

C₂–C₈ NMHCs over the Eastern Mediterranean: Seasonal variation and impact on regional oxidation chemistry

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ABSTRACT

More than 2500 measurements of C₂–C₈ non-methane hydrocarbons (NMHCs) have been conducted at Finokalia sampling station on the island of Crete over a thirty-month period (September 2003–February 2006), to investigate the factors controlling NMHC levels and estimate their role in the oxidizing capacity of the Eastern Mediterranean atmosphere. Atmospheric concentrations of NMHCs range from below the detection limit (5 pptv) to a few ppbv and present a hydroxyl radical (OH) driven seasonal pattern with lower values during summer. The diel variability was also influenced by the reaction of the NMHC with the OH radical, exhibiting a nighttime maximum and a midday or early afternoon minimum. Long-lived compounds demonstrate higher concentrations under the influence of the northern sector (European continent), indicating that besides chemistry, transport significantly contributes to NMHCs levels in the area. Based on the observed NMHCs diurnal cycles, mean OH radical levels of 3.5×10^6 molecules cm⁻³ have been derived for May–October period.

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1. Introduction

A large number of volatile organic compounds (VOCs) of various complexity and chemical reactivity have been detected in the atmosphere at urban, rural and marine areas. VOCs include methane and non-methane hydrocarbons (NMHCs) as well as oxygen and nitrogen containing organic gases like alcohols, ethers, ketones, aldehydes, organic nitrates and amines (Williams, 2004). VOCs are emitted into the troposphere from both anthropogenic (fuel and biomass burning, vehicles, solvent usage, oil refineries) and natural (vegetation and seawater) sources. On the global scale, emissions from terrestrial vegetation of biogenic volatile organic compounds (BVOCs) such as isoprene, terpenes and oxygenated organic compounds are estimated to be about 1150 Tg C y⁻¹ (Guenther et al., 1995; Atkinson and Arey, 2003) almost 10 times higher than the anthropogenic sources of about 100 Tg C y⁻¹ (Atkinson and Arey, 2003).

VOCs react rapidly with hydroxyl radicals (OH) and depending on their chemical structure also with ozone (O₃) and nitrate radicals (NO₃). In the presence of sufficient nitrogen oxides (NO_x), VOC oxidation leads to photochemical O₃ formation. The atmospheric oxidation of VOC, initiated by the aforementioned three major oxidants in the troposphere, involves chains of chemical reactions and a multitude of gas phase products such as peroxy acetyl nitrate (PAN), organic nitrate compounds (RONO₂), carbonyl and carboxylic compounds. Several VOCs are also known to contribute to the secondary organic aerosol (SOA) formation since some of their oxidation products are semivolatile (e.g. Kanakidou et al., 2005). The overall reactivity of VOCs, determines their respective impact on regional oxidation chemistry.

This work presents a thirty-month study of the occurrence and fate of light (C₂–C₈) NMHCs at a rural marine location in the eastern Mediterranean (Crete island, Greece) using three different analytical systems. The major aims of this study are: i) to understand the factors that control the seasonal and diel variation of NMHCs levels in the area and ii) to evaluate the role of NMHCs in the regional oxidation chemistry. It is the first time that such an extensive dataset of NMHCs and related parameters is collected and analyzed for the Mediterranean an area, which is characterized by high levels of ozone and OH radicals (Kouvarakis et al., 2000; Lelieveld et al., 2002).

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2. Experimental

2.1. NMHCs sampling and the Finokalia site

The hydrocarbon measurements were conducted at Finokalia sampling station (35°20'N, 25°40'E) located on the north coast of the island of Crete, Greece, 70 km to the East of the capital city, Heraklion. The site is exposed to the sea from 270° to 90° (W–E). A detailed description of the Finokalia sampling site and the prevailing meteorological conditions has been reported elsewhere (Mihalopoulos et al., 1997; Gerasopoulos et al., 2005).

Three different analytical systems were used and several C₂–C₈ NMHCs have been measured. Sampling periods as well as data coverage are reported in Table 1. For the whole sampling period air samples were compressed into stainless steel canisters on a weekly or biweekly basis. Canister samples collected from September 2003 to July 2004 have been analyzed for benzene and toluene and from July 2004 to February 2006 for saturated C₂–C₈ NMHCs, acetylene and benzene. In addition, from February 2004 to October 2004, 2450 direct hourly measurements of saturated C₂–C₆ NMHCs (see Table 1) have been performed in-situ. Unsaturated C₂–C₄ NMHCs have been measured with this system only during September and October 2004.

2.2. NMHCs analysis

Three gas chromatography systems were used for quantifying the 23 different C₂–C₈ NMHCs shown in Table 1.

2.2.1. GC–MS system – benzene/toluene detection

A gas chromatograph coupled with a mass spectrometric detector (GC–MS 6890/5963, Agilent Technology) has been used for measurements of benzene and toluene in the air samples collected in canisters from September 2003 to July 2004. For each analysis 1000 ml of air (flow: 30–40 ml min⁻¹) were taken from the canisters via a stainless steel line. To remove the humidity the air sample passed through a magnesium perchlorate (Cl₂MgO₈) dryer, maintained at 50 °C. The hydrocarbons were cryogenically pre-concentrated on a 10 cm length trap containing glass beads (Uni-beads) that was kept at –70 °C by using a Neslab cc-100 circulation cooler. The pre-concentrated air sample was thermally desorbed at 200 °C and backflush-injected into a 40 m proprietary Crossbond phase capillary column (Restek, Rtx-VMS, 0.18 mm ID, 1.0 μm dF) located inside the temperature controlled oven of the chromatograph. Within the first four minutes of the analytical procedure the column was kept at 50 °C, then heated at a rate of 9 °C min⁻¹ to reach 100 °C and afterwards at a rate of 40 °C min⁻¹ until 230 °C. This temperature was kept constant until the end of the analysis.

Table 1
Details of the sampling and analysis systems of the air samples collected at Finokalia station.

Time scale	Sampling frequency	Sample no Data coverage	Gas Chromatograph	NMHCs
September 2003–July 2004	Canisters Weekly/biweekly	34 85%	GC–MS	Benzene, toluene
February 2004– October 2004	Direct Hourly	2450 60%	GC–FID (automatic)	C ₂ –C ₆ ^a
July 2004– February 2006	Canisters Weekly/biweekly	47 60%	GC–FID	C ₂ –C ₈ ^b

^a For whole period measurements for propane, n-/iso-butane, n-/iso-pentane, n-hexane and 2,2-/2,3-dimethyl-butane. From September to October 2004 ethene, acetylene, propene, 1-butene and trans-/cis-2-butene have been also measured.

^b Ethane, acetylene, propane, n-/iso-butane, n-/iso/cyclo-pentane, n-/cyclo-hexane, 2,2-/2,3-dimethyl-butane, 2-/3-methyl-pentane, n-heptane, n-octane and benzene.

One analysis lasted about 15 min. Benzene and toluene were detected by a mass spectrometer (MSD) that was connected at the end of the capillary column and operated in single ion mode (SIM).

