

Isoprene above the Eastern Mediterranean: Seasonal variation and contribution to the oxidation capacity of the atmosphere

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Abstract

Isoprene is one of the most important biogenic volatile organic compounds with large terrestrial emissions and comparatively a small oceanic source on a global scale. This marine source seems to strongly depend on environmental parameters such as phytoplankton abundance, light, temperature, wind speed, and thus, to be highly variable. However, this source can consequently affect the chemistry of the marine boundary layer on a local or mesoscale. The present study investigates the factors that control isoprene levels and estimates the marine source of isoprene and its role in the oxidizing capacity of the atmosphere at a coastal site in the East Mediterranean. More than 2000 measurements of isoprene have been conducted at Finokalia sampling station on the island of Crete over an 8-month period from February to October 2004. Isoprene varies between 5 and 1200 pptv with the highest values observed in summer. The origin of the air masses determines the atmospheric abundance and the prevailing source of isoprene. According to chemical box model calculations, during daytime the isoprene observed under marine conditions is reducing hydroxyl (OH) and hydroperoxy (HO₂) radicals by up to 26% and 13%, respectively, whereas, it can increase the sum of peroxy radicals by a factor of 4. At night, isoprene of marine origin is depressing nitrate radicals by up to 25% and increases the low nighttime levels of OH and HO₂ radicals by up to 25% and 30%, respectively. The seawater emissions of isoprene in the area are estimated between 10⁸ and 6 × 10⁹ molecules cm⁻² s⁻¹ with a strong seasonal variability.

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1. Introduction

Volatile organic compounds (VOCs) are very reactive against hydroxyl (OH) radicals, ozone (O₃), and nitrate radicals (NO₃). Their oxidation in the

atmosphere contributes to O₃ formation when sufficient NO_x is available. It is also a source of peroxy radicals (RO₂), peroxy acetyl nitrate (PAN), and a variety of other compounds affecting the oxidation capacity of the atmosphere. Several VOCs oxidation is known to produce secondary organic aerosol that affect climate, and thus, VOC oxidation also exerts an impact on the energy balance of the Earth (Kanakidou et al., 2005).

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VOCs are emitted to the troposphere from both anthropogenic (vehicle emissions, fuel and biomass burning, industrial facilities, solvent usage, and oil refineries) and natural sources (vegetation and seawater). While on global scale, VOCs emissions from anthropogenic sources are estimated at about 100 Tg C y^{-1} (Atkinson and Arey, 2003), natural sources are responsible of larger emission by one order of magnitude (1150 Tg C y^{-1} ; Guenther et al., 1995; Atkinson and Arey, 2003) of biogenic volatile organic compound (BVOCs) such as isoprene, terpenes, and oxygenated organic compounds.

Isoprene (2-methyl-1,3-butadiene) is one of the most important BVOCs with emissions estimated between 220 and 503 Tg C y^{-1} (Muller, 1992; Guenther et al., 1995). These emissions show both light and temperature dependence and approach maximum values during midday (Guenther et al., 1991). Isoprene is highly reactive with an atmospheric lifetime of few minutes to few hours (Atkinson and Arey, 2003). The major sources of isoprene are emissions from deciduous trees; thus, over forested areas isoprene mixing ratios can raise up to several ppbv (Apel et al., 2002; Rinne et al., 2002). Besides terrestrial vegetation, other isoprene sources include emissions by heterotrophic bacteria (Kuzma et al., 1995), by marine phytoplankton (Shaw et al., 2003) and by seaweeds (Broadgate et al., 2004). Several authors (Bonsang et al., 1992; Ratte et al., 1998; Shaw et al., 2003; Broadgate et al., 2004; Palmer and Shaw, 2005) estimated the isoprene flux from the ocean into the atmosphere between 0.1 and 1.2 Tg C y^{-1} . These values although small compared to terrestrial fluxes could significantly influence atmospheric chemistry in remote marine and maritime rural regions (Ayers et al., 1997; Carslaw et al., 2000).

