





27     **Abstract**

28     Biogenic volatile organic compounds (BVOCs) from terrestrial vegetation and marine  
29     organisms contribute to photochemical pollution and affect the radiation budget, cloud  
30     properties and precipitation via secondary organic aerosol formation. Their emission  
31     from both marine and terrestrial ecosystems is substantially affected by climate  
32     change in ways that are currently not well characterized. The Eastern Mediterranean  
33     Sea was identified as a climate change “hot spot”, making it a natural laboratory for  
34     investigating the impact of climate change on BVOC emission from both terrestrial  
35     and marine vegetation. We quantified the mixing ratios of a suite of volatile organic  
36     compounds (VOCs), including isoprene, dimethyl sulfide (DMS), acetone,  
37     acetaldehyde and monoterpenes, at a mixed vegetation site ~4km from the  
38     southeastern tip of the Levantine Basin, where the sea surface temperature maximizes  
39     and ultra-oligotrophic conditions prevail. The measurements were performed between  
40     July and October, 2015, using a proton-transfer-reaction–time-of-flight mass  
41     spectrometer. The analyses were supported by the Model of Emissions of Gases and  
42     Aerosols from Nature (MEGAN 2.1). For isoprene and DMS mixing ratios, we  
43     identified a dominant contribution from the seawater. Our analyses further suggest a  
44     major contribution at least for monoterpenes from the seawater. Our results indicate  
45     that the Levantine Basin greatly contributes to isoprene emission, corresponding with  
46     mixing ratios of up to ~9 ppbv several km inland from the sea shore. This highlights  
47     the need to update air-quality and climate models to account for the impact of sea  
48     surface temperature (SST) on marine isoprene emission. The DMS mixing ratios were  
49     one-to-two orders of magnitude lower than those measured in 1995 in the same area,  
50     suggesting a dramatic decrease in emission due to changes in the species composition  
51     induced by the rise in SST.



52 **1. Introduction**

53 Biogenic volatile organic compounds (BVOCs) emitted from terrestrial vegetation  
54 and marine organisms significantly affect air pollution and health via increasing  
55 regional photochemical O<sub>3</sub> pollution (Curci et al., 2009), enhancing local O<sub>3</sub> removal  
56 via chemical reaction (Calfapietra et al., 2013) and serving as precursors for  
57 secondary organic aerosol (SOA) formation (Griffin et al., 1999; Lang-Yona et al.,  
58 2010; Ren et al., 2017). Considering the large global emission rate of BVOCs, mostly  
59 from terrestrial vegetation (700–1000 TgC year<sup>-1</sup>; Laothawornkitkul et al., 2009),  
60 biogenic SOA formation further impacts the radiation budget, precipitation, and  
61 climate (Chiemchaisri et al., 2001; Wuebbles et al., 1989). BVOC oxidation likewise  
62 increases CO<sub>2</sub> levels, as a direct product, and methane concentrations, by reducing the  
63 oxidation capacity (Penuelas et al., 2010).

64 Only a minor fraction of all BVOCs (>10,000) have sufficient reactivity and  
65 emissions to play an important role in the climate and photochemistry (Guenther,  
66 2002). Here, we focus on some of the important emitted reactive BVOCs, including 2-  
67 methyl-1,3-butadiene (isoprene), dimethyl sulfide (DMS), and some oxygenated  
68 VOCs (OVOCs). Emission of isoprene from vegetation has received a lot of attention  
69 in recent years, because this compound has the highest global emission rates among  
70 all reactive BVOCs from vegetative sources (Guenther, 2002), and due to its high  
71 photochemical reactivity and contribution to SOA amounts, estimated to be at least  
72 27-48% of total global SOA formation (Carlton et al., 2009; Meskhidze and Nenes,  
73 2007). It is also well recognized that isoprene is emitted from seawater, too (Bonsang  
74 et al., 1992; Goldstein and Galbally, 2007; Kameyama et al., 2014; Liakakou et al.,  
75 2007; Matsunaga et al., 2002), by marine organisms, including phytoplankton,  
76 seaweeds and microorganisms (Alvarez et al., 2009; Broadgate et al., 2004;



77 Kameyama et al., 2014; Kuzma et al., 1995). Although the emission rates of isoprene  
78 into the marine boundary layer (MBL) are substantially smaller than terrestrial  
79 emissions, 0.1–1.9 TgC year<sup>-1</sup> (Arnold et al., 2009; Palmer and Shaw, 2005) vs. 400–  
80 750 TgC year<sup>-1</sup> (Arneth et al., 2008; Guenther et al., 2006, 2012), they play an  
81 important role in SOA formation (Hu et al., 2013) and photochemistry (Liakakou et  
82 al., 2007) in the marine environment, particularly in more remote areas (Ayers et al.,  
83 1997; Carslaw et al., 2000).

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

92 OVOCs, including aldehydes, alcohols, ketones and carboxylic acids, can  
93 induce tropospheric O<sub>3</sub> formation via RO<sub>2</sub> formation (Monks et al., 2015; Müller and  
94 Brasseur, 1999; Singh, 2004) and act as OH precursors, particularly in the upper  
95 troposphere (Lary and Shallcross, 2000; Singh et al., 1995; Wennberg et al., 1998).  
96 Similarly to isoprene and DMS, OVOCs serve as precursors to SOA formation  
97 (Blando and Turpin, 2000).