2.2.2. Automatic in-situ GC–FID system – C₂–C₆ NMHCs detection

An automatic gas chromatograph (Chromatrap GC, Chromato Sud, France) equipped with a flame ionisation detector (FID) has been used for the in-situ measurements of 2450 continuous hourly measurements of C₂–C₆ NMHCs from February to October 2004. For each analysis, 250 ml of ambient air was drawn into the system from 3 m above the ground via a stainless steel inlet line with a flow rate of 65 ml min⁻¹ (air sample integrated over about 4 min). The air sample passed first through a Nafion dryer to remove the humidity and then hydrocarbons were pre-concentrated at –15 °C on a 2.25 mm i.d., 6 cm length trap filled with: Carboxen 1000 (50 mg), Carbopack B (10 mg) and Carbotrap C (10 mg). This procedure is described in detail elsewhere (Touaty, 1999; Gabard, 2002). The pre-concentrated air sample was thermally desorbed and directly injected in a 50 m Al₂O₃/Na₂SO₄ column (Varian Inc., Ultimetal PLOT column, 0.53 mm ID, 10.0 μm dF) located inside the heated oven of the GC. Within the first minute of the analytical procedure, the oven temperature rose from 38 °C to 40 °C. Afterwards a constant heating rate of 20 °C min⁻¹ was applied and the temperature reached 199 °C by the end of the analysis time. C₂–C₆ hydrocarbons were detected by an FID and the detection limit has been determined to be 5 pptv. The alkane measurements have been performed during the entire period, whereas C₂ and C₄ alkenes have been measured only for the September–October 2004 period.

2.2.3. GC–FID system – C₂–C₈ NMHCs detection

A semiautomatic gas chromatograph (Varian Star 3400 CX) equipped with an FID, operated at the University of Crete, has been used to measure C₂–C₈ NMHCs in the 47 ambient air samples collected in stainless steel canisters from July 2004 to February 2006. For each analysis 300–600 ml of air was drawn into the device from the canisters via a stainless steel line at a flow rate of 35–40 ml min⁻¹ (air sample integrated over approximately 10 min). The air sample was passed through a magnesium perchlorate (Cl₂MgO₈) dryer to remove water and then hydrocarbons were pre-concentrated on a 'U'-shaped stainless steel 1/8" diameter trap filled with Tenax TA 60/80 mesh. The trap was placed inside a EtOH/Liquid N₂ mixture which maintained a temperature close to –120 °C. The pre-concentrated air sample was thermally desorbed with boiling water (100 °C) and transferred via backflushing to a second shorter 'U'-shaped stainless steel 1/16" diameter pre-concentration trap. This trap was filled with glass beads 60/80 mesh and placed in liquid N₂ (–196 °C). After the second desorption with boiling water, the sample was directly injected in a 50 m Al₂O₃/KCl capillary column (Restek, Rt-Alumina 0.53 mm ID, 6.0 μm dF) column located inside the heated oven of the GC. For the first minute the oven temperature was held constant at 40 °C. Afterwards the temperature was increased at a rate of 10 °C min⁻¹ until it reached 120 °C, at which point it was held constant for 5 min. In the second step, the temperature was increased to 160 °C at a rate of 25 °C min⁻¹ and was held at this temperature for 5 min. Finally, the temperature was raised from 160 °C to 180 °C at 25 °C min⁻¹ and then held constant until end of the analysis. The detection limit has been determined to be circa 4 pptv, based on the minimum integrated baseline peak assuming a signal to noise ratio of 3.

2.2.4. Calibration

A gas mixture containing 1-ppmv levels of fifty-five C₂–C₉ VOCs (# 22964-Restek, Spectra Gases), including 25 compounds detectable by our GC–FID (C₂–C₆ alkenes, n- and iso-alkanes, and isoprene), has been used for the identification of the compounds of interest for both

GC–FID systems. A certified standard gas mixture (commercialized by Air Liquide, France with stated accuracy of 2%), provided by the Laboratoire des Sciences du Climat et de l'Environnement, CNRS/CEA, France, containing 96 ppmv of ethane, 102 ppmv ethene, 103 ppmv propane and 101 ppmv n-butane has been used as the primary calibration standard. 100–300 μl of this primary standard were regularly (weekly) injected into the automatic GC–FID, and 50 μl into the second semiautomatic GC–FID with a pressure-lock syringe. Based on the linearity in the response of the FID detector with respect to the carbon number of the measured C_2 – C_4 hydrocarbons, it was deemed feasible to quantify heavier NMHC in the C_5 – C_6 range, at ppbv levels, with accuracy better than 1%. For the GC–MS a gaseous standard mixture containing 198 pptv of benzene and 47 pptv of toluene has been used for the identification of these compounds. 500 ml of this standard were analyzed following the same procedure as for the ambient air samples.

2.3. Other measurements

In addition to light hydrocarbons, the meteorological parameters (wind speed and direction, total solar radiation (W) and temperature), radon-222 (^{222}Rn), and ozone were continuously monitored (Gerasopoulos et al., 2005). Furthermore, nitrate radicals were measured during the first period of the experiment (Vrekoussis et al., 2007). The HYSPLIT model (Hybrid Single-Particle Lagrangian Integrated Trajectory Model; www.arl.noaa.gov/ready/hysplit4.html; Draxler and Hess, 1998) has been used to calculate air masses back trajectories arriving at Finokalia at 1000 m above sea level to avoid orographic interferences at lower heights and to be continuously within the boundary layer (BL) of the region, which mostly ranges between 1000 and 1300 m with no significant diel or seasonal variation (Gerasopoulos et al., 2006).

2.4. Model description

The chemistry model used in this study is a condensed chemical mechanism, which, apart from the background $\text{O}_3/\text{NO}_x/\text{OH}/\text{CO}$ and CH_4 chemistry, also takes into account the oxidation chemistry of C_1 – C_5 hydrocarbons as described in details at Liakakou et al. (2007). The NMHC concentrations vary hourly according to the observations.

3. Results

3.1. Annual variation of C_2 – C_8 NMHCs

The C_2 – C_8 NMHCs monitored at Finokalia during the period September 2003–February 2006 can be classified into three major categories: i) saturated C_2 – C_8 compounds such as ethane, propane, n-butane, iso-butane, n-pentane, iso-pentane, cyclo-pentane, n-hexane, cyclo-hexane, 2,2-dimethyl-butane, 2,3-dimethyl-butane, 2-methyl-pentane, 3-methyl-pentane, n-heptane and n-octane, ii) unsaturated C_2 – C_4 NMHCs namely ethene, acetylene, propene, 1-butene, trans-2-butene and cis-2-butene iii) benzene and toluene. Fig. 1 depicts the partly discontinuous hourly measurements of selected C_3 – C_6 NMHCs by the automatic GC–FID as well as their daily mean values. Atmospheric concentrations range from below the detection limit (5 pptv) to a few ppbv and present a clear seasonal pattern with higher values during winter. Statistical analysis of the measurements and comparison to literature data on a seasonal basis is presented in Table 2. Summertime concentrations are in good agreement with previous short-term measurements in the area (Gros et al., 2003). The mean seasonal levels of the saturated light hydrocarbons are lower in comparison with those reported from urban (Moschonas et al., 2001) and

forested Mediterranean areas (Bonsang and Kanakidou, 2001). In contrast, arctic marine regions show comparable winter and fall values and lower summer values (Hakola et al., 2006). Acetylene, which is mainly of anthropogenic origin, shows levels four times lower than previously reported over mainland Greece (Moschonas and Glavas, 2000). Finally, the measured aromatic hydrocarbons, benzene and toluene, were observed in lower concentration than earlier measurements in urban areas (Moschonas et al., 2001), although in the same range as those from less polluted regions (Hakola et al., 2006).

