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Tropospheric OH and Cl levels deduced from non-methane hydrocarbon measurements in a marine site

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Abstract

In situ continuous hourly measurements of C_2-C_8 non-methane hydrocarbons ($NMHC_S$) have been performed from March to October 2006 at two coastal locations on the island of Crete, in the Eastern Mediterranean. Well defined diurnal variations were observed for several short lived $NMHC_S$ (including ethene, propene, n-butane, n-pentane, n-hexane, 2-methyl-pentane). The daytime concentration of hydroxyl (OH) radicals estimated from these experimental data varied from 1.3×10^6 to $\sim4.0\times10^6$ radical cm^{-3}, in good agreement with box-model simulations. In addition the relative variability of various hydrocarbon pairs (at least 7) was used to derive the tropospheric levels of Cl atoms. The Cl atom concentration has been estimated to range between 0.6×10^4 and 4.7×10^4 atom cm^{-3}, in good agreement with gaseous hydrochloric acid (HCl) observations in the area. Such levels of Cl atoms can be of considerable importance for the oxidation capacity of the troposphere on a regional scale.

1 Introduction

Non-methane hydrocarbons ($NMHC_S$), as trace gas species, play an important role in the photochemistry of the atmosphere by influencing the concentration of the hydroxyl (OH), hydro-peroxyl (HO_2) radicals and ozone. Indeed, under favourable conditions, including high solar radiation and nitrogen oxides, NMHC oxidation may lead to the production of ozone (Crutzen, 1974; Logan et al., 1981; Collins et al., 2002; Jenkin et al., 2002; Derwent et al., 2003). In addition, the oxidation of several hydrocarbons is known to produce secondary organic aerosol (SOA) that could affect human health, visibility and the Earth's energy balance (Kanakidou et al., 2005).

Light $NMHC_S$ (C_2-C_8) include a large number of trace gases with lifetimes ranging from hours to few months. In the past, measurements of various hydrocarbons with different chemical behaviour toward OH radicals and Cl atoms were used by several groups to estimate atmospheric oxidant levels, e.g. OH radicals and Cl atoms (Kanakidou et al., 1989; Wingenter et al., 1996; Derwent et al., 1999; Bonsang and Kanakidou, 2001). For example OH radical levels during night-time were estimated by Bonsang et al. (1987) through NMHC vertical profile measurements performed in a forested site. From changes in the concentration patterns of $NMHC_S$ measured during tropospheric ozone depletion events in the Arctic spring, Cl and Br atom levels in the range of 3–8×10^4 and 3–6×10^7 atoms cm^{-3}, respectively, were deduced (Jobson et al., 1994; Ramacher et al., 1999). Recently, Read et al. (2007) reported for the Antarctic boundary layer, Cl and Br atoms concentrations in the range of 1.7×10^3–3.4×10^4 and 4.8×10^6–9.6×10^7 atoms cm^{-3}, respectively.

The atmosphere of the eastern Mediterranean is characterised by high insolation, humidity and ozone levels throughout the year (Kouvarakis et al., 2000; Gerasopoulos et al., 2005). Such conditions can lead to OH levels as high as 1×10^7 radical cm^{-3} measured around noon in August 2001 (Berresheim et al., 2003).

In addition, Mihalopoulos et al. (1997) and Kouvarakis et al. (2002) reported for the same area a significant chloride deficit in the aerosol phase relative to sodium, indicating potential presence of Cl atoms in the gas phase. Indeed, this deficit is attributed to the reactions of sodium chloride (NaCl) with acidic species such as sulphuric acid (H_2SO_4) and nitric acid (HNO_3) present also at relatively high levels in the Mediterranean atmosphere (Bardouki et al., 2003; Metzger et al., 2006). These reactions lead to the formation of gaseous hydrochloric acid (HCl), which through reaction with OH radicals is producing Cl atoms in the gas phase (Sander and Crutzen, 1996; Vogt et al., 1996; Wingenter et al., 1996).

In the present work we estimate the levels of OH radical and Cl atom based on the NMHC measurements performed at two coastal sites on the island of Crete, located in the eastern Mediterranean. The levels are inferred through the relative variability of selected measured hydrocarbons and chemical box model simulations. Their possible importance for the oxidation capacity of the troposphere is discussed.

2 Experimental

2.1 Site and experimental procedure

In situ measurements of C_2 to C_8 NMHC$_S$ were conducted at two coastal locations on the island of Crete: the monitoring station of the University of Crete (Finokalia) and the University campus (Heraklion). These two sites are refereed in the text as natural and rural respectively, following Putaud et al. (2004) definition. The University campus is located at a rural area, 5 km inland from the N coast of the island, westward to the main city of Crete, Heraklion, and is occasionally affected by emissions of the city. The air monitoring station at Finokalia is a remote background site located in the N coast of the island but 70 km eastward of Heraklion city. In order to avoid important local influences measurements of NMHC$_S$ were performed at both sites during periods with prevalent N-NW winds of speed higher than 5 m s^{-1}. From March to October 2006, intensive sampling and analyses were performed at the University campus through campaigns consisting of 2 to 3 days per month (250 samples). From the 26 July to the 4 August 2006 an intensive sampling was also performed at Finokalia with hourly measurements from 07:00 to 22:00 every day, summer local time (140 samples).