This work presents an 8-month study of the occurrence and fate of isoprene at a rural marine location in the Eastern Mediterranean (Crete island (Greece)). The major aims of this study are:

- (i) to understand the factors that control the isoprene levels in the area;
- (ii) to estimate the magnitude of the marine source of isoprene;
- (iii) to evaluate the role of this isoprene source in the oxidation capacity of the atmosphere on a regional basis by using a 0-D chemical model.

It is the first time that such an extensive data set of isoprene and related parameters is collected and

analyzed for the Eastern Mediterranean, an area characterized by high levels of ozone and OH radicals (Kouvarakis et al., 2000; Lelieveld et al., 2002).

2. Experimental

2.1. The site

Hydrocarbon measurements from C_2 to C_6 , including isoprene, were conducted at Finokalia sampling station ($35^\circ 20' \text{N}$, $25^\circ 40' \text{E}$) located on the coast of the island of Crete, Greece, exposed to the sea from 270° – 90° (W–E). A detailed description of the Finokalia sampling site and the prevailing meteorological conditions are reported elsewhere (Mihalopoulos et al., 1997; Kouvarakis et al., 2000; Gerasopoulos et al., 2005).

2.2. Isoprene measurements

More than 2000 continuous hourly measurements of isoprene have been performed by means of an automatic gas chromatograph (Chromatrap GC by Chromato Sud, France) from February to October 2004. Thus, the data coverage during this 8 months period was 33%. For each analysis, 250 ml of air were drawn from about 3 m above the ground via a stainless-steel inlet with a flow rate of 65 ml min^{-1} (air sample integrated over about 4 min). The air sample passed through a Nafion dryer to remove the humidity and then hydrocarbons were preconcentrated at -15°C on a 2.25 mm id, 6 cm length trap containing as adsorbents: Carboxen 1000 (50 mg), Carbopack B (10 mg), and Carbotrap C (10 mg). This procedure adapted from the Airmotec instrument and developed by ChromatoSud is described elsewhere (Touaty, 1999; Gabard, 2002). Then the pre-concentrated air sample was thermally desorbed and directly injected in an $\text{Al}_2\text{O}_3/\text{Na}_2\text{SO}_4$ capillary column located inside the heated oven of the GC. Within the first minute of the analytical procedure, the oven temperature was raised from 38 to 40°C . Afterwards, a constant heating rate of $20^\circ \text{C min}^{-1}$ was applied and the temperature reached 199°C by the end of the analysis. C_2 – C_6 hydrocarbons including isoprene were detected by a flame ionization detector (FID). The detection limit has been estimated at 5 pptv. A gas mixture containing 1 ppmv levels of 55 C_2 – C_9 VOCs, (# 22964-Restek, Spectra Gases) and including 25 compounds in the analytical range of the GC instrument (C_2 – C_6

alkenes, *n*- and iso-alkanes, and isoprene) have been used for the identification of the compounds of interest. A certified standard gas mixture containing 100 ppmv of ethane, ethylene, propane, and *n*-butane has been used as the primary calibration standard. 100–300 μ l of this primary standard were regularly (weekly) injected with a pressure-lock syringe. Taking into account the linearity of the FID detector with respect to the carbon number of the molecules detected, this calibration based on the detector response to C₂–C₄ hydrocarbons is also suitable to quantify heavier NMHC in the C₅–C₆ range, at ppbv levels, with an accuracy better than 1%. The performances of this procedure have been previously checked by comparison with injections of a primary standard of isoprene, details are given in a previous paper (Bonsang and Kanakidou 2001). In addition to light hydrocarbons, meteorological parameters (wind speed and direction, total solar radiation (*W*), temperature, and relative humidity) and radon-222 (²²²Rn) activities were continuously monitored (Gerasopoulos et al., 2005). Air masses back trajectories were calculated by the HYSPLIT model (Hybrid Single-Particle Lagrangian Integrated Trajectory Model; <http://www.arl.noaa.gov/ready/hysplit4.html>; Draxler and Hess, 1998) for 1000 m above sea level to avoid orographic interferences at lower heights and to be consistently within the boundary layer of the region which mostly ranges between 1000 and 1300 m.