3.2. Seasonal variation of C_2 – C_8 NMHCs and factors controlling their fate

Fig. 2a–f depict the monthly mean values of selected NMHCs and their standard deviation from September 2003 to February 2006 derived from the canister samples and analyzed with GC–MS and semiautomatic GC–FID chromatography systems. All the compounds demonstrate a distinct seasonal cycle characterized by summer minimum and winter maximum, which is consistent with previously reported trends (Borbon et al., 2002; Yang et al., 2005; Sahu and Lal, 2006). Isoprene has been examined in detail elsewhere (Liakakou et al., 2007) but is included in Fig. 2g as an example of biogenic compound. It is the only NMHC that demonstrates a summertime maximum, as its emission rate is strongly dependent on light and temperature. The increased light intensity in summer also promotes the highest OH radical levels and the monthly mean OH concentrations calculated by the chemical box model are shown in Fig. 2h (Liakakou et al., 2007). As a consequence the loss rate of NMHCs through reaction with OH maximizes in summer. Thus most NMHCs exhibit minimum concentrations during summer, which indicates that the seasonality in sinks is more important than possible seasonality in emissions.

Based on the in-situ observations of NO_3 radical (Vrekoussis et al., 2007) and O_3 (Gerasopoulos et al., 2005, 2006) and the levels of OH deduced from the chemical box model (Liakakou et al., 2007) the NMHC lifetimes have been calculated with respect to these three oxidants (Table 3). The lifetime in all cases is driven primarily by the OH abundance and therefore it is shorter during summer than during winter. Lifetimes vary from a few hours for propene and long chain hydrocarbons up to several days for benzene, acetylene and short chain saturated compounds such as ethane and propane. Generally for the saturated NMHCs, the lifetime decreases with carbon atoms and methyl-substitution following the decreasing stability of the carbon-hydrogen bond. The presence of double bonds and rings reduces the lifetimes even more as H-atom addition can also occur rapidly.

According to Jobson et al. (1999) the variability of a compound is related to the sources and sinks via the equation $\text{Sln}(X) = A\tau^{-b}$, where $\text{Sln}(X)$ is the standard deviation of the natural logarithm of the concentration of hydrocarbon X, τ is the lifetime of hydrocarbon X and A and b are fitting parameters. The parameter b expresses the dependence of variability on lifetime. Values of b around 0 indicate vicinity to sources areas and higher values close to 0.5 remote locations. The parameter A relates to the mass age. Application of this hydrocarbon variability concept to our dataset obtained at Finokalia from February to October 2004 leads to A and b values equal to 0.48 and 0.28, respectively. The parameter A is lower than the previously measured (0.85) at Finokalia during August 2001 (MINOS campaign; Gros et al., 2003). On the other hand no significant difference was observed for b that was found equal to 0.23 during the MINOS campaign, in line with the fact that Finokalia represents an intermediate site between remote location and source area.

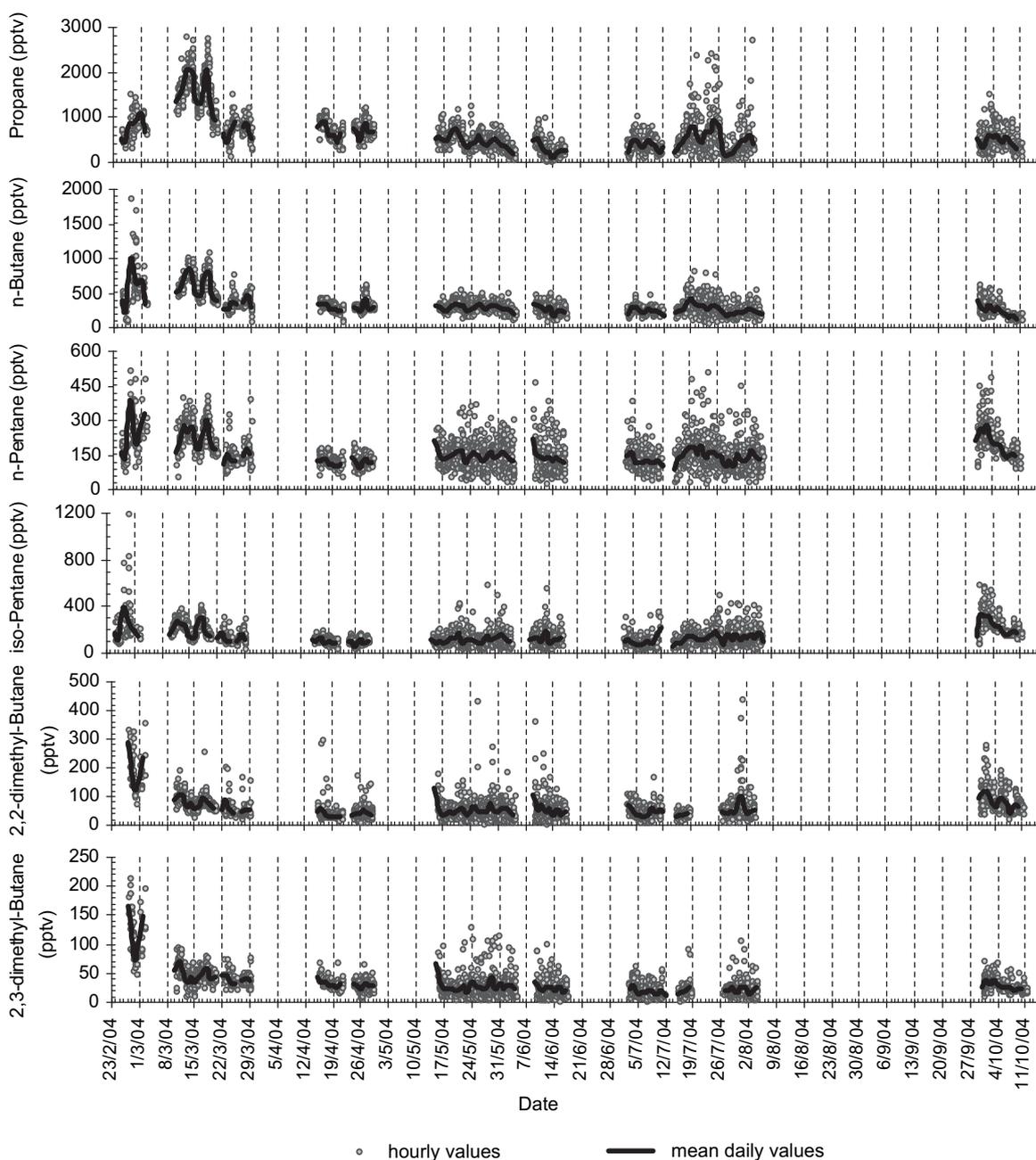


Fig. 1. Selected C₃–C₆ NMHC hourly and mean daily observations at Finokalia, Crete, Greece, from February 2004 to October 2004.