98 Emission of BVOCs from both terrestrial and marine sources is fundamentally  
99 influenced by climate changes. For instance, most BVOC emissions from terrestrial  
100 vegetation tend to increase exponentially with temperature (T) (Goldstein et al., 2004;  
101 Guenther et al., 1995; Monson et al., 1992; Niinemets et al., 2004; Tingey et al.,



102 1990), while drought can negate the effect of temperature on the emission rate from  
103 vegetation (Holopainen and Gershenson, 2010; Llusia et al., 2015; Peñuelas and  
104 Staudt, 2010; Schade et al., 1999). Seawater acidification and sea surface temperature  
105 (SST) increases significantly affect BVOCs in various ways, including by altering the  
106 biodiversity, spatial and temporal distribution and physiological activity of marine  
107 organisms, influences that are currently not well characterized (Beaugrand et al.,  
108 2008, 2010; Bijma et al., 2013; Bopp et al., 2013; Dani and Loreto, 2017).  
109 Accordingly, the effect of climate change on BVOC emissions into the MBL is  
110 largely unknown (Boyce et al., 2010; Dani and Loreto, 2017).

111 The Eastern Mediterranean Basin has been recognized as a highly responsive  
112 region to climate change and has been aptly named a primary “climate change  
113 hotspot” (Giorgi, 2006; IPCC, 2007; Lelieveld et al., 2012). Being both warm and  
114 oligotrophic, it gives rise to the dominance of unicellular and small plankton such as  
115 cyanobacteria (Krom et al., 2010; Rasconi et al., 2015), making it an attractive site to  
116 study the impact of anthropogenic stress and climate change on marine BVOC  
117 emissions.

118 At the southeastern tip of the Mediterranean Basin is the Levantine Basin,  
119 which is ultra-oligotrophic and the warmest region in the Mediterranean Sea (Shaltout  
120 and Omstedt, 2014; Azov, 1986; Krom et al., 2010; Psarra et al., 2000; Sisma-Ventura  
121 et al., 2017; Yacobi et al., 1995), particularly in its northern section (Efrati et al.,  
122 2013; Koç et al., 2010). This region has experienced a significant increase in SST  
123 during the last decade ( $+0.12 \pm 0.07$  °C year<sup>-1</sup> (Ozer et al., 2016), with temperatures  
124 exceeding 30°C 2 km from the coastline in 2015 (IOLR, 2015).

125 Most of the surface BVOC measurements at the Eastern Mediterranean are  
126 from Finokalia, Crete (Kouvarakis and Mihalopoulos, 2002; Liakakou et al., 2007).



127 To the best of our knowledge, only a few measurements of BVOCs were performed in  
128 the Levantine Basin, including BVOC emissions in Cyprus (e.g., Debevec et al.,  
129 2017; Derstroff et al., 2017) and DMS measurements in Israel (Ganor et al., 2000).

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

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## 139 **2. Methods**

### 140 *2.1 Measurement site*

141 Field measurements were performed in Ramat Hanadiv Nature Park (33°33'19.87"N,  
142 32°56'50.25"E). The measurement site is situated at the edge of the park's memorial  
143 garden. This site is located about 3.6 km from the Mediterranean shore, 120 m above  
144 sea level. The characteristics of the park are described in detail by Li et al. (2018) and  
145 briefly in Fig. 1. The nature park consists of mixed natural Mediterranean vegetation:  
146 *Quercus calliprinos* (~25%), *Pistacia lentiscus* (~20%), the sclerophyll *Phillyrea*  
147 *latifolia* (broad-leaved phillyrea) (~7.5%), invasive species (~10%), *Cupressus* (5%),  
148 *Sarcopoterium spinosum* (~2%), *Rhamnus lycioides* (~2%) and *Calicotome villosa*  
149 (~1%). The park's western part features a few scattered *Pinus halepensis* (<5%)  
150 combined with planted pine (*Pinus halepensis* and *Pinus brutia*) and cypress  
151 (Massada et al., 2012). During the measurements, the average canopy height was



152 ~4.5 m, the leaf area index was ~1.3 and the vegetation cover fraction was ~0.5. The  
153 site is exposed to various anthropogenic contributions: Two highways are located  
154 1.5 km and 2.5 km west of the measurement site, a power plant (“Hadera”) is at a  
155 distance of 11 km south of site, and a major industrial zone (Haifa) is 30 km to the  
156 north. Aquaculture farms totaling ~6 km in length, located 3.2 km to the west of the  
157 site, could potentially also contribute to BVOCs at the site.

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160

161 **Figure 1. Satellite images of the measurement site at Ramat Hanadiv Nature Park.** Left: Location  
162 of the measurement site (red dot). Right: Zoom-in on the surrounding area of the measurement site (red  
163 dot). Background imagery from ©Google Earth.

164

## 165 2.2 Field Measurements

166 The field measurements were taken at the Ramat Handiv site from the summer until  
167 the late autumn of 2015 (July 6–October 12, 2015). The set of instruments included a  
168 platform for eddy covariance measurements of BVOCs, O<sub>3</sub>, carbon dioxide (CO<sub>2</sub>) and  
169 water vapor (H<sub>2</sub>O), trace-gases mixing ratios, including O<sub>3</sub>, NO<sub>x</sub>, SO<sub>2</sub> and CO, and  
170 basic meteorological conditions, using an air-conditioned mobile laboratory and two  
171 towers (Fig. S2). The sampling routine and schematic of the setup were described in  
172 (Li et al., 2018) and are summarized in Fig. S2.



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

177           The PTR-ToF-MS was placed inside an air-conditioned mobile laboratory, and  
178 ambient air was pulled at a rate of about 35 l min<sup>-1</sup> through an external PFA Teflon  
179 tube (3/8" OD, 5/16" ID) and subsampled by the PTR-ToF-MS at a rate of 0.5 l min<sup>-1</sup>  
180 via a 1/16" OD (1 mm ID) polyetheretherketone (PEEK) tube. The instrument inlet  
181 and drift-tube were heated to 80°C, the drift pressure was set to 2.3 mbar, and the  
182 voltage to 600 V; all the settings were maintained at constant levels throughout the  
183 measurements, corresponding to the E/N ratio of 140 Td.