Air samples were analysed by a gas chromatograph (GC, Varian Star 3400) equipped with an FID detector. For each analysis 990 ml of air were drawn from about 5 m above the ground via a stainless steel inlet at a flow rate of 50 ml min^{-1} (air sample integrated over 20 min). The sample firstly passed via a trap filled with magnesium perchlorate ($Mg(ClO_4)_2$) to remove the humidity and then the hydrocarbons were trapped on Tenax TA cooled at about –100°C. The collected sample was thermally desorbed into another trap containing glass beads kept at –196°C. After an enrichment period of two minutes the content of the second trap was injected (via thermal desorption) into an Rt-Alumina PLOT capillary column (Al_2O_3/KCl, 50 m length, 0.53 mm ID and 6.0 μm df). The column was initially kept at 40°C for one minute and then the following temperature program was applied: increase at 120°C at a rate of 10°C min^{-1}, hold time

5 min; increase at 160 °C at a rate of 25°C min^{-1}, hold time 5 min; increase at a final temperature of 180°C at a rate of 25°C min^{-1}. The total analysing time was 40 min.

A gas mixture containing 1 ppmv of fifty-five C_2-C_9 NMHC$_S$ (22964-Restek, Spectra Gases) was used for the identification of the compounds of interest. A certified gas standard mixture containing 100 ppmv of ethane, ethene, propane and n-butane was used as primary calibration standard and was injected daily with a pressure-lock syringe. The detection limit was estimated to be of about 5 pptv and the accuracy of the measurements of about 10%.

During the summer intensive campaign at Finokalia, aerosol and gaseous samples have been collected using the filter pack technique, for the analyses of HNO_3, HCl and NH_3. The filter pack consists of a succession of 3-filters, namely Teflon, glass fibber filter (GFF) and cellulose, the last two impregnated with sodium carbonate (Na_2CO_3) and citric acid, respectively. In total 30 filter samples (sampling frequency of 3 samples per day) were analysed by ion chromatography (details of the analytical procedure are given in Economou and Mihalopoulos, 2002).

2.2 Model description

The chemistry model used to calculate the OH radical levels is a condensed chemical mechanism which, apart from the background O_3/NO_x/OH/CO and CH_4 chemistry, takes also into account the oxidation chemistry of C_2-C_5 NMHC$_S$ including isoprene and dimethyl sulphide. The hydrocarbon chemical scheme used in the present study is an update of the Poisson et al. (2001) scheme to IUPAC recommendations (Atkinson et al., 2006) and includes NO_3 radical and some surface reactions as described by Tsigaridis and Kanakidou (2002) and Vrekousis et al. (2004, 2006). No direct heterogeneous ozone losses are taken into account whereas NO_x and RO_x heterogeneous losses are parameterized as explained by Tsigaridis and Kanakidou (2002) and Vrekoussis et al. (2004).

Hourly mean observations of O_3, CO, NO, NO_2, JNO_2, JO^1D, temperature, relative humidity (RH) and wind speed, from the background air monitoring station (Finokalia) have been used as input to the model. Ethene, propene, ethane, propane and butanes diurnal mean mixing ratios, measured in the area in 2004 (Liakakou, 2007), are adopted in the model as initial conditions. Formaldehyde (HCHO) mixing ratios have been initialised to 1 ppbv (Lelieveld et al., 2002). This model version has been previously applied to evaluate on a seasonal basis the impact of isoprene chemistry on the oxidizing capacity of the area (Liakakou et al.; 2007).

3 Results

3.1 Seasonal and diurnal variations of NMHC_S

Figures 1 and 2 show examples of the datasets obtained during the present work and used for the experimental estimation of the OH radicals. The hydrocarbon levels determined during the present study are in good agreement with earlier reported observations for the Mediterranean area (Moschonas and Glavas, 2000; Gros et al., 2003). Figure 1 depicts the diurnal variability of relatively long lived (ethane, propane, Fig. 1a) and short lived (i-pentane, n-pentane, Fig. 1b) NMHC_S, measured at Finokalia during the campaign in summer 2006. Both ethane and propane do not show any clear diurnal variability and changes in their patterns are mainly influenced by the long range transport due to their relatively long lifetimes toward OH radicals (τ_{ethane}=11.5 days and τ_{propane}=2.9 days, for a mean OH of 4×10^6 radicals cm^{-3}). On the opposite a clear diurnal variation is observed for the shorter lived NMHC_S, i- and n-pentane, with minimum around 19:00, summer local time, especially during days when no significant changes occurred in the wind speed (Fig. 1b). Measurements at Finokalia with a Laser Imaging Detection And Ranging (LIDAR) system showed no significant changes in the boundary layer height during the daytime (Chourdakis, personal communication, 2006) and thus, the diurnal variability of the short lived NMHC_S is attributed to local photochemistry.

The monthly variability of afore mentioned hydrocarbons, measured at the University campus from March to October 2006, is presented in Fig. 2. Species as ethane, propane (Fig. 2a) and i-pentane, n-pentane (Fig. 2b) show a clear seasonal variability with a distinct minimum during the warm season, mainly attributed to photochemistry. However, several other factors like transport, emissions, boundary layer height can control the observed diurnal and seasonal variability of the $NMHC_S$. Detailed analysis of these factors will be presented elsewhere.