Given the wide range of the lifetimes of NMHCs, the atmospheric transport of air masses of different origin could contribute to the seasonal trend in NMHC levels. The following investigation was limited to the continuous hourly measurements since they offer better statistics; and propane, n-/iso-butane, n-/iso-pentane, n-hexane and 2,2-/2,3-dimethylbutane have been investigated. The air masses arriving at the Finokalia station have been characterized based on a back-trajectory analysis for the studied period. The number of incidents of northern air masses exceeds that of southern and western air masses while the eastern air masses are rare. Three major groups of air masses were considered: (i) the “north” (or N, NE, NW) sector indicative of transport from industrialized areas of W. and E. Europe, (ii) the “south” (or S, SE, SW) sector indicating transport from desert areas of N. Africa and (iii) the western sector which represents the marine Mediterranean.

Propane is selected as a long-lived and 2,3-dimethyl-butane as a short-lived compound, with mean lifetimes of 3.9 days and less than 1 day respectively (Table 3). Then for each compound the seasonal cycle is extracted per wind sector (Fig. 3). Fig. 3 indicates the same seasonality for the NMHCs, with Fig. 2, regardless of air mass origin. In both figures NMHCs present maximum values during winter that decrease in spring and minimize in summer. Concentrations of the longer-lived propane are higher under the northern sector relative to the southern and western, indicating an enhanced role of long-range transport of pollutants over the local and marine sources respectively. In contrast there is no evident difference with the wind sector in the concentrations for the shorter-lived 2,3-dimethyl-butane, indicating no significant additional contribution from long-range sources, to the atmospheric abundance of this NMHC.

Table 2

NMHC measurements and comparison with concentrations at different rural and remote locations over Europe reported in literature (values in pptv), on seasonal basis.

Season (year) location area	Summer (2004–2006) Finokalia, Greece marine	Summer (2001) Finokalia, Greece marine	Summer Thessaloniki Greece (290–680 m height)	Summer (1996) Messorougion Greece (mountain)	Summer (1994) Portugal (forested)	Summer (1999) Finland (marine)	Winter (2004–2006) Finokalia Greece (marine)	Winter (1999) Finland (marine)	Fall (2004–2006) Finokalia Greece (marine)	Fall (1996) Messorougion Greece (mountain)
Ref.	This work	Gros et al., 2003	Moschonas et al., 2001	Moschonas and Glavas, 2000	Bonsang and Kanakidou, 2001	Hakola et al., 2006	This work	Hakola et al., 2006	This work	Moschonas and Glavas, 2000
NMHCs group										
i) Saturated C ₂ –C ₈										
Ethane	1353 ± 598				1057	942	2432 ± 936	2795	1952 ± 836	
Propane	418 ± 322	235 ± 121	360–580	640 ± 330	856	167	757 ± 306	1487	471 ± 264	950 ± 420
iso-Butane	451 ± 115	72 ± 178		40 ± 20	248	55	544 ± 192	359	174 ± 89	70 ± 30
n-Butane	258 ± 96	86 ± 93	80–1310	110 ± 70	498	82	561 ± 326	679	235 ± 117	320 ± 180
iso-Pentane	121 ± 71	97 ± 278	10–850	90 ± 80	319	35	221 ± 173	264	227 ± 96	110 ± 60
n-Pentane	140 ± 68	36 ± 64	90–540	40 ± 30	227	18	210 ± 98	165	196 ± 76	70 ± 50
cyclo-Pentane	40 ± 24				96		29 ± 13		38 ± 4	
n-Hexane	96 ± 68		30–170	40 ± 40	116	4	602 ± 254	43	95 ± 39	50 ± 20
2-Methylpentane	64 ± 48			60 ± 30	83		163 ± 118		135 ± 82	40 ± 10
3-Methylpentane	52 ± 53		80–270	140 ± 100	66		40 ± 16		52 ± 50	40 ± 20
2,2-Dimethylbutane	50 ± 40		40–120	20 ± 10			159 ± 91		80 ± 45	10 ± 0
2,3-Dimethylbutane	22 ± 15			80 ± 60			102 ± 49		28 ± 11	240 ± 10
n-Heptane	32 ± 21		10–120	20 ± 10			37 ± 23		52 ± 50	40 ± 10
cyclo-Hexane	9 ± 4		0–220	10 ± 10			20 ± 12		18 ± 5	10 ± 10
n-Octane	47 ± 33		20–310	10 ± 10			106 ± 95		65 ± 54	0 ± 0
ii) Aromatic C ₆ –C ₇										
Benzene	118 ± 41	101 ± 56	210–610	80 ± 60		80	269 ± 58	254	231 ± 102	170 ± 100
Toluene	141 ± 95		180–1270	160 ± 130			174 ± 285		174 ± 188	130 ± 70
iii) Unsaturated C ₂ –C ₄										
Acetylene									229 ± 71	960 ± 490
Ethene									75 ± 27	
Propene									235 ± 68	60 ± 40
1-Butene									53 ± 18	
cis-2-Butene									15 ± 6	20 ± 10
trans-2-Butene									22 ± 9	10 ± 0