184           The PTR-ToF-MS raw hdf5 (h5) files were preprocessed by a set of routines  
185 included in the *ptrwid* processing suite within an Interactive Data Language (IDL)  
186 environment and described in detail in Holzinger, 2015. Further data processing was  
187 performed by customized multi-step Matlab (Mathworks Inc.) postprocessing  
188 routines, which included processing of calibrations, zero air, and ambient  
189 measurements, chemical formula assignment, and comprehensive quality control  
190 similar to Tang et al., 2016. The list of compounds inferred from chemical formulas  
191 and further analysis (e.g., correlation matrix, diel variability, and fragmentation  
192 patterns) is shown in Table S2. The uncertainties are listed according to whether a  
193 compound was explicitly calibrated, an accurate proton reaction rate constant was  
194 used (Sect. S1; Cappellin et al., 2012; Yuan et al., 2017), or a default reaction rate  
195 constant ( $2.5 \times 10^{-9}$  cm sec<sup>-1</sup>) for unidentified ions was employed (not reported here).

196           **Measurements of other trace gases and micrometeorology:** Complementary  
197 measurements included the quantification of mixing ratios of carbon monoxide (CO),



198 sulfur dioxide (SO<sub>2</sub>), nitrogen oxides (NO<sub>x</sub> ≡ NO + NO<sub>2</sub>) and ozone (O<sub>3</sub>), using  
199 models 48i, 43s, 42i and 49i, respectively (Thermo Environmental Instruments Inc.,  
200 Waltham, MA, USA), with manufacturer-reported limits of detection of 4.0 ppm, 0.1  
201 ppbv, 0.4 ppbv and 1.0 ppbv, respectively. These monitors were periodically  
202 calibrated to avoid drift in their accuracy. Trace-gas mixing ratios were recorded by a  
203 CR1000 data logger at a frequency of 1 min. Wind speed and wind direction were  
204 measured using an R. M. Young Wind Monitor 05103 (R.M. Young, Traverse City,  
205 MI, USA), the air temperature and relative humidity with a Campbell CS500 probe  
206 (Campbell Scientific, Logan, UT, USA), and the global radiation with a Kipp &  
207 Zonen CM3 Pyranometer (Kipp & Zonen, Delft, Netherlands). The measured data  
208 were recorded by a CR10X data logger (Campbell Scientific) at 10 Hz frequency.  
209 Overall, the measurements resulted in 20 days of high-quality, complete data, which  
210 were divided into six different periods due to instrument downtime (see Sect. S1).

211

### 212 2.3 Model simulations of BVOC emission

213 The Model of Emissions of Gasses and Aerosols from Nature version 2.1  
214 (MEGANv2.1; Guenther et al., 2012) was applied to estimate the emission flux of  
215 BVOCs from the nature park, according to the vegetation type, and the on-site  
216 measured solar radiation, temperature, soil moisture, vegetation-cover fraction and  
217 leaf area index, using the following general formula to estimate the emission flux of  
218 species *i* (F<sub>*i*</sub>):

$$219 F_i = \gamma_i \sum \varepsilon_{i,j} \chi_j ,$$

220 where  $\varepsilon_{i,j}$  is the emission factor (representing the emission under standard  
221 conditions) of vegetation type *j*,  $\gamma_i$  is the emission activity factor, which reflects the  
222 impact of environmental factors and phenology, and  $\chi_j$  represents the vegetation



223 effective fractional coverage area. The landscape average emission factor was  
224 estimated using the observed plant species composition at the field site (see Sect. 2.1).  
225 The major driving variables of the model are solar radiation, calculated leaf  
226 temperature, leaf age, soil moisture, and leaf area index. The actual measured  
227 parameters at Ramat Hanadiv were used as input to the model, including vegetation  
228 and soil type, vegetation coverage, fraction and leaf area index, soil water content and  
229 *in situ*-measured meteorological data. Note that only the nature park was simulated by  
230 MEGANv2.1, while potential emissions from a nearby, relatively small "Memorial  
231 Garden" were not taken into account.

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233

### 234 **3. Results and discussion**

#### 235 *3.1 Seasonal and diel trends in measured BVOCs*

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



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

Day of Year (calendric day)	T (°C)	PAR (W/m <sup>2</sup> )	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

243

244 \* See Table S1 for data availability and exclusion.

245 \*\* Discussed only in relation to Fig. 3 considering irregular meteorological conditions.

246

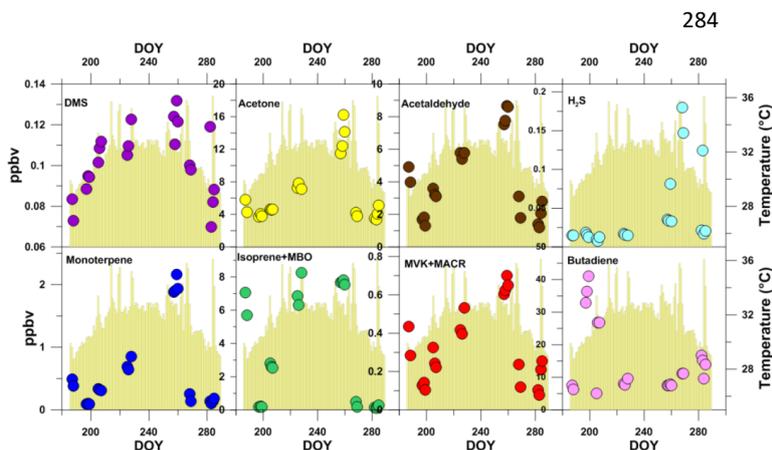
247 Fig. 3 presents both VOCs dominated by biogenic sources (BVOCs) and VOCs  
248 dominated by anthropogenic emission sources (AVOCs), although no compound can be  
249 regarded as exclusively biogenic or anthropogenic. The former include monoterpenes  
250 (MTs; m/z=137.133, m/z=95.086, m/z=81.070),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



