



## Non-Methane Volatile Organic Compounds in the Background Atmospheres of a Southern European Mountain Site (Mt. Cimone, Italy): Annual and Seasonal Variability

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### ABSTRACT

Since January 2010 continuous high-frequency in situ measurements of a range of anthropogenic Non-Methane Volatile Organic Compounds (NMVOCs) has been carried out at the World Meteorological Organisation Global Atmospheric Watch observatory at Mt. Cimone, on the highest peak of the Italian Northern Apennines, at the border between the Po Valley and the Mediterranean Basin. Five-year (2010–2014) time series of eleven NMVOCs, including aromatic and aliphatic species, have been analysed in order to derive average mixing ratios and detect annual and seasonal variability. Recent studies conducted in Europe, mainly in urban areas, have reported a decrease in atmospheric NMVOCs. Here we investigate how the decline in emissions, due to the implementation of air pollution policies, is reflected in the annual variability of NMVOC mixing ratios measured at a regional background location. Analysis of temporal trends for well-mixed conditions showed statistically significant decreases in ethyne, n-pentane and ethyl-benzene, while no significant trends were found for propane, butanes, i-pentane, toluene and xylenes. The seasonal variability of NMVOCs has been studied showing clear seasonal cycles for longer lived compounds and cycles with smaller seasonal amplitudes for shorter-lived species. We used the propane time series to describe the seasonal cycle and to verify to what extent the mixing ratios of propane have been depleted by OH oxidation. We found that, during the summer, different transport times to the receptors and different source distribution are the main responsible for the relatively low integrated OH concentrations at Mt. Cimone.

**Keywords:** Volatile hydrocarbons; Air quality; Hydroxyl radical; Long-term observations.

### INTRODUCTION

Non-Methane Volatile Organic Compounds (NMVOCs) play a key role in the chemistry of the atmosphere being involved in the formation of localised urban smog, regional scale ozone pollution and secondary organic aerosol (SOA) formation. In addition NMVOCs control the concentration of the hydroxyl radical (OH) (Monks *et al.*, 2009), the principal oxidizing agent in the troposphere hence strongly affecting the quality of ambient air as well as the climate. NMVOCs are emitted by both anthropogenic and biogenic sources. However, while on a global scale VOC emissions

are dominated by biogenic sources (Guenther *et al.*, 2006) in urban areas the anthropogenic emissions (mainly fossil fuel related) are the principal contributor to VOC sources (Barletta *et al.*, 2005).

Emission inventories of NMVOCs are available to be used by the modelling community in order to predict the impact of NMVOC emissions on local air quality (Colette *et al.*, 2012) and climate (Kanakidou *et al.*, 2005). However, the emissions of NMVOCs are generally not very well represented in emission inventories and their speciation has a high level of uncertainty (Lewis *et al.*, 2013). Therefore, reliable high temporal resolution measurements of NMVOCs are strongly needed. This has been recognised by Global Atmosphere Watch (GAW) of the World Meteorological Organization (WMO) (WMO, 2007; Helmig *et al.*, 2009), which included NMVOCs among the long-term monitoring parameters to be measured, as well as by regional programmes such as the European Monitoring and Evaluation

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Programme (EMEP) (Tørseth *et al.*, 2012).

In Europe, long-term measurements of NMVOCs are carried out mostly at urban and rural sites and only at a few remote sites. European studies have reported decreases in NMVOCs concentration monitored at urban-rural (Derwent *et al.*, 2003; Plass-Dulmer and Berresheim, 2007; Sauvage *et al.*, 2009) and at remote sites (Grant *et al.*, 2011; Hakola *et al.*, 2006) with a substantial decline observed during the period 1980–2000, due to a significant change in anthropogenic emissions resulting from the implementation of reduction policies, like vehicle emission control technologies and reduction in industrial and domestic solvent usage (Dollard *et al.*, 2007; Worton *et al.*, 2012).

However, the various European monitoring programmes lack coordination. In order to overcome this problem, the EU FP7 infrastructure project ACTRIS (Aerosols, Clouds, and Trace gases Research InfraStructure Network) is supporting an activity aimed at integrating and harmonising NMVOCs measurements, thus creating a sustainable and reliable observation network for highly time-resolved data across Europe (Hoerger *et al.*, 2015). Within this framework, high frequency measurements of eleven NMVOCs are conducted at the Global GAW-WMO station of Monte Cimone (CMN) located in the Italian North Western Apennines at 2165 m above sea level (asl). Although in the last 15 years several short term campaigns have been conducted in Southern Europe (Moschonas and Glavas, 2000; Liakakou *et al.*, 2009; Seco *et al.*, 2013), CMN is the southernmost site in Europe where NMVOCs are measured continuously. Moreover, CMN is the only site with continuous observations of NMVOCs overlooking the Po Valley, one of the most urbanised and industrialised areas in Europe that can be considered as a distributed megacity (WMO, 2012). Emissions from megacities affect air quality at a local and a regional scale and can influence atmospheric chemistry at the global scale (Monks *et al.*, 2009).

In Table 1 we report the list of the compounds monitored at CMN in order of their OH reaction coefficients ( $K_{OH}$ ) and their respective atmospheric lifetimes ( $\tau_{OH}$ ). They include ethyne, five alkanes and five aromatics. All compounds primarily originate from various anthropogenic activities, mainly combustion processes (e.g., vehicle exhausts and man-made biomass burning); production, treatment, storage, and distribution of fossil fuels, industrial processes (solvent) and landfills (Barletta *et al.*, 2005). Ethyne is used as a tracer for anthropogenic emissions because it is solely derived from combustion (Lee *et al.*, 2006), propane is mainly emitted from natural gas leakages while butanes and pentanes are emitted mainly from petrol evaporation (Kansal, 2009). Benzene is a component of unburned fossil fuels and a by-product of the incomplete combustion of other hydrocarbons in fossil fuels (Schauer *et al.*, 2002) and has been strictly regulated because it is a Class 1 human carcinogen. Toluene, being widely used as a feedstock and solvent, is mainly emitted from industry and is one of the most important aromatic compounds for ozone formation (Derwent *et al.*, 2003). The xylenes and ethyl-benzene are used as solvents in paints and coating (Borbon *et al.*, 2004) and are also

**Table 1.** Compounds monitored at CMN, rate coefficients and atmospheric lifetimes with respect to OH reactivity. The 298 K rate and lifetimes are taken from Atkinson and Arey (2003),  $OH = 2 \times 10^6$  molecules  $cm^{-3}$  (12-h daytime average).