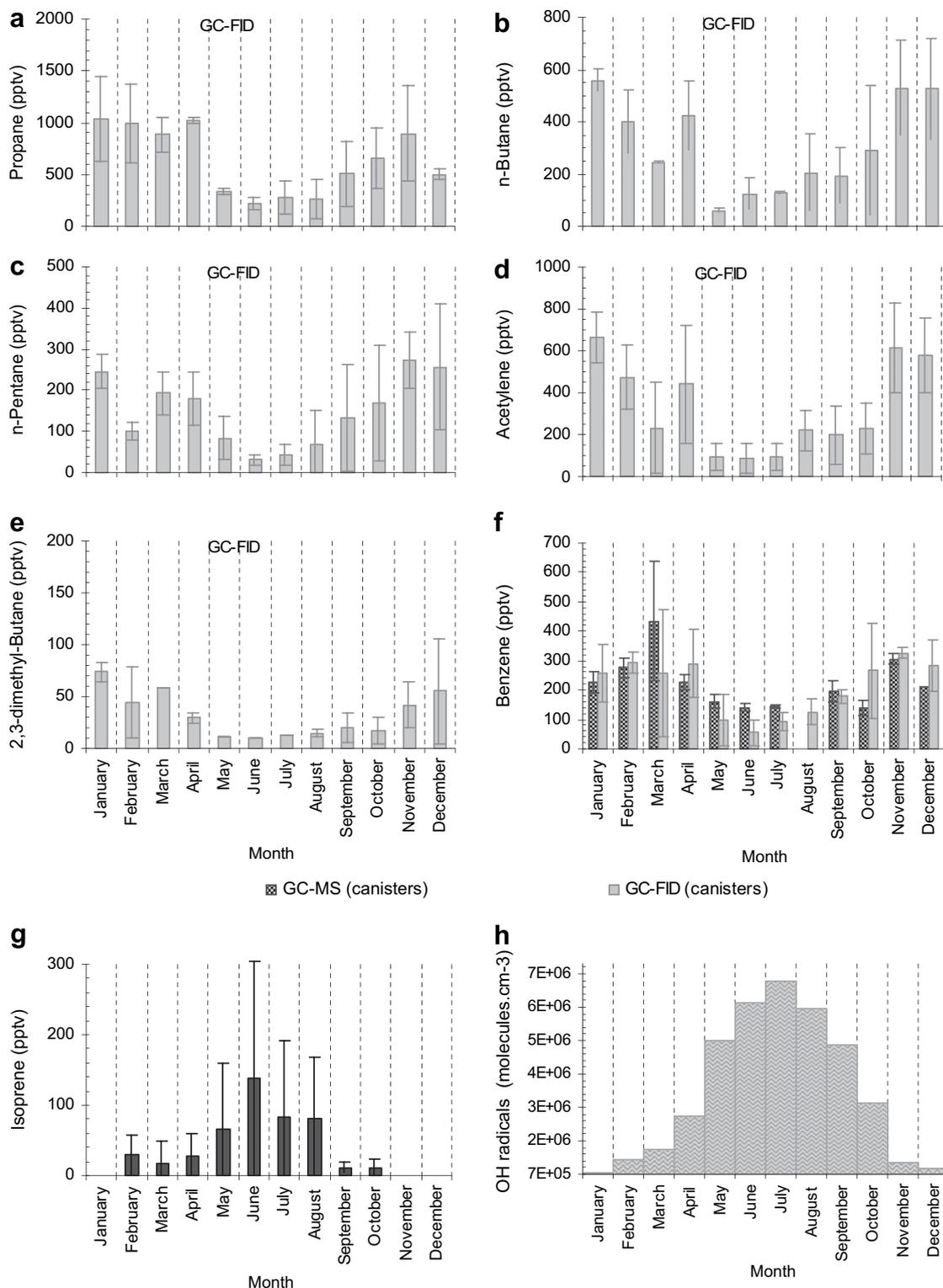


Fig. 2. (a–f) Monthly mean observations (and standard deviations) for selected NMHCs from canisters at Finokalia station from September 2003 to February 2006, (g) isoprene mean seasonal cycle and (h) mean seasonal variation of hydroxyl radicals are taken from Liakakou et al. (2007).

The observed seasonal patterns of NMHC have been further examined to distinguish between the role of transport and chemistry in the Eastern Mediterranean region. As previously stated (see Fig. 2) NMHCs (with the exception of isoprene) show minimum levels in summer when OH radical maximizes. Assuming steady NMHC sources in the region throughout the year and that the OH

radical is the predominant sink for NMHC, the ratio of the maximum to the minimum annual level of NMHC should be proportional to the corresponding OH ratio, i.e. $[\text{NMHC}]_{\text{max}}/[\text{NMHC}]_{\text{min}} = [\text{OH}]_{\text{max}}/[\text{OH}]_{\text{min}}$. Contribution of other oxidants to NMHC oxidation would result into higher ratio and thus in, $[\text{NMHC}]_{\text{max}}/[\text{NMHC}]_{\text{min}} > [\text{OH}]_{\text{max}}/[\text{OH}]_{\text{min}}$. In the case of

Table 3NMHC lifetimes calculated based on OH, NO₃ and O₃ concentration for 288 K (values in years, days, hours and minutes).

Lifetime	t (OH) ^a	t (NO ₃) ^b	t (O ₃) ^c
NMHCs group			
i) Saturated C ₂ –C ₈			>2854 y (2303 y–3692 y)
Ethane	17.0 d (7.2 d–41.7 d)	48.1 y (15.3 y–189.4 y)	
Propane	3.9 d (1.6 d–9.5 d)	6.9 y (2.2 y–27.1 y)	
iso-Butane	2.0 d (20.2 h–4.9 d)	4.5 y (1.4 y–17.9 y)	
n-Butane	1.8 d (18.1 h–4.4 d)	10.5 y (3.3 y–41.3 y)	
iso-Pentane	1.2 d (11.9 h–2.9 d)	3.0 y (345.5 d–11.7 y)	
n-Pentane	1.1 d (11.3 h–2.7 d)	5.5 y (1.8 y–21.8 y)	
cyclo-Pentane	20.4 h (8.6 h–2.1 d)		
n-Hexane	19.5 h (8.2 h–2.0 d)	4.4 y (1.4 y–17.2 y)	
2-Methylpentane	19.5 h (8.2 h–2.0 d)	2.7 y (310.9 d–10.5 y)	
3-Methylpentane	19.5 h (8.2 h–2.0 d)	2.2 y (254.4 d–8.6 y)	
2,2-Dimethylbutane	1.9 d (19.2 h–4.6 d)		
2,3-Dimethylbutane	17.5 h (7.4 h–1.8 d)	1.1 y (127.2 d–4.3 y)	
n-Heptane	15 h (6.3 h–1.5 d)	3.2 y (1.0 y–12.6 y)	
cyclo-Hexane	14.5 h (6.1 h–1.5 d)	3.4 y (1.1 y–13.5 y)	
n-Octane	12.5 h (5.3 h–1.3 d)	2.5 y (294.6 d–10.0 y)	
ii) Unsaturated C ₂ –C ₄			
Acetylene	4.2 d (1.8 d–10.3 d)	4.8 y (1.5 y–18.9 y)	2.9 y (2.3 y–3.7 y)
Ethene	11.9 h (5.0 h–1.2 d)	2.3 y (273.0 d–9.2 y)	6.6 d (5.3 d–8.5 d)
Propene	3.8 h (1.6 h–9.4 h)	18.5 d (5.9 d–72.8 d)	1.0 d (20.0 h–1.3 d)
1-Butene	3.2 h (1.4 h–7.9 h)	13.0 d (4.1 d–51.2 d)	1.1 d (20.9 h–1.4 d)
cis-2-Butene	1.8 h (48 min–4.4 h)	12.0 h (3.8 h–2.0 d)	2.0 h (1.6 h–2.6 h)
trans-2-Butene	1.6 h (42 min–3.9 h)	10.8 h (3.4 h–1.8 d)	1.3 h (1.1 h–1.7 h)
iii) Aromatic C ₆ –C ₈			>2.9 y (2.3 y–3.7 y)
Benzene	3.5 d (1.5 d–8.5 d)	16.0 y (5.1 y–63.1 y)	
Toluene	18.0 h (7.6 h–1.8 d)	6.9 y (2.2 y–27.1 y)	

^a 10-h daytime concentration OH 3.9×10^6 molecules cm⁻³.^b 12-h nighttime concentration NO₃ 0.2 – 2.0×10^8 molecules cm⁻³.^c 24-h concentration O₃ 1.2×10^{12} molecules cm⁻³.

additional summertime sources, e.g. transport, the low summertime NMHC levels would increase and therefore the corresponding NMHC ratio would decrease, $[\text{NMHC}]_{\text{max}}/[\text{NMHC}]_{\text{min}} < [\text{OH}]_{\text{max}}/[\text{OH}]_{\text{min}}$. The $[\text{NMHC}]_{\text{max}}/[\text{NMHC}]_{\text{min}}$ ratio is calculated for each NMHC under the same air mass influence (Northern winds which prevails in our area) using the observed seasonal cycles. February and July are selected to represent the maximum and minimum level periods. The same ratio is also calculated for the OH radicals based on the box model simulated values, with February and July being the minimum and maximum OH level periods, respectively. The winter summer ratio for all hydrocarbons, is always lower (0.8–4.8) than the calculated OH ratio (5.8). Based on the aforementioned argumentation we conclude that additional emissions during summertime significantly contributes (up to 60%) to the seasonal variation of NMHCs.