259 The dominating source behavior for BVOCs is reflected in their diurnal cycle, which was  
260 characterized by an increase in their mixing ratios from morning to around noontime or  
261 afternoon, followed by a gradual decrease until sunset (see Figs. S5-S9). We found  
262 similar day-to-day trends in the mixing ratios of all BVOCs, particularly of acetone,  
263 acetaldehyde and the MTs. This strongly reinforces the predominantly biogenic origin  
264 for these four species, considering that MTs are expected to be primarily emitted from  
265 biogenic sources in the studied area, in the absence of any nearby wood industry. H<sub>2</sub>S  
266 and butadiene show significantly different trends in the mixing ratios, suggesting a  
267 dominating anthropogenic contribution for these species, with a potential contribution  
268 from microbial activity (Misztal et al., 2018).

269 Overall, the day-to-day trend in the BVOC mixing ratios appears to follow the  
270 temperature, but exhibits only a relatively weak correlation with daily temperature  
271 variation (Fig. 3). DMS showed the strongest correlation with the average daytime  
272 temperature ( $r^2=0.27$ ; see Sect. 3.2.2), corresponding to a significant increase in the  
273 mixing ratios between early summer (DOY=188) and the end of summer (DOY=254),  
274 which decreased during autumn (DOY=255 to DOY=283). The other BVOCs, except for  
275 isoprene+MBO, showed a gradual increase in their mixing ratios during summer (DOY  
276 197-260), and a decrease during autumn (DOY 268-285), which can be explained by the  
277 correlation with T (Fig. 3). We attribute the extreme mixing ratios during DOY 257-260  
278 to extreme meteorological conditions; this period was characterized by high wind speeds  
279 and relatively low solar radiation, which can facilitate a shallow boundary layer and, in  
280 turn, higher VOC mixing ratios (see Sect. S4).

281 While the diurnal profile of isoprene+MBO suggests a predominantly biogenic source  
282 (Fig. 5), its day-to-day mixing ratios showed higher variability, which was quite different  
283 from both DMS and the other BVOCs.



