling ~6 km in length, located 3.2 km to the west of the site, could potentially also contribute to BVOCs at the site.

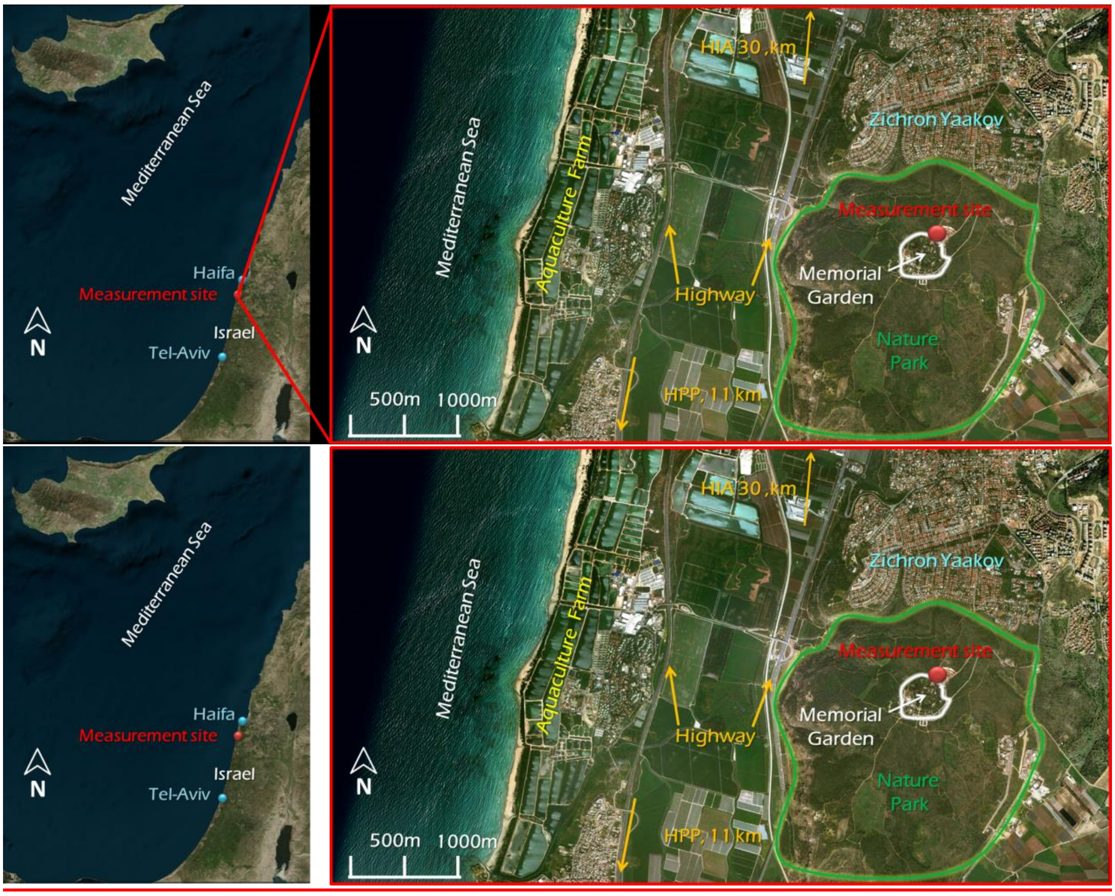


Figure 1. Satellite images of the measurement site at Ramat Hanadiv Nature Park. Left: Location of the measurement site (red dot). Right: Zoom-in on the surrounding area of the measurement site (red dot).

2.2 *Field ~~Measurements~~ measurements*

The field measurements were taken at the Ramat Hanadiv site from the summer until the late autumn of 2015 (6 July ~~6~~ 12 October ~~12,~~ 2015). ~~–~~The set of instruments included a platform for eddy covariance measurements of BVOCs, O_3, carbon dioxide (CO_2) and water vapor (H_2O), trace-gas~~es~~ mixing ratios, including O_3, NO_X, SO_2 and CO, and basic meteorological conditions, using an air-conditioned mobile laboratory and two towers (Fig. S2). Note that due to technical problems, VOC fluxes were not evaluated. The sampling routine and schematic of the setup were described in (Li et al., 2018) and are summarized in Fig. S2.

Measurement and analysis of VOC concentrations: VOC measurements were conducted using a proton transfer reaction time-of-flight mass spectrometer (PTR-ToF-MS 8000 Ionicon Analytik GmbH, Innsbruck, Austria). A detailed description of the instrument can be found in Graus et al. (2010) and Jordan et al. (2009).

The PTR-ToF-MS was placed inside an air-conditioned mobile laboratory, and ambient air was pulled at a rate of about 35 l min^{-1} through an external PFA Teflon tube (3/8" OD, 5/16" ID) and subsampled by the PTR-ToF-MS at a rate of 0.5 l min^{-1} via a 1/16" OD (1 mm ID) polyetheretherketone (PEEK) tube. The instrument inlet and drift-tube were heated to 80ºC, the drift pressure was set to 2.3 mbar, and the voltage to 600 V; all ~~the~~ settings were maintained at constant levels throughout the measurements, corresponding to ~~the~~ an E/N ratio of 140 Td. Measured data were recorded by a computer at 10 Hz.

The PTR-ToF-MS was calibrated every 1-2 days for background (zero), and weekly for sensitivity (span), subject to technical limitations (see Table S1). Background (zero) calibration was conducted by sampling ambient air which was passed through a catalytic converter heated to 350°C. Sensitivity calibration was performed using gas standards (Ionicon Analytik GmbH, Austria) containing methanol (0.99±8% ppmv), acetonitrile (0.99±6% ppmv), acetaldehyde (0.95±5% (ppmv), ethanol (1.00±5% ppmv), acrolein (1.01±5% ppmv), acetone (0.98±5% ppmv), isoprene (0.95±5% ppmv), crotonaldehyde (1.01±5% ppmv), 2-butanone (0.99±5% ppmv), benzene (0.99±5% ppmv), toluene (0.99±5% ppmv), o-xylene (1.02±6% ppmv), chlorobenzene (1.01±5% ppmv), α-pinene (1.01±5% ppmv) and 1,2-dichlorobenzene (1.02±5% ppmv) to obtain gas mixtures ranging from 1-10 ppbv. Mixing ratios of compounds for which no gas standard was available were calculated using default reaction rate constants (see Sect. S1). The PTR-ToF-MS raw hdf5 (h5) files were preprocessed by a set of routines included in the *ptrwid* processing suite within an Interactive Data Language (IDL) environment and described in detail in Holzinger, 2015. Further data processing was performed by customized multi-step Matlab (Mathworks Inc.) postprocessing routines, which included processing of calibrations, zero air, and ambient measurements, chemical formula assignment, and comprehensive quality control similar to Tang et al~~., ~~. (2016). The list of compounds inferred from chemical formulas and further analysis (e.g., correlation matrix, diel variability, and fragmentation patterns) is shown in Table S2. The uncertainties are listed according to whether a compound was explicitly calibrated and an accurate proton reaction rate constant ~~was ~~used (Sect. S1-; Cappellin et al., 2012~~a~~; Yuan et al., 2017)~~–~~, or a default reaction rate constant (2.5 × 10^{-9} cm s^{-1}) for unidentified ions was employed (not reported here).

Measurements of other trace gases and micrometeorology: Complementary measurements included the quantification of mixing ratios of carbon monoxide (CO), sulfur dioxide (SO_2), nitrogen oxides ($NO_x \equiv NO + NO_2$) and ozone (O_3), using models 48i, 43s, 42i and 49i, respectively (Thermo Environmental Instruments Inc., Waltham, MA, USA), with manufacturer-reported limits of detection of 4.0 ppm, 0.1 ppbv, 0.4 ppbv and 1.0 ppbv, respectively. These monitors were periodically calibrated to avoid drift in their accuracy. Trace-gas mixing ratios were recorded by a CR1000 data logger (Campbell Scientific, Logan, UT, USA) at a frequency of 1 min. Wind speed and wind direction were measured using an R.~~-~~M. Young Wind Monitor 05103 (R.M. Young, Traverse City, MI, USA), the air temperature and relative humidity with a CS500 probe (Campbell Scientific), and the global radiation with a Kipp & Zonen CM3 Pyranometer (Kipp & Zonen, Delft, Netherlands). These measured data were recorded with a CR10X data logger (Campbell Scientific) at 10-~~Hz~~ min frequency. Overall, the measurements resulted in 20 days of high-quality, complete data, which were divided into six different periods due to instrument downtime (see Sect. S1).

2.3 *Model simulations of BVOC emission*

The Model of Emissions of Gasses and Aerosols from Nature version 2.1 (MEGAN v2.1; Guenther et al., 2012) was applied to estimate the emission flux of BVOCs from the nature park, according to the vegetation type, and the on-site measured solar radiation, temperature, soil moisture, vegetation-cover fraction and leaf area index, using the following general formula to estimate the emission flux of species i (F_i):

$$F_i = \gamma_i \sum \varepsilon_{i,j,} \chi_j \ ,$$

where $\varepsilon_{i,j,}$ is the emission factor (representing the emission under standard conditions) of vegetation type j, γ_i is the emission activity factor, which reflects the impact of environmental factors and phenology, and χ_j represents the vegetation effective fractional coverage area. The landscape average emission factor was estimated using the observed plant species composition at the field site (see Sect. 2.1). The major driving variables of the model are solar radiation, calculated leaf temperature, leaf age, soil moisture, and leaf area index. The actual measured parameters at Ramat Hanadiv were used as input to the model, including vegetation and soil type, vegetation coverage, fraction and leaf area index, soil water content and *in situ*-measured meteorological data. Note that only the nature park was simulated by MEGAN_v2.1, while potential emissions from a nearby, relatively small "Memorial Garden" were not taken into account.

3. Results and discussion

3.1 *Seasonal and diel trends in measured BVOCs*

Figure ~~3~~ 2 presents the daytime average mixing ratios for selected VOCs measured in the field, along with the corresponding daytime average temperature. The presented data are not continuous, due to instrument unavailability, and were, therefore, separated into seven different measurement periods during the year 2015, as shown in Table 1.

Table 1. Measurement periods and corresponding daytime mean of meteorological parameters used for the analyses*

Day of ~~Year~~ year (calendric day)	**T (°C)**	**PAR (W/m^2)**	**RH (%)**	**WDD (°)**	**WDS (m/s)**
187-188 (6-7 July)	26.5	522.0	69.2	283.2	3.3
197-199 (16-18 July)	27.7	477.1	73.2	251.2	3.2
205-207 (24-26 July)	29.6	533.4	66.6	319.6	4.4
225-226 (13-14 August)	29.6	481.6	65.3	288.2	3.0
257-260 (14-17 September)**	29.7	395.4	69.1	320.6	3.9
268-269 (25-26 September)	29.3	461.0	56.0	324.2	3.7
282-285 (9-12 October)	28.6	397.7	53.1	329.3	3.5

* See Table S1 for data availability and exclusion.

** Discussed only in relation to Fig. ~~3~~ 2 considering irregular meteorological conditions (see Sect. S6).

Fig~~.~~ure ~~3~~ 2 presents both VOCs dominated by biogenic sources (BVOCs) and VOCs dominated by anthropogenic emission sources ~~(AVOCs)~~, although no compound can be regarded as exclusively biogenic or anthropogenic. The former include ~~monoterpenes (~~MTs~~;~~ (m/z=137.133, m/z=95.086, m/z=81.070), isoprene+2-~~Methyl~~methyl-3-buten-2-ol (MBO) (m/z=69.071), ~~dimethyl sulfide (~~DMS~~;~~ (m/z=63.062), acetone (m/z=59.049), acetaldehyde (m/z=45.033) and the sum of methyl vinyl ketone and methacrolein (MVK+MACR; m/z=71.048) (Janson and de Serves, 2001; Kanda et al., 1995; Karl et al., 2003; Park et al., 2013b). The latter include 1,3-butadiene (m/z=55.055) (Filipiak et al., 2013) and hydrogen sulfide (H_2SH^+;m/z=34.995) (Li et al., 2014). It is interesting to note that both MVK and MACR can have an anthropogenic source and be an oxidation product of isoprene (Fares et al., 2015; Jardine et al., 2013). Furthermore, this signal may ~~correspond~~ receive contributions from~~to 2,3~~ dihydrofurans.

The dominating source behavior for BVOCs is reflected in their diurnal cycle, which was characterized by an increase in their mixing ratios from morning to around noontime or afternoon, followed by a gradual decrease until sunset (see Figs. ~~S5~~S3~~-~~ ~~S9~~S~~8~~9). We found similar day-to-day trends in the mixing ratios of all BVOCs, particularly of acetone, acetaldehyde and the MTs. This strongly reinforces the predominantly biogenic origin for these four species, considering that MTs are expected to be primarily emitted from biogenic sources in the studied area, in the absence of any nearby wood industry. H_2S and butadiene show significantly different trends in the mixing ratios, suggesting a dominating anthropogenic contribution for these species, with a potential contribution from microbial activity (Misztal et al., 2018).