3.2 Estimation of the OH radical levels from NMHC variability

The measurements performed at both sites revealed a clear decaying trend for the short lived $NMHC_S$ over the daytime. The absence of variation in the boundary layer height at Finokalia during the studied period and the selection of periods with no changes in air masses origin and with high wind speed assure the applicability of a steady-state hypothesis. The diurnal variation of selected short lived $NMHC_S$ (ethene, propene, n-pentane, n-hexane, 2-methyl-pentane) has been therefore used to estimate the levels of the OH radicals.

Figure 3 shows a typical example of the procedure applied to estimate the OH radical concentration from the decay of the hydrocarbons measured at Finokalia. For this purpose, the observed decreasing trend during daytime has been attributed to the reaction of the hydrocarbons only with OH radicals (Fig. 3a).

The concept

Assuming steady-state conditions, the decay in the concentration of a hydrocarbon from its initial concentration (C_o) at the beginning of the day to that after a time t (C), due to its reaction with OH radicals and Cl atoms, is described by the equation:

$$C=C_0 \times e^{-(k_{OH}[OH]+k_{Cl}[Cl])\times t} \quad (1)$$

By applying a natural logarithm, Eq. (1) leads to Eq. (2) in the form:

$$\ln\frac{C_0}{C}=(k_{OH}[OH] + k_{Cl}[Cl]) \times t \tag{2}$$

When the reaction with Cl is negligible and the decay of the hydrocarbon is determined only by its reaction with OH, then Eq. (3) can be derived:

$$\ln\frac{C_0}{C}=k_{OH}[OH] \times t \tag{3}$$

In this case, the slope of the regression between $\ln(C_o/C)$ as a function of the time t and the reaction rate k_{OH}, allows the estimate of the mean OH concentration over the studied period t (Fig. 3b). Such analysis can be performed based on observations of selected short lived $NMHC_S$. The criteria used for this selection is a high reactivity toward OH radicals compared to other atmospheric oxidants, for instance Cl atoms and ozone (Atkinson and Arey, 2003; Atkinson et al., 2006).

Thus, a 12-h median value of 4.0×10^6 radical cm^{-3} (standard deviation (σ) of the data $\pm 0.6\times10^6$ radical cm^{-3}) was derived from the diurnal variation of ethene, propene, n-pentane, n-hexane and 2-methyl pentane. It is worth noting that n-butane leads to much higher OH levels (almost a factor of 2 higher than the other $NMHC_S$, Fig. 3a) which can be explained by its higher k_{Cl}/k_{OH} ratio than that of other studied hydrocarbons (further discussed in Sect. 3.3).

The concentration of the OH radicals was also derived for the rural site (University campus) by using the above described concept. The results are presented in Table 1. The OH radical levels at this site are estimated to range from 1.3×10^6 (low insolation period) to about 3.4×10^6 radical cm^{-3} (high insolation period). These experimentally derived OH levels agree reasonably well with those derived from the 0-D box model presented also in Table 1. For instance the experimentally derived value of $4.0\times10^6\pm0.6\times10^6$ radical cm^{-3}, for the natural marine site during July/August 2006, is within 10% of the average value of 4.4×10^6 calculated by the 0-D box model for the same period.

The coherence between the experimentally derived OH concentrations and the model calculations indicate that under appropriate meteorological conditions, measurements of NMHC$_S$ can provide a useful tool for the estimation of the OH radical concentration.

3.3 Estimation of Cl atom levels from NMHC variability

3.3.1 Evidence for Cl atom chemistry

Apart OH radicals, halogen atoms can also contribute to the decay of the hydrocarbons during daytime, as shown in Eq. (1). Indication of the presence of halogen atoms in the atmosphere can be obtained through examination of pairs of compounds that have almost identical reaction rates with respect to OH radicals and very different reaction rates with respect to Cl atoms, e.g. i-butane and n-butane (n-butane reaction with Cl atoms proceeds almost twice as fast as the reaction of Cl with i-butane).

An examination of i-butane/n-butane ratio versus n-butane levels illustrates the dominant radical chemistry acting on specific air masses. A constant i-butane/n-butane ratio with the increase of n-butane, independent of the NMHC atmospheric abundance, implies only OH radical chemistry. In addition a constant i-butane/n-butane ratio and an increasing in i-butane/third hydrocarbon (e.g. propane) ratio would also imply only OH radical influence. On the other hand, a significant Cl chemistry involved in the sink of those hydrocarbons would determine the reverse to be true (Hopkins et al., 2002; Read et al., 2007).

Based on NMHC observations at both sites i-butane/n-butane ratio is plotted against n-butane (Fig. 4a). As the ratio varies between 0.3 and 3 for the rural site and 0.6 and 3 for the natural site, this is clearly indicating the presence of Cl atoms in the area. Similar conclusion can be drawn from Fig. 4b that depicts i-butane/n-butane vs. i-butane/propane (Fig. 4b) under low and high insolation conditions based on all available observations. In addition, the pattern in Fig. 4b demonstrates also the increased importance of Cl chemistry during the high compared to the low insolation period.

There is no appropriate analytical method that allows the direct measurement of Cl atom at levels of 10^3–10^5 atoms cm^{-3} such as those expected in the atmosphere (Singh et al., 1996; Wingenter et al., 1996; Rudolph et al., 1997; Read et al., 2007). In the afore mentioned works the Cl atom levels were mainly deduced by using indirect methods such as analysis of logarithmic ratios plots for various NMHC pairs (Wingenter et al., 1996; Rudolph et al., 1997) or final global distributions of ethane and tetrachloroethene (Rudolph et al., 1996).