2.3. Model description

The chemistry model is a condensed chemical mechanism, which, apart from the background O₃/NO_x/OH/CO and CH₄ chemistry, also takes into account the oxidation chemistry of C₁–C₅ nonmethane hydrocarbons including isoprene and sulfur compounds. For the isoprene chemical reaction scheme the following assumptions were made: (i) the six peroxy radicals formed by the reaction of isoprene with OH radicals are “lumped” to one species, (ii) ketones and aldehydes as MVK and MACR are explicitly treated in the model, and (iii) all PAN-like compounds are represented by PAN. The hydrocarbon chemical scheme is presented in detail by Poisson et al. (2001). Observed diurnal variations based on hourly mean values of O₃, CO, NO, NO₂, JNO₂, JO¹D, temperature, relative humidity (RH), and wind speed are used as input to the model for each month. In addition, in the model NO and NO₂ are forced every 5 min by

the corresponding hourly mean observations. Isoprene concentrations vary hourly according to the observations but are kept constant within each hour interval. Ethene, propene, ethane, propane, and butane diurnal mean mixing ratios measured in the area during the studied period (February–October 2004; Mihalopoulos and Bonsang, unpublished data) are adopted in the model. HCHO initial mixing ratios are taken equal to 1 ppbv (Lelieveld et al., 2002). No direct heterogeneous ozone losses are taken into account in the model whereas NO_z and RO_x heterogeneous losses are parameterized as described by Tsigaridis and Kanakidou (2002) and Vrekoussis et al. (2004). For the present study, simulations have been performed for each month of the studied period by taken into account and by neglecting isoprene occurrence in the atmosphere. Two repetitive diurnal cycles have been simulated in each model run. The first one is used as spin-up time and the results of the second one are analyzed in the present study.

3. Results

3.1. Annual, seasonal, and diurnal variations of isoprene

Fig. 1 depicts the time series (discontinuous hourly measurements) of isoprene at Finokalia during the period February–October 2004. Atmospheric isoprene concentrations range from below the detection limit (5 pptv) to 1200 pptv and present a clear seasonal pattern with higher values during summer. Statistical analysis of the isoprene measurements is presented in Table 1. Fig. 2a depicts the monthly mean isoprene values and their standard

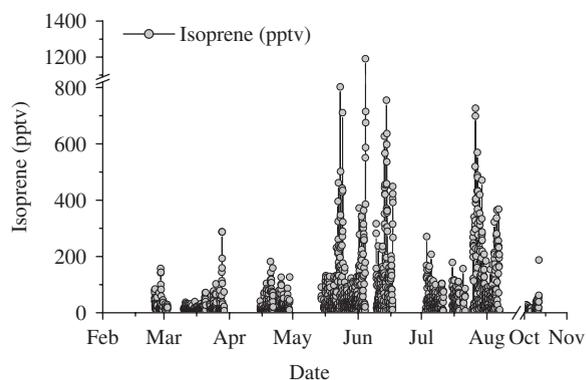
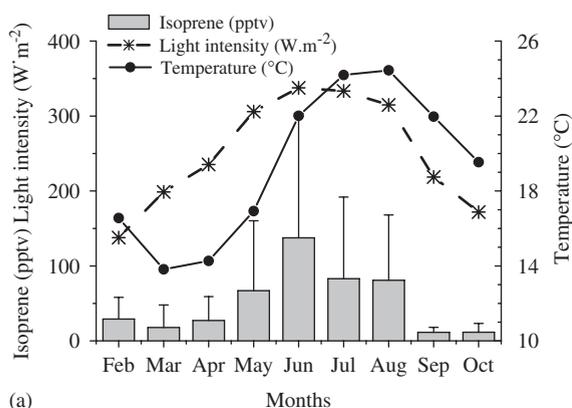


Fig. 1. Isoprene observations at Finokalia, Crete, Greece, from February to October 2004.