Overall, the day-to-day trend in the BVOC mixing ratios appears to follow the temperature, but exhibits only a relatively weak correlation with daily temperature variation (Fig. ~~3~~2). DMS showed the strongest correlation with the average daytime temperature (r^2=0.27; see Sect. 3.2.2), corresponding to a significant increase in the mixing ratios between early summer (0.072±0.005 ppb, day of year (DOY) 188) and the end of summer (0.19±0.040 ppb, DOY 254), which decreased during the autumn (0.17±0.015 ppb, DOY 255 to 0.066±0.011 ppb, DOY 283). The other BVOCs, except for isoprene+MBO, showed a gradual increase in their average mixing ratios during the summer and early autumn (DOY ~~197~~198-~~260~~269; acetone from 3.74±0.767 ppbv to 4.33±0.471 ppbv~~,~~, acetaldehyde from 1.64±0.595 ppbv to 3.09±0.496 ppbv, MT from 0.089±0.021 ppbv to 0.237±0.120 ppbv, MVK+MACR from 0.125±0.048 ppbv to 0.252±0.070 ppbv), and ~~a decrease during~~lower average mixing ratios in the autumn and early winter (DOY ~~268~~270-~~285~~286; DMS~~,~~ 0.091±0.026 ppbv, acetone 3.96±1.04 ppbv, acetaldehyde~~,~~ 1.86±0.97 ppbv, MT 0.139±0.064 ppbv, isoprene+MBO 0.182±0.093 ppbv, MVK+MACR 0.153±0.098 ppbv), which can be explained by the correlation with air temperature (Fig. ~~3~~2). During DOY– 257~~-~~–260, BVOCs showed elevated mixing ratios (daytime averages for DMS, acetone, acetaldehyde, H_2S, MT, isoprene+MBO and MVK+MACR were 0.122±0.016 ppbv, 13.6±3.26 ppbv, 8,1~~38~~40±1.18 ppbv, 0.046±0.021 ppbv, 1.97±0.215 ppbv, 7.68±0.218 ppbv and 0.644±0.084 ppbv, respectively), 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. ~~We attribute the extreme mixing ratios during DOY 257-260 to extreme meteorological conditions; this period was characterized by high wind speeds and relatively low solar radiation, which can facilitate a shallow boundary layer and, in turn, higher VOC mixing ratios (see Sect. S4).~~

~~While t~~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. ~~5~~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.

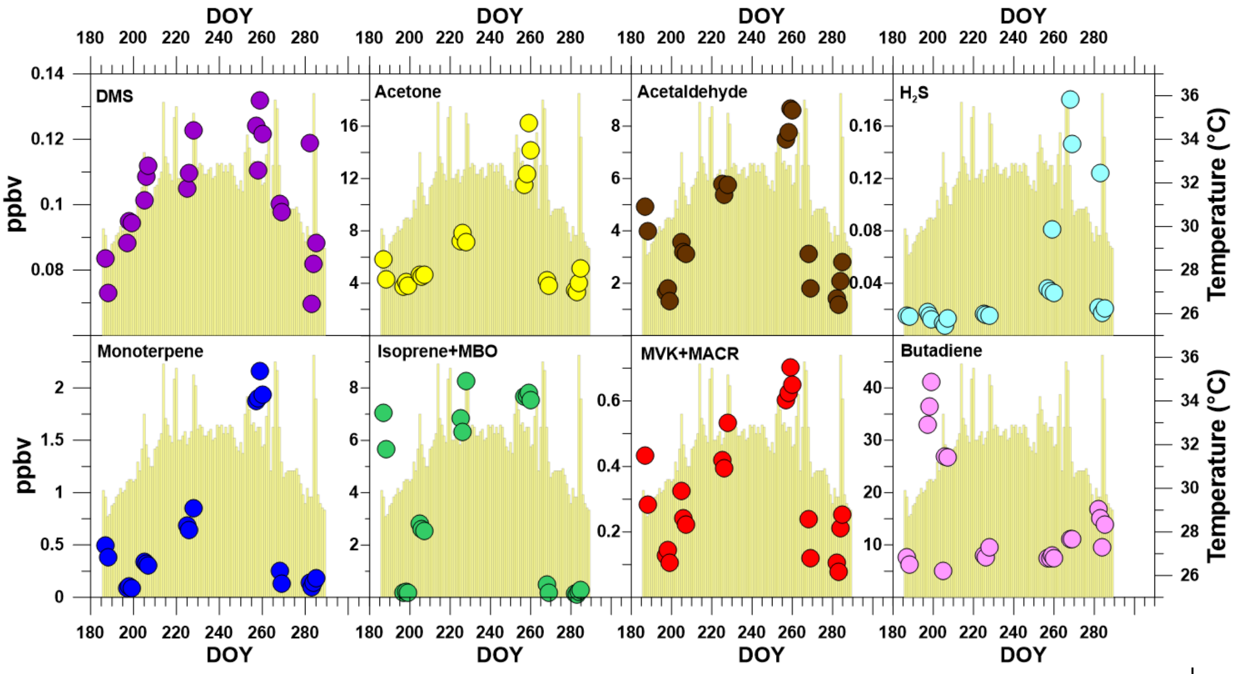
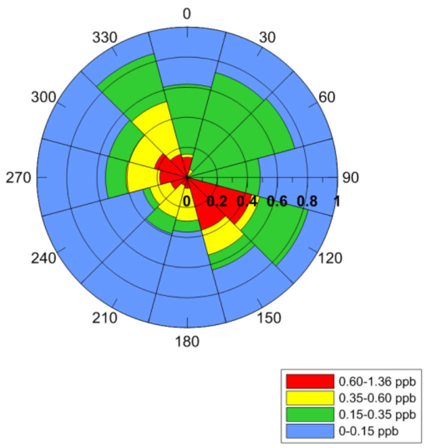


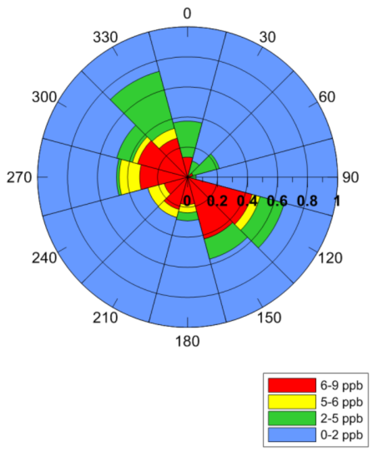
Figure ~~3~~2. The daytime average of selected VOCs. Yellow bars indicate the average daily temperature. DOY indicates the day of the year. For average diurnal profiles, see Fig. ~~S5~~S3-~~S9~~S9.

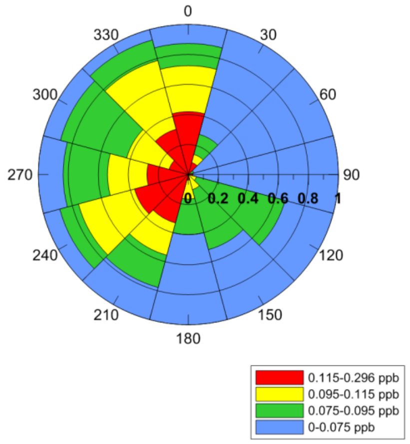
3.2 *Origin of the BVOCs*

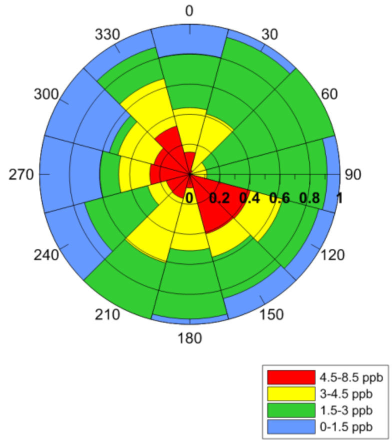
To explore the potential sources of the BVOCs, we calculated for each wind sector the percentage of time corresponding with several mixing-ratio ranges, individually for each species (Fig. ~~4~~3). Our findings indicate elevated mixing ratios for westerly and southeasterly wind components. The relatively elevated mixing ratios from the southeast can be attributed to emissions from the memorial garden, where frequent thinning of the vegetation can contribute to the generally elevated mixing ratios of plant-wounding BVOCs ~~such as~~ which may include acetaldehyde, MVK, MACR, acetone, MT ~~hexenal and hexanal~~ (e.g., Brilli et al., 2011, 2012; Goldstein et al., 2004; Ormeño et al., 2011; Portillo-Estrada et al., 2015) and possibly isoprene ~~from this direction~~(e.g., Kanagendran et al., 2018). While methanol, hexanal and hexenal measurements also indicated elevated mixing ratios from the southeast, our analysis did not clearly indicate higher excess of these green~~–~~-lea~~ves~~ved species from the southeast, compared to the other wounding BVOCs (Sect. S7). The elevated mixing ratios from the west may point to an additional contribution from marine origin, such as the Mediterranean Sea and/or the aquaculture farms, considering that the measurement site is surrounded by nearly homogeneous vegetation in all directions except for the memorial garden (Fig. 1). We found a smaller relative contribution of DMS from the southeast compared to the other BVOCs. ~~The MEGANv2.1 simulations suggested~~ The MEGAN v2.1 simulations indicated that the known plant species in the nature park should not be a significant source of isoprene~~no significant emission of isoprene from the nature park;~~ . 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.

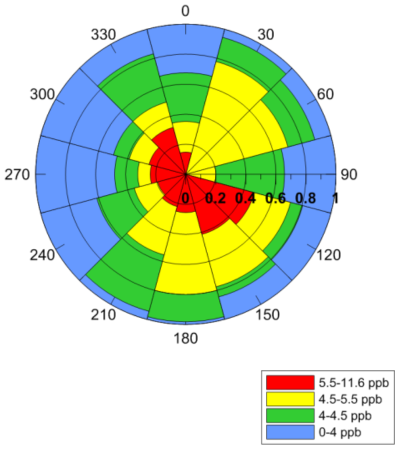
~~t~~The relatively strong contribution of isoprene+MBO from the southeast can be attributed to MBO emissions from conifer trees (Gray et al., 2003) in the memorial garden. Similar trends in the day-to-day variation of MVK+MACR, isoprene oxidation products, and isoprene+MBO (Fig. ~~3~~2) could imply the contribution of the memorial garden to isoprene emission~~,~~ .~~but~~ However, ~~this possibility is ruled out by kinetic analysis~~ kinetic analysis indicated that the isoprene emission from the memorial garden is much too small to account for the observed MVK+MACR ~~which is~~ associated with transported air masses from the memorial garden (see Sect. ~~S2~~S4). 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. The origin of DMS is further addressed in Sect. 3.2.2.

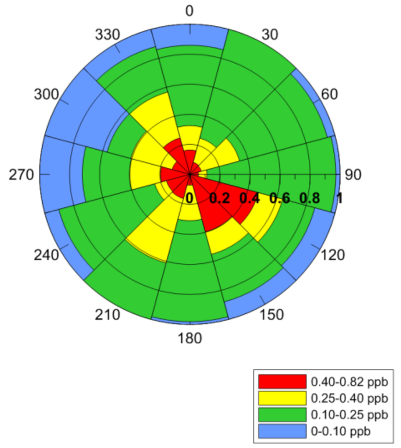

Monoterpene emission source direction (%)


Isoprene+MBO emission source direction (%)


DMS emission source direction (%)


Acetaldehyde emission source direction (%)


Acetone emission source direction (%)


MVK+MACR emission source direction (%)

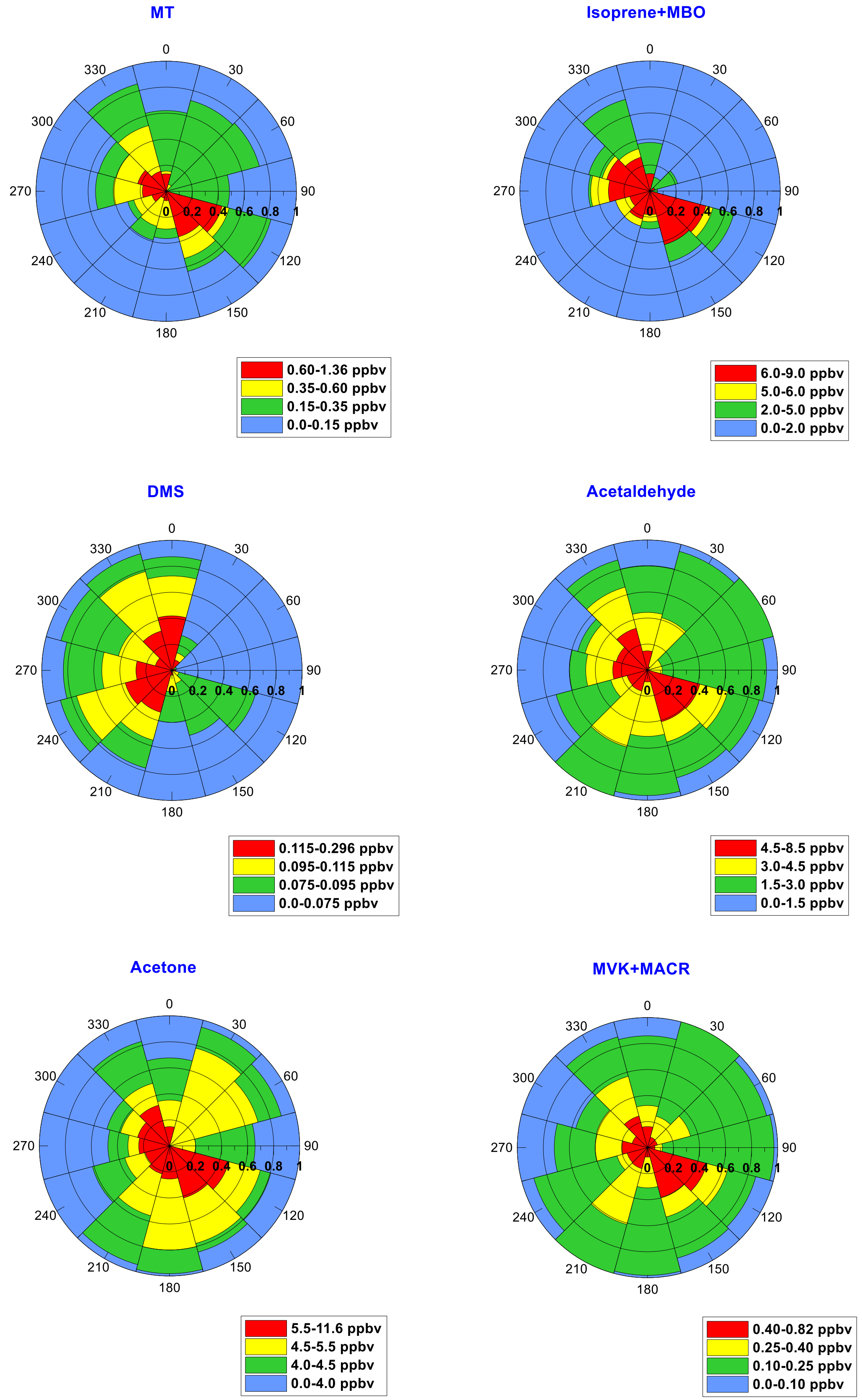


Figure 43. BVOC mixing ratios as a function of the contribution from each wind sector during the daytime. The radial dimension represents the fraction of time, for each wind sector, during which the mixing ratios were within a certain range, as specified in the color key.