3.3.2 The concept of indirect Cl determination

The analysis in the present study is based on the concept described by Rudolph et al. (1997). Hydrocarbon variability is interrelated with their reactivity toward OH radicals and Cl atoms through logarithmic approaches outlined here below. The dependence between the natural logarithms of the ratios of different NMHC concentrations is described under ideal conditions by a linear relationship as follows:

$$\ln\frac{[A]}{[C]} = a \times \ln\frac{[B]}{[C]} + b \qquad (4)$$

where [A], [B] and [C] denote the concentrations of the hydrocarbons measured in the same air sample. When both OH radical and Cl atom reactions are involved in the atmospheric removal of the hydrocarbons the slope, *a*, in Eq. (4) can be calculated by the expression

$$a_{\mathrm{Cl,OH}} = \left(\frac{(k_{\mathrm{OH}})_C + r\,(k_{\mathrm{Cl}})_C - (k_{\mathrm{OH}})_A - r\,(k_{\mathrm{Cl}})_A}{(k_{\mathrm{OH}})_C + r\,(k_{\mathrm{Cl}})_C - (k_{\mathrm{OH}})_B - r\,(k_{\mathrm{Cl}})_B}\right) \qquad (5)$$

where k denotes the rate constants of the specific hydrocarbon (A, B, C) toward OH radicals or Cl atoms and r is the ratio between the Cl atom and OH radical concentrations (r = [Cl]/[OH]). Using Eq. (5) the following expression can be derived in order to calculate the [Cl]/[OH] ratio

$$\frac{[\mathrm{Cl}]}{[\mathrm{OH}]} = \frac{a_{\mathrm{Cl,OH}}\left((k_{\mathrm{OH}})_C - (k_{\mathrm{OH}})_B\right) + (k_{\mathrm{OH}})_A - (k_{\mathrm{OH}})_C}{a_{\mathrm{Cl,OH}}\left((k_{\mathrm{Cl}})_B - (k_{\mathrm{Cl}})_C\right) + (k_{\mathrm{Cl}})_C - (k_{\mathrm{Cl}})_A} \tag{6}$$

3.3.3 Experimentally derived Cl levels

Based on the above described concept, as an example, Fig. 5 presents the logarithm of the ratio (n-butane/benzene) as a function of the logarithm of the ratio (n-pentane/benzene) based on the data collected at Finokalia during the summer campaign. These hydrocarbons have been also analysed in detail by Rudolph et al. (1997). If NMHC variability is driven only by the reaction with OH radicals, the slope of the regression depicted in Fig. 5 should equal 0.44 as derived from the corresponding ratios of the reaction rate constants of the compounds against OH. In the case of exclusive reaction with Cl atoms the slope of the above presented regression would change to 0.80. These ideal slopes are different from those earlier reported by Rudolph et al. (1997) mainly due to recent literature updates in the reaction rate constants that have been adopted for the present study. However, the slope derived from the NMHC observations in the present work is equal to 0.64±0.07 ($\pm\sigma$), which is not significantly different from the value of 0.58±0.02 reported by Rudolph et al. (1997). Consequently, the [Cl]/[OH] ratio of 1.3×10^{-2}, estimated from the 0.64 slope, is in very good agreement with the value of 1.2×10^{-2} reported by Rudolph et al. (1997).

The procedure described above has been applied to all possible pairs of NMHC_S and only slopes with significant correlation coefficients (r>0.85) were retained for further investigation. Table 2 reports the median of [Cl]/[OH] ratio derived for each month as well as the number of the hydrocarbon pairs used for this determination. For each month the concentrations of the Cl atoms were determined using both the ratios of [Cl]/[OH] and the levels of the OH radicals experimentally deduced. The derived Cl atom levels range from 0.6×10^4 (low insolation period) to 4.7×10^4 atoms cm^{-3} (high insolation period). Moreover, the continuous measurements performed at the rural site indicate that Cl seasonal distribution follow well the variability of the OH radicals (Fig. 6).

It is interesting to note the difference in Cl atom concentrations derived for summer time at the natural site (Finokalia, median of 2.3×10^4, standard deviation of data, σ, $\pm$ 1.9×10^4 atoms cm^{-3}) and at the rural area (University campus, Heraklion, median of 4.5×10^4 standard deviation of data, σ, $\pm$ 2.7×10^4 atoms cm^{-3}). Although influence from local anthropogenic sources could account for the higher values observed at the rural site, more work is clearly needed in order to examine this hypothesis.

Cl atom concentrations have been also calculated as suggested by Singh et al. (1996). Values were obtained based on the normalization of the night-time/daytime hydrocarbon differences relative to carbon monoxide concentration (CO) derived from the data set obtained at Finokalia during summer. A median value of 4.1 (standard deviation of data, σ, $\pm1.2\times10^4$ atoms cm^{-3}) has been obtained using this approach, which has increased our confidence on the estimated levels of Cl atoms presented in Table 2.

