

**A five year record of  
NMHC measurements  
at Mace Head**

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# A five year record of high-frequency in situ measurements of non-methane hydrocarbons at Mace Head, Ireland

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## Abstract

Continuous high-frequency in situ measurements of a range of non-methane hydrocarbons have been made at Mace Head since January 2005. Mace Head is a background Northern Hemispheric site situated on the eastern edge of the Atlantic. Five year measurements (2005–2009) of eleven non-methane hydrocarbons, namely C<sub>2</sub>–C<sub>5</sub> alkanes, benzene, toluene, ethyl-benzene and the xylenes, have been separated into baseline Northern Hemispheric and European polluted air masses, among other sectors. Seasonal cycles in baseline Northern Hemispheric air masses and European polluted air masses arriving at Mace Head have been studied. Baseline air masses show a broad summer minima between June and September for shorter lived species, longer lived species show summer minima in July/August. All species displayed a winter maxima in February. European air masses showed baseline elevated mole fractions for all non-methane hydrocarbons, largest elevations (of up to 360 ppt for ethane maxima) from baseline data were observed in winter maxima, with smaller elevations observed during the summer. Analysis of temporal trends using the Mann-Kendall test showed small (<6%/year) but statistically significant decreases in the butanes, i-pentane and o-xylene between 2005 and 2009 in European air. Toluene was found to have an increasing trend of 34%/year in European air. No significant trends were found for any species in baseline air.

## 1 Introduction

The role of non-methane hydrocarbons (NMHCs) in the production of tropospheric ozone was first reported in 1956 by Haagen-Smit and Fox NMHC as a classification includes alkanes, alkenes, alkynes and aromatic species, all of which form ozone by reaction with the hydroxyl radical (OH) in the presence of nitrogen oxides (NO<sub>x</sub> where NO<sub>x</sub> = NO+NO<sub>2</sub>). NO<sub>x</sub>, which is emitted mainly by fossil fuel combustion, is an essential component in the ozone formation cycle, in the absence of NO<sub>x</sub> ozone cannot

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be formed in the troposphere. Tropospheric ozone is a harmful pollutant which has negative effects on human health and vegetation. Background tropospheric ozone in the Northern Hemisphere has been reported to be increasing by 0.49 ppb/year with a current background Northern Hemispheric mole fraction of  $\sim 42$  ppb (Simmonds et al., 2004). To assess if recent increases in tropospheric ozone can be linked to changes in NMHC mole fractions one needs to analyse a long-term record of NMHC measurements. These measurements must be made at a background location to minimise the effects of local pollution on data and enable effective analyses of long-term trends and seasonal cycles. It is difficult to elucidate trends and seasonal cycles from urban measurement records because of almost continually elevated NMHC mole fractions from local pollution.

This paper reports on continuous high-frequency measurements of a range of NMHCs conducted at Mace Head from January 2005 to December 2009. These measurements extend those reported by Yates et al. (2010) from January 2005 to December 2006. This longer dataset enables the assessment of long-term trends of NMHC species. NMHCs reported include  $C_2$ – $C_5$  alkanes, isoprene, benzene, toluene, xylenes and ethyl-benzene. These data provide information on long-term trends and seasonal cycles of NMHCs in background Northern Hemispheric air. Individual measurements are sorted using a Lagrangian dispersion model to separate clean background air from regionally polluted European air masses and those transported from southerly latitudes. Yearly and seasonal trends are assessed and variations and anomalies in baseline air masses accounted for.

## 2 Experimental

### 2.1 Measurement location

The Mace Head atmospheric research station ( $53^{\circ}20' N$ ,  $9^{\circ}54' W$ ) is situated on the west coast of Ireland (Fig. 1). At the station, numerous ambient air measurements

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are made as part of the Advanced Global Atmospheric Gases Experiment (AGAGE) (Cunnold et al., 1997; Prinn et al., 2000) and the Global Atmospheric Watch network (GAW). It is one of only a few clean background western European stations, thus providing an essential baseline input for inter-comparisons with continental Europe, whilst also acting as a baseline site representative of Northern Hemispheric air. Prevailing winds from the west to southwest sector bring clean background air to the site. Polluted European air masses as well as tropical maritime air masses cross the site periodically. Mace Head is therefore uniquely positioned for resolving these air masses and for comparative studies of their constitution. Galway is the closest city, with a population of 72 000, sitting 50 km to the east whilst the area immediately surrounding Mace Head is very sparsely populated providing very low local anthropogenic emissions. The sample inlet is located 10 m inland from the shoreline, sampling at 10 metres above sea level, through stainless steel lines attached to a meteorological tower. The area surrounding Mace Head is generally wet and boggy with areas of exposed rock (Dimmer et al., 2001).