3.2.1 Origin apportionment of measured isoprene+MBO

Potential anthropogenic emission sources of isoprene+MBO: The indication from the MEGAN v2.1 simulations that the known plant species in the nature park are not a significant source of isoprene~~,~~ may suggest~~s~~ a significant contribution of the measured isoprene from anthropogenic sources. ~~As~~Moreover, as demonstrated in Sect. 3.1, the isoprene+MBO day-to-day variations differed from those of most of the other BVOCs, with remarkably high variations in its mixing ratios, ranging from 0.03 ppbv to nearly 9 ppbv (Fig. ~~3~~2; Table S3~~), —~~). These day-to-day variations apparently masked the seasonal correlation of isoprene with ~~–while the seasonal variation in its mixing ratios did not correlate with~~ temperature (see Fig. ~~S12~~S10). Two highways to the west (Fig. 1) are the major potential anthropogenic isoprene~~-~~ emission sources at the site. The low correlation between the diurnal profile of isoprene ~~and with~~and those of acetonitrile, benzene, toluene, and carbon monoxide (see Figs. ~~S10~~S1~~1~~2~~-~~-S1~~6~~7 and S18) strongly supports no significant contribution to isoprene mixing ratios from traffic on the two highways~~ to the west (Fig. 1)~~, considering that ~~the latter threeCO~~ benzene, toluene and carbon monoxide can be used as ~~an~~ indicators for ~~incomplete combustion of fossil fuels~~emission from transportation. The ~~Positive Matrix Factorization model (PMF) further predicted that isoprene+MBO has a common source with other BVOCs and not with AVOCs~~ dominant contribution of biogenic over anthropogenic sources to isoprene is further discussed in the following~~(see Fig. S3)~~.

Potential biogenic emission sources of isoprene+MBO: Figure~~.~~ 4 presents a scatter plot of isoprene+MBO mixing ratios vs. T for the six measurement periods. For the two periods with high and low isoprene+MBO mixing ratios, there was a clear typical biogenic diurnal trend, with a maximum around noontime. This finding reinforces the notion that isoprene+MBO originates predominantly from biogenic sources. We did not, however, observe a positive correlation between isoprene+MBO mixing ratios and air *T* in all six periods (Table 1). Furthermore, in most cases, we found no exponential increase in isoprene+MBO with air *T*, as is expected in the case of a nearby local biogenic source (e.g., Bouvier-Brown et al., 2009; Fares et al., 2009, 2010, 2012; Goldstein et al., 2004; Guenther et al., 1993; Kurpius and Goldstein, 2003; Richards et al., 2013). This might be related to the fact that the m69 signal is affected by the mixing ratios of both isoprene and MBO emitted locally and further away, while the local air temperature did not reflect changes of more distant leaf temperatures or SSTs. Therefore, ~~in the following~~ we ~~do~~partitioned the~~ a partitioning of~~ isoprene+MBO signal.

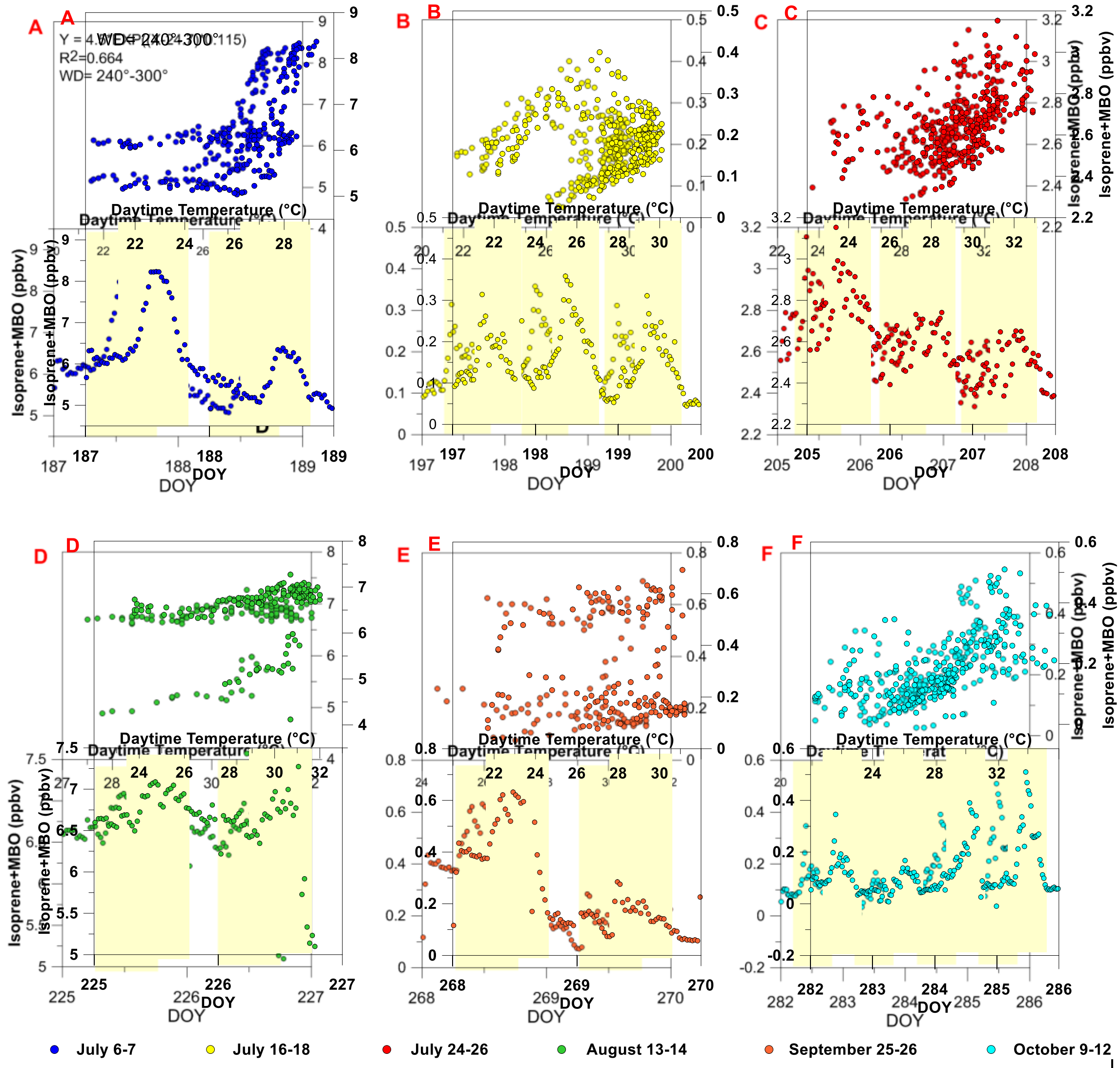


Figure ~~5~~4. Isoprene+MBO (m69) diurnal average mixing ratios and time series. (A-F) ~~The regressionr~~Regression scatter of ~~between the~~ measured MBO+isoprene (ISP+MBO) ~~and~~ vs. ~~T~~ temperature (upper panels) and the time series of isoprene+MBO (lower panels) for the six measurement periods: DOY 187~~-~~-188 (A), DOY 197~~-~~-199 (B), DOY 205~~-~~-207 (C), DOY 225~~-~~-226 (D), DOY 268~~-~~-269 (E), DOY 282~~-~~-285 (F). The ~~regression~~ scatter ~~between~~ of the measured MBO+isoprene ~~and~~ vs. ~~T~~ temperature (upper panels) excludes measurements associated with wind direction from the memorial garden (90~~°-~~°-150°).

Partitioning of isoprene+MBO signal: We used the fact that MBO can ~~be~~ also be detected at m/z=87.0805 (m87), which typically accounts for 13-25% of the total

MBO signal (Kaser et al., 2013; Park et al., 2013a, 2012, 2013b) to learn about the ratio between the isoprene and MBO mixing ratios. Note that other species, in addition to MBO, including methyl propyl ketone, pentanal, and other $C_5H_{10}O$ compounds may contribute to the m87 signal~~, in addition to MBO~~. Hence, we refer in the following to ~~the~~ m/z=87 as MBO* to reflect this fact. Figure ~~6a~~ 5~~a~~A presents the mixing ratios for m69 vs. m87/m69. Periods with high mixing ratios for m69 were associated with a very low m87/m69 ratio (less than 2%), which suggests that the emissions are predominantly of isoprene. Fig~~.~~ure ~~6a~~ 5~~a~~A also indicates ~~also~~ that m87/m69>25% was mostly measured during the nighttime, twilight and early morning. ~~-~~For low m69, the ratio matches the typical MBO ~~typical~~ ratio, m87/m69, which ranges between 13~~-~~ and 25% or higher (Fig. ~~6a~~5aA). ~~Furthermore, in those relatively low m69 mixing ratio periods, the ratio between the measured m69 and the MT relative signals match the [MBO]/[MT] from MEGANv2.1. This reinforces the hypothesis that high isoprene+MBO mixing ratios predominantly result from isoprene emission, whereas low mixing ratios are primarily from local vegetation MBO emissions.~~

Isoprene origin: Figure ~~7~~ 6 further presents the diurnal profile for m87/m69<13%, as well as the corresponding mixing ratios versus ~~T~~temperature, separately for each measurement day. Interestingly, some of the measurement days presented in Fig. ~~5~~ 4 were associated with no m87/m69<13%, which is why there are fewer measurement days in Fig. ~~7~~ 6 than in Fig. ~~5~~4. The diurnal profiles in Fig. ~~7~~ 6 support a biogenic origin for isoprene, although they were more scattered for 25-27 ~~of~~ July. Fig~~.~~ure ~~7~~ 6 also demonstrates the positive correlation between the isoprene mixing ratio and ~~T~~ temperature during all measurement days, while ~~in~~ on several days, a sharp increase in isoprene with ~~T~~ temperature occurred for T>~26-28°C (e.g., 6,7 July and 16 August). In general, a higher correlation with temperature was obtained for m87/m69<13% (Fig. ~~7~~6) than for all m69 signals (i.e., Fig. ~~7~~ 6 vs. Fig. ~~5~~4), reinforcing the biogenic origin ~~for~~ of isoprene with a relatively strong dependency on ~~T~~temperature. Furthermore, regression of m87/m69>13% with ~~T~~ temperature does not indicate a clear dependency of mixing ratios on ~~T~~temperature, suggesting different emission controls for the MBO* and isoprene (see Fig. ~~S4~~S21). While ~~The~~ the MBO* mixing ratios tended to be controlled by both ~~T~~ temperature and solar radiation, ~~while~~ isoprene was predominantly governed by the former, in agreement with a previous study (see Kaser et al., 2013).

To study the origin of isoprene, we analyzed the fraction of time for which m87/m69<13% vs. wind direction (Fig. ~~6b~~5~~b~~B). We found that m87/m69<13% predominantly corresponds with a western origin. These results suggest a significant contribution of isoprene from the sea or the aquaculture farm located ~~at~~ to the west of the measurement site (Fig. 1), considering that the measurement site is nearly homogeneously surrounded by mixed-Mediterranean vegetation, except for the memorial garden to the southeast. Furthermore, MEGAN v2.1 simulations predicted a negligible emission rate for isoprene from the nature park. In addition, the relatively high day-to-day variation in isoprene mixing ratios (Fig. 6) further support emission induced by marine organisms.