3.3.4 Consistency of the derived Cl atom levels with other Cl_x measurements

Previous works conducted at Finokalia and other locations in the Eastern Mediterranean report significant chloride (Cl) deficit compared to sodium (Na) (Mihalopoulos et al., 1997; Kocak et al., 2004). The observed Cl pattern indicates clear seasonal variability with higher deficit values during summer (Kocak et al., 2004), attributed to the reactions of sea-salt with the acidic species, mainly sulphuric acid (H_2SO_4) and nitric acid (HNO_3), both presenting a summer maximum. These reactions form HCl in the gas phase which can produce Cl atoms through the $HCl + OH \rightarrow Cl + H_2O$ reaction. However, HCl is also formed through the reactions of various hydrocarbons (RH) with Cl atoms ($RH + Cl \rightarrow R + HCl$, where R is an alkyl radical).

Measurements of gaseous HCl were performed at Finokalia using the filter pack technique during the summer campaign. The HCl measured values range from about 2 to 6 ppbv (average 3.0 ± 2.1 ppbv, n=30). Similar levels have been measured at Finokalia using the Coffer and denuder techniques (Mihalopoulos, unpublished data) during long-term measurements from June 2001 to June 2002. These data revealed a well defined seasonal variability of HCl with values of about 2 ppbv during winter to 5 ppbv during summer. The mean measured value of 3.0±2.1 ppbv for 26 July to 4 August 2006, seems to be in a good agreement with the values determined during the warm seasons in 2001 and 2002.

For the marine atmosphere a Cl/HCl ratio of the order of 2.0×10^{-6} is expected (see for instance Sander, http://www.mpch-mainz.mpg.de/~sander/ and Pszenny et al., 2004). Using the measured HCl concentrations from the present work and the above ratio, Cl atom levels in the range of 9.8×10^{4} to 3.0×10^{5} atom cm^{-3} can be estimated. This Cl atom estimate should be viewed as upper limit since the available sampling techniques for gaseous HCl (filter packs, denuders, Coffers) could collect other acidic Cl-containing compounds in addition to the gaseous HCl. However, the derived Cl atom levels are in reasonable agreement with the Cl concentrations indirectly estimated from the measured NMHC variability.

3.4 Possible implications on regional atmospheric chemistry

Table 3 presents the lifetime of selected NMHC_S relative to OH radicals and Cl atoms based on the oxidant concentrations derived during this work. The data in Table 3 clearly reveal that OH radical and, in lesser extend Cl atom levels, control the lifetime for most of the studied hydrocarbons with the exception of few long lived NMHC_S (ethane and propane). However the conditions at Finokalia, with Cl deficit in the aerosol phase and high OH radical levels during summer, prevail also at other locations around Mediterranean (Kocak et al., 2004; Kouyoumdjian and Saliba, 2006). Under these circumstances it is expected that Cl atoms at levels as those estimated in the present work would have a more regional significance, and could be the main oxidant controlling the lifetime of long lived hydrocarbons, including methane (CH_4), in the area. Indeed based on our calculations Cl atoms can increase the removal of CH_4 from the atmosphere by about 8% compared to the amount of CH_4 removed by OH radicals.

4 Conclusions

Continuous hourly in situ measurements of C_2 to C_8 NMHC$_S$ (45 compounds) were performed on the island of Crete in the Eastern Mediterranean, at a coastal rural site, from March to October 2006, and at a natural marine site, from 26 July to 4 August 2006. The large data-set (140 measurements in a marine area during an intensive campaign and more than 250 analyses at a rural site) was used to estimate oxidants levels in the atmosphere over the investigated area.

The levels of the OH radicals were derived from the diurnal variation of short lived NMHC$_S$ under given air masses origin. The daytime OH radical concentrations were found to range from 1.3×10^6 up to 4.0×10^6 radical cm^{-3}, in good agreement with 0-D box-model simulations.

Cl atom levels were also estimated using the relative variability of various pairs of NMHC$_S$ (on average 8 pairs). The determined concentrations of the Cl atoms range from 0.6×10^4 to 4.7×10^4 atoms cm^{-3}, in line with the observed levels of gaseous HCl in the area.

Our results indicate that, under well defined and uniform meteorological conditions, NMHC measurements provide a useful tool to estimate OH and Cl levels in the atmosphere. In addition, the estimated significant levels of Cl atoms can considerably contribute to the oxidation of methane and other long lived hydrocarbons (ethane, propane) in the troposphere of the investigated region.

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Table 1. Monthly OH radical mixing ratios (median value and standard deviation) estimated from the variability of selected NMHC$_S$ (ethene, propene, n-pentane, n-hexane and 2-methyl pentane) and calculated by a chemical box model.

Site	Month	OH radical concentration (12 h) radical cm^{-3}			
		N	present work		0-D model box
			median	Standard deviation of estimates (σ)	marine
rural	March	5	1.3E+06	0.5E+06	1.0E+06
	April	5	2.2E+06	0.7E+06	1.7E+06
	May	4	2.5E+06	1.5E+06	3.0E+06
	June	4	3.2E+06	1.4E+06	4.1E+06
	July	4	3.4E+06	1.3E+06	4.5E+06
	August	4	3.3E+06	1.9E+06	3.9E+06
	September	4	2.6E+06	0.9E+06	3.2E+06
	October	5	1.7E+06	0.6E+06	2.0E+06
marine	July/August	5	4.0E+06	0.6E+06	~ 4.4E+06

N – number of the hydrocarbons used in the estimation.

Table 2. Median [Cl]/[OH] ratios, number of pairs of $NMHC_S$ used for the Cl/OH estimation, the derived monthly mean Cl atom concentrations and the associated uncertainty expressed as standard deviation of the estimates.