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

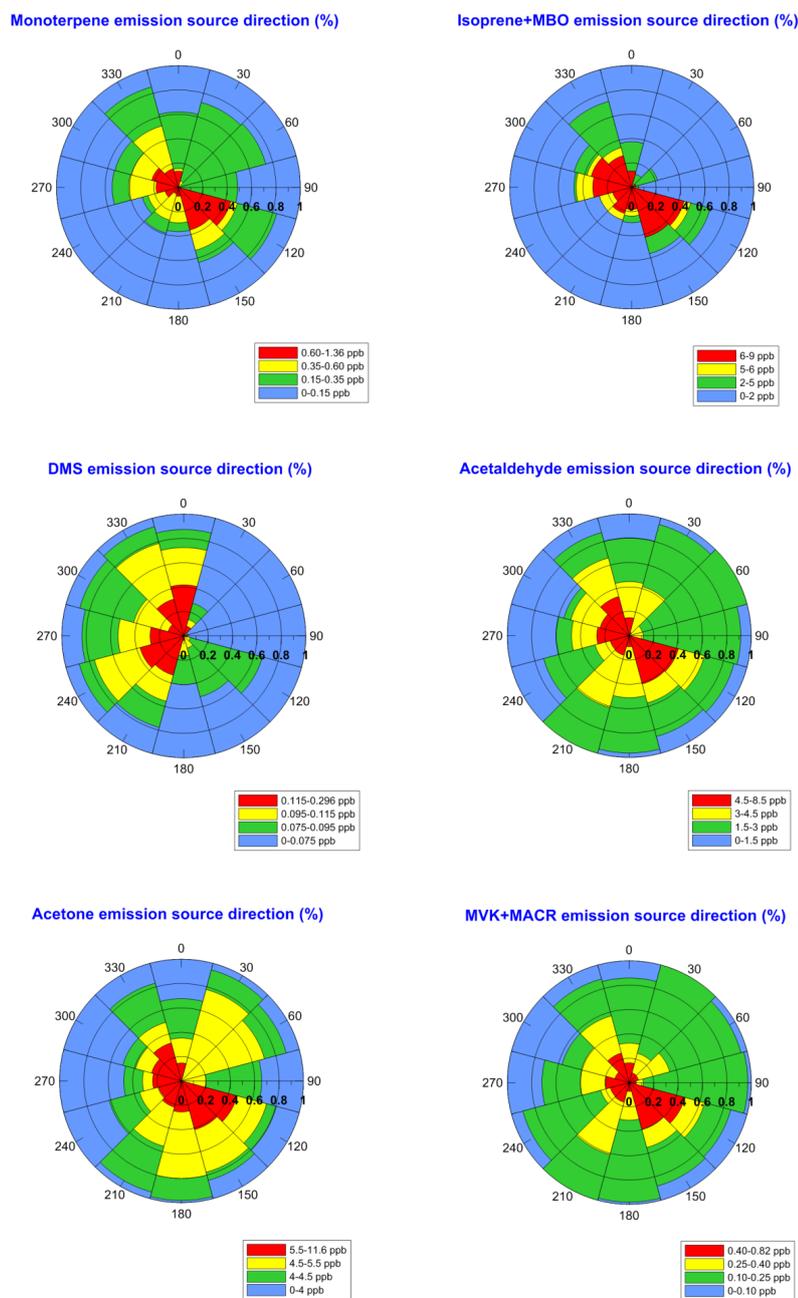
295

### 296 3.2 Origin of the BVOCs

297 To explore the potential sources of the BVOCs, we calculated for each wind sector the  
298 percentage of time corresponding with several mixing-ratio ranges, individually for  
299 each species (Fig. 4). Our findings indicate elevated mixing ratios for westerly and  
300 southeast wind components. The relatively elevated mixing ratios from the southeast  
301 can be attributed to emissions from the memorial garden, where frequent thinning of  
302 the vegetation can contribute to the generally elevated mixing ratios of plant-  
303 wounding BVOCs such as hexenal and hexanal (e.g., Brillì et al., 2011; Ormeño et al.,  
304 2011; Portillo-Estrada et al., 2015) from this direction. The elevated mixing ratios  
305 from the west may point to an additional contribution from marine origin, such as the  
306 Mediterranean Sea and/or the aquafarms, considering that the measurement site is  
307 surrounded by nearly homogeneous vegetation in all directions except for the  
308 memorial garden (Fig. 1). We found a smaller relative contribution of DMS from the  
309 southeast compared to the other BVOCs. The MEGANv2.1 simulations suggested no  
310 significant emission of isoprene from the nature park; the relatively strong



311 contribution of isoprene+MBO from the southeast can be attributed to MBO  
312 emissions from conifer trees (Gray et al., 2003) in the memorial garden. Similar  
313 trends in the day-to-day variation of MVK+MACR, isoprene oxidation products, and  
314 isoprene+MBO (Fig. 3) could imply the contribution of the memorial garden to  
315 isoprene emission, but this possibility is ruled out by kinetic analysis (see Sect. S2).  
316 The elevated mixing ratios of isoprene+MBO from the west may be attributed to the  
317 emission of isoprene from marine organisms, as discussed in Sect. 3.2.1. The origin of  
318 DMS is further addressed in Sect. 3.2.2.



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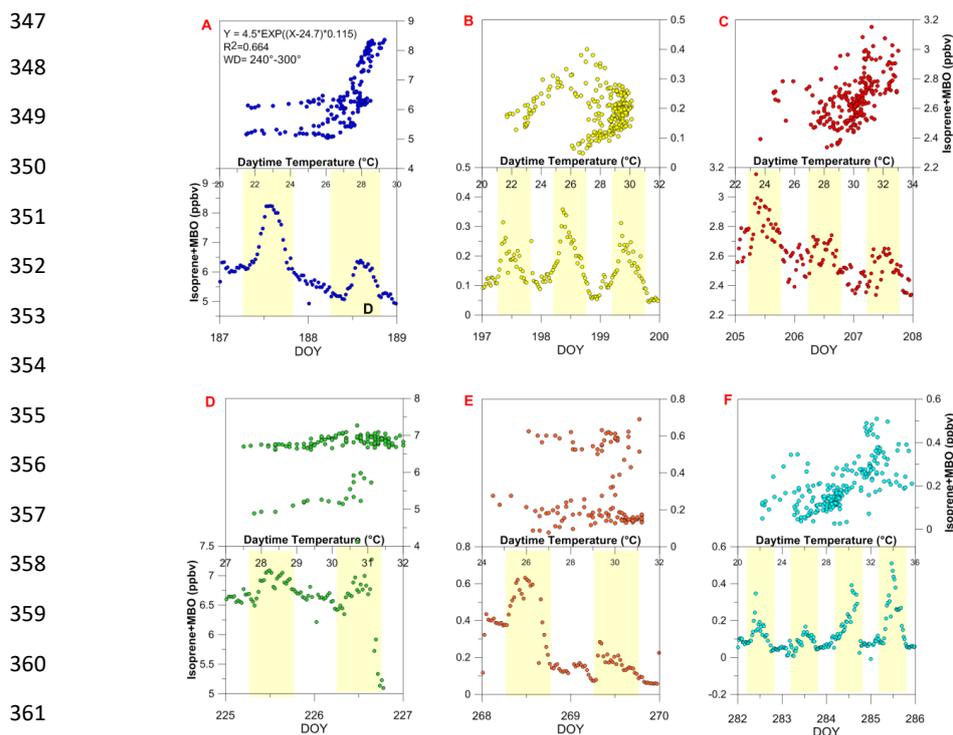
**Figure 4.** BVOC mixing ratios as a function of the contribution from each wind sector. The radial dimension represents the fraction of time for each wind sector, for which the mixing ratios were within a certain range, as specified in the legend.



323 *3.2.1 Origin apportionment of measured Isoprene+MBO*

324 As demonstrated in Sect. 3.1, the isoprene+MBO day-to-day variations differed from  
325 those of most of the BVOCs, with remarkably high variations in its mixing ratios,  
326 ranging from 0.03 ppbv to nearly 9 ppbv (Fig. 3), while the seasonal variation in its  
327 mixing ratios did not correlate with temperature (see Fig. S12). The low correlation  
328 between the diurnal profile of isoprene and carbon monoxide (see Fig. S10) strongly  
329 supports no significant contribution to isoprene mixing ratios from traffic on the two  
330 highways to the west (Fig. 1), considering that CO can be used as an indicator for  
331 incomplete combustion of fossil fuels. The Positive Matrix Factorization model  
332 (PMF) further predicted that isoprene+MBO has a common source with other BVOCs  
333 and not with AVOCs (see Fig. S3).

334 Figure. 5 presents the regressions of isoprene+MBO mixing ratios vs. T for the  
335 six measurement periods. For the two periods with high and low isoprene+MBO  
336 mixing ratios, there was a clear typical biogenic diurnal trend, with a maximum  
337 around noontime. This finding reinforces the notion that isoprene+MBO originates  
338 predominantly from biogenic sources. We did not, however, observe a positive  
339 correlation between isoprene+MBO mixing ratios and air T in all six periods (Table  
340 1). Furthermore, in most cases, we found no exponential increase in isoprene+MBO  
341 with air T, as is expected in the case of a nearby local biogenic source (e.g., Bouvier-  
342 Brown et al., 2009; Fares et al., 2009, 2010, 2012; Goldstein et al., 2004; Guenther et  
343 al., 1993; Kurpius and Goldstein, 2003; Richards et al., 2013). This might be related  
344 to the fact that the m69 signal is affected by the mixing ratios of both isoprene and  
345 MBO emitted locally and further away, while the local air temperature did not reflect  
346 changes of more distant leaf temperatures or SSTs.