In some cases (~4% of the time), elevated m87/m69~~>~~<13% was also recorded ~~also~~ from the southwest and northwest, which according to simulations by HYSPLIT, can be entirely attributed to transport from either the sea or the aquaculture farms (see Fig. ~~S11~~S20). The relatively small fraction of time ~~for~~ during which m87/m69<13% ~~is~~ was from the southeast can be attributed to the emission of isoprene, while most of the elevated isoprene+MBO from this direction (Fig. 3)~~,~~ can be attributed to MBO from conifers.~~.~~

A

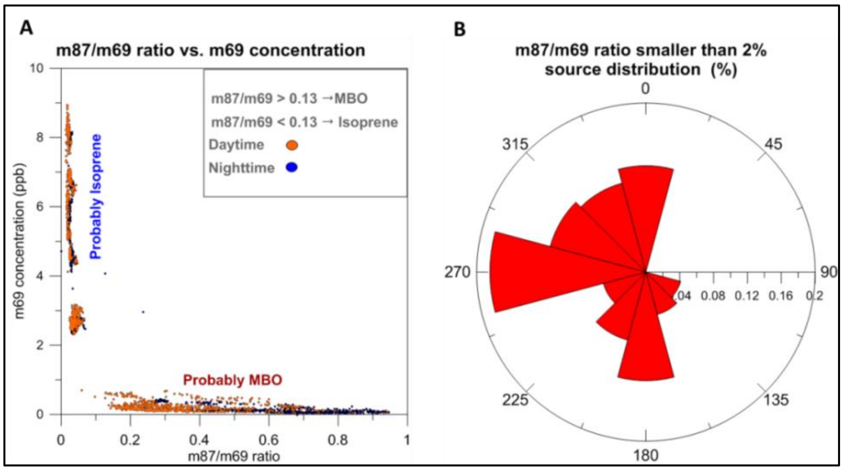


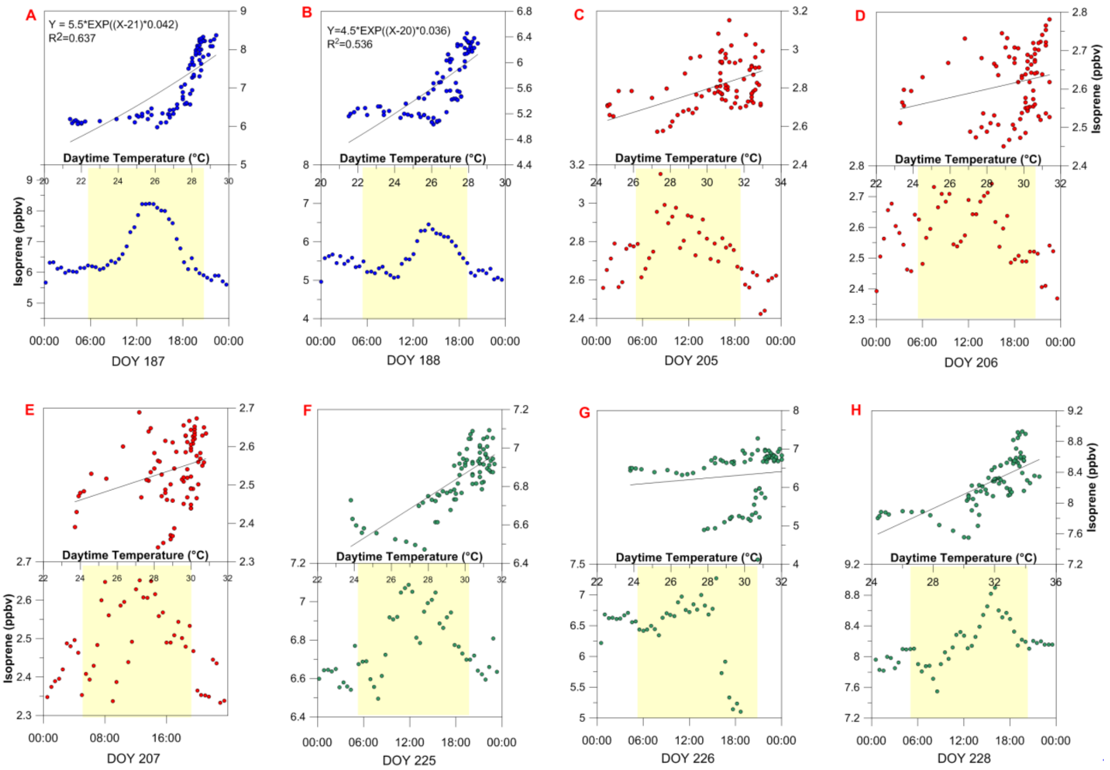
Figure ~~6~~5. Isoprene and MBO* origins. (~~a~~A) Scatter plot of m69 mixing ratios as a function of the m87/m69 ratio. Low and high ratios indicate a predominant contribution of MBO* (see definition in section 3.2.1) and isoprene, respectively. The orange dots were measured during the daytime and the dark blue dots during the night~~time~~. (~~b~~B) Fraction of time for each wind sector for which m87/m69 was <13%~~.~~.

Two facts support isoprene~~+MBO~~ predominant sea origin rather than the aquaculture farms. First, back trajectories using HYSPLIT show no lower mixing ratios for m87/m69<2%, ~~isoprene+MBO~~ also in cases when the air masses were transported from the sea but not over the aquaculture farms compared to transport of air masses over the aquaculture (e.g., Fig. ~~5~~ 4 and Fig. ~~S11~~S20). Second, marine organisms have relatively short life cycles, typically a few days (Tyrrell, 2001), and would likely have a variable source strength from the aquaculture farms, which would not ~~explain~~ coincide with the similar measured m87/m69<2% ~~isoprene+MBO~~ mixing ratios for different wind directions during a specific day. Our measurements indicated no dependence of high m87/m69<2% ~~isoprene+MBO~~ mixing ratios on wind direction during the day, reinforcing the sea's dominant role in isoprene emission, rather than the aquaculture farms. 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.

Interestingly, the isoprene mixing ratios during the nighttime remained relatively high (~5~~-~~-6 ppb) (Fig. ~~6a~~5~~a~~A), possibly due to relatively small oxidative sink strength during the night. The daytime and nighttime isoprene lifetime can be estimated based on its reaction with OH, NO_3 and O_3. We estimated the average daytime OH and nighttime NO_3 concentrations, based on the MINOS campaign in Finokalia, Crete (Berresheim et al., 2003; Vrekoussis et al., 2004), at $4.5 \cdot 10^{6}\ \frac{molec}{cm^3}$ (Berresheim et al., 2003), and $1.1 \cdot 10^{8}\ \frac{molec}{cm^3}$ (Vrekoussis et al., 2004), respectively. Using these concentrations, the reported rate constants for isoprene with OH and NO_3 of $1 \cdot 10^{-10}\ \frac{cm^3}{molec \cdot s}$ (Stevens et al., 1999) and $5.8 \cdot 10^{-13}\ \frac{cm^3}{molec \cdot s\cancel{ec}}$ (Winer et al., 1984), respectively, and measured O_3 levels, we obtained daytime and nighttime isoprene lifetimes of ~37 min and ~3.8 h, respectively. Considering the relatively moderate decrease in the measured isoprene during the night (Figs. S11~~-~~-S16), ~~T~~this result indicates stronger isoprene emissions ~~occurring~~ during the daytime, but does not rule out nighttime isoprene emissions.

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 ~$4.9 \cdot 10^{-5}$ and $1.7 \cdot 10^{-2}$ ppbv ·

s^{-1} (average $5.2 \cdot 10^{-3} \pm 5.6 \cdot 10^{-3}$ ppbv $\cdot$ s^{-1}) and between $-1.3 \cdot 10^{-3}$ and $1.3 \cdot 10^{-3}$ (average~~d~~ $-1.6 \cdot 10^{-6}$ppbv $\cdot$ s^{-1} $\pm 1.4 \cdot 10^{-5}$ ppbv $\cdot$ s^{-1}), supporting a much smaller isoprene production rate during the night vs. daytime.



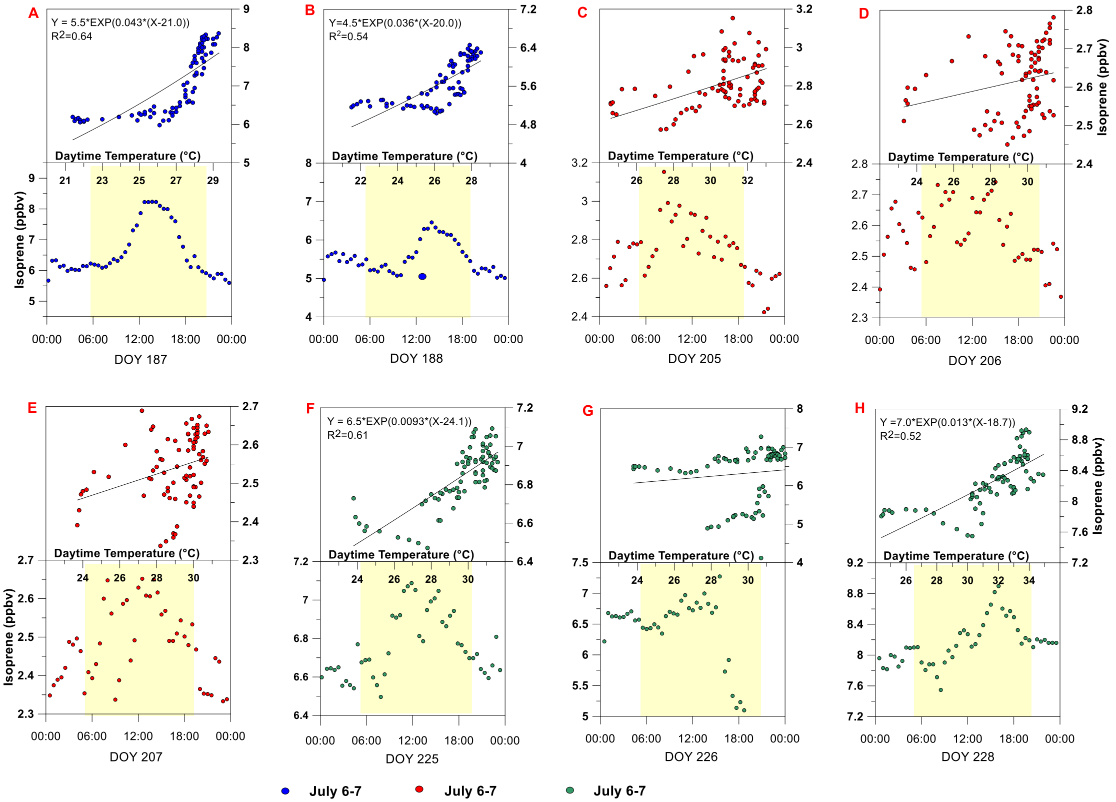


Figure ~~7~~6. Isoprene (m87/m~~9~~69<13%) diurnal average mixing~~-~~ ratio ~~diurnal average~~ and dependence on temperature. Upper panels show ~~regression~~ scatter plot between measured m87/m96<13% and ~~T~~temperature, as well as the corresponding regression equation and nonlinear exponential coefficient

(R^2) in cases when $R^2>0.50$. Lower panels present that of m87/m96<13%. Yellow shaded area represents daylight hours.

3.2.2 Origin and characterization of DMS emission

The discussion in Section 3.1 suggests that DMS is primarily emitted from the west, pointing to a dominant marine emission source, with the less elevated mixing ratios probably associated with emission from vegetation. According to the MEGAN v2.1 simulation, the natural park's vegetation is a potent source of DMS (average flux=0.477 $\frac{mg}{m^2\cdot hr}$), slightly higher than the flux measured from insolated branches (Jardine et al., 2015; Yonemura et al., 2005), while our analysis points to a stronger emission from the memorial garden (see Fig. ~~4~~3). As with isoprene, insensitivity of DMS mixing ratios to wind direction, for westerly winds, rules out a significant contribution of the aquaculture farms to the measured DMS~~,~~. This suggests that the sea is a major source for DMS, with an apparently ~~a~~ strong dependency on ~~T~~ temperature (Figs. ~~3~~2, ~~4~~3). DMS showed much less day-to-day variations in its mixing ratios compared to isoprene and other BVOCs. This corresponded with a clear day-to-day correlation of DMS mixing ratios with ~~T~~ air temperature (Fig. 2). Figure ~~8~~ 7 demonstrates a clear increase in the mixing ratios with ~~T~~ air temperature, throughout the measurement period. Note that no significant dependency of DMS on global solar radiation was observed.

The DMS mixing ratios peaked at ~0.18 ppbv. This figure is about an order of magnitude lower than at the ocean surface (Tanimoto et al., 2014), about an order of magnitude lower than in the Southern Ocean (Koga et al., 2014), slightly lower than the maximum concentrations in the south Indian Ocean (Aumont et al., 2010), and similar to the maximum concentrations on the coasts of Tasmania (Aumont et al., 2010). 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 ~~which~~ 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.