Site	Month	y/x	[Cl]/[OH]	n	[Cl] atom cm^{-3}	σ
rural	March	0.76	0.5E-02	8	0.6E+04	0.4E+04
	April	0.87	1.1E-02	9	2.4E+04	2.0E+04
	May	0.92	1.4E-02	7	3.5E+04	3.2E+04
	June	0.79	1.4E-02	8	4.6E+04	3.7E+04
	July	0.82	1.3E-02	7	4.7E+04	3.0E+04
	August	0.75	1.3E-02	6	4.3E+04	2.3E+04
	September	0.89	1.0E-02	7	3.6E+04	2.5E+04
	October	0.89	1.1E-02	9	1.2E+04	1.0E+04
marine	July/August	0.75	0.7E-02	15	2.3E+04	1.9E+04

n – number of pairs used in the estimation.

Table 3. Hydrocarbon chemical reactivity with regard to OH radicals and Cl atoms, ratio of the reaction rate of each hydrocarbon with Cl to that with OH, contribution of Cl reaction to the total destruction of the hydrocarbon by OH radicals and Cl atoms, lifetime of the selected NMHC$_S$ due to oxidation by OH radicals and Cl atoms.

CH_4&NMHCs	k_{Cl}^{a} cm^3 molec^{-1} s^{-1}	k_{OH}^{a} cm^3 molec^{-1} s^{-1}	k_{Cl}/k_{OH}	%Cl^{b}	lifetime toward^{c} Cl	lifetime toward^{c} OH
methane	1.00E-13	6.40E-15	16	8.2	14 y	1.5 y
ethane	5.90E-11	2.50E-13	238	57.6	8.5 d	11.5 d
propane	1.40E-10	1.00E-12	139	44.6	3.5 d	2.9 d
n-butane	2.10E-10	2.40E-12	87	33.5	2.4 d	1.2 d
acetylene	2.00E-10	2.50E-12	80	31.5	2.5 d	1.2 d
i-butane	1.40E-10	1.90E-12	74	29.8	3.5 d	1.5 d
n-pentane	2.50E-10	3.80E-12	66	27.4	2.0 d	18 h
n-hexane	3.00E-10	5.20E-12	58	24.9	1.5 d	13 h
i-pentane	2.00E-10	3.90E-12	51	22.8	2.5 d	18 h
cyclo-hexane	3.10E-10	7.00E-12	44	20.3	1.6 d	10 h
ethene	1.00E-10	8.50E-12	12	6.3	5.3 d	9 h
benzene	1.50E-11	1.20E-12	12	6.7	33 d	2.4 d
toluene	5.90E-11	5.60E-12	11	5.7	80 d	12 h
(m+p)-xylene	1.50E-10	1.40E-11	11	5.8	3.3 d	5 h
propene	2.40E-10	2.60E-11	9	5.0	2.1 d	2.5 h

[a] The reaction rate constants are from Atkinson and Arey (2003), Atkinson et al. (2006).

[b] The data in the column refers to the importance of the NMHC$_S$ reaction with Cl atoms vs. their total reaction toward OH radicals and Cl atoms. The percentage was calculated according to the (k_{Cl}[Cl]/(k_{Cl}[Cl]+k_{OH}[OH]) expression.

[c] In the calculation of the selected NMHC lifetime toward Cl atoms or OH radicals were used the upper limits in their concentration (2.3×10^4 Cl atoms cm^{-3} and 4.0×10^6 OH radicals cm^{-3}) as determined in the present experimental work for summer time.

