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 $1.7 \cdot 10^{-2}$ ppbv $\cdot$ 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 $-1.6 \cdot 10^{-6}$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" (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?

Answer:

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).

References:

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