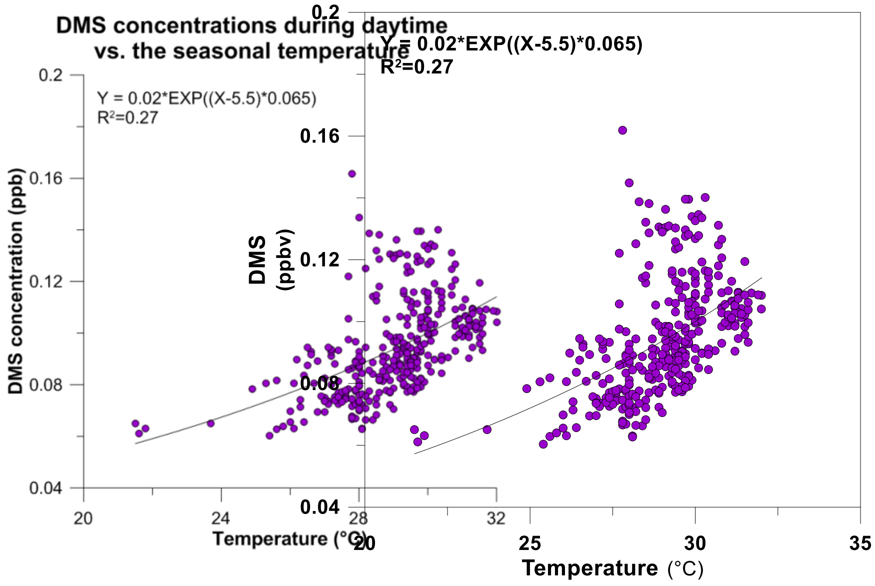


Figure ~~8~~7. Daytime DMS mixing ratios from the western sector (marine source) as a function of the temperature along the measurement campaign. An exponential fit between the two is included.

3.2.3 Origin and characterization of other BVOCs

Our findings in Figure ~~3~~ 2 strongly suggest a common source for other BVOCs with isoprene. We could not, however, use a wind-direction-based analysis to indicate BVOCs' origin from the sea, since both sea and vegetation are located to the west of the measurement point (see Fig. 1), and in contrast to isoprene, the other BVOCs were indicated by MEGAN v2.1 to be locally emitted. Furthermore, those BVOCs were less variable with wind direction than was isoprene. We used MT summer measurements from two other sites in Israel to assess whether MTs are likely to be transported to the measurement site.

We used the ratio between MT flux and mixing ratio at the three sites as a basis to address this inquiry. Note that according to the MEGAN v2.1 simulations (see Sect. 2.3), the MT emissions in Ramat Hanadiv were driven by *Quercus calliprinos* (48.1%), *Pistacia lentiscus* (19.8%), *Phillyrea latifolia* (7.12%) and *Cupressus* spp. (6.17%), ~~–~~as well as other species (see Sect. S5), in contrast to the two *Pinus halepensis* plantations, Birya and Yatir. While the fact that MT is not emitted by the same vegetation species should not significantly affect our analysis, we recognize that there may be differences in the MT composition and atmospheric oxidation capacity at the three sites which would influence MT lifetimes and lead to some differences in the flux~~-~~-to~~-~~-concentration ratios. According to MEGAN_v2.1, the average and maximal daytime MT flux were 59 $\frac{\mu g}{m^2 \cdot hr}$ and 152 $\frac{\mu g}{m^2 \cdot hr}$, respectively. While this predicted average flux is lower than the mean MT measurements in the Birya and Yatir ~~*Pinus halepensis Mill.*~~ forests ~~in Israel~~ (~200 $\frac{\mu g}{m^2 \cdot hr}$ and 800 $\frac{\mu g}{m^2 \cdot hr}$, respectively; Seco et al., 2017), the corresponding measured mixing ratios in our study are generally higher than those measured in those two sites, where in only a few cases the MT mixing ratios reached above 0.5 ppbv for Birya, and the maximum was 0.2 ppbv in Yatir. Note that the higher mixing ratios in our study, as compared with these two sites, were associated with wind direction, either from the memorial garden or from the western sector (Fig. ~~4~~3). This supports a relatively small local contribution of MTs in our study compared with seawater.

3.3 *Concentrations of isoprene and DMS originating from the Levantine Basin*

Previous studies demonstrated the trade-off between DMS and isoprene in the marine boundary layer, due to species distribution and climate, suggesting that most regions are a source of either isoprene or DMS, but not both. While isoprene is emitted from species that are more abundant in warmer regions and low-to-middle latitudes, DMS is predominantly emitted in colder regions and higher latitudes (Dani and Loreto, 2017). This is in agreement with the relatively high isoprene/DMS mixing ratios in our study. The SST in the Levantine Basin is relatively high, exceeding 30°C in August 2015 at a distance of 2km from the coastline (IOLR, 2015). Further, SST plays a significant role in determining which phytoplankton will dominate, and for a given marine organisms population higher temperature and solar radiation tends to enhance their BVOC emission, including DMS and isoprene (Dani and Loreto, 2017). The strong emission of isoprene from the Levantine Basin can be attributed primarily to its relatively high SST, considering the well-known correlation of isoprene emission with SST (Dani and Loreto, 2017; Exton et al., 2013).

The relatively warm and oligotrophic sea enables cyanobacteria to become a large fraction of marine primary production and phytoplankton (Krom et al., 2010; Paerl and Otten, 2013; Pedrotti et al., 2017; Sarma, 2013) in the Levantine Basin, that favors, in turn, emission of isoprene over other BVOCS, including DMS. Previous measurements have indicated the presence of cyanobacteria in the Levantine Basin during the summer of 2015 (Herut, 2016), with the cyanobacteria *Synechococcu*s and *Prochlorococcus* being the most abundant phytoplankton along the coasts of Israel during August 2015. A laboratory experiment demonstrated the emission of isoprene from the latter (Shaw et al., 2003). Other micro-organisms in the Levantine Basin (mostly dinoflagellates and diatoms) are generally less abundant. *Thalassiosira pseudonana* diatoms are also abundant along the coasts of Israel, which raises the possibility that the emission of isoprene from the sea is also influenced by this species. A laboratory experiment using PTR-MS indicated the emission of isoprene, as well as methanol, acetone and acetaldehyde from *Thalassiosira pseudonana* diatoms, but isoprene is the only one among these that is not consumed by bacterioplankton within the water column (Halsey et al., 2017).

DMS can be also emitted by diatoms, but at lower rates under warmer conditions (Dani and Loreto, 2017; Levasseur et al., 1994). In addition, DMS is a common microbial VOC, formed in various marine environments by bacterial decomposition of dimethylsulfoniopropionate (DMSP) (Bourne et al., 2013; Howard et al., 2008). DMS in the marine boundary layer is mostly emitted by dinoflagellates and haptophyte coccolithophores. Dinoflagellates, as well as *Thalassiosira pseudonana* diatoms, were constantly observed along the coast in estuary zones several kilometers from the measurement site (Herut, 2016). This might explain the relatively minor day-to-day variations in the mixing ratios of DMS (Fig. ~~3~~2), which, in turn, resulted in a relatively high correlation of the mixing ratios with T throughout the measurement periods. Cyanobacteria blooms and collapses depend on the nutrient supply and have no seasonality (Paerl and Otten, 2013), which can be an additional reason for the fluctuations in isoprene.

4. Conclusions

Our findings indicate that high isoprene emission from the Eastern Mediterranean Sea contributes up to ~9 ppb several km inland from the sea shore. The apparently strong emission of isoprene can be attributed primarily to the relatively high SST of the Levantine Basin, considering the well-known correlation of isoprene emission with SST growth conditions (Dani and Loreto, 2017; Exton et al., 2013). Furthermore, isoprene mixing ratios tended to strongly increase with diurnal increases in ~~T~~air temperature, but there was no correlation with solar radiation. Our analysis points to cyanobacteria as a dominant source for the isoprene emission, as are other possible marine microbiomes, supporting previous findings (Arnold et al., 2009; Bonsang et al., 2010; Dani and Loreto, 2017; Hackenberg et al., 2017; Shaw et al., 2003). Measured DMS mixing ratios were lower by 1-2 orders of magnitude than those measured in 1995 (Ganor et al., 2000) in the same area during the same season, suggesting a strong impact of SST on the decadal change in DMS emissions via changes in species composition. Considering that, according to IPCC, ocean SST is expected to rise by 5°C by the year 2100 (Hoegh-Guldberg et al., 2014), efforts are required to adequately represent the complex dependency of marine BVOC emissions, such as isoprene and DMS, on SST, to improve the predictability of both air-quality and climate models. Our study results indicate that this increase in SST can significantly increase the emission of isoprene into the MBL. This can greatly affect air quality, considering its high photochemical reactivity, with particularly negative implications in urbanized coastal areas, where on-shore wind typically occurs during the daytime, controlled by the sea-land breeze. Furthermore, elevated isoprene emission is expected from coastal areas where coastal upwelling can significantly affect biological activity, which was shown to correlate with BVOC emissions (Gantt et al., 2010).

Comprehensive evaluation of the impact of marine organism emissions on both the atmospheric chemistry and radiative budget should rely on a suite of gases. Along with the high isoprene levels, relatively low DMS mixing ratios were observed under the studied conditions, which supports previous studies that have indicated a general contrasting spatial distribution, partially controlled by SST and latitude (Yokouchi et al., 1999) and lower DMS emission under relatively low temperature (Dani and Loreto, 2017). While DMS and isoprene emissions are influenced in a contrasting manner by changes in SST, both tend to rise in response to a SST increase for a given phytoplankton population (Dani and Loreto, 2017), as supported by this study.

Significant contribution of oceanic emission of other BVOCs, such as acetone, acetaldehyde and monoterpenes have been also reported by previous studies. We found supporting indications for dominant emission of MT from the Levantine Basin, further suggesting significant emission of other BVOCs from this source. The analyses also indicate that estuaries play a potentially important role in facilitating the emission of DMS, and probably additional BVOCs, by maintaining a suitable environment for phytoplankton growth. In agreement with a previous study (Goldstein et al., 2004), our analyses suggest that thinning may play an important role in facilitating BVOC emissions, a mechanism which should be taken into consideration especially in urban areas with cultivated parks and gardens.

This study demonstrates that most of the VOCs studied here are controlled by both anthropogenic and marine and terrestrial biogenic emission sources, highlighting the need for the strict identification of the origin and representative models for both emission source types. Our study further highlights the Levantine Basin’s capability to serve as a natural laboratory for studying both anthropogenic stress and climate change on marine BVOC emissions. More comprehensive research is required to directly address the impact of oligotrophication and increased SST on marine BVOC emissions.

Data availability. Data are available upon request from the corresponding authors Eran Tas (eran.tas@mail.huji.ac.il) and Erick Fredj (erick.fredj@gmail.com).

Author contribution. ET designed the experiments, MG and GL carried the field measurements out and PM and EF led the calibration, quality control and data processing. AG setup the MEGAN_v2.1 model. CD and ET led the analyses with contributions from all co-authors. ET and CD prepared the manuscript with contributions from all co-authors.

Competing interests. The authors declare that they have no conflict of interest.

Acknowledgements

We want to greatly thank the crew of Ramat Hanadiv and Gil Lerner for supporting the measurements. This study was supported by the Israel Science Foundation, Grant No. 1787/15. E.T. holds the Joseph H. and Belle R. Braun Senior Lectureship in Agriculture.

References

Alvarez, L. A., Exton, D. A., Timmis, K. N., Suggett, D. J. and McGenity, T. J.: Characterization of marine isoprene-degrading communities, Environ. Microbiol., 11(12), 3280–3291, doi:10.1111/j.1462-2920.2009.02069.x, 2009.

Andreae, M. O.: Ocean-atmosphere interactions in the global biogeochemical sulfur cycle, Mar. Chem., 30(C), 1–29, doi:10.1016/0304-4203(90)90059-L, 1990.

Arneth, A., Monson, R. K., Schurgers, G., Niinemets, Ü. and Palmer, P. I.: Why are estimates of global terrestrial isoprene emissions so similar (and why is this not so for monoterpenes)?, Atmos. Chem. Phys., 8(16), 4605–4620, doi:10.5194/acp-8-4605-2008, 2008.

Arnold, S. R., Spracklen, D. V, Williams, J., Yassaa, N., Sciare, J., Bonsang, B., Gros, V., Peeken, I., Lewis, A. C., Alvain, S. and Alvain, M.: Evaluation of the global oceanic isoprene source and its impacts on marine organic carbon aerosol, Atmos. Chem. Phys., 9(4), 1253–1262, doi:10.5194/acp-9-1253-2009, 2009.

Aumont, O., Belviso, S., Moulin, C., Sciare, J., von Kuhlmann, R., Cosme, E., Boucher, O., Pham, M., Lawrence, M. G., Bopp, L., Reddy, M. S. and Venkataraman, C.: Sensitivity study of dimethylsulphide (DMS) atmospheric concentrations and sulphate aerosol indirect radiative forcing to the DMS source representation and oxidation, Atmos. Chem. Phys. Discuss., 2(4), 1181–1216, doi:10.5194/acpd-2-1181-2002, 2010.

Ayers, G. P., Cainey, J. M., Gillett, R. W. and Ivey, J. P.: Atmospheric sulphur and cloud condensation nuclei in marine air in the Southern Hemisphere, Philos. Trans. R. Soc. B Biol. Sci., 352(1350), 203–211, doi:10.1098/rstb.1997.0015, 1997.

Azov, Y.: Seasonal patterns of phytoplankton productivity and abundance in nearshore oligotrophic waters of the Levant Basin (Mediterranean), J. Plankton Res., 8(1), 41–53, doi:10.1093/plankt/8.1.41, 1986.