3.3. Diel variation of C₂–C₈ NMHCs

NMHCs diel cycles can be extracted from the hourly data measured by the automatic GC. For every day, the data was normalized to the 24 h mean values. Then the monthly mean diurnal cycles are calculated and presented with the dots in Fig. 4. Based on meteorological observations March and July have been selected to represent the cold and the warm season respectively. The diel pattern of the monthly mean hourly values is also displayed (see lines in Fig. 4). NMHCs were selected based on their lifetime, increasing from 2,3-dimethylbutane (≈ 18 h) to propane (≈ 4 d):

$$\tau_{2,3\text{-Dimethylbutane}} < \tau_{n\text{-Pentane}} < \tau_{n\text{-Butane}} < \tau_{\text{Propane}}$$

Summertime diel cycles (in July) for saturated hydrocarbons are in general agreement with literature data (Bonsang and Kanakidou, 2001; Hopkins et al., 2005; Yang et al., 2005; Durana

et al., 2006; Sahu and Lal, 2006). They demonstrate nighttime maxima and midday or early afternoon minima reflecting the losses by OH radicals that maximize around noon (Fig. 5a). With increasing NMHC reactivity and consequently decreasing lifetime, the diel amplitude derived as the ratio of the nighttime maximum to the daytime minimum concentration also increases. This indicates that photochemistry is driving the diurnal cycle of NMHC rather than advection. ²²²Rn similar to propane (3.9 days) lifetime can be used as a tracer of continental origin in both horizontal and vertical direction. In order to eliminate the impact of local sources and study only cases of long-range transport, cases of air masses originating from north are selected (Fig. 5b). In this respect May was an ideal month with several days under Northern sector influence when long-range transport dominates over photochemistry for propane levels. As it concerns the diurnal variability both, propane and radon exhibit similar variation with an afternoon minimum. This minimum is correlated with air masses vertical transport from the free troposphere (Gerasopoulos et al., 2006) pointing the importance of both horizontal and vertical transport as a determinant process for the variations in the longer-lived hydrocarbons.

For the unsaturated hydrocarbons we use the data acquired by the automatic chromatograph measurements that are available for October 2004. The lifetimes of unsaturated NMHCs are shorter than those of alkanes and increase from trans-2-butene (about 1 h) to acetylene (about 4 days):

$$\tau_{\text{trans-2-Butene}} < \tau_{\text{cis-2-Butene}} < \tau_{1\text{-Butene}} < \tau_{\text{Propene}} < \tau_{\text{Ethene}} < \tau_{\text{Acetylene}}$$

Thus, acetylene is the only studied unsaturated NMHC that could be affected by transport, assuming constant sources, as it is the longest-lived (almost 4 days). The lifetimes of the other unsaturated NMHCs range from 1 h up to one day. The values are

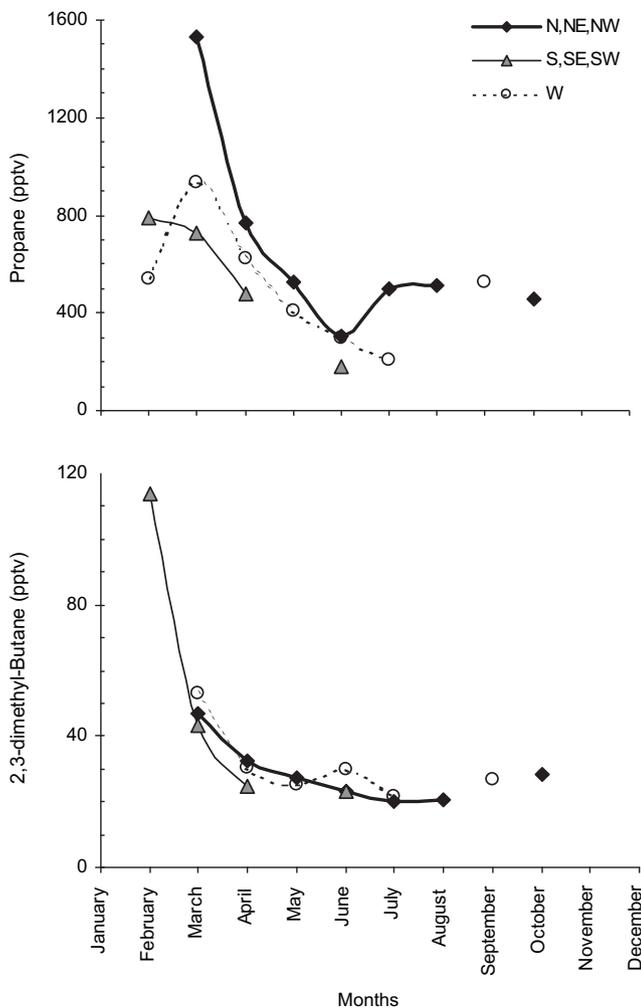


Fig. 3. Observed seasonal variability of propane and 2,3-dimethyl-butane at Finokalia for the three major wind sectors.

also normalized by the 24-h mean. The monthly mean diurnal cycles deduced afterwards are presented in Fig. 6.

In October, daytime levels (Fig. 6) are in general lower than during night. Early afternoon (around 18:00 local time) minima and late night maxima are observed for all hydrocarbons. However, besides this common diel pattern more subtle differences can be observed. For example acetylene's diel variability is insignificant with the maximum/minimum ratio around 1.1, indicating consequently small photochemical consumption. On the other hand the ratio for propene and butene is 1.2 and 1.3 respectively, indicating that chemistry becomes more important for the heavier hydrocarbons.

3.4. NMHCs impact on the regional tropospheric chemistry

3.4.1. Hydroxyl radical levels derived from the diurnal variability of the NMHCs

The key role of hydroxyl radical in determining the level of NMHC and their diurnal variability has been discussed in the previous sections especially for the longer chain/shorter-lived compounds. Under northern air mass influence that minimizes the impact of local sources, the atmospheric levels of compounds such as n-butane, n-/iso-pentane and n-hexane is determined by the hydroxyl radical abundance. The average OH level can be thus