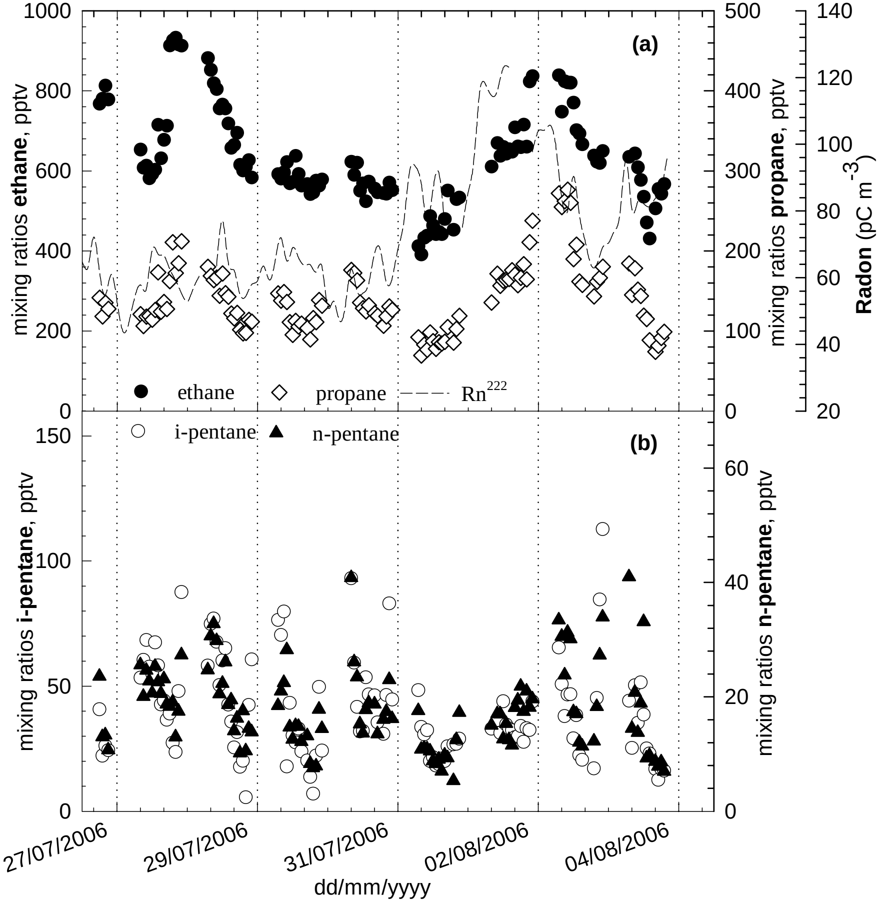

Fig. 1. Variability of ethane, propane **(a)**, i-pentane and n-pentane **(b)** measured in a marine area from 26 July to 4 August 2006 (Finokalia).

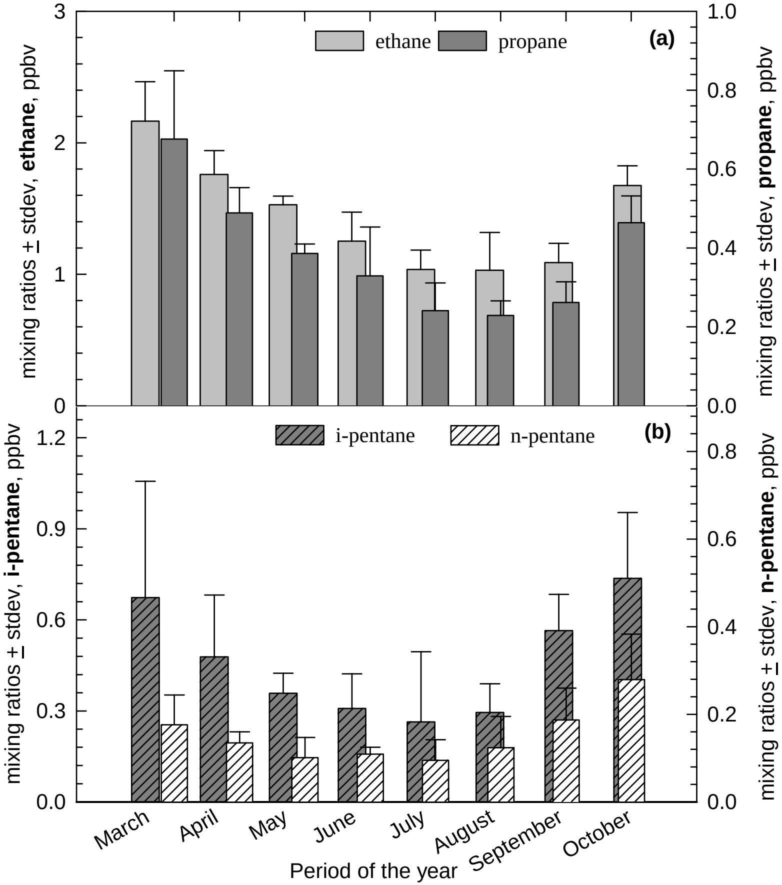

Fig. 2. Monthly variability of ethane, propane **(a)**, i-pentane and n-pentane **(b)** measured at a rural site (University campus, Heraklion) from March to October 2006.

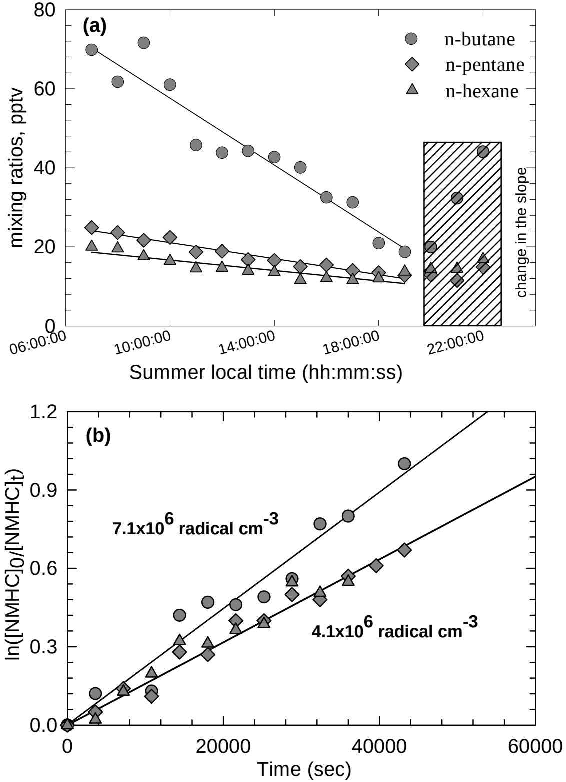

Fig. 3. Typical example of the kinetic analysis applied for the estimation of the OH radical concentration at a marine site. Decaying trend of selected hydrocarbons **(a)** and the dependence of ln(C_0/C) vs. time **(b)**.