## 2.2 Instrumentation

The system couples an Agilent 6890 gas chromatograph (GC)/5973 mass selective detector (MSD) with a low-temperature, cryogen-free pre-concentration system (Medusa). This self-contained cryogenic technology is essential due to the inaccessibility of field locations and difficulty of obtaining consumables such as liquid nitrogen. The ambient air sample inlet is situated 10 m up a 20 m high tower. Ambient air is flushed through an inlet line, made of 1/4 instrument-grade stainless steel tubing, a portion of this air is delivered to the Medusa inlet where a backpressure regulator controls the sample pressure at 1.5 bar and vents at ~2 L/min (Miller et al., 2008). Analysis of each 2 L sample of ambient air was alternated with analysis the same volume of reference gas (also delivered to the Medusa at 1.5 bar) to determine and correct for short term instrumental drift, resulting in 12 fully calibrated air samples per day. At the heart of the Medusa is a Polycold “Cryotiger” cold end which maintains a minimum trapping

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temperature of  $-175^{\circ}\text{C}$ , even with a substantial heat load, using a simple single-stage compressor with a proprietary mixed-gas refrigerant. This cold end conductively cools a copper baseplate which supports two traps to about  $-165^{\circ}\text{C}$ . By using aluminium standoffs of limited thermal conductivity to connect the traps to the cold head, each trap can independently be heated resistively to any temperature from  $-165^{\circ}\text{C}$  to  $+200^{\circ}\text{C}$  or more, while the baseplate remains cold. The use of two traps with extraordinarily wide programmable temperatures ranges, coupled with the development of appropriate trap absorbents, permits the desired analytes from 2 L air samples to be effectively separated from more-abundant gases in the air matrix that would otherwise interfere with chromatographic separation or mass spectrometric detection, such as  $\text{N}_2$ ,  $\text{O}_2$ , Ar,  $\text{H}_2\text{O}$ ,  $\text{CO}_2$ ,  $\text{CH}_4$ , Kr and Xe. Importantly, the dual traps also permit the analytes to be purified of interfering compounds by fractional distillation and re-focusing from the larger first-stage trap (T1) onto a smaller trap (T2) at very low temperatures, so that the resulting injections to the Agilent 5973 GC-MS are sharp and reproducible. A detailed description of Medusa sampling is presented in Miller et al. (2008).

The instrument is controlled by GCWerks™ custom designed software (<http://gcwerks.com/>) which automates all the instrument parameters (valves, trap temperatures, MSD etc.), displays chromatograms, performs peak integration and gives graphical and tabulated displays of all results. For maximum sensitivity in routine field monitoring the MSD is operated in Selective Ion Monitoring (SIM) mode. This cycles the MSD through selected target and qualifier ion masses during the specified windows of elution in the chromatogram.

In this study, hydrocarbon measurements carried out at Mace Head since 2005 are reported. The Medusa-GCMS which measures NMHCs was originally developed to make high frequency in situ measurements for the determination of atmospheric lifetimes and emissions of various compounds related to the Montreal and Kyoto Protocols. The Medusa measures a wide range of halocarbons, NMHCs and sulfur compounds involved in ozone depletion and climate forcing (Miller et al., 2008). A network of five Medusa systems are located at remote field stations around the world (Mace