**Figure 5.** Isoprene+MBO (m69) diurnal average mixing ratios and time series. (A-F) The regression between the measured MBO+isoprene (ISP+MBO) and T (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 between the measured MBO+isoprene and T (upper panels) excludes measurements associated with wind direction from the memorial garden (90°-150°).

We used the fact that MBO can be also 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. Figure 6a 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. 6a indicates also that  $m87/m69 > 25\%$  was mostly measured during nighttime, twilight and early



376 morning. For low  $m_{69}$ , the ratio matches the MBO typical ratio,  $m_{87}/m_{69}$ , which  
377 ranges between 13-25% or higher (Fig. 6a). Furthermore, in those relatively low  $m_{69}$   
378 mixing ratio periods, the ratio between the measured  $m_{69}$  and the MT relative signals  
379 match the  $[MBO]/[MT]$  from MEGANv2.1. This reinforces the hypothesis that high  
380 isoprene+MBO mixing ratios predominantly result from isoprene emission, whereas  
381 low mixing ratios are primarily from local vegetation MBO emissions.

382 Figure 7 further presents the diurnal profile for  $m_{87}/m_{69} < 13\%$ , as well as the  
383 corresponding mixing ratios versus  $T$ , separately for each measurement day.  
384 Interestingly, some of the measurement days presented in Fig. 5 were associated with  
385 no  $m_{87}/m_{69} < 13\%$ , which is why there are fewer measurement days in Fig. 7 than in  
386 Fig. 5. The diurnal profiles in Fig. 7 support a biogenic origin for isoprene, although  
387 they were more scattered for 25-27 of July. Fig. 7 also demonstrates the positive  
388 correlation between the isoprene mixing ratio and  $T$  during all measurement days,  
389 while in several days a sharp increase in isoprene with  $T$  occurred for  $T > \sim 26-28^\circ\text{C}$   
390 (e.g., 6,7 July and 16 August). In general, a higher correlation with temperature was  
391 obtained for  $m_{87}/m_{69} < 13\%$  (Fig. 7) than for all  $m_{69}$  signals (i.e., Fig. 7 vs. Fig. 5),  
392 reinforcing the biogenic origin for isoprene with a relatively strong dependency on  $T$ .  
393 Furthermore, regression of  $m_{87}/m_{69} > 13\%$  with  $T$  does not indicate a clear  
394 dependency of mixing ratios on  $T$ , suggesting different emission controls for the  
395 MBO and isoprene (see Fig. S4). The MBO mixing ratios tended to be controlled by  
396 both  $T$  and solar radiation, while isoprene was predominantly governed by the former,  
397 in agreement with a previous study (see Kaser et al., 2013).

398 To study the origin of isoprene, we analyzed the fraction of time for which  
399  $m_{87}/m_{69} < 13\%$  vs. wind direction (Fig. 6b). We found that  $m_{87}/m_{69} < 13\%$   
400 predominantly corresponds with a western origin. These results suggest a significant



401 contribution of isoprene from the sea or the aquaculture farm located at the,  
402 considering that the measurement site is nearly homogeneously surrounded by mixed-  
403 Mediterranean vegetation, except for the memorial garden to the southeast.  
404 Furthermore, MEGANv2.1 simulations predicted a negligible emission rate for  
405 isoprene from the nature park.

406 In some cases (~4% of the time), elevated  $m_{87}/m_{69} > 13\%$  was recorded also  
407 from the southwest and northwest, which according to simulations by HYSPLIT can  
408 be entirely attributed to transport from either the sea or the aquaculture farms (see Fig.  
409 S11). The relatively small fraction of time for which  $m_{87}/m_{69} < 13\%$  is from the  
410 southeast can be attributed to the emission of MBO from conifers.

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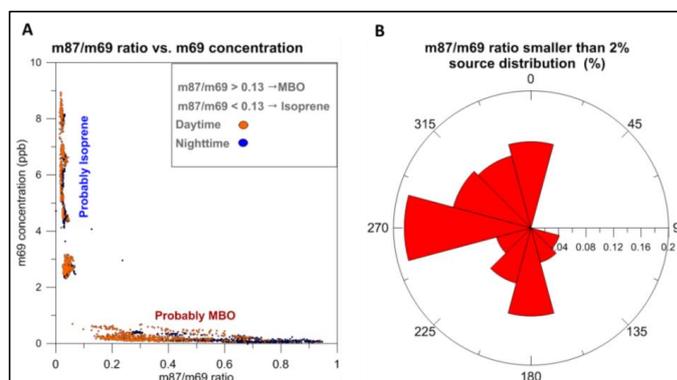
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420 **Figure 6.** Isoprene and MBO origins. (a) Scatter plot of m69 mixing ratios as a function of the  
421 m87/m69 ratio. Low and high ratios indicate a predominant contribution of MBO and isoprene,  
422 respectively. The orange dots were measured during the daytime and the dark blue during the nighttime  
423 (b) Fraction of time for each wind sector for which m87/m69 was <13%.