Species	$K_{OH}$ (298K) ( $cm^3$ molecules $^{-1}$ s $^{-1}$ )	$\tau_{OH}$ (days)
Ethyne	$8.20 \times 10^{-13}$	14
Propane	$1.09 \times 10^{-12}$	11
Benzene	$1.22 \times 10^{-12}$	9.5
i-butane	$2.12 \times 10^{-12}$	5.5
n-butane	$2.36 \times 10^{-12}$	4.9
i-pentane	$3.60 \times 10^{-12}$	3.2
n-pentane	$3.80 \times 10^{-12}$	3.0
Toluene	$5.63 \times 10^{-12}$	2.1
Ethyl-benzene	$7.00 \times 10^{-12}$	1.7
o-xylene	$1.36 \times 10^{-11}$	0.9
m,p-xylene	$1.90 \times 10^{-11}$	0.6

emitted in vehicle exhausts (Monod *et al.*, 2001; Lewis *et al.*, 2013).

The NMVOCs monitored at CMN are characterised by a range of different atmospheric lifetimes, which determine the extent of transport from the source region (Heard, 2007): long-lived species undergo long-range transport and short-lived species contribute to ambient levels over a much smaller domain. The more reactive species contribute to regional photochemistry near emission sources favouring the transport of air-masses rich in  $O_3$  during summer months (Cristofanelli *et al.*, 2015).

Seasonal variability of NMVOCs in the troposphere is driven by various factors such as emission strength, removal and transport processes and meteorological conditions. As pointed out by Pozzer *et al.* (2010), the seasonal changes in the anthropogenic emissions of NMVOCs are thought to be small, due to their relatively constant release from fossil fuel combustion and leakage from oil and natural gas production. As a consequence, seasonal cycles of NMVOCs are mainly driven by removal processes, the most important of which is the reaction with OH radicals (Atkinson, 2000). In the Northern Hemisphere winter accumulation of NMVOCs is generally observed and is consistent with a simple model in which hydrocarbons are emitted by man-made sources and are removed by OH, whose levels in winter are much lower than in summer. As a consequence, the phase of the hydrocarbons seasonal cycles for each species would reflect their rate of reaction with OH: more reactive hydrocarbons would peak earlier in winter and drop faster in spring than the least reactive compounds (Goldstein *et al.*, 1995).

In this paper we report five-years continuous high-frequency measurements of eleven NMVOCs conducted at CMN from January 2010 to December 2014. The time series provide useful information on the annual and seasonal variability of NMVOCs at a site considered to be strategic for investigating the influence of anthropogenic emissions from a megacity-like environment on the surrounding regions and its potential influence on air quality and atmospheric oxidation capacity.

## METHODS

### Measurement Site

The Italian Climate Observatory “O. Vittori” (44°12' N, 10°42' E, 2165 m a.s.l.) is part of the GAW program of the WMO. It is located on the top of Mt. Cimone (2165 m a.s.l.), the highest peak of the North Western Italian Apennines and it is the only high mountain station for atmospheric research located south of the Alps and the Po basin. The measurement site can be mostly considered representative of the background conditions of the South European free troposphere (Bonasoni *et al.*, 2000). However during the summer, CMN can be influenced by the more effective (with respect to the other seasons) convective uplift of air masses from the Planetary Boundary Layer (PBL) through vertical mixing and the local mountain wind system (Cristofanelli *et al.*, 2015). The vicinity of the Po valley, one of the major polluted areas in Europe, makes this site particularly suitable for studying changes of atmospheric composition on a regional scale. CMN is also affiliated to the AGAGE (Advanced Global Atmospheric Gases Experiment) network, whose aim is to measure over the globe at high frequency the most important ozone depleting gases (Maione *et al.*, 2013) and almost all of the significant climate altering fluorinated gases (see e.g. Stohl *et al.*, 2009).

### Analytical Procedure and Calibration

At CMN, observations of the eleven NMVOCs in ambient air are conducted via gas chromatography–mass spectrometry (GC–MS) preceded by on-line sample enrichment using adsorbent material, following a method described in Maione *et al.* (2013). A GC–MS Agilent 6850–5975 has been equipped with an auto-sampling/pre-concentration device (Markes International, UNITY2-Air Server2) to enrich the NMVOCs on a focussing trap filled with four different adsorbing materials. The pre-concentration is achieved at sub-ambient temperature (–30°C): for that reason the sample moisture (for both real air and working standard) is reduced by the use of a Nafion drier tube. The trapped compounds are then thermally desorbed at 310°C in a Helium carrier gas flow at 1.6 mL min<sup>–1</sup> and injected and separated on a PLOT column, J&W GASPRO 25 m × 0.32 mm, at the initial oven temperature of 49°C for 6 minutes, then increased by 10 °C min<sup>–1</sup> up to 150°C and then by 20 °C min<sup>–1</sup> up to

240°C. The MS detector is operating in selective ion mode (SIM). Annual mean percent relative standard deviations (%RSD) are evaluated from the repeated working standard measurements (RSD over 1 year). Absolute total uncertainty (TU, coverage factor = 2), in ppt, is calculated including the certified uncertainty in the standard gas mixing ratio that propagates along the calibration chain. Limits of detection (LODs), (Signal to Noise, S/N > 3) and limits of quantitation, LOQs (S/N > 10) have been indirectly estimated on the chromatogram of the working standard run. The obtained RSD, LOD and LOQ values are reported in Table 2.