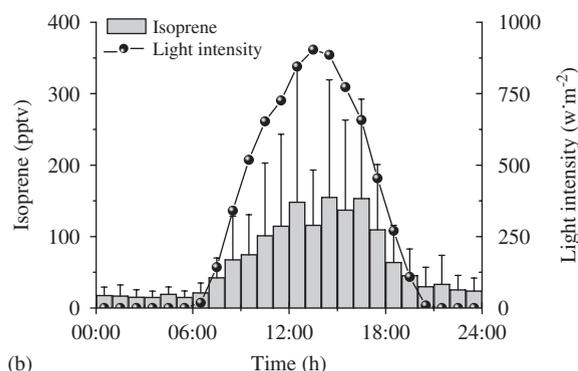
Table 1

Statistical analysis of isoprene levels observed during this work (values in pptv). B.L. is below the detection limit estimated to be 5 pptv

Statistical data						
Month	Mean	St. Dev.	Min	Max	Day mean	Night mean
February	29.1	28.9	7.3	157.3	39.9	17.1
March	17.8	30.1	BL	287.4	28.2	8.7
April	27.1	32.0	BL	181.8	41.8	12.1
May	66.9	93.4	BL	802.5	109.2	26.6
June	137.5	166.1	BL	1190.8	231.6	55.5
July	83.0	108.9	BL	726.4	128.7	32.4
August	80.9	87.2	BL	367.8	120.3	44.4
September	11.5	6.6	6.5	27.0	12.7	8.7
October	11.6	11.7	BL	62.1	15.9	6.5



(a)



(b)

Fig. 2. (a) Monthly mean observations of isoprene (and standard deviation), light intensity and temperature at Finokalia station from February to October 2004 and (b) Hourly mean observations of isoprene (and their standard deviation) for the month of May 2004 and of the light intensity as a function of the local time.

deviation in conjunction with the temperature and light intensity variation. The monthly mean concentration of isoprene minimizes in autumn and maximizes in summer. However, the observed

seasonal pattern is slightly misleading, since February 2004 has been an exceptional month with unusual high temperature and insolation (Fig. 2a). The monthly mean variations of isoprene seem to be related with those of temperature and insolation. However, significant correlation is observed only with insolation ($r^2 = 0.84$) since insolation rapidly decreases after August. The role of insolation is clearly shown in Fig. 2b that depicts the monthly mean diurnal variation of isoprene in May in conjunction with the light intensity. Photosynthetic production from both the terrestrial and the marine biota (Guenther et al., 1993; Shaw et al., 2003) is a well-known source of isoprene. However, nighttime levels exhibit a seasonality similar to the daytime ones (Table 1). Owing to the very short lifetime of isoprene (of the order of 0.6–2 h; see below) it is unlikely that these levels correspond to a residual background of isoprene produced during daytime. Thus, they could be explained by a potential additional factor controlling isoprene production, besides photosynthesis, most probably temperature.

The monthly mean (Fig. 2a) and the annual mean (60 ± 100 pptv) levels of isoprene observed at Finokalia are in good agreement with the few values reported in literature for marine locations of the Northern hemisphere and especially with those for similar latitudes (Sharma et al., 2000; Matsunaga et al., 2002; Table 2).

3.2. Factors controlling isoprene levels

3.2.1. Lifetime of isoprene in the Mediterranean atmosphere

The evaluation of the isoprene lifetime enables a first identification of the factors that control isoprene levels in the Mediterranean atmosphere. Since isoprene is oxidized by OH and NO₃ radicals and O₃, its lifetime has been estimated using the in situ observations of NO₃ radicals and O₃, and the levels of OH which have been deduced from the observations of O₃ and of the frequency of its photo dissociation to O¹D (JO¹D) and a chemical box model (Vrekoussis et al., 2004, 2006). Table 3 summarizes the mean calculated isoprene lifetime during day and during night as well as its minimum and maximum values for each month of the studied period. Isoprene lifetime varies between 36 min during daytime in summer and a few hours during nighttime in winter. Although relatively short, this lifetime enables atmospheric transport to affect isoprene levels in the atmosphere. Thus, isoprene

Table 2
Isoprene concentrations at different worldwide locations (values in pptv)