Beaugrand, G., Edwards, M., Brander, K., Luczak, C. and Ibanez, F.: Causes and projections of abrupt climate-driven ecosystem shifts in the North Atlantic, Ecol. Lett., 11(11), 1157–1168, doi:10.1111/j.1461-0248.2008.01218.x, 2008.

Beaugrand, G., Edwards, M. and Legendre, L.: Marine biodiversity, ecosystem functioning, and carbon cycles, Proc. Natl. Acad. Sci., 107(22), 10120–10124, doi:10.1073/pnas.0913855107, 2010.

Berresheim, H., Plass-Dülmer, C., Elste, T., Mihalopoulos, N. and Rohrer, F.: OH in the coastal boundary layer of Crete during minos: Measurements and relationship with ozone photolysis, Atmos. Chem. Phys., 3(3), 639–649, doi:10.5194/acp-3-639-2003, 2003.

Bijma, J., Pörtner, H. O., Yesson, C. and Rogers, A. D.: Climate change and the oceans - What does the future hold?, Mar. Pollut. Bull., 74(2), 495–505, doi:10.1016/j.marpolbul.2013.07.022, 2013.

Blando, J. D. and Turpin, B. J.: Secondary organic aerosol formation in cloud and fog droplets: A literature evaluation of plausibility, Atmos. Environ., 34(10), 1623–1632, doi:10.1016/S1352-2310(99)00392-1, 2000.

Bonsang, B., Polle, C. and Lambert, G.: Evidence for marine production of isoprene, Geophys. Res. Lett., 19(11), 1129–1132, doi:10.1029/92GL00083, 1992.

Bonsang, B., Gros, V., Peeken, I., Yassaa, N., Bluhm, K., Zoellner, E., Sarda-Esteve, R. and Williams, J.: Isoprene emission from phytoplankton monocultures: the relationship with chlorophyll-a, cell volume and carbon content, Environ. Chem., 7(6), 554, doi:10.1071/en09156, 2010.

Bopp, L., Resplandy, L., Orr, J. C., Doney, S. C., Dunne, J. P., Gehlen, M., Halloran, P., Heinze, C., Ilyina, T., Séférian, R., Tjiputra, J. and Vichi, M.: Multiple stressors of ocean ecosystems in the 21st century: Projections with CMIP5 models, Biogeosciences, 10(10), 6225–6245, doi:10.5194/bg-10-6225-2013, 2013.

Bouvier-Brown, N. C., Goldstein, A. H., Gilman, J. B., Kuster, W. C. and de Gouw, J. A.: In-situ ambient quantification of monoterpenes, sesquiterpenes, and related oxygenated compounds during BEARPEX 2007: implications for gas- and particle-phase chemistry, Atmos. Chem. Phys., 9(15), 5505–5518, doi:10.5194/acp-9-5505-2009, 2009.

Boyce, D. G., Lewis, M. R. and Worm, B.: Global phytoplankton decline over the past century., Nature, 466(7306), 591–6, doi:10.1038/nature09268, 2010.

Brilli, F., Ruuskanen, T. M., Schnitzhofer, R., Müller, M., Breitenlechner, M., Bittner, V., Wohlfahrt, G., Loreto, F. and Hansel, A.: Detection of plant volatiles after leaf wounding and darkening by proton transfer reaction “time-of-flight” mass spectrometry (ptr-tof), PLoS One, 6(5), doi:10.1371/journal.pone.0020419, 2011.

Brilli, F., Hörtnagl, L., Bamberger, I., Schnitzhofer, R., Ruuskanen, T. M., Hansel, A., Loreto, F. and Wohlfahrt, G.: Qualitative and quantitative characterization of volatile organic compound emissions from cut grass, Environ. Sci. Technol., 46(7), 3859–3865, doi:10.1021/es204025y, 2012.

Broadgate, W. J., Malin, G., Küpper, F. C., Thompson, A. and Liss, P. S.: Isoprene and other non-methane hydrocarbons from seaweeds: A source of reactive hydrocarbons to the atmosphere, Mar. Chem., 88(1–2), 61–73, doi:10.1016/j.marchem.2004.03.002, 2004.

Calfapietra, C., Fares, S., Manes, F., Morani, A., Sgrigna, G. and Loreto, F.: Role of Biogenic Volatile Organic Compounds (BVOC) emitted by urban trees on ozone concentration in cities: A review, Environ. Pollut., 183(x), 71–80, doi:10.1016/j.envpol.2013.03.012, 2013.

Cappellin, L., Karl, T., Probst, M., Ismailova, O., Winkler, P. M., Soukoulis, C., Aprea, E., Märk, T. D., Gasperi, F. and Biasioli, F.: On quantitative determination of volatile organic compound concentrations using proton transfer reaction time-of-flight mass spectrometry, Environ. Sci. Technol., 46(4), 2283–2290, doi:10.1021/es203985t, 2012.

Carlton, A. G., Wiedinmyer, C. and Kroll, J. H.: A review of Secondary Organic Aerosol (SOA) formation from isoprene, Atmos. Chem. Phys., 9(14), 4987–5005, doi:10.5194/acp-9-4987-2009, 2009.

Carslaw, N., Jacobs, P. J. and Pilling, M. J.: Understanding radical chemistry in the marine boundary layer, Phys. Chem. Earth, Part C Solar, Terr. Planet. Sci., 25(3), 235–243, doi:10.1016/S1464-1917(00)00011-8, 2000.

Chiemchaisri, W., Visvanathan, C. and Jy, S. W.: Effects of trace volatile organic compounds on methane oxidation, Brazilian Arch. Biol. Technol., 44(2), 135–140, doi:10.1590/S1516-89132001000200005, 2001.

Curci, G., Beekmann, M., Vautard, R., Smiatek, G., Steinbrecher, R. and Theloke, J.: Modelling study of the impact of isoprene and terpene biogenic emissions on European ozone levels, Atmos. Environ., 43(7), 1444–1455, doi:10.1016/J.ATMOSENV.2008.02.070, 2009.

Dani, K. G. G. S. and Loreto, F.: Trade-Off Between Dimethyl Sulfide and Isoprene Emissions from Marine Phytoplankton, Trends Plant Sci., 22(5), 361–372, doi:10.1016/j.tplants.2017.01.006, 2017.

Debevec, C., Sauvage, S., Gros, V., Sciare, J., Pikridas, M., Stavroulas, I., Salameh, T., Leonardis, T., Gaudion, V., Depelchin, L., Fronval, I., Sarda-Esteve, R., Baisnée, D., Bonsang, B., Savvides, C., Vrekoussis, M. and Locoge, N.: Origin and variability in volatile organic compounds observed at an Eastern Mediterranean background site (Cyprus), Atmos. Chem. Phys., 17(18), 11355–11388, doi:10.5194/acp-17-11355-2017, 2017.

Derstroff, B., Hüser, I., Bourtsoukidis, E., Crowley, J. N., Fischer, H., Gromov, S., Harder, H., H Janssen, R. H., Kesselmeier, J., Lelieveld, J., Mallik, C., Martinez, M., Novelli, A., Parchatka, U., Phillips, G. J., Sander, R., Sauvage, C., Schuladen, J., Stönner, C., Tomsche, L., Williams, J. and Derstroff bettinaderstroff, B.: Volatile organic compounds (VOCs) in photochemically aged air from the eastern and western Mediterranean, Atmos. Chem. Phys, 17, 9547–9566, doi:10.5194/acp-17-9547-2017, 2017.

Efrati, S., Lehahn, Y., Rahav, E., Kress, N., Herut, B., Gertman, I., Goldman, R., Ozer, T., Lazar, M.

and Heifetz, E.: Intrusion of coastal waters into the pelagic eastern Mediterranean: In situ and satellite-based characterization, Biogeosciences, 10(5), 3349–3357, doi:10.5194/bg-10-3349-2013, 2013.

Exton, D. A., Suggett, D. J., McGenity, T. J. and Steinke, M.: Chlorophyll-normalized isoprene production in laboratory cultures of marine microalgae and implications for global models, Limnol. Oceanogr., 58(4), 1301–1311, doi:10.4319/lo.2013.58.4.1301, 2013.

Fares, S., Mereu, S., Scarascia Mugnozza, G., Vitale, M., Manes, F., Frattoni, M., Ciccioli, P., Gerosa, G. and Loreto, F.: The ACCENT-VOCBAS field campaign on biosphere-atmosphere interactions in a Mediterranean ecosystem of Castelporziano (Rome): Site characteristics, climatic and meteorological conditions, and eco-physiology of vegetation, Biogeosciences, 6(6), 1043–1058, doi:10.5194/bg-6-1043-2009, 2009.

Fares, S., McKay, M., Holzinger, R. and Goldstein, A. H.: Ozone fluxes in a Pinus ponderosa ecosystem are dominated by non-stomatal processes: Evidence from long-term continuous measurements, Agric. For. Meteorol., 150(3), 420–431, doi:10.1016/j.agrformet.2010.01.007, 2010.

Fares, S., Weber, R., Park, J. H., Gentner, D., Karlik, J. and Goldstein, A. H.: Ozone deposition to an orange orchard: Partitioning between stomatal and non-stomatal sinks, Environ. Pollut., 169, 258–266, doi:10.1016/j.envpol.2012.01.030, 2012.

Fares, S., Paoletti, E., Loreto, F. and Brilli, F.: Bidirectional Flux of Methyl Vinyl Ketone and Methacrolein in Trees with Different Isoprenoid Emission under Realistic Ambient Concentrations, , doi:10.1021/acs.est.5b00673, 2015.

Filipiak, W., Sponring, A., Filipiak, A., Baur, M., Troppmair, J. and Amann, A.: Volatile Biomarkers: Non-Invasive Diagnosis in Physiology and Medicine, Elsevier., 2013.

Fogg, G. E.: Review Lecture - Picoplankton, Proc. R. Soc. London. Ser. B. Biol. Sci., 228(1250), 1–30, doi:10.1098/rspb.1986.0037, 1986.

Gage, D. A., Rhodes, D., Nolte, K. D., Hicks, W. A., Leustek, T., Cooper, A. J. L. and Hanson, A. D.: A new route for synthesis of dimethylsulphoniopropionate in marine algae, Nature, 387(6636), 891–894, doi:10.1038/43160, 1997.

Ganor, E., Foner, H. A., Bingemer, H. G., Udisti, R. and Setter, I.: Biogenic sulphate generation in the Mediterranean Sea and its contribution to the sulphate anomaly in the aerosol over Israel and the Eastern Mediterranean, Atmos. Environ., 34(20), 3453–3462, doi:10.1016/S1352-2310(00)00077-7, 2000.

Gantt, B., Meskhidze, N., Zhang, Y. and Xu, J.: The effect of marine isoprene emissions on secondary organic aerosol and ozone formation in the coastal United States, Atmos. Environ., 44(1), 115–121, doi:10.1016/J.ATMOSENV.2009.08.027, 2010.

Giorgi, F.: Climate change hot-spots, Geophys. Res. Lett, 33, 8707, doi:10.1029/2006GL025734, 2006.

Goldstein, A. H. and Galbally, I. E.: Known and Unexplored Organic Constituents in the Earth’s Atmosphere, Environ. Sci. Technol., 41(5), 1514–1521, doi:10.1021/es072476p, 2007.

Goldstein, A. H., Mckay, M., Kurpius, M. R., Schade, G. W., Lee, A., Holzinger, R. and Rasmussen, R. A.: Forest thinning experiment confirms ozone deposition to forest canopy is dominated by reaction with biogenic VOCs, , doi:10.1029/2004GL021259, 2004.

Graus, M., Müller, M. and Hansel, A.: High resolution PTR-TOF: Quantification and Formula Confirmation of VOC in Real Time, J. Am. Soc. Mass Spectrom., 21(6), 1037–1044, doi:10.1016/j.jasms.2010.02.006, 2010.

Gray, D. W., Lerdau, M. T. and Goldstein, A. H.: INFLUENCES OF TEMPERATURE HISTORY, WATER STRESS, AND NEEDLE AGE ON METHYLBUTENOL EMISSIONS. [online] Available from: https://pdfs.semanticscholar.org/3240/cf36bb34db04129310281aad9aae48ecc40f.pdf (Accessed 28 January 2019), 2003.

Griffin, R. J., Cocker, D. R., Flagan, R. C. and Seinfeld, J. H.: Organic aerosol formation from the oxidation of biogenic hydrocarbons, J. Geophys. Res. Atmos., 104(D3), 3555–3567, doi:10.1029/1998JD100049, 1999.

Guenther, A.: The contribution of reactive carbon emissions from vegetation to the carbon balance of terrestrial ecosystems, Chemosphere, 49(8), 837–844, doi:10.1016/S0045-6535(02)00384-3, 2002.

Guenther, A., Hewitt, C. N., Erickson, D., Fall, R., Geron, C., Graedel, T., Harley, P., Klinger, L., Lerdau, M., Mckay, W. A., Pierce, T., Scholes, B., Steinbrecher, R., Tallamraju, R., Taylor, J. and Zimmerman, P.: A global model of natural volatile organic compound emissions, J. Geophys. Res., 100(D5), 8873, doi:10.1029/94JD02950, 1995.

Guenther, A., Karl, T., Harley, P., Wiedinmyer, C., Palmer, P. I. and Geron, C.: Estimates of global terrestrial isoprene emissions using MEGAN (Model of Emissions of Gases and Aerosols from Nature), Atmos. Chem. Phys., 6(11), 3181–3210, doi:10.5194/acp-6-3181-2006, 2006.