Ambient air samples are taken every two hours and each sample takes about 26 minutes to collect. The sample analyses are bracketed by working standard analyses, in order to detect and correct for short-term instrumental drift. These working standards are air samples that are pumped during relatively clean-background conditions into 35-l electro-polished stainless steel canisters (Essex Cryogenics, Missouri, USA) using a modified oil-free compressor (SA-3 or SA-6Rix California, USA) up to ~60 bar. The tanks are humidified with purified water during the pumping process in order to improve the stability of the compounds (Miller *et al.*, 2008) and to ensure a close similarity in composition between the ambient air samples and the reference standard. The working standards are calibrated against a primary reference standard prepared by NPL (National Physical Laboratory, Teddington, UK). The gas mixture contains thirty hydrocarbons with certified concentrations around 4 ppb; absolute concentrations are propagated to a lower concentration standard in air, that is used to calibrate the working standard. The GC-MS system is fully automated via the Linux-based chromatography software (GCWerks, gcwerks.com) adopted by the AGAGE programme.

### Evaluation of Well-Mixed Conditions

CMN, although recognised as a remote station, is sometimes affected by nearby emissions, in particular from the highly polluted Po valley. Nearby emissions give rise to changes in mixing ratios on a short time scale, corresponding to a non-well-mixed state. Therefore, for deriving the long-term variability of the NMVOCs, it is necessary to identify the mixing ratios corresponding to a well-mixed state. For the identification of concentrations corresponding to well mixed conditions we used a statistical method based on a

**Table 2.** RSD, LODs and LOQs for the twelve NMVOCs considered in this study.

Species	% RSD	TU (k = 2) (ppt)	LOD (ppt)	LOQ (ppt)
Ethyne	1.9	12.3	1.82	6.08
Propane	2.9	23.2	17.5	58.3
Benzene	0.7	6.8	0.05	0.17
i-butane	1.5	4.1	0.80	2.67
n-butane	1.3	12.6	0.92	3.05
i-pentane	1.3	3.8	0.40	1.35
n-pentane	2.6	4.8	0.79	2.64
Toluene	1.3	3.3	0.05	0.17
Ethyl-benzene	1.7	2.8	0.12	0.41
o-xylene	1.9	2.8	0.12	0.41
m,p-xylene	2.2	4.8	0.11	0.34

two-step procedure (Giostra *et al.*, 2011), the first step consisting of a detrending of the time series using an appropriate time interval (one month), the second one aimed at estimating the amplitude of the overall error, which includes the instrumental error and the natural variability, through the assumption that such overall error follows a Gaussian distribution. The overall observed probability distribution function (pdf) can be decomposed into the sum of a Gaussian and a Gamma distribution with the Gaussian corresponding to the well-mixed state and the Gamma corresponding to the non-well-mixed state. The method has been originally applied to the analysis of long-lived compounds (namely, hydrochlorofluorocarbons). Nevertheless, such approach can also be used for compounds with lifetimes ranging from a few hours to a few days, under the condition that the distance among emission sources is up to 50–100 km, for compounds with lifetimes in the range of a few hours. Such distances can be greater for compounds with longer lifetimes. In other words, the emission field surrounding the receptor should be, at the mesoscale, discontinuous but distributed in an adequately homogeneous way. Such a condition is verified at CMN, as well as at the rural to remote continental European receptors. More details on the applicability of the method to the analysis of short-lived compounds is given in Appendix 1.

Yearly variability in the NMVOCs time series was calculated with the non-parametric seasonal Kendall test (Hirsch *et al.*, 1982). The test is based on the null hypothesis of no trend against the hypothesis of the existence of a trend. The level of statistical significance used here is 0.05. The polynomial reported in Simmonds *et al.* (2004) is employed to obtain the best fits of the monthly means of well mixed data, used to evaluate the seasonal cycles.

## RESULTS AND DISCUSSION

### *Long-Term Variability of NMVOCs at CMN*

The time series of the eleven NMVOCs monitored at CMN are reported in Fig. 1, where data pertaining to well-mixed conditions are indicated by the black dots, whereas grey dots identify concentrations corresponding to polluted air masses. In the past few years, several studies have been published reporting long-term NMVOC measurements in urban, rural and remote sites across Europe (Pluss-Dulmer *et al.*, 2007; Sauvage *et al.* 2009, von Schneidermesser *et al.*, 2010; Grant *et al.*, 2011). A direct comparison with NMVOC levels measured at CMN would not be feasible, because all the published data refer to studies that ended before the start of the measurements at CMN. Nevertheless, such comparisons could help in evaluating how changes in atmospheric concentration trends over different time frames can reflect the impact of the implementation of air pollution control policies (mainly based on vehicular traffic) on atmospheric composition at the European scale.

We have calculated 5-year (2010–2014) average mixing ratios and long-term variability (trends) of eleven NMVOCs monitored at CMN using background data only and all data. In Table 3 the average mixing ratios at CMN and at

other European remote, rural and urban sites reported in the recent literature are shown. Table 4 reports the respective long term variability (trends).

### *NMVOC Mixing Ratios*

At CMN propane is the dominant compound. As already observed in the United States by Russo *et al.* (2008), natural gas or LPG (liquefied petroleum gas) emissions have been identified as a major source of anthropogenic VOCs in the atmosphere of the Northern Hemisphere. In contrast, ethylbenzene and the xylenes show the lowest atmospheric concentrations. Benzene is the most abundant aromatic compound measured in the background air at CMN, followed by toluene, ethylbenzene and the xylenes. The presence of background concentrations of these highly reactive compounds is indicative of the presence of a number of widespread sources in the receptor domain.