Location/date	Area	Mean	Literature
Western North Pacific May 2001	Marine	45	Matsunaga et al. (2002)
Baltic Sea/Uto 1993–1994			
Winter	Marine	26	Laurila and HaKola (1996)
Spring		29	
Summer		7	
Autumn		4	
Happo/Japan			
Autumn 1998	Marine/rural	32	Sharma et al. (2000)
Summer 1998		343	
Messorouigion/Greece			
May 1996 and May 1997	Rural forested	4	Moschonas and Glavas (2000)
June and September 1996		780	
October 1996		4	
Finokalia/Greece			
Annual	Rural/marine	60	This work
Winter 2004		18	
Spring 2004		41	
Summer 2004		100	
Autumn 2004		12	

Table 3
The mean isoprene lifetime during day and nighttime as well as the range (minimum and maximum values)

Months	$\tau_{\text{Day}}(\text{h})$	$\tau_{\text{Night}}(\text{h})$
February	1.9 (1.0–15.2)	11.5 (10.2–12.6)
March	2.0 (1.1–13.5)	3.5 (2.6–7.3)
April	1.2 (0.8–7.5)	5.3 (4.0–6.5)
May	0.8 (0.5–4.7)	1.9 (1.0–4.1)
June	0.6 (0.4–13.6)	1.7 (1.3–4.0)
July	0.6 (0.4–13.8)	2.8 (2.3–3.6)
August	0.7 (0.4–15.1)	1.8 (1.4–2.5)
September	0.7 (0.4–9.6)	1.9 (1.6–2.6)
October	1.1 (0.5–13.8)	4.1 (3.8–4.5)

levels in the area can be affected both from oceanic and from terrestrial sources depending on the wind direction. Note however, that, on global scale, emissions of isoprene from the terrestrial biosphere are almost three orders of magnitude higher than its marine emissions (Palmer and Shaw, 2005).

3.2.2. The role of atmospheric transport

Given the short lifetime of isoprene (less than 4 h) the impact of the atmospheric transport has been studied with regard to (i) the air masses origin and (ii) the wind speed.

Isoprene relation with the air masses origin: The air masses arriving at Finokalia station are char-

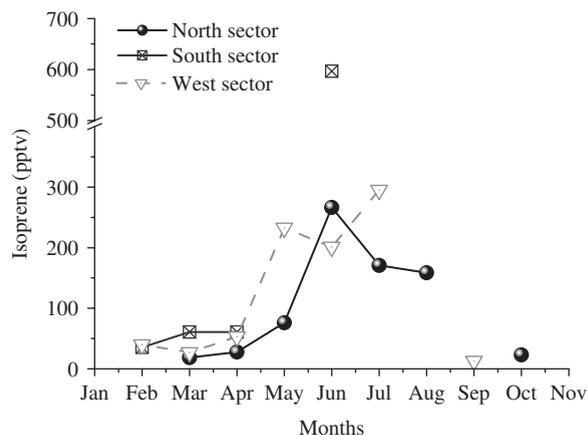


Fig. 3. Observed seasonal variability of daytime isoprene levels at Finokalia for the three distinct wind sectors.

acterized based on 24 h back-trajectories analysis for the studied period. The impact of air masses origin on the seasonal variation of isoprene at Finokalia is clearly seen in Fig. 3 where daytime (8–18 h) isoprene levels are plotted as a function of the month and category of the observed air mass. Focusing on the month of June when almost all possible origins of air masses arriving at Finokalia have been observed isoprene mixing ratios are by about a factor of 3.5 higher when air masses originate from the SW (terrestrial sector) compared

with the N and NW (marine sectors). Under SW winds, the air masses sweep part of the island that is covered by vegetation (mainly olive trees) before reaching the station. Although the seasonality in isoprene levels, shown in Fig. 1, remains after the air masses selection, the amplitude of the seasonal variation is changing and strongly depends on the air masses origin. More precisely, the highest amplitude is observed for the W and S sectors (influenced by the island).