424

425 Two facts support isoprene+MBO predominant sea origin rather than the aquaculture  
426 farms. First, back trajectories using HYSPLIT show no lower mixing ratios for  
427 isoprene+MBO also in cases when the air masses were transported from the sea but  
428 not over the aquaculture farms compared to transport of air masses over the

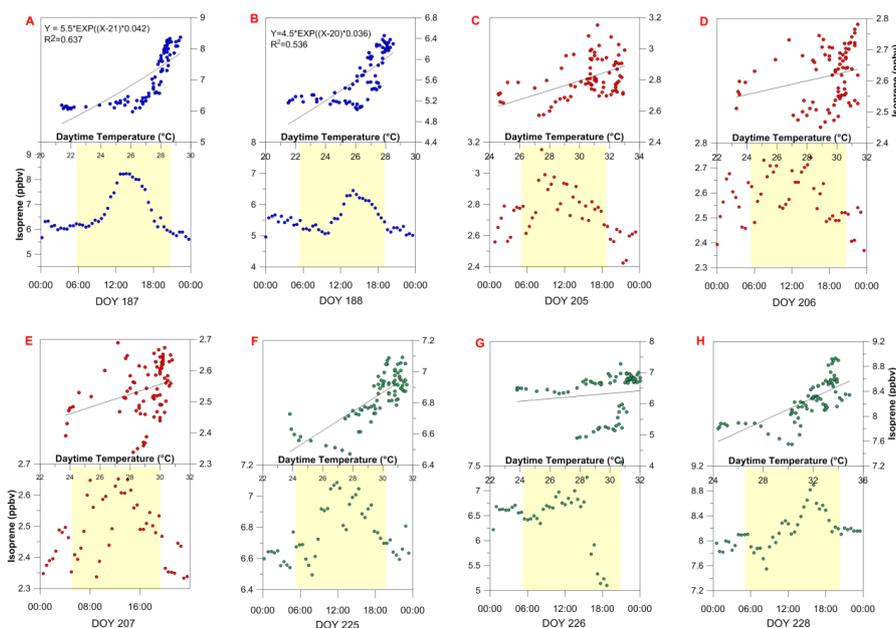


429 aquaculture (e.g., Fig. 5 and S11). Second, marine organisms have relatively short  
430 life cycles, typically a few days (Tyrrell, 2001), and would likely have a variable  
431 source strength from the aquaculture farms, which would not explain the similar  
432 isoprene+MBO mixing ratios for different wind directions during a specific day. Our  
433 measurements indicated no dependence of high isoprene+MBO mixing ratios on wind  
434 direction during the day, reinforcing the sea's dominant role in isoprene emission,  
435 rather than the aquaculture farms.

436 Interestingly, the isoprene mixing ratios during the nighttime remained  
437 relatively high (~5-6 ppb) (Fig. 6a), the reason for which could be a relatively small  
438 oxidative sink strength during the night. The daytime and nighttime isoprene lifetime  
439 can be estimated based on its reaction with OH, NO<sub>3</sub> and O<sub>3</sub>. We estimated the  
440 average daytime OH and nighttime NO<sub>3</sub> concentrations, based on the MINOS  
441 campaign in Finokalia, Crete (Berresheim et al., 2003; Vrekoussis et al., 2004), at  
442  $4.5 \cdot 10^6 \frac{\text{molec}}{\text{cm}^3}$  (Berresheim et al., 2003), and  $1.1 \cdot 10^8 \frac{\text{molec}}{\text{cm}^3}$  (Vrekoussis et al.,  
443 2004), respectively. Using these concentrations, the reported rate constants for  
444 isoprene with OH and NO<sub>3</sub> of  $1 \cdot 10^{-10} \frac{\text{cm}^3}{\text{molec}\cdot\text{sec}}$  (Stevens et al., 1999) and  $5.8 \cdot$   
445  $10^{-13} \frac{\text{cm}^3}{\text{molec}\cdot\text{sec}}$  (Winer et al., 1984), respectively, and measured O<sub>3</sub> levels, we  
446 obtained daytime and nighttime isoprene lifetimes of ~37 min and ~3.8 h,  
447 respectively. This result points to isoprene emission occurring during the daytime.



448



449

450 **Figure 7.** Isoprene ( $m_{87}/m_{96} < 13\%$ ) mixing-ratio diurnal average and dependence on temperature.  
451 Upper panels show regression between measured  $m_{87}/m_{96} < 13\%$  and T, and lower panels present that  
452 of  $m_{87}/m_{96} < 13\%$ . Yellow shaded area represents daylight hours.

453

### 454 3.2.2 Origin and characterization of DMS

455 The discussion in Section 3.1 suggests that DMS is primarily emitted from the west,  
456 pointing to a dominant marine emission source, with the less elevated mixing ratios  
457 probably associated with emission from vegetation. According to the MEGANv2.1  
458 simulation, the natural park's vegetation is a potent source of DMS (average  
459 flux =  $0.477 \frac{mg}{m^2 \cdot hr}$ ), slightly higher than the flux measured from insolated branches  
460 (Jardine et al., 2015; Yonemura et al., 2005), while our analysis points to a stronger  
461 emission from the memorial garden (see Fig. 4). As for isoprene, our analysis of DMS  
462 mixing ratios with respect to wind direction rules out a significant contribution of the  
463 aquafarms to the measured DMS, suggesting that the sea is a major source for DMS,



464 with apparently a strong dependency on T (Figs. 3, 4). DMS showed much less day-  
465 to-day variations in its mixing ratios compared to isoprene and other BVOCs. This  
466 corresponded with a clear day-to-day correlation of DMS mixing ratios with T. Figure  
467 8 demonstrates a clear increase in the mixing ratios with T, throughout the  
468 measurement period. Note that no significant dependency of DMS on global solar  
469 radiation was observed.