In general, we observe that background mixing ratios at CMN are in line with the remote site of MHD. Because of the small atmospheric trends exhibited at the two sites, the difference in the time frames of the two contiguous measurement periods can be considered negligible. When considering the averaged whole data set, CMN exhibits concentration values that are in line with the European rural sites when we take into account the trend values reported in Table 4, and with MHD European air masses as reported in Grant *et al.* (2011) (not shown).

### *NMVOC Long Term Variability*

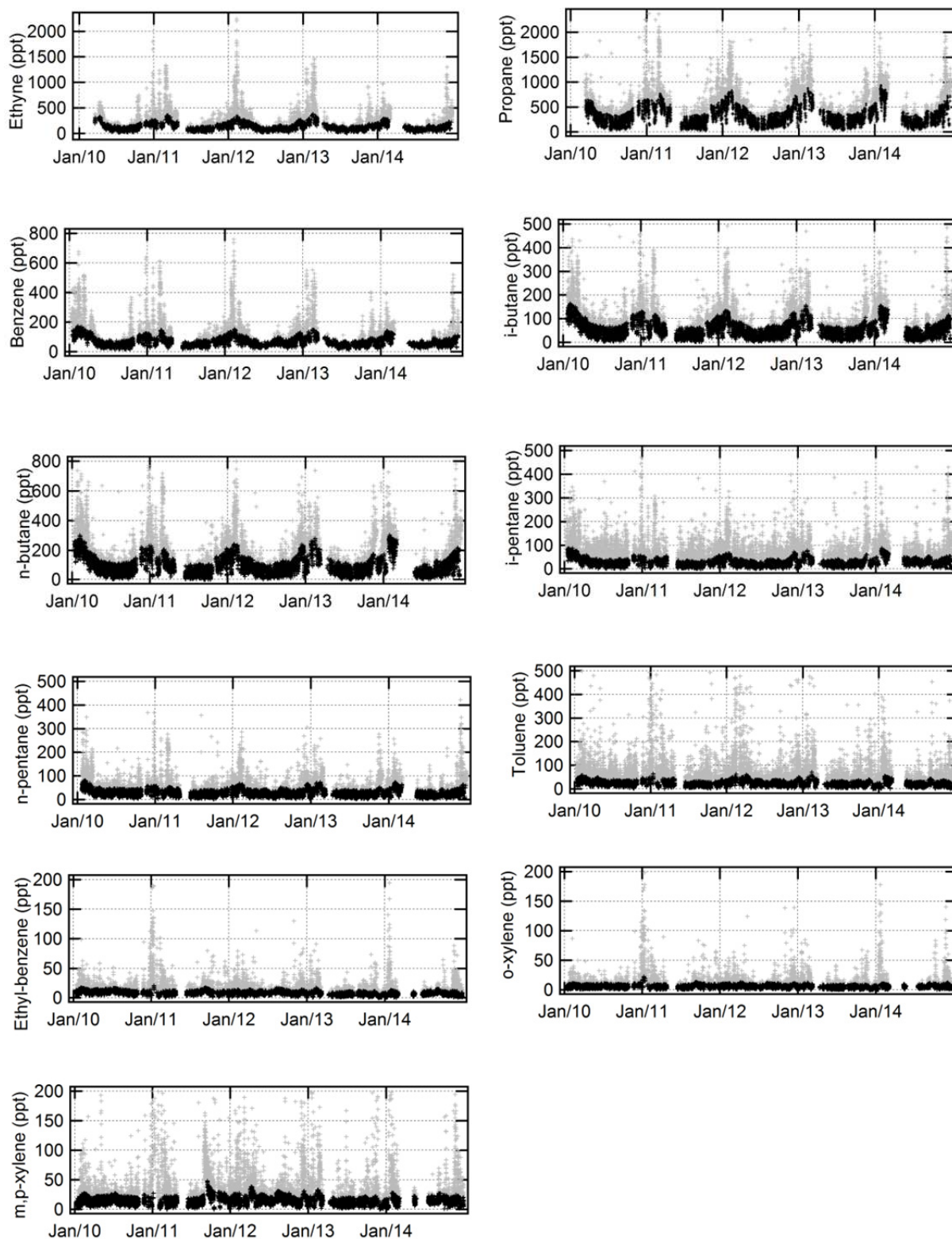
At CMN, over the 5-years of observations, an overall decreasing trend of the NMVOC atmospheric mixing ratios is observed. It should be noted that a five year period is not long enough to allow a robust evaluation of the atmospheric trends, as reflected in the low level of statistical significance that we found for some of the calculated trends, especially in the sub-set of the background data that includes fewer data with respect to the all-data set. Nevertheless, we report these data for comparison with other European records.

Atmospheric ethyne has dramatically decreased in Europe since the late 90s due to the emission reduction policies related to abatement measures on exhaust emissions from motor vehicles (Dollard *et al.*, 2007). When our measurements started, the reduction measures had been well established for more than a decade. Nevertheless, we still found a statistically significant decreasing trend in the background mixing ratios of 2.7% per year. This could be due to the slow turnover of the vehicle fleet regulated by the Euro vehicle emission regulations and the increased stringency in these regulations (Directive 91/441/EC and following directives and regulations), that led to an increase in the efficiency of catalysts in petrol-engined cars. An even larger decrease (5.6% per year) is found when all data are considered, reflecting a decrease of fresh emissions. However, this last value is not statistically significant, which is likely to be due to the larger variability in the all data set.

Although propane (both background and all data) does not exhibit a statistically significant trend at CMN, the values and the signs of the trends are similar to those recorded at other European sites, suggesting that similar causes

influence the CMN concentrations. Propane is emitted mainly from natural gas leakages and not from car exhaust, and emission reduction policies, that have mainly focused on the traffic sector have not affected to a large extent

anthropogenic propane emissions. This is also reflected by previous measurements carried out at rural/urban sites that recorded the smallest decreasing trend among all the compounds considered.



**Fig. 1.** NMVOC time series at CMN from January 2010 until December 2014. Black dots represent baseline data. Grey dots indicate enhancements above the baseline.