Guenther, A. B., Zimmerman, P. R., Harley, P. C., Monson, R. K. and Fall, R.: Isoprene and monoterpene emission rate variability: Model evaluations and sensitivity analyses, J. Geophys. Res., 98(D7), 12609, doi:10.1029/93JD00527, 1993.

Guenther, A. B., Jiang, X., Heald, C. L., Sakulyanontvittaya, T., Duhl, T., Emmons, L. K. and Wang, X.: The Model of Emissions of Gases and Aerosols from Nature version 2.1 (MEGAN2.1): an extended and updated framework for modeling biogenic emissions, Geosci. Model Dev., 5(6), 1471–1492, doi:10.5194/gmd-5-1471-2012, 2012.

Hackenberg, S. C., Andrews, S. J., Airs, R., Arnold, S. R., Bouman, H. A., Brewin, R. J. W., Chance, R. J., Cummings, D., Dall’Olmo, G., Lewis, A. C., Minaeian, J. K., Reifel, K. M., Small, A., Tarran, G. A., Tilstone, G. H. and Carpenter, L. J.: Potential controls of isoprene in the surface ocean, Global Biogeochem. Cycles, 31(4), 644–662, doi:10.1002/2016GB005531, 2017.

Halsey, K. H., Giovannoni, S. J., Graus, M., Zhao, Y., Landry, Z., Thrash, J. C., Vergin, K. L. and de Gouw, J.: Biological cycling of volatile organic carbon by phytoplankton and bacterioplankton, Limnol. Oceanogr., 62(6), 2650–2661, doi:10.1002/lno.10596, 2017.

Herut, B. and all scientific group of I.: The National Monitoring Program of Israel’s Mediterranean waters – Scientific Report for 2015., 2016.

Hoegh-Guldberg, O., Cai, R., Poloczanska, E. S., Brewer, P. G., Sundby, S., Hilmi, K., Fabry, V. J., Jung, S., Perry, I., Richardson, A. J., Brown, C. J., Schoeman, D., Signorini, S., Sydeman, W., Zhang, R., van Hooidonk, R., McKinnell, S. M., Turley, C., Omar, L., Cai, R., Poloczanska, E., Brewer, P., Sundby, S., Hilmi, K., Fabry, V., Jung, S., Field, C., Dokken, D., Mach, K., Bilir, T., Chatterjee, M., Ebi, K., Estrada, Y., Genova, R., Girma, B. and Kissel, E.: The Ocean. In: Climate Change 2014: Impacts, Adaptation, and Vulnerability. Part B: Regional Aspects. Contribution of Working Group II to the Fifth Assessment Report of the Intergovernmental Panel on Climate Change, Intergov. Panel Clim. Chang., 2(Fifth), doi:10.1017/CBO9781107415386.010, 2014.

Holopainen, J. K. and Gershenzon, J.: Multiple stress factors and the emission of plant VOCs, Trends Plant Sci., 15(3), 176–184, doi:10.1016/j.tplants.2010.01.006, 2010.

Holzinger, R.: PTRwid: A new widget tool for processing PTR-TOF-MS data, Atmos. Meas. Tech., 8(9), 3903–3922, doi:10.5194/amt-8-3903-2015, 2015.

Hu, Q. H., Xie, Z. Q., Wang, X. M., Kang, H., He, Q. F. and Zhang, P.: Secondary organic aerosols over oceans via oxidation of isoprene and monoterpenes from Arctic to Antarctic, Sci. Rep., 3, 1–7, doi:10.1038/srep02280, 2013.

IOLR: Israel Oceanographic & Limnological Research (IOLR) Mediterranean GLOSS #80 station., 2015.

IPCC: Climate Change 2007 - Impacts, Adaptation and Vulnerability The., 2007.

Janson, R. and de Serves, C.: Acetone and monoterpene emissions from the boreal forest in northern

Europe, Atmos. Environ., 35(27), 4629–4637, doi:10.1016/S1352-2310(01)00160-1, 2001.

Jardine, K., Yañez-Serrano, A. M., Williams, J., Kunert, N., Jardine, A., Taylor, T., Abrell, L., Artaxo, P., Guenther, A., Hewitt, C. N., House, E., Florentino, A. P., Manzi, A., Higuchi, N., Kesselmeier, J., Behrendt, T., Veres, P. R., Derstroff, B., Fuentes, J. D., Martin, S. T. and Andreae, M. O.: Dimethyl sulfide in the Amazon rain forest, Global Biogeochem. Cycles, 29(1), 19–32, doi:10.1002/2014GB004969, 2015.

Jardine, K. J., Meyers, K., Abrell, L., Alves, E. G., Yanez Serrano, A. M., Kesselmeier, J., Karl, T., Guenther, A., Chambers, J. Q. and Vickers, C.: Emissions of putative isoprene oxidation products from mango branches under abiotic stress., J. Exp. Bot., 64(12), 3697–708, doi:10.1093/jxb/ert202, 2013.

Jordan, A., Haidacher, S., Hanel, G., Hartungen, E., Herbig, J., Märk, L., Schottkowsky, R., Seehauser, H., Sulzer, P. and Märk, T. D.: An online ultra-high sensitivity Proton-transfer-reaction mass-spectrometer combined with switchable reagent ion capability (PTR+SRI−MS), Int. J. Mass Spectrom., 286(1), 32–38, doi:10.1016/j.ijms.2009.06.006, 2009.

Kameyama, S., Yoshida, S., Tanimoto, H., Inomata, S., Suzuki, K. and Yoshikawa-Inoue, H.: High-resolution observations of dissolved isoprene in surface seawater in the Southern Ocean during austral summer 2010–2011, J. Oceanogr., 70(3), 225–239, doi:10.1007/s10872-014-0226-8, 2014.

Kanda, K. I., Tsuruta, H. and Tsuruta, H.: Emissions of sulfur gases from various types of terrestrial higher plants, Soil Sci. Plant Nutr., 41(2), 321–328, doi:10.1080/00380768.1995.10419589, 1995.

Karl, T., Guenther, A., Spirig, C., Hansel, A. and Fall, R.: Seasonal variation of biogenic VOC emissions above a mixed hardwood forest in northern Michigan, Geophys. Res. Lett., 30(23), n/a-n/a, doi:10.1029/2003GL018432, 2003.

Kaser, L., Karl, T., Schnitzhofer, R., Graus, M., Herdlinger-Blatt, I. S., DiGangi, J. P., Sive, B., Turnipseed, A., Hornbrook, R. S., Zheng, W., Flocke, F. M., Guenther, A., Keutsch, F. N., Apel, E. and Hansel, A.: Comparison of different real time VOC measurement techniques in a ponderosa pine forest, Atmos. Chem. Phys., 13(5), 2893–2906, doi:10.5194/acp-13-2893-2013, 2013.

Kettle, A. J. and Andreae, M. O.: Flux of dimethylsulfide from the oceans: A comparison of updated data sets and flux models, J. Geophys. Res. Atmos., 105(D22), 26793–26808, doi:10.1029/2000JD900252, 2000.

Koç, M., Kubilay, N., Tuğrul, S. and Mihalopoulos, N.: Atmospheric nutrient inputs to the northern levantine basin from a long-term observation: Sources and comparison with riverine inputs, Biogeosciences, 7(12), 4037–4050, doi:10.5194/bg-7-4037-2010, 2010.

Koga, S., Nomura, D. and Wada, M.: Variation of dimethylsulfide mixing ratio over the Southern Ocean from 36°S to 70°S, Polar Sci., 8(3), 306–313, doi:10.1016/j.polar.2014.04.002, 2014.

Kouvarakis, G. and Mihalopoulos, N.: Seasonal variation of dimethylsulfide in the gas phase and of methanesulfonate and non-sea-salt sulfate in the aerosols phase in the Eastern Mediterranean atmosphere, Atmos. Environ., 36(6), 929–938, doi:10.1016/S1352-2310(01)00511-8, 2002.

Krom, M. D., Emeis, K. C. and Van Cappellen, P.: Why is the Eastern Mediterranean phosphorus limited?, Prog. Oceanogr., 85(3–4), 236–244, doi:10.1016/j.pocean.2010.03.003, 2010.

Kurpius, M. R. and Goldstein, A. H.: Gas-phase chemistry dominates O3 loss to a forest, implying a source of aerosols and hydroxyl radicals to the atmosphere, Geophys. Res. Lett., 30(7), doi:10.1029/2002GL016785, 2003.

Kuzma, J., Nemecek-Marshall, M., Pollock, W. H. and Fall, R.: Bacteria produce the volatile hydrocarbon isoprene, Curr. Microbiol., 30(2), 97–103, doi:10.1007/BF00294190, 1995.

Lana, A., Bell, T. G., Simó, R., Vallina, S. M., Ballabrera-Poy, J., Kettle, A. J., Dachs, J., Bopp, L., Saltzman, E. S., Stefels, J., Johnson, J. E. and Liss, P. S.: An updated climatology of surface dimethlysulfide concentrations and emission fluxes in the global ocean, Global Biogeochem. Cycles, 25(1), n/a-n/a, doi:10.1029/2010GB003850, 2011.

Lang-Yona, N., Rudich, Y., Mentel, T. F., Bohne, A., Buchholz, A., Kiendler-Scharr, A., Kleist, E., Spindler, C., Tillmann, R. and Wildt, J.: The chemical and microphysical properties of secondary organic aerosols from Holm Oak emissions, Atmos. Chem. Phys., 10(15), 7253–7265, doi:10.5194/acp-10-7253-2010, 2010.

Laothawornkitkul, J., Taylor, J. E., Paul, N. D. and Hewitt, C. N.: Biogenic volatile organic compounds in the Earth system: Tansley review, New Phytol., 183(1), 27–51, doi:10.1111/j.1469-8137.2009.02859.x, 2009.

Lary, D. J. and Shallcross, D. E.: Central role of carbonyl compounds in atmospheric chemistry, J. Geophys. Res. Atmos., 105(D15), 19771–19778, doi:10.1029/1999JD901184, 2000.

Lelieveld, J., Hadjinicolaou, P., Kostopoulou, E., Chenoweth, J., El Maayar, M., Giannakopoulos, C., Hannides, C., Lange, M. A., Tanarhte, M., Tyrlis, E. and Xoplaki, E.: Climate change and impacts in the Eastern Mediterranean and the Middle East, Clim. Change, 114(3–4), 667–687, doi:10.1007/s10584-012-0418-4, 2012.

Levasseur, M., Gosselin, M. and Michaud, S.: A new source of dimethylsulfide (DMS) for the arctic atmosphere: ice diatoms, Mar. Biol., 121(2), 381–387, doi:10.1007/BF00346748, 1994.

Li, Q., Gabay, M., Rubin, Y., Fredj, E. and Tas, E.: Measurement-based investigation of ozone deposition to vegetation under the effects of coastal and photochemical air pollution in the Eastern Mediterranean, Sci. Total Environ., 645, 1579–1597, doi:10.1016/j.scitotenv.2018.07.037, 2018.

Li, R., Warneke, C., Graus, M., Field, R., Geiger, F., Veres, P. R., Soltis, J., Li, S.-M., Murphy, S. M., Sweeney, C., Pétron, G., Roberts, J. M. and De Gouw, J.: Measurements of hydrogen sulfide (H 2 S) using PTR-MS: calibration, humidity dependence, inter-comparison and results from field studies in an oil and gas production region, Atmos. Meas. Tech, 7, 3597–3610, doi:10.5194/amt-7-3597-2014, 2014.

Liakakou, E., Vrekoussis, M., Bonsang, B., Donousis, C., Kanakidou, M. and Mihalopoulos, N.: Isoprene above the Eastern Mediterranean: Seasonal variation and contribution to the oxidation capacity of the atmosphere, Atmos. Environ., 41(5), 1002–1010, doi:10.1016/J.ATMOSENV.2006.09.034, 2007.

Llusia, J., Roahtyn, S., Yakir, D., Rotenberg, E., Seco, R., Guenther, A. and Peñuelas, J.: Photosynthesis, stomatal conductance and terpene emission response to water availability in dry and mesic Mediterranean forests, Trees - Struct. Funct., 30(3), 749–759, doi:10.1007/s00468-015-1317-x, 2015.

Massada, A. B., Kent, R., Blank, L., Perevolotsky, A., Hadar, L. and Carmel, Y.: Automated segmentation of vegetation structure units in a Mediterranean landscape, Int. J. Remote Sens., 33(2), 346–364, doi:10.1080/01431161.2010.532173, 2012.

Matsunaga, S., Mochida, M., Saito, T. and Kawamura, K.: In situ measurement of isoprene in the marine air and surface seawater from the western North Pacific, Atmos. Environ., 36(39–40), 6051–6057, doi:10.1016/S1352-2310(02)00657-X, 2002.

Meskhidze, N. and Nenes, A.: Phytoplankton and cloudiness in the southern ocean, Science (80-.)., 314(5804), 1419–1423, doi:10.1126/science.1131779, 2007.

Misztal, P. K., Lymperopoulou, D. S., Adams, R. I., Scott, R. A., Lindow, S. E., Bruns, T., Taylor, J. W., Uehling, J., Bonito, G., Vilgalys, R. and Goldstein, A. H.: Emission Factors of Microbial Volatile Organic Compounds from Environmental Bacteria and Fungi, , doi:10.1021/acs.est.8b00806, 2018.