Given the short lifetime of isoprene, it is unlikely that isoprene emissions from the close-by upwind lands contribute to the isoprene levels measured when air masses originate from the marine sector (NW–NE sectors; hereafter as N sector). Indeed, the travel time from Peloponnesus, which is the nearest upwind land, to Crete and thus to the sampling station is at least 6 h. Moschonas and Glavas (2000) reported at Peloponnesus a summertime mean isoprene level of 780 pptv. Assuming a travel time of air masses of 6 h and a summertime isoprene lifetime of 0.6 h (Table 2), the contribution of a medium range transported isoprene to the measured levels is not expected to exceed 1 pptv, which is two orders of magnitude lower than the mid-day observations in summer. Thus, the isoprene levels measured under marine sector influence correspond to regional marine emissions.

Isoprene relation with the wind speed: Fig. 4 illustrates the hourly average values for isoprene during day as a function of wind speed from May to August. Low wind speed favors the impact of local (terrestrial) sources on isoprene. Especially, for wind

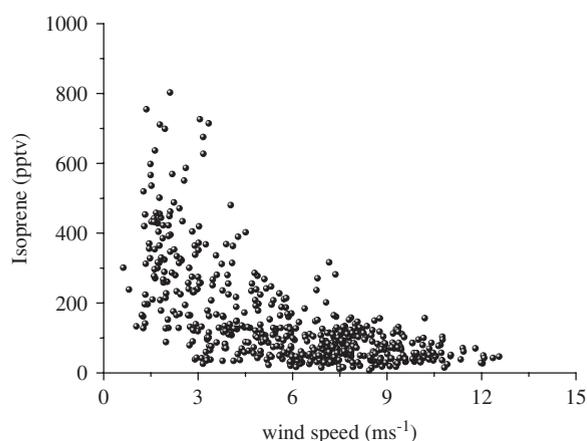


Fig. 4. Isoprene dependence on wind speed for all wind directions observed from May through August 2004 based on daytime hourly mean values.

speed (u) below 4 m s^{-1} , isoprene increases exponentially, whereas, for wind speed above 4 m s^{-1} isoprene does not show any dependence on wind speed and remains almost constant. Therefore, in order to exclude isoprene observations potentially influenced by nearby terrestrial emissions, the measurements performed when wind speed was below 4 m s^{-1} have been neglected from the following data interpretation. Thus, the discussion is limited to the data collected in air masses from the marine sector and with wind speed higher than 4 m s^{-1} .

3.2.3. Light and temperature dependence

Isoprene emissions are conditioned by photosynthesis rate, which maximizes at noon and ceases at night. The impact of light intensity and of temperature on isoprene emissions is examined in Figs. 5 and 6 respectively, using only data obtained under pure marine conditions (N sector and $u > 4 \text{ m s}^{-1}$). In Fig. 5, all day and nighttime data are reported whereas, for the correlation with temperature (Fig. 6) only the daytime data have been used. Note also that since seawater temperature data are not available, air temperature data have been used in Fig. 6. Isoprene levels demonstrate an exponential increase with the light intensity (Fig. 5) and with temperature (Fig. 6) as those observed for terrestrial plants indicating similar influence of insolation and temperature on the marine phytoplankton in agreement with experiments performed using phytoplanktonic cultures (Shaw et al., 2003). Note that in Fig. 6 when only nighttime data are used, similar behavior with

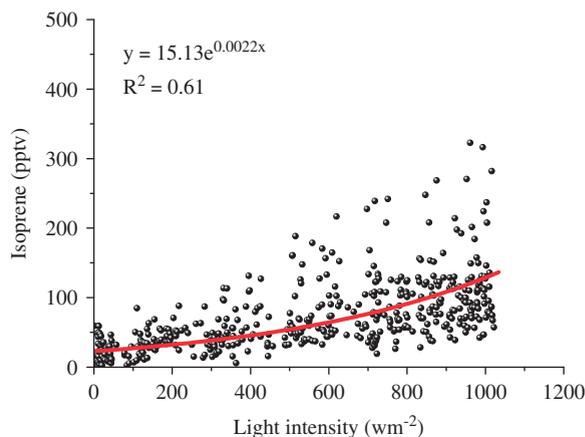


Fig. 5. Isoprene level dependence on light intensity for the months of May through August 2004 based on day and nighttime data collected under marine conditions (marine sector and wind speed $> 4 \text{ m s}^{-1}$).