**Table 3.** Comparison between average NMVOC mixing ratios at CMN and other European sites.

Compound	European Remote						European Remote/Rural/Urban		
	Average mixing ratios: background only			Average mixing ratios: all data			Average mixing ratios: all data		
	CMN 2010–2014 this study	MHD (Grant et al., 2011) 2005–2009	CMN 2010–2014 this study All Data	Rural Germany (Pluss-Dulmer et al., 2007) 1999–2005	Rural French (Sauvage et al., 2009) 1997–2006	Rural UK (von Schneidmesser et al., 2010) 1998–2008	Urban UK (von Schneidmesser et al., 2010) 1998–2009		
Ethylene	115	-	185	518	521	230	1300		
Propane	291	263	406	602	672	610	2700		
Benzene	57	66	89	161	168	88	320		
i-butane	49	35	73	136	-	170	1200		
n-butane	90	95	139	239	371	260	2000		
i-pentane	49	27	84	172	210	140	1600		
n-pentane	23	26	42	89	111	81	540		
Toluene	33	-	109	125	163	120	1000		
Ethyl-benzene	7	-	15	21	33	36	140		
o-xylene	5	-	19	18	32	32	200		
m,p-xylene	12	-	38	43	69	59	790		

**Table 4.** NMVOC trends (% y<sup>-1</sup>) at CMN compared to urban rural and remote sites across Europe.

Compound	European Remote Background						European Remote/Rural/Urban		
	Average mixing ratios: background only			Average mixing ratios: all data			Average mixing ratios: all data		
	CMN 2010–2014 this study	MHD (Grant et al., 2011) 2005–2008	CMN 2010–2014 this study All Data	Rural Germany (Pluss-Dulmer et al., 2007) 1999–2005	Rural French (Sauvage et al., 2009) 1997–2006	Rural UK (von Schneidmesser et al., 2010) 1998–2008	Urban UK (von Schneidmesser et al., 2010) 1998–2009		
Ethylene	-2.7 <sup>a</sup>	-	-5.6 <sup>b</sup>	-3 <sup>a</sup>	-	-7 <sup>a</sup>	-15 <sup>a</sup>		
Propane	0.6 <sup>b</sup>	6 <sup>b</sup>	-4.5 <sup>b</sup>	-4 <sup>a</sup>	-	-3 <sup>a</sup>	-3 <sup>a</sup>		
Benzene	-1.2 <sup>b</sup>	-1 <sup>a</sup>	-1.3 <sup>b</sup>	-4 <sup>a</sup>	-4 <sup>b</sup>	-12 <sup>a</sup>	-26 <sup>a</sup>		
i-butane	-1.3 <sup>b</sup>	1 <sup>b</sup>	-3.1 <sup>a</sup>	-6 <sup>a</sup>	-	-	-14 <sup>a</sup>		
n-butane	-2.4 <sup>b</sup>	<1 <sup>b</sup>	-3.6 <sup>b</sup>	-5 <sup>a</sup>	-	-6 <sup>a</sup>	-17 <sup>a</sup>		
i-pentane	1.2 <sup>b</sup>	<1 <sup>b</sup>	-3.5 <sup>a</sup>	-6 <sup>a</sup>	-4 <sup>a</sup>	-8 <sup>a</sup>	-		
n-pentane	-5.7 <sup>a</sup>	<1 <sup>b</sup>	-2.7 <sup>a</sup>	-5 <sup>a</sup>	-	-2 <sup>a</sup>	-12 <sup>a</sup>		
Toluene	-3.3 <sup>b</sup>	-	-3.6 <sup>a</sup>	-6 <sup>a</sup>	-6 <sup>a</sup>	-9 <sup>a</sup>	-22 <sup>a</sup>		
Ethyl-benzene	-8.7 <sup>a</sup>	-	-1.2 <sup>a</sup>	-8 <sup>a</sup>	-	-3 <sup>a</sup>	-25 <sup>a</sup>		
o-xylene	-3.0 <sup>b</sup>	-	-0.2 <sup>b</sup>	-9 <sup>a</sup>	-	-3 <sup>a</sup>	-23 <sup>a</sup>		
m,p-xylene	-3.7 <sup>b</sup>	-	-0.1 <sup>b</sup>	-8 <sup>a</sup>	-	-5 <sup>a</sup>	-20 <sup>a</sup>		

a = level of significance < 0.05; b = not statistically significant.

For benzene, decreasing trends are observed at CMN during 2004–2014 of 1.2 and 1.3% in the background and in the all data set, neither of which is statistically significant. This lack of statistical significance and the low absolute values suggest that benzene levels have now reached a steady state in the remote atmosphere and also that fresh emissions influencing CMN are not varying over the measurement period. Benzene is the most regulated among the monitored compounds, and stringent reduction measures in Europe have been implemented two decades ago on its use as solvent and feedstock (1488/94 Commission Regulation, 200/69/CE European Directive) and in the reformulation of gasoline content and the use of catalytic converters in exhaust systems of petrol-engined vehicles (1998/70/CE European Directive). That is reflected in the decreasing trends recorded at urban sites during the first decade of this century (von Schneidmesser *et al.*, 2010), and which are much faster than those observed in recent years at remote sites (Grant *et al.*, 2011 and this work).

C<sub>4</sub>-C<sub>5</sub> alkane background trends are not statistically significant except for n-pentane. In the all-data set the decrease is around 3% per year, a value that is statistically significant with the exception of n-butane. This behaviour of C<sub>4</sub>-C<sub>5</sub> alkanes, that are the main components of evaporated petrol, is consistent with reduction measures set by the EU legislation. The first Directive (94/63/EC) on the control of VOC emissions resulting from the storage of petrol and its distribution from terminals to service stations was followed in 2009 by further reduction measures (set by Directive 2009/126/EC) on Stage II petrol vapour recovery during refuelling of motor vehicles at service stations. It is likely that these latest reduction measures are responsible for the downward trend that we are still observing. The reason why n-pentane shows a statistically significant decrease of 5.7 in the background data and a smaller decreasing rate

(2.7%) in the whole set it is not clear and suggests that local sources impacting CMN are changing more slowly than those in the wider European region.