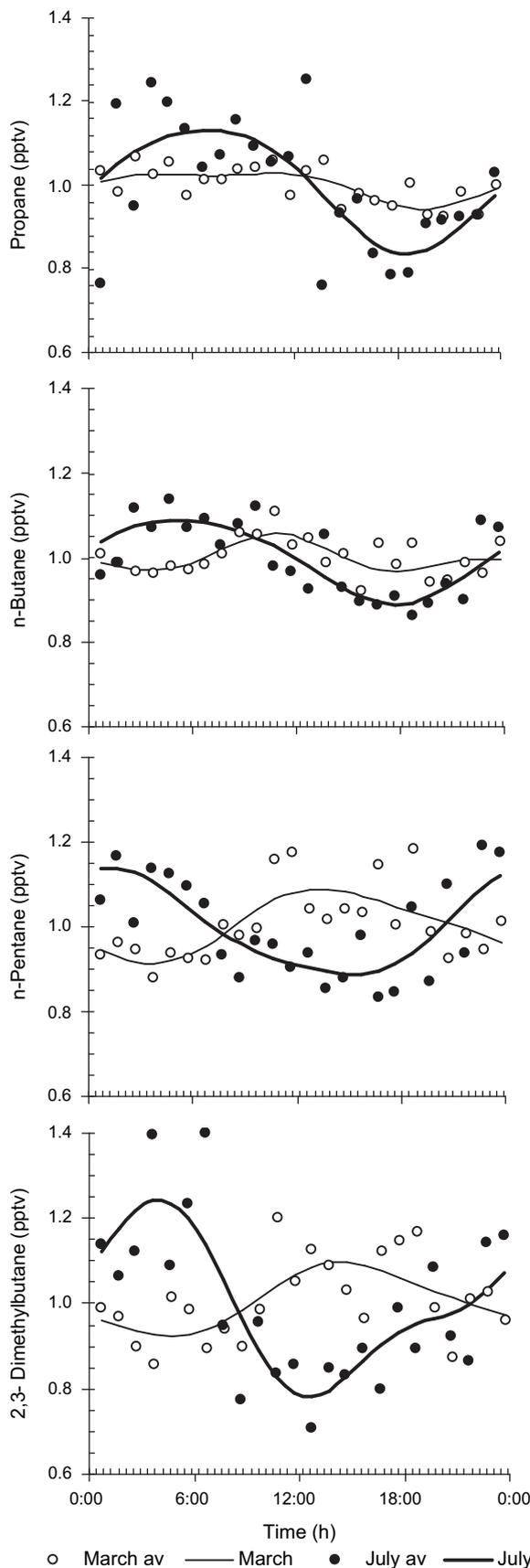


Fig. 4. Normalized monthly mean diel patterns for selected NMHCs.

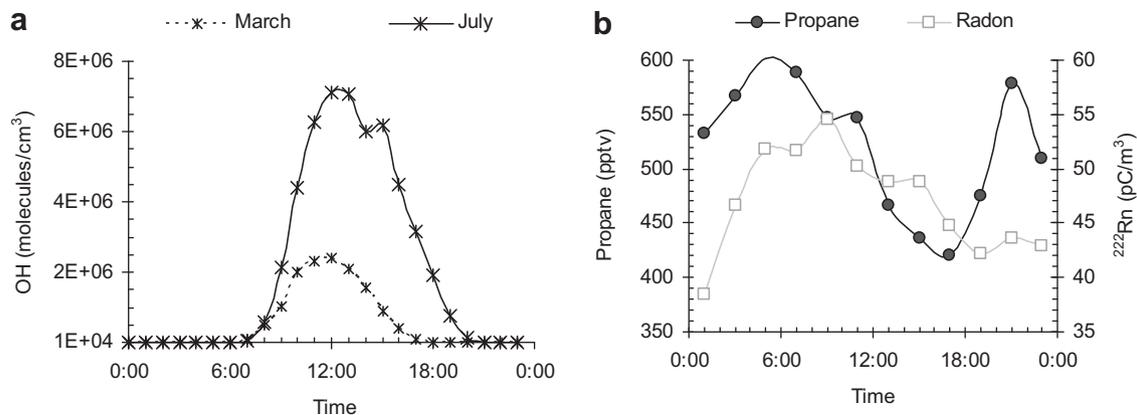


Fig. 5. Factors affecting NMHCs diel variation: (a) Seasonal variation of OH radicals calculated by the chemical box model for March and July and (b) role of transport elucidated by comparison between propane's and radon's diel variation during May.

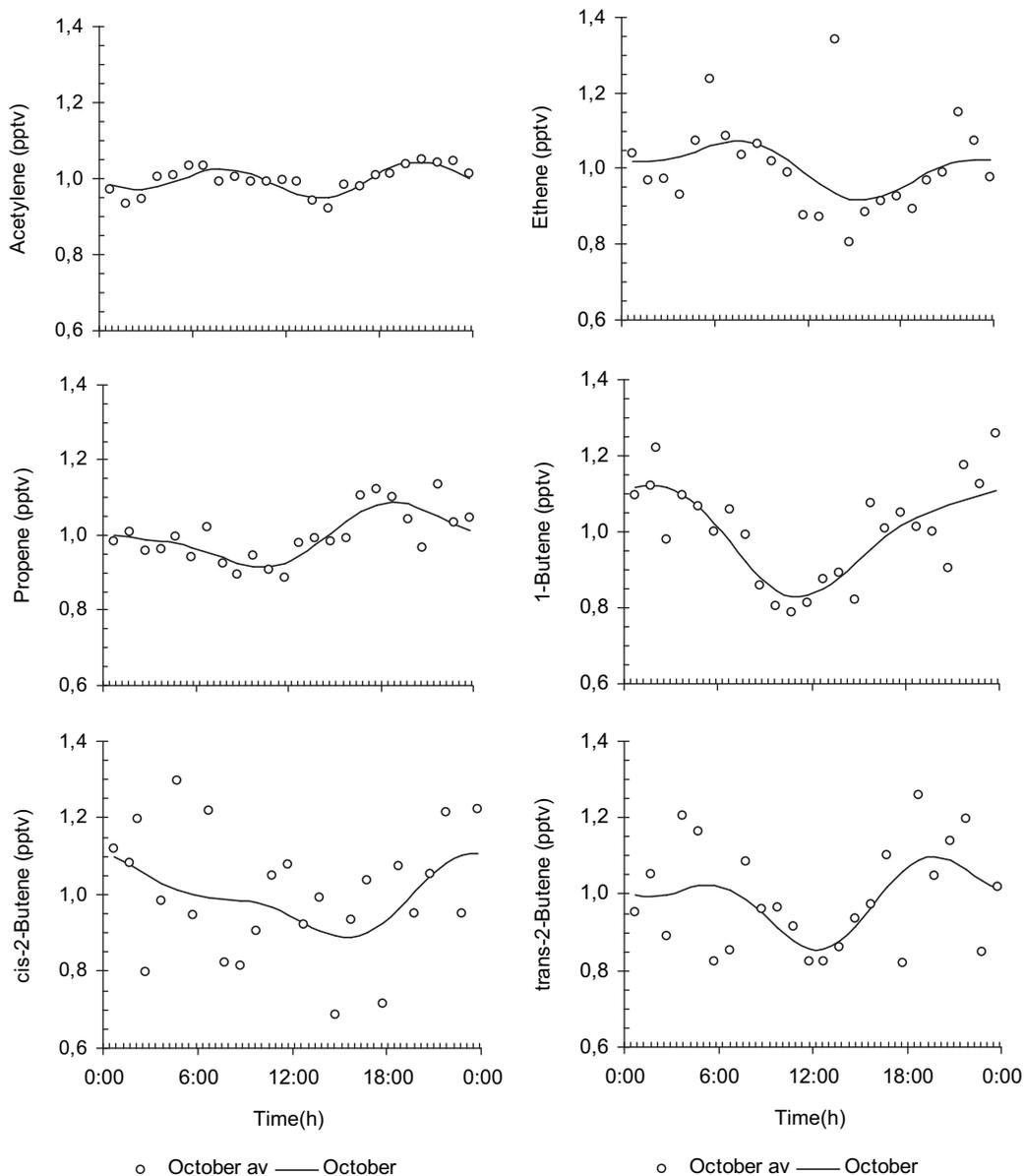


Fig. 6. Mean diel cycles for unsaturated NMHCs during October.

