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C_2–C_8 NMHCs over the Eastern Mediterranean: Seasonal variation and impact on regional oxidation chemistry

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ABSTRACT

More than 2500 measurements of C_2–C_8 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.

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 (O_3) and nitrate radicals (NO_3). In the presence of sufficient nitrogen oxides (NO_x), VOC oxidation leads to photochemical O_3 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 ($RONO_2$), 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 (C_2–C_8) 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 C_2–C_8 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 C_2–C_8 NMHCs, acetylene and benzene. In addition, from February 2004 to October 2004, 2450 direct hourly measurements of saturated C_2–C_6 NMHCs (see Table 1) have been performed in-situ. Unsaturated C_2–C_4 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 C_2–C_8 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 (Cl_2MgO_8) dryer, maintained at 50 °C. The hydrocarbons were cryogenically pre-concentrated on a 10 cm length trap containing glass beads (Unibeads) 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 um 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. 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).

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.

2.2.2. Automatic in-situ GC–FID system – C_2–C_6 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 C_2–C_6 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 Al_2O_3/Na_2SO_4 column (Varian Inc., Ultimetal PLOT column, 0.53 mm ID, 10.0 um 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. C_2–C_6 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 C_2 and C_4 alkenes have been measured only for the September–October 2004 period.

2.2.3. GC–FID system – C_2–C_8 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 C_2–C_8 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 (Cl_2MgO_8) 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 N_2 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 N_2 (−196 °C). After the second desorption with boiling water, the sample was directly injected in a 50 m Al_2O_3/KCl capillary column (Restek, Rt-Alumina 0.53 mm ID, 6.0 um 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 C_2–C_9 VOCs (# 22964-Restek, Spectra Gases), including 25 compounds detectable by our GC–FID (C_2–C_6 alkenes, n- and iso-alkanes, and isoprene), has been used for the identification of the compounds of interest for both