For toluene (all data) the trend observed at CMN is –3.6% per year. This is consistent with the EU VOC Solvent Emission Directive (1999/13/CE European Directive with amending) limiting NMVOCs used in the formulation of organic solvents. We have not observed statistically significant changes in the toluene baseline values.

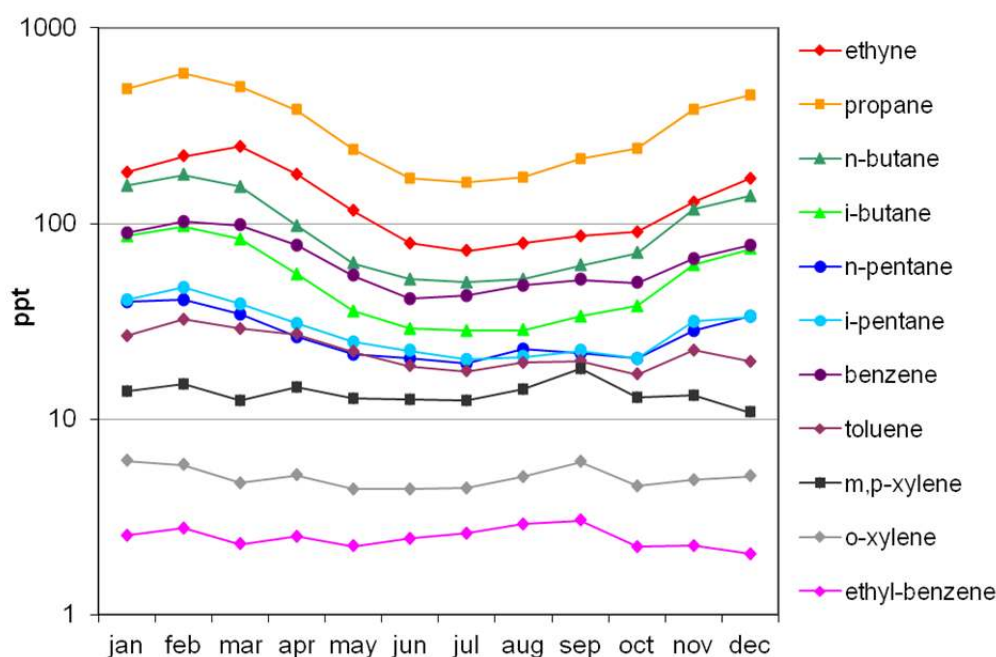
A similar behaviour is observed for ethyl-benzene, with a statistically significant decreasing trend of 8.7 and 1.2% per year in the background and all data set, respectively, an indication that the local sources impacting the CMN are changing more slowly than those contributing to the background. This could be ascribed to the differences in behaviour of the emission sources, in particular the solvent sector which is mainly responsible for the emissions of this compound.

At CMN the xylenes decreasing trends, both all data and background data, are not statistically significant.

### Seasonal Cycle of NMVOCs

Fig. 2 shows the observed background seasonal variability of NMVOCs at CMN together with the best fit of the data. The least reactive species (ethyne, propane, benzene, butanes and pentanes) show significant seasonal variations with maxima in wintertime (December, January and February - DJF) and minima in summertime (June, July and August - JJA), consistent with the OH removal mechanism. More reactive species, toluene, ethyl benzene and xylenes show a much smaller seasonal variability, as already observed by other authors (Moschonas and Glavas, 2000; Li *et al.*, 2005).

In contrast to Derwent *et al.* (2012), who described at MHD a faster spring-summer decline for the more reactive compounds, the background monthly average mixing ratios of



**Fig. 2.** Seasonal Cycles of NMVOCs at CMN, monthly averages of background data, over 2010–2014 (typical year).

the fast-reacting compounds recorded at CMN did not show the same early decline but, on the contrary, seasonal cycles become less pronounced with increasing OH-reactivity.

In order to understand this behaviour, we plotted the relative winter maxima, i.e., the ratio of winter seasonal maximum to average mixing ratio, against the OH reaction rate coefficients. As can be seen in Fig. 3 the plot shows how relative winter maxima decrease steadily with increasing OH-reactivity.

Considering that the NMVOC atmospheric lifetimes determine the range of transport from the source region, it can be hypothesized that in summertime NMVOCs with shorter atmospheric lifetimes would be less influenced by air mass history and more influenced by European emissions with respect to long-lived species. Ethyne, propane, benzene, butanes and pentanes have a relatively low reactivity with OH radicals and their background mixing ratios depend more on long range transport than on regional emissions. Due to their relatively long lifetimes, they might also be emitted in other continents and oxidized during transport. Toluene, ethyl-benzene and xylenes, being very reactive species, react close to their sources and their background mixing ratios are determined mainly by European emission source strengths. The impact of European sources on the NMVOC mixing ratios is therefore greater for the more reactive compounds, explaining the decrease in the seasonal variability with the increase in reactivity with OH radicals. Furthermore, aromatic compounds like toluene, ethyl-benzene and xylenes, being major components of solvents might also have a higher evaporative release during the warmer months (Liakakou *et al.*, 2009).

### Impact of Photochemistry

In order to further investigate the impact of OH radical on the NMVOCs seasonal cycles, we have compared the alkanes monthly means in the well-mixed (baseline) data

observed at CMN with the baseline data at MHD, situated on the eastern edge of Atlantic. As can be seen from Table 5 the average winter maxima at the two stations are within an order of magnitude but the average summer (minima) concentrations at CMN are at least one order of magnitude higher than those recorded at MHD. Differences in the absolute magnitude of seasonal cycles can be attributed to the distinct features of the two sites, in terms of location and transport regimes.