derived from NMHC observations and compared to the box model estimations. An additional restriction, facilitating this data interpretation, is the selection of the high insolation period, from May to October. The hydroxyl radical level [OH] is derived from the diurnal pattern of the above-mentioned four NMHCs and the following equation (1):

$$[\text{OH}] = \frac{\ln\left(\frac{C_{\max}}{C_{\min}}\right)}{k_{\text{OH}} \times t} \quad (1)$$

resulting from combination of equations (2) and (3):

$$C_{\min} = C_{\max} \times \exp\left(-\frac{t}{\tau}\right) \quad (2)$$

and

$$\tau = \frac{1}{k_{\text{OH}}[\text{OH}]} \quad (3)$$

with C_{\max} and C_{\min} the maximum and minimum concentration as it is extracted from the selected NMHCs diurnal cycles, t the time

interval between these two points and k_{OH} the rate constant of the reaction of each of the selected NMHCs with OH radical. The hydroxyl radical production rate increases from sunrise (6:00 GMT) until noon (13:00 GMT) and then decreases as the light intensity decreases (20:00 GMT, Fig. 5a), while NMHC presents the reverse variation (Fig. 4) indicative of their photochemical consumption. Applying equation (2) for the periods 6:00–13:00 (morning) and 14:00–20:00 (afternoon) and assuming insignificant change in BL, the hydroxyl radicals required for the observed NMHCs consumption are calculated. The monthly mean concentration for each of the two periods and their mean are depicted in Fig. 7 in comparison with the box model results. Using equation (2) and the NMHC diurnal cycles the derived mean OH concentration from May to October 2004 equals 3.5×10^6 molecules cm^{-3} . This value is comparable with the 3.8×10^6 molecules cm^{-3} calculated by the model. With July as the only exception, the model estimation ranges within the limits of the calculations based on the observed NMHCs diurnal cycles. Furthermore, the OH radicals calculated for August are in good agreement with Berresheim's mean OH radical level of 4.5×10^6 molecules cm^{-3} estimated for the area during August 2001 (Berresheim et al., 2003).

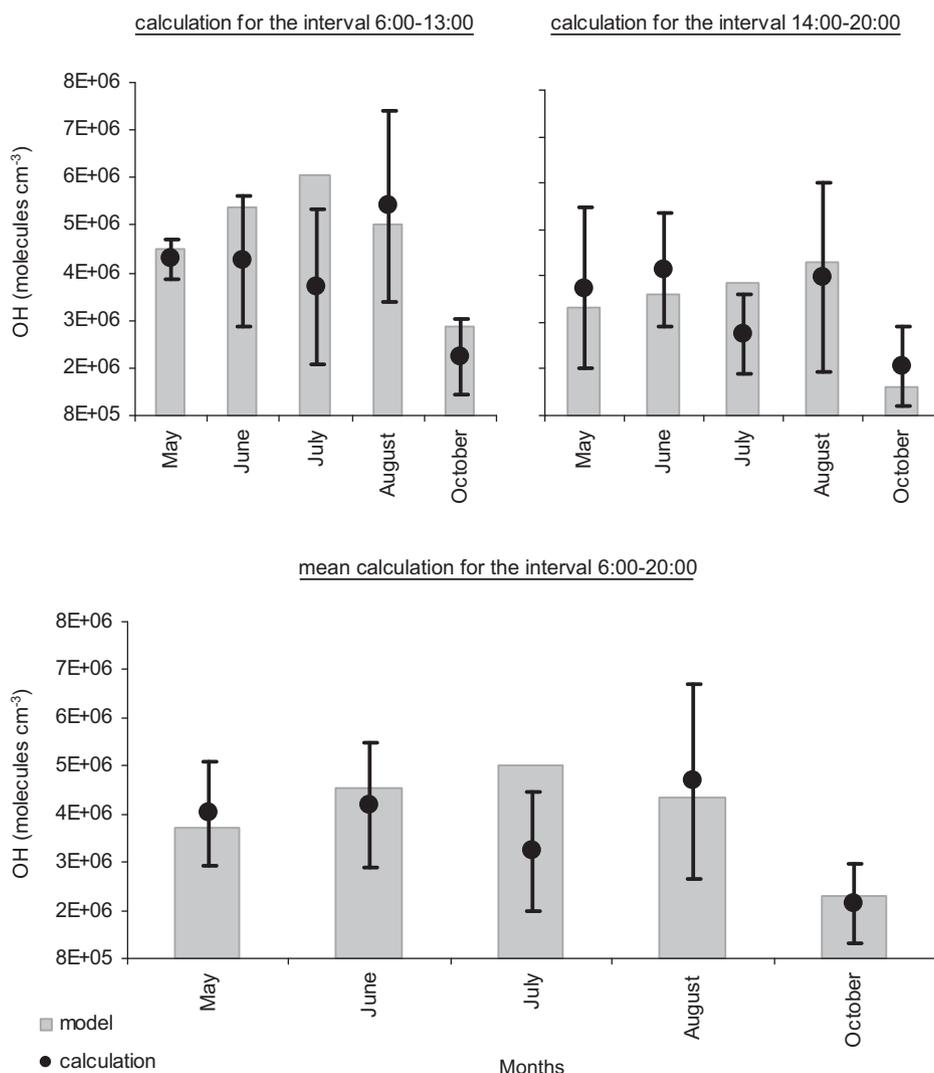


Fig. 7. Hydroxyl radical level calculation based on the diel NMHCs cycles and comparison with the model estimation for the time interval (a) 6:00–13:00/morning, (b) 14:00–20:00/afternoon and (c) 6:00–20:00/all daytime.

4. Conclusions

Measurements of non-methane hydrocarbons with 2–8 carbon atoms (C₂–C₈ NMHCs) have been conducted on North-Eastern Crete from September 2003 to February 2006. C₂–C₈ saturated, C₂–C₄ unsaturated and C₆–C₇ aromatic NMHCs concentrations range from below the detection limit (5 pptv) to a few ppbv, in good agreement with the limited number of measurements reported for the area. They demonstrate a distinct seasonal cycle characterized by summer minimum and winter maximum, driven by the seasonal variation of the OH radicals. The impact of OH is also observed on the NMHCs diel variability with NMHC nighttime maxima and midday or early afternoon minima.

Given the wide range of NMHCs lifetimes (from few hours to several weeks) the role of air masses origin on NMHCs levels has been also investigated. For the longer-lived compounds their concentration was found to be higher under the northern sector (W and E. Europe) relative to the southern (N. Africa) and western ones (Mediterranean sea). In contrast, no significant influence of air masses origin was found on the concentrations of the shorter-lived compounds.

An estimation of the levels of OH radicals, based on the diurnal variability of NMHCs, was also performed. A mean OH concentration of 3.5×10^6 molecules cm⁻³ was derived for the May–October period. This value is comparable with the 3.8×10^6 molecules cm⁻³ calculated for the same period using a box model.

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