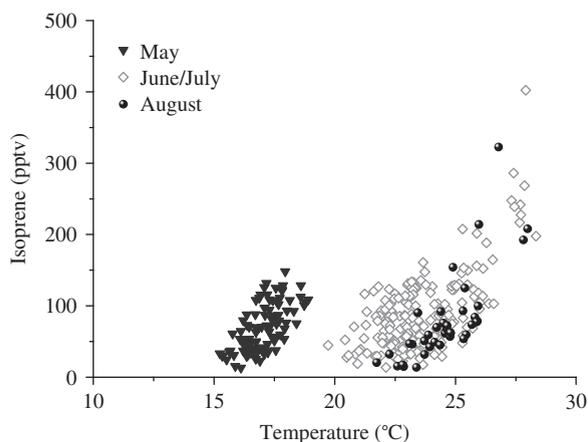


Fig. 6. Dependence of isoprene levels on temperature (only daytime data).

temperature is obtained. However, the fact that the mean isoprene levels during nighttime are a factor of four lower compared to daytime (Table 1) indicates that the role of temperature in determining isoprene levels is smaller compared to insolation. In Fig. 6, the different behavior of isoprene during May compared to the summer months is noticeable and probably indicates a difference in biological production process.

3.3. Isoprene contribution to regional tropospheric chemistry

The impact of isoprene levels observed under pure marine conditions (N sector with $u > 4 \text{ m s}^{-1}$) on the regional tropospheric chemistry and more precisely on the levels of nitrate (NO_3), hydroxyl (OH), hydroxyl peroxy (HO_2), and peroxy ($\text{RO}_x = \text{HO}_2 + \text{alkylperoxy radicals}$) radicals and formaldehyde (HCHO) has been investigated using a 0-D chemical model. For this purpose, simulations have been performed by considering and by neglecting the presence of isoprene in the boundary layer. The calculated percent differences between the two simulations are presented in Table 4 for each month of the sampling period and distinction is made between daytime and nighttime results. Positive sign denotes an increase when the observed isoprene levels are taken into account in the model, whereas negative sign indicates a decrease. As expected, consideration of isoprene leads to a decrease in NO_3 levels by up to 25% due to NO_3 consumption by isoprene and by its oxidation products like methacrolein. However, with regard

Table 4

The impact of isoprene chemistry on the oxidation capacity of the atmosphere in the boundary layer at Finokalia during night and day

Months	Time	% (NO_3) ^a	% (OH)	% (HO_2)	% (RO_x)	% (HCHO)
February	Absence of sea sector air masses with strong wind speed					
March	Day	-1	-3	-2	+38	0
	Night	-6	+13	+8	+1	0
April	Day	-1	-8	-5	+110	+1
	Night	-6	+15	+13	+4	0
May	Day	-2	-17	-10	+282	+3
	Night	-15	+20	+21	+15	0
June	Day	-3	-26	-13	+393	+7
	Night	-25	+25	+30	+22	0
July	Day	-3	-17	-8	+288	+5
	Night	-17	+13	+13	+9	0
August	Day	-2	-20	-9	+280	+6
	Night	-16	+18	+23	+16	0
September	Absence of sea sector air masses with strong wind speed					
October	Day	0	-3	-2	+39	0
	Night	-5	+4	+3	+2	0

RO_x stands for the sum of hydroperoxy radicals and alkylperoxy radicals.

^aThe NO_3 levels computed for daytime are below the pptv levels in all cases.

to OH and HO_2 , a clear distinction can be made between nighttime and daytime isoprene chemistry. During daytime, a decrease up to 26% (for OH) and 13% (for HO_2) has been calculated, while during night an opposite effect, i.e. an increase of up to 25% and 30%, respectively, has been deduced. Thus, for both day and night conditions the role of isoprene on OH and HO_2 levels is significant. The role of isoprene becomes extremely important in the case of RO_x , where almost a four-fold increase has been calculated during daytime. During nighttime the impact of isoprene is modest due to its low levels and thus, consideration of isoprene in the 0-D model leads to RO_x increase of up to 22%. As mentioned in Section 2.3 the six first generation peroxy radicals from the reaction of isoprene with OH radicals are “lumped” to one species (ISO2) and this explains the increase of RO_x when isoprene is taken into account by the model. Finally, the percent contribution of isoprene observed under marine conditions to the HCHO levels in the area is relatively small since the maximum calculated increase in HCHO is only 7%, i.e., about 70 pptv of HCHO.