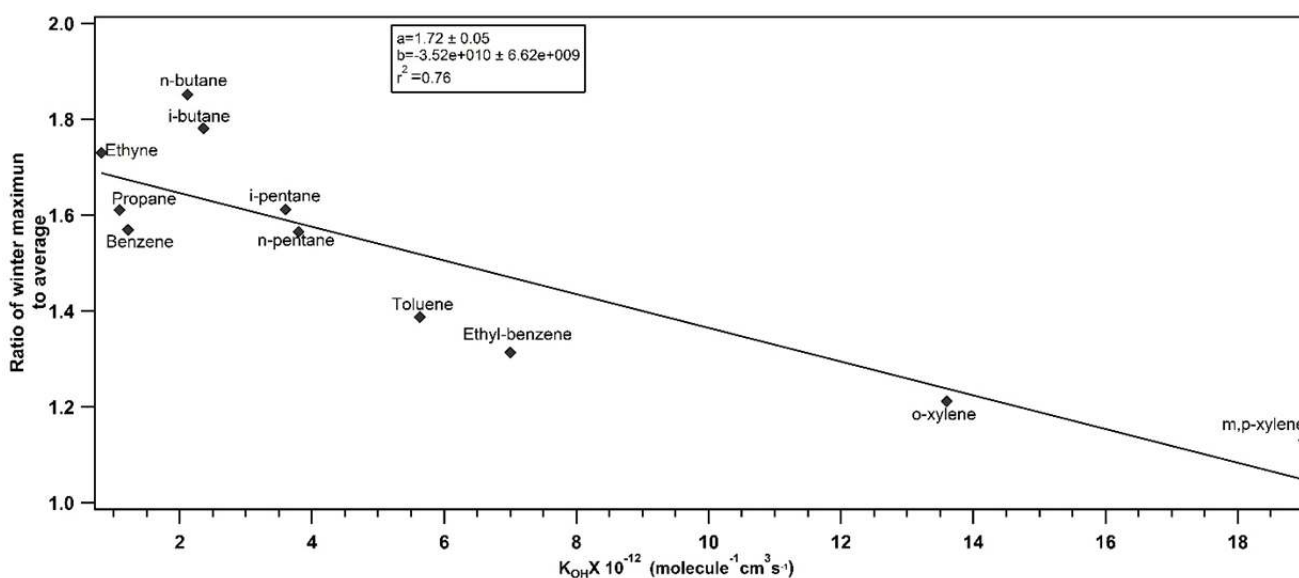
The ‘photochemical clock’ model proposed by Rudolph and Johnen, 1990, can be used to describe the seasonal cycle and to verify/check the extent to which the mixing ratios of these alkanes have been depleted by OH oxidation. This simple model is based on the assumptions that 1) in winter the light alkanes, like propane and ethane (this last not measured at CMN), are scarcely affected by OH oxidation; 2) the transport to the receptor occurs in the absence of mixing with fresh emissions (i.e., baseline conditions are occurring). If these two assumptions were valid, the mixing ratios measured at the receptor would reflect the impact of the OH sink.

The rate of removal of a generic alkane AH is described by Eq. (1). Taking the winter maximum as the initial concentration  $[AH]_0$ , we obtain the monthly time integrated OH radical concentration  $[OH]_t$ , Eq. (2).

$$d[AH]/dt = -k[OH][AH] \quad (1)$$

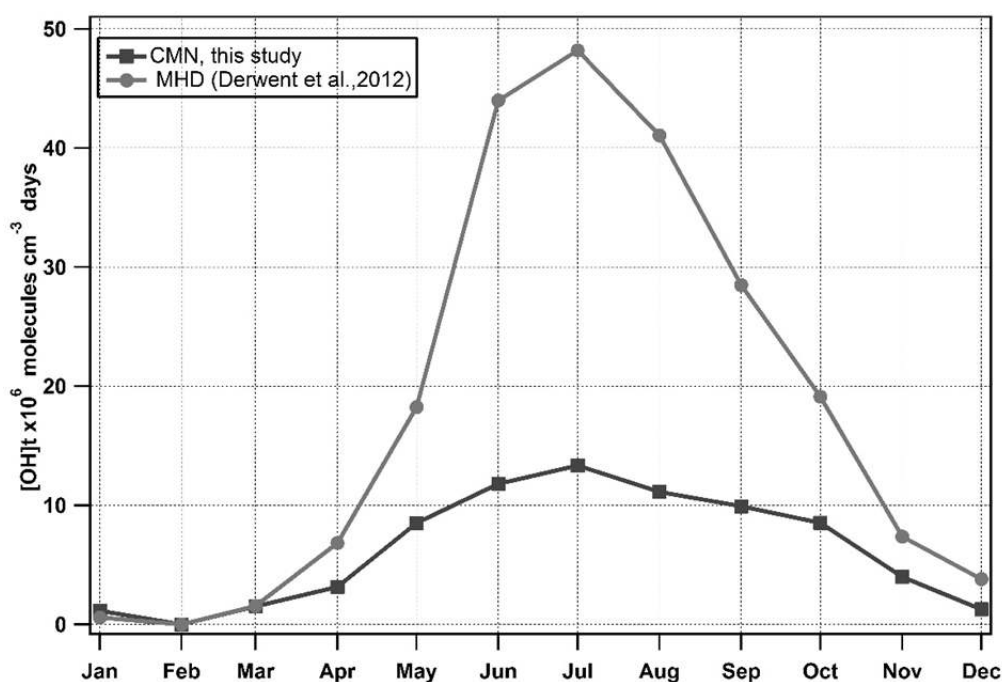
$$\ln([AH])/[AH]_0 = -k[OH]t \quad (2)$$

We used propane because, due to its lower reactivity with OH radicals compared to the other VOCs, it is possible to hypothesize that during the winter its oxidation is negligible, while for the butanes and pentanes it becomes significant. Fig. 4 shows a comparison of the seasonal cycles of the time-integrated OH radical concentrations  $[OH]_t$  obtained



**Fig. 3.** Linear fit of winter maxima (background data) of the observed seasonal cycles of NMVOCs versus their OH rate coefficients.