Monks, P. S., Archibald, A. T., Colette, A., Cooper, O., Coyle, M., Derwent, R., Fowler, D., Granier, C., Law, K. S., Mills, G. E., Stevenson, D. S., Tarasova, O., Thouret, V., Von Schneidemesser, E., Sommariva, R., Wild, O. and Williams, M. L.: Tropospheric ozone and its precursors from the urban to the global scale from air quality to short-lived climate forcer, Atmos. Chem. Phys, 15, 8889–8973, doi:10.5194/acp-15-8889-2015, 2015.

Monson, R. K., Jaeger, C. H., Ill, W. W. A., Driggers, E. M., Silver, G. M. and Fall, R.: Relationships among Isoprene Emission Rate, Photosynthesis, and Isoprene Synthase Activity as Influenced by

Temperature1. [online] Available from: https://www.ncbi.nlm.nih.gov/pmc/articles/PMC1080324/pdf/plntphys00702-0385.pdf (Accessed 21 October 2018), 1992.

Müller, J. F. and Brasseur, G.: Sources of upper tropospheric HOx: A three-dimensional study., 1999.

Niinemets, Ü., Loreto, F. and Reichstein, M.: Physiological and physicochemical controls on foliar volatile organic compound emissions, Trends Plant Sci., 9(4), 180–186, doi:10.1016/j.tplants.2004.02.006, 2004.

Ormeño, E., Goldstein, A. and Niinemets, Ü.: Extracting and trapping biogenic volatile organic compounds stored in plant species, TrAC - Trends Anal. Chem., 30(7), 978–989, doi:10.1016/j.trac.2011.04.006, 2011.

Ozer, T., Gertman, I., Kress, N., Silverman, J. and Herut, B.: Interannual thermohaline (1979–2014) and nutrient (2002–2014) dynamics in the Levantine surface and intermediate water masses, SE Mediterranean Sea, Glob. Planet. Change, 151, 60–67, doi:10.1016/j.gloplacha.2016.04.001, 2016.

Paerl, H. W. and Otten, T. G.: Harmful Cyanobacterial Blooms: Causes, Consequences, and Controls, Microb. Ecol., 65(4), 995–1010, doi:10.1007/s00248-012-0159-y, 2013.

Palmer, P. I. and Shaw, S. L.: Quantifying global marine isoprene fluxes using MODIS chlorophyll observations, Geophys. Res. Lett, 32, 9805, doi:10.1029/2005GL022592, 2005.

Park, J.-H., Goldstein, A. H., Timkovsky, J., Fares, S., Weber, R., Karlik, J. and Holzinger, R.: Eddy covariance emission and deposition flux measurements using proton transfer reaction &amp;ndash; time of flight &amp;ndash; mass spectrometry (PTR-TOF-MS): comparison with PTR-MS measured vertical gradients and fluxes, Atmos. Chem. Phys., 13(3), 1439–1456, doi:10.5194/acp-13-1439-2013, 2013a.

Park, J. H., Fares, S., Weber, R. and Goldstein, A. H.: Biogenic volatile organic compound emissions during BEARPEX 2009 measured by eddy covariance and flux-gradient similarity methods, Atmos. Chem. Phys., 14(1), 231–244, doi:10.5194/acp-14-231-2014, 2012.

Park, J. H., Goldstein, A. H., Timkovsky, J., Fares, S., Weber, R., Karlik, J. and Holzinger, R.: Active atmosphere-ecosystem exchange of the vast majority of detected volatile organic compounds, Science (80-.)., 341(6146), 643–647, doi:10.1126/science.1235053, 2013b.

Pedrotti, M. L., Mousseau, L., Marro, S., Passafiume, O., Gossaert, M. and Labat, J.-P.: Variability of ultraplankton composition and distribution in an oligotrophic coastal ecosystem of the NW Mediterranean Sea derived from a two-year survey at the single cell level, edited by S. Duperron, PLoS One, 12(12), e0190121, doi:10.1371/journal.pone.0190121, 2017.

Penuelas, J., Rutishauser, T. and Filella, I.: Phenology feedbacks on climate change, Science (80-.)., 324(May 2009), 887–888, 2010.

Peñuelas, J. and Staudt, M.: BVOCs and global change, Trends Plant Sci., 15(3), 133–144, doi:10.1016/j.tplants.2009.12.005, 2010.

Portillo-Estrada, M., Kazantsev, T., Talts, E., Tosens, T. and Niinemets, Ü.: Emission Timetable and Quantitative Patterns of Wound-Induced Volatiles Across Different Leaf Damage Treatments in Aspen (Populus Tremula), J. Chem. Ecol., 41(12), 1105–1117, doi:10.1007/s10886-015-0646-y, 2015.

Psarra, S., Tselepides, A. and Ignatiades, L.: Primary productivity in the oligotrophic Cretan Sea (NE Mediterranean): Seasonal and interannual variability, Prog. Oceanogr., 46(2–4), 187–204, doi:10.1016/S0079-6611(00)00018-5, 2000.

Rasconi, S., Gall, A., Winter, K. and Kainz, M. J.: Increasing Water Temperature Triggers Dominance of Small Freshwater Plankton., PLoS One, 10(10), e0140449, doi:10.1371/journal.pone.0140449, 2015.

Ren, Y., Qu, Z., Du, Y., Xu, R., Ma, D., Yang, G., Shi, Y., Fan, X., Tani, A., Guo, P., Ge, Y. and Chang, J.: Air quality and health effects of biogenic volatile organic compounds emissions from urban green spaces and the mitigation strategies, Environ. Pollut., 230, 849–861, doi:10.1016/j.envpol.2017.06.049, 2017.

Richards, N. A. D., Arnold, S. R., Chipperfield, M. P., Miles, G., Rap, A., Siddans, R., Monks, S. A. and Hollaway, M. J.: The Mediterranean summertime ozone maximum: Global emission sensitivities and radiative impacts, Atmos. Chem. Phys., 13(5), 2331–2345, doi:10.5194/acp-13-2331-2013, 2013.

Sarma, T. A.: Handbook of cyanobacteria, CRC Press. [online] Available from: https://books.google.co.il/books?id=BlHSBQAAQBAJ&dq=cyanobacteria+mediterranean+oligotrophic&hl=iw (Accessed 18 March 2019), 2013.

Schade, G. W., Goldstein, A. H. and Lamanna, M. S.: Are Monoterpene Emissions influenced by Humidity?, Geophys. Res. Lett., 26(14), 2187–2190, doi:10.1029/1999GL900444, 1999.

Seco, R., Karl, T., Turnipseed, A., Greenberg, J., Guenther, A., Llusia, J., Peñuelas, J., Dicken, U., Rotenberg, E., Kim, S. and Yakir, D.: Springtime ecosystem-scale monoterpene fluxes from Mediterranean pine forests across a precipitation gradient, Agric. For. Meteorol., 237–238, 150–159, doi:10.1016/j.agrformet.2017.02.007, 2017.

Shaltout, M. and Omstedt, A.: Recent sea surface temperature trends and future scenarios for the Mediterranean Sea, Oceanologia, 56(3), 411–443, doi:10.5697/OC.56-3.411, 2014.

Shaw, S. L., Chisholm, S. W. and Prinn, R. G.: Isoprene production by Prochlorococcus, a marine cyanobacterium, and other phytoplankton, Mar. Chem., 80(4), 227–245, doi:10.1016/S0304-4203(02)00101-9, 2003.

Simo, R.: Production of atmospheric sulfur by oceanic plankton: Biogeochemical, ecological and evolutionary links, Trends Ecol. Evol., 16(6), 287–294, doi:10.1016/S0169-5347(01)02152-8, 2001.

Singh, H. B.: Analysis of the atmospheric distribution, sources, and sinks of oxygenated volatile organic chemicals based on measurements over the Pacific during TRACE-P, J. Geophys. Res., 109(D15), D15S07, doi:10.1029/2003JD003883, 2004.

Singh, H. B., Kanakidou, M., Crutzen, P. J. and Jacob, D. J.: High concentrations and photochemical fate of oxygenated hydrocarbons in the global troposphere, Nature, 378(6552), 50–54, doi:10.1038/378050a0, 1995.

Sisma-Ventura, G., Bialik, O. M., Yam, R., Herut, B. and Silverman, J.: pCO2 variability in the surface waters of the ultra-oligotrophic Levantine Sea: Exploring the air–sea CO2 fluxes in a fast warming region, Mar. Chem., 196(June), 13–23, doi:10.1016/j.marchem.2017.06.006, 2017.

Stefels, J., Steinke, M., Turner, S., Malin, G. and Belviso, S.: Environmental constraints on the production and removal of the climatically active gas dimethylsulphide (DMS) and implications for ecosystem modelling, in Phaeocystis, major link in the biogeochemical cycling of climate-relevant elements, pp. 245–275, Springer Netherlands, Dordrecht., 2007.

Stevens, P., L'Esperance, D., Chuong, B. and Martin, G.: Measurements of the kinetics of the OH-initiated oxidation of isoprene: Radical propagation in the OH + isoprene + O2 + NO reaction system, Int. J. Chem. Kinet., 31(9), 637–643, doi:10.1002/(SICI)1097-4601(1999)31:9<637::AID-KIN5>3.0.CO;2-O, 1999.

Tang, X., Misztal, P. K., Nazaroff, W. W. and Goldstein, A. H.: Volatile organic compound emissions from humans indoors, Environ. Sci. Technol., 50(23), 12686–12694, doi:10.1021/acs.est.6b04415, 2016.

Tanimoto, H., Kameyama, S., Iwata, T., Inomata, S. and Omori, Y.: Measurement of air-sea exchange of dimethyl sulfide and acetone by PTR-MS coupled with gradient flux technique, Environ. Sci. Technol., 48(1), 526–533, doi:10.1021/es4032562, 2014.

Tingey, D. T., Turner, D. P. and Weber, J. A.: Factors Controlling the Emissions of Monoterpenes and Other Volatile Organic Compounds, in Trace Gas Emissions by Plants, pp. 93–119., 1990.

Tyrrell, T.: Redfield Ratio, Encycl. Ocean Sci., 677–686, doi:10.1016/B978-012374473-9.00271-X, 2001.

Vogt, M. and Liss, P. S.: Dimethylsulfide and climate, Geophys. Monogr. Ser., 187, 197–232, doi:10.1029/2008GM000790, 2009.

Vrekoussis, M., Kanakidou, M., Mihalopoulos, N., Crutzen, P. J., Lelieveld, J., Perner, D., Berresheim, H. and Baboukas, E.: Role of the NO 3 radicals in oxidation processes in the eastern Mediterranean troposphere during the MINOS campaign, Atmos. Chem. Phys. Atmos. Chem. Phys., 4, 169–182 [online] Available from: www.atmos-chem-phys.org/acp/4/169/ (Accessed 30 May 2018), 2004.

Wennberg, P. O., Hanisco, Jaegle, Jacob, Hintsa, Lanzendorf, Anderson, Gao, Keim, Donnelly, Negro, Fahey, McKeen, Salawitch, Webster, May, Herman, Proffitt, Margitan, Atlas, Schauffler, Flocke, McElroy and Bui: Hydrogen Radicals, Nitrogen Radicals, and the Production of O3 in the Upper Troposphere, Science (80-.)., 279(5347), 49–53, doi:10.1126/science.279.5347.49, 1998.

Winer, A. M., Atkinson, R. and Pitts, J. N.: Gaseous nitrate radical: Possible nighttime atmospheric sink for biogenic organic compounds, Science (80-.)., 224(4645), 156–159, doi:10.1126/science.224.4645.156, 1984.

Wuebbles, D. J., Grant, K. E., Connell, P. S. and Penner, J. E.: The role of atmospheric chemistry in climate change, J. Air Waste Manag. Assoc., 39(1), 22–28, doi:10.1080/08940630.1989.10466502, 1989.

Yacobi, Y. Z., Zohary, T., Kress, N., Hecht, A., Robarts, R. D., Waiser, M., Wood, A. M. and Li, W. K. W.: Chlorophyll distribution throughout the southeastern Mediterranean in relation to the physical structure of the water mass, J. Mar. Syst., 6(3), 179–190, doi:10.1016/0924-7963(94)00028-A, 1995.

Yokouchi, Y., Li, H. and Machida, T.: eastern Indian Ocean , and Southern Ocean)' Comparison with dimethyl sulfide and bromoform, J. Geophys. Res., 104, 8067–8076, 1999.

Yonemura, S. Sandoval-Soto, L. Kesselmeier, J. Kuhn, U. von Hobe, M. Yakir, D. Kawashima, S.: Uptake of Carbonyl Sulfide (COS) and Emission of Dimethyl Sulfide (DMS) by Plants, APGC, 45(4), 17–24 [online] Available from: www.biologiezentrum.at (Accessed 5 December 2018), 2005.

Yuan, B., Koss, A. R., Warneke, C., Coggon, M., Sekimoto, K. and De Gouw, J. A.: Proton-Transfer-Reaction Mass Spectrometry: Applications in Atmospheric Sciences, Chem. Rev., 117(21), 13187–13229, doi:10.1021/acs.chemrev.7b00325, 2017.