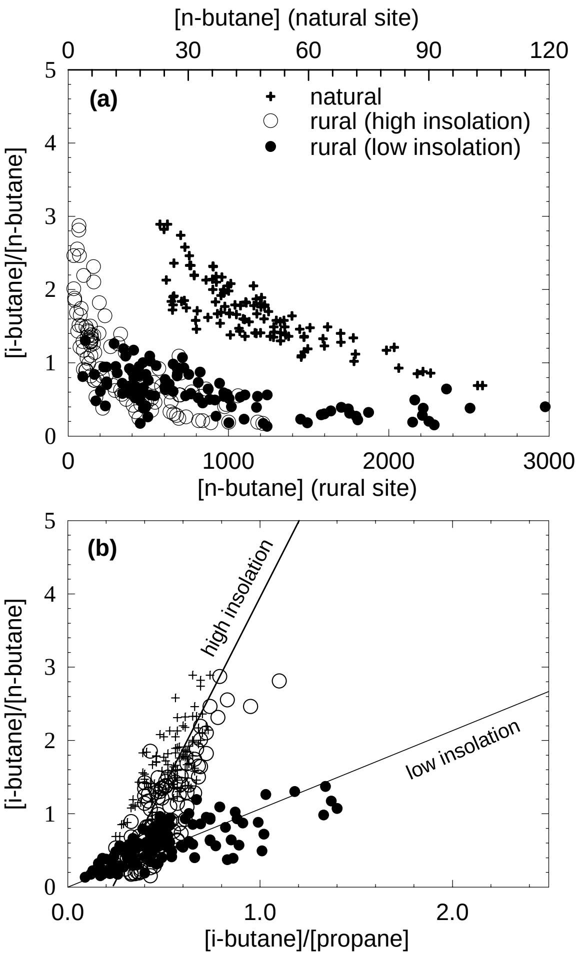

Fig. 4. Plots of i-butane/n-butane vs. n-butane **(a)** and i-butane/n-butane vs. i-butane/propane **(b)** during high and low insolation periods.

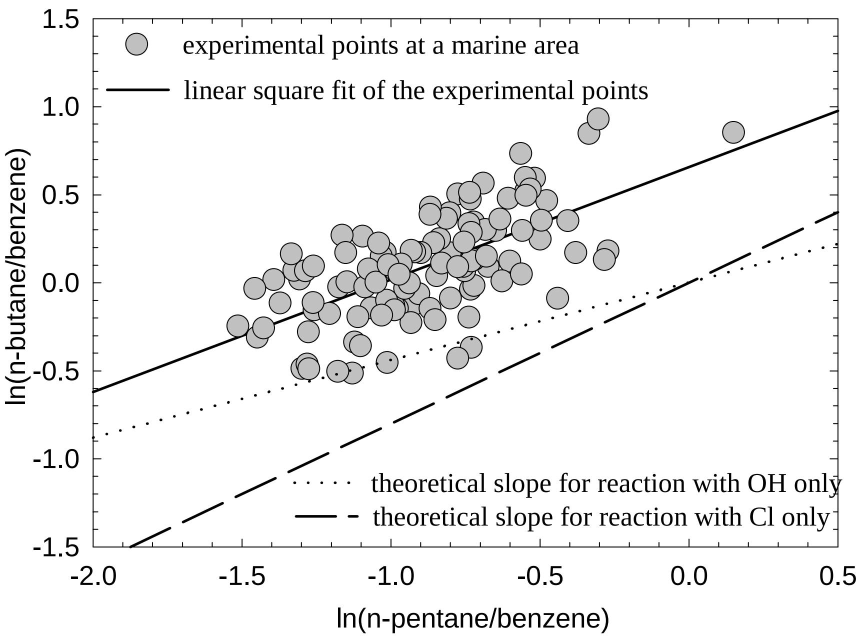

Fig. 5. Plot of ln(n-butane/benzene) vs. ln(n-pentane/benzene).

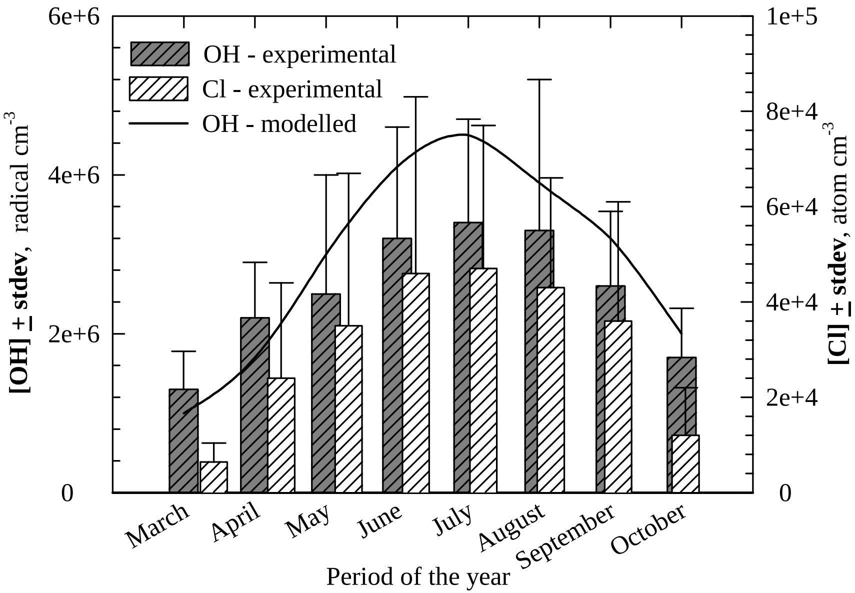

Fig. 6. Seasonal distribution of the experimentally determined Cl atom levels compared to the experimentally and theoretically derived OH radical concentrations.