3.4. Isoprene seawater fluxes

A first estimate of the marine isoprene fluxes has been made by using the 0-D chemical model. For this purpose, the flux required to maintain the observed isoprene levels has been calculated. The estimated marine isoprene fluxes range between 10^8 molecules $\text{cm}^{-2}\text{s}^{-1}$ during March and 6×10^9 molecules $\text{cm}^{-2}\text{s}^{-1}$ during June. These values, which are more than two orders of magnitude lower compared to terrestrial fluxes from mainland Greece (Simeonidis et al., 1999), are in the high range of the oceanic isoprene fluxes reported by Palmer and Shaw (2005), 10^7 – 10^9 molecules $\text{cm}^{-2}\text{s}^{-1}$. These authors calculated the isoprene oceanic emissions using: (i) the empirical equation between isoprene and chl “a” derived from culture experiments and (ii) chl “a” levels from satellite observations. However, that approach might not be appropriate for the E. Mediterranean for two reasons:

Firstly, it is well established that chl “a” in the eastern Mediterranean has a subsurface maximum below 30 m depth with levels 3–4 times higher than at surface, which is not seen by satellites. Thus, the isoprene levels estimated using the surface chl “a” derived from satellite observations could be underestimated by at least a factor of three (Psarra et al., 2000).

Secondly, Yokouchi et al. (1999) reported that isoprene in the marine atmosphere behaves similar to dimethylsulfide (DMS), a biogenic compound produced by seawater. DMS levels in the E. Mediterranean sea are found (Mihalopoulos et al., unpublished data) not to be directly related to the surface chl “a” levels and in general, to be higher than expected from the DMS/chl “a” ratios reported for the open oceans. These observations indicate that processes not linked to chl “a” might be responsible for the DMS levels observed in the E. Mediterranean, like for instance bacterial activity. Since Kuzma et al. (1995) have reported that bacterial activity in the seawater produces isoprene, this process could explain the high levels of isoprene observed in the present work.

4. Conclusions

Intensive isoprene measurements conducted on North-Eastern Crete from February to October 2004, demonstrated isoprene levels between 5 and 1200 pptv with an annual mean mixing ratio of 60 ± 100 pptv representative for marine locations.

The seasonal variation of isoprene is shown to be strongly dependent on light and in a lesser extent on temperature. In addition, isoprene levels in the area are found to depend on air masses origin and wind speed. South-western air masses enhance isoprene concentration by a factor of 3.5 compared with the marine sectors (N and NW) because of their terrestrial impact. Isoprene concentration also increases exponentially for wind speeds below 4 m s^{-1} , whereas above this level the observed isoprene variability is almost negligible. Marine emissions of isoprene maximize during late spring and summer depicting biogenic formation of isoprene.

Based on the observations of isoprene, its impact on the oxidation capacity of the atmosphere has been investigated by using a 0-D chemistry model. Isoprene is depressing the NO_3 levels by up to 25% and slightly increasing the HCHO levels. OH and HO_2 radicals are reduced by isoprene chemistry by up to 26% and 13%, respectively during day, while during night an increase of up to 25% and 30% has been estimated. Isoprene is a major contributor to RO_x that can be increased by up to 4-fold due to isoprene daytime oxidation. Finally, the marine isoprene flux has been calculated between 10^8 and 6×10^9 molecules $\text{cm}^{-2}\text{s}^{-1}$. These values are significantly higher than estimates using only surface chl “a” levels indicating probably the role of other biological processes in isoprene formation as has been observed for DMS in the E. Mediterranean.

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