**Fig. 4.** Comparison between time-integrated OH concentrations estimated at CMN (2010–2014) (black line) and MHD (2005–2009) (grey line).

with the propane ‘clock equations’ at MHD (Derwent *et al.*, 2012) and at CMN. The plot shows a good agreement at the two stations for [OH]*t* during the winter months, while during the summer at CMN the [OH]*t* is up to five times lower than at MHD. This result does not necessarily provide evidence of differences in [OH] concentration at the two sites. Rather an indication of the different transport times to the receptors and different source distribution: at CMN in summertime the propane background mixing ratios are also influenced by emissions characterised by short-to-medium range transport time from all directions, intercepting one of the most populated and industrialised regions in Europe, whereas at MHD baseline levels mostly correspond to long range transport across the North Atlantic Ocean.

## SUMMARY AND CONCLUSIONS

In Europe, whilst a number of sporadic NMVOC measurement campaigns at background sites have been made, and some long-term records do exist, most routine and long-term observations continue to be focused on urban centres, reflecting concerns over air quality and population exposures. However, increasing efforts are made to establish trends in the background atmosphere through the WMO Global Atmosphere Watch programme. In this article we report five years of NMVOC observations conducted at a southern European mountain site and we discuss their annual and seasonal variability. The characterisation of the NMVOCs at remote locations is important for the understanding of the impact of changes in emissions on a regional scale. Toluene, xylenes and ethyl-benzene are useful in checking the strength of the ‘solvent use’ sector. Propane, ethyne and benzene, are used as indicators of the

degree of emissions linked to fossil fuel consumption. NMVOC background mixing ratios at CMN show a slight decrease in the period 2010–2014, probably due the emission controls implemented in Europe during the past two decades. A seasonal variation in the background concentrations at CMN is observed with winter maxima and summer minima. The investigation of NMVOC seasonal cycles at CMN has highlighted the influence of European emissions on the atmospheric composition and the dominant role of mixing in accounting for the seasonal changes in NMVOC levels.

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## APPENDIX

Here we discuss some details of the method proposed for the identification of the background concentrations of

short-lived compounds such as NMVOCs. First we summarise the constraints for the well-mixed condition. A well-mixed state is reached when the concentration produced by an emission is homogeneous over the whole domain: i.e., measuring the concentration at a given point in the domain in subsequent times, a Dirac delta probability density function (pdf) is obtained. In the case of real measurements, the pdf is not a Dirac delta but a Gaussian whose  $\sigma$  (standard deviation) is given by the instrumental error. The homogeneity of the concentration field is reached under the conditions that the domain is confined and that the source is not emitting anymore or, with a weaker constraint, that many time scales  $T_S$  have passed since the release, where  $T_S$  is the time scale representative of the largest spatial scale in the domain. Going from the theoretical to the real case, the spatial distribution of a concentration given by an emission source in a confined domain after many  $T_S$  (i.e.,  $t \gg T_S$ ) will never be homogeneous but will be approximated by a flat Gaussian (characterised by a large  $\sigma$  values). The concentration measured as a function of time in a point of the domain is not distributed as a Dirac delta, but as a Gaussian that is the narrower, the closer the theoretical conditions are met.

In general, the pdf of the concentration measured in a given point in the domain is then given by a Gaussian (sum of all Gaussians produced by the sources, whose contributions are “quasi” well mixed), and by a second distribution that includes the contributions of those sources whose emissions are not giving rise to well-mixed concentrations. In the method proposed by Giostra *et al.* (2011) we assume that this second pdf can be described by a gamma distribution (but a lognormal pdf could be used as well to describe this distribution).

But, which value  $T_S$  has in the free troposphere? Keeping in mind the free troposphere can be, as a first approximation, characterised by quasi 2D turbulence, and keeping in mind the temporal scale of intra-hemispheric phenomena,  $T_S$  is  $15\text{dd} < T_S < 60\text{ days}$ . In other words, since the well mixed condition can be reached only when  $t \gg T_S$ , we can consider as being well mixed only those concentrations given by those compounds that, after having been emitted, travelled for times much greater than those defined above before reaching the receptor.

Can Compounds with lifetime  $\tau \ll T_S$  (as in the case of NMVOCs in summertime) produce a background concentration in the above sense? This is true if further conditions/approximations are respected.

The need of a quasi-homogeneous concentration in the domain can be satisfied (as a first guess), assuming that the distance between two contiguous sources is smaller than the spatial scale typical of the relative dispersion of the single sources. Here we assume that the sources have the same strength. It should be useful, but not necessary, to define the concept of equivalent source, i.e., those sources that, independently from their strength and distance from the receptor, give rise to equivalent average mixing ratios at the receptor.

A spatial distance between two sources up to  $L < 2\sigma_x$  represents a sufficient condition to produce in the domain

(for a practical use, in the neighbourhood of the receptor) a quasi-homogeneous concentration profile. Here  $\sigma_x^2$  represents the mean square separation for two particles simultaneously released from an emission source. In 2D turbulence,  $\sigma_x^2$  is described as:

$$\sigma_x^2(t) \approx e^{t/1.35} \text{ (Wells } et al., 2008) \text{ for } t \ll T_S.$$

The exponential behaviour of the separation at short times is consistent with the inertial range of the enstrophy in 2D turbulence. For  $t \ll T_S$  (i.e., 1–2 hours) we obtain that sources at a distance  $L$  up to 50–100 km ( $2\sigma_x$ ) will produce at the receptor a quasi-homogeneous concentration spatial profile. Therefore, the contributions of these sources as a function of time will follow a Gaussian pdf, representing the well-mixed state at the receptor. The proposed method is able to distinguish the mixing ratio values referring to the Gaussian pdf (background) from those referring to a gamma pdf (not well mixed state).

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