470 The DMS mixing ratios peaked at  $\sim 0.18$  ppbv. This figure is about an order of  
471 magnitude lower than at the ocean surface (Tanimoto et al., 2014), about an order of  
472 magnitude lower than in the Southern Ocean (Koga et al., 2014), slightly lower than  
473 the maximum concentrations in the south Indian Ocean (Aumont et al., 2010), and  
474 similar to the maximum concentrations on the coasts of Tasmania (Aumont et al.,  
475 2010). Interestingly, the mixing ratios measured in this study are lower by about 1-2  
476 orders of magnitude than those measured in the same region during August 1995  
477 (Ganor et al., 2000), which could be attributed to a change in the marine biota as a  
478 consequence of seawater warming.



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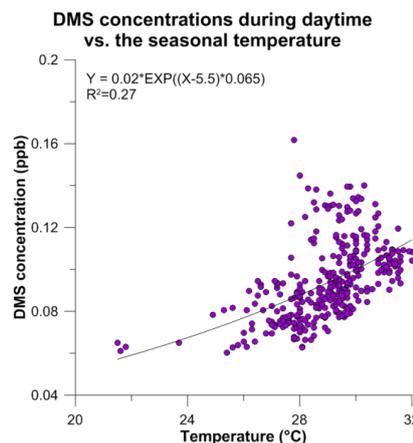
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**Figure 8.** Daytime DMS mixing ratios from the western sector (marine source) as a function of the temperature along the measurement campaign. An exponential fit between the two is included.

490

### 491 3.2.3 Origin and characterization of other BVOCs

492

Our findings in Figure 3 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 MEGANv2.1 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. According to MEGANv2.1, the average and maximal daytime MT flux were  $59 \frac{\mu\text{g}}{\text{m}^2 \cdot \text{hr}}$  and  $152 \frac{\mu\text{g}}{\text{m}^2 \cdot \text{hr}}$ , respectively. While this predicted average flux is lower than the mean MT measurements in the Birya and Yatir *Pinus halepensis* Mill. forests in Israel ( $\sim 200 \frac{\mu\text{g}}{\text{m}^2 \cdot \text{hr}}$  and  $800 \frac{\mu\text{g}}{\text{m}^2 \cdot \text{hr}}$ , 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

505



506 higher mixing ratios in our study, as compared with these two sites, were associated  
507 with wind direction, either from the memorial garden or from the western sector (Fig.  
508 4). This supports a relatively small local contribution of MTs in our study compared  
509 with seawater.

510

### 511 *3.3 Concentrations of isoprene and DMS originating from the Levantine Basin*

512 Previous studies demonstrated the trade-off between DMS and isoprene in the marine  
513 boundary layer, due to species distribution and climate, suggesting that most regions  
514 are a source of either isoprene or DMS, but not both. While isoprene is emitted from  
515 species that are more abundant in warmer regions and low-to-middle latitudes, DMS  
516 is predominantly emitted in colder regions and higher latitudes (Dani and Loreto,  
517 2017). This is in agreement with the relatively high isoprene/DMS mixing ratios in  
518 our study. The SST in the Levantine Basin is relatively high, exceeding 30°C in  
519 August 2015 at a distance of 2km from the coastline (IOLR, 2015). Further, SST  
520 plays a significant role in determining which phytoplankton will dominate, and for a  
521 given marine organisms population higher temperature and solar radiation tends to  
522 enhance their BVOC emission, including DMS and isoprene (Dani and Loreto, 2017).  
523 The strong emission of isoprene from the Levantine Basin can be attributed primarily  
524 to its relatively high SST, considering the well-known correlation of isoprene  
525 emission with SST (Dani and Loreto, 2017; Exton et al., 2013).

526 The relatively warm and oligotrophic sea enables cyanobacteria to become a  
527 large fraction of marine primary production and phytoplankton (Krom et al., 2010;  
528 Paerl and Otten, 2013; Pedrotti et al., 2017; Sarma, 2013) in the Levantine Basin, that  
529 favors, in turn, emission of isoprene over other BVOCS, including DMS. Previous  
530 measurements have indicated the presence of cyanobacteria in the Levantine Basin



531 during the summer of 2015 (Herut, 2016), with the cyanobacteria *Synechococcus* and  
532 *Prochlorococcus* being the most abundant phytoplankton along the coasts of Israel  
533 during August 2015. A laboratory experiment demonstrated the emission of isoprene  
534 from the latter (Shaw et al., 2003). Other micro-organisms in the Levantine Basin  
535 (mostly dinoflagellates and diatoms) are generally less abundant. *Thalassiosira*  
536 *pseudonana* diatoms are also abundant along the coasts of Israel, which raises the  
537 possibility that the emission of isoprene from the sea is also influenced by this  
538 species. A laboratory experiment using PTR-MS indicated the emission of isoprene,  
539 as well as methanol, acetone and acetaldehyde from *Thalassiosira pseudonana*  
540 diatoms, but isoprene is the only one among these that is not consumed by  
541 bacterioplankton within the water column (Halsey et al., 2017).

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



555 **4. Conclusions**

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



579 affect biological activity, which was shown to correlate with BVOC emissions (Gantt  
580 et al., 2010).

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

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

601 This study demonstrates that most of the VOCs studied here are controlled by  
602 both anthropogenic and marine and terrestrial biogenic emission sources, highlighting  
603 the need for the strict identification of the origin and representative models for both



604 emission source types. Our study further highlights the Levantine Basin's capability  
605 to serve as a natural laboratory for studying both anthropogenic stress and climate  
606 change on marine BVOC emissions. More comprehensive research is required to  
607 directly address the impact of oligotrophication and increased SST on marine BVOC  
608 emissions.

609

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

612

613 **Author contribution.** ET designed the experiments, MG and GL carried the field  
614 measurements out and PM and EF led the calibration, quality control and data  
615 processing. AG setup the MEGANv2.1 model. CD and ET led the analyses with  
616 contributions from all co-authors. ET and CD prepared the manuscript with  
617 contributions from all co-authors.

618

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

620

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