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Head, Ireland; Ragged Point, Barbados; Cape Grim, Tasmania; Cape Mataula, American Samoa; and Trinidad Head, California) operated by the Advanced Global Atmospheric Gases Experiment (AGAGE) since 2003 providing 12 in situ ambient measurements per day (<http://agage.eas.gatech.edu/>). The Medusa-GCMS at Mace Head initially measured the NMHCs; ethane, benzene and toluene. The suite of NMHCs measured was extended in 2005 by Yates (2007) to also include: propane, n-butane, i-butane, n-pentane, i-pentane, isoprene, ethyl-benzene, m and p-xylene and o-xylene. Modifications made to the Medusa-GCMS to extend the number of compounds measured are detailed in Yates (2007). NMHC measurements are limited in number in order to leave the Medusa-GCMS AGAGE measurements of CFCs, PFCs, HFCs, HCFCs and SF<sub>6</sub> uncompromised. It is essential that any additional measurements do not interfere with measurements of AGAGE core species. Alkene measurements are recorded using this system, but research shows that there is production of alkene artefacts from the Nafion drier (pentene and butenes) (Boudries et al., 1994). Since the Medusa-GCMS uses two Nafion driers to dry air samples prior to pre-concentration alkene measurements have not been attempted with this system.

Ethane was detected with the MSD in selected ion monitoring mode (SIM) using a target ion, C<sub>2</sub>H<sub>2</sub><sup>+</sup> (*m/z* 65), propane C<sub>3</sub>H<sub>5</sub><sup>+</sup> (*m/z* 41), i-butane C<sub>3</sub>H<sub>6</sub><sup>+</sup> (*m/z* 43), n-butane, i-pentane and n-pentane C<sub>2</sub>H<sub>2</sub><sup>+</sup> (*m/z* 65), benzene C<sub>6</sub>H<sub>6</sub><sup>+</sup> (*m/z* 78), toluene, ethylbenzene, o-, m-, p-xylene C<sub>7</sub>H<sub>7</sub><sup>+</sup> (*m/z* 91). Blanks and laboratory air were measured weekly to check for contamination of the instruments working environment. Blank corrections were applied to benzene and toluene based on average blank concentration over specific time periods using the GCWerks™ software. Instrument precision is an indicator of the detectors response over a period of time. Precision was calculated from the standard-standard ratios of concurrent standard analyses. Table 1 shows precisions and limits of detection of the range of NHMCs measured where the limit of detection is calculated as three times of the mean blank. NMHC measurements from another AGAGE Medusa GC-MS instrument situated at the Scripps institution of Oceanography, USA have been reported by Mühle et al. (2007).

## 2.2.1 Calibration

Working standards (quaternary standards) are prepared by compressing background ambient air at Mace Head, into 35 L electropolished stainless steel canisters (Essex Cryogenics, Missouri, USA) using a modified oil-free compressor (SA-3, RIX California, USA). This ensures that NMHC mole fractions in quaternary standards are close in concentration to air sample values at Mace Head minimising sample matrix non-linearities. The quaternary standards are used to bracket each air measurement in an attempt to minimise detector response non-linearities. In addition tertiary standards (air filled at Trinidad Head, California and calibrated for halocarbons at Scripps Institution of Oceanography (SIO) against their primary calibration scales) are analysed weekly against the quaternary standards. The quaternary working gases are calibrated over the course of their use in the field by analyses against the tertiary standards. The NMHC quaternary calibration is linked by analysis of tertiary standards against an NMHC primary standard (O'Doherty et al., 2004). The NMHC primary standard was made by accurate volumetric dilution of a ppb mole fraction synthetic standard (Apel Reimer USA) to ppt mole fractions, to mimic ambient NMHC mole fractions observed at this background site. Analysis of the NMHC primary standard against each new tertiary standard from SIO enables application of NMHC mole fractions measured on the Medusa.

## 3 Results

NMHC species measured by the Medusa-GCMS include; ethane, propane, i-butane, n-butane, i-pentane, n-pentane, benzene, toluene, ethyl-benzene, concomitant m and p-xylene and o-xylene. NMHC data from January 2005 to December 2009 is shown in Fig. 2. These data were sorted into air mass origins using the NAME Lagrangian atmospheric dispersion model (Jones et al., 2007) using the technique described in Manning et al. (2003). This classified measurements into different sector types:

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baseline (westerly or north westerly airflow), European polluted, southerly transport, mixed (when air was from a variety of sectors), and local (times when there were low wind speeds and stable air so sources and sinks in the local region would significantly impact the observations).

To calculate air mass sectors the NAME dispersion model is run backwards to estimate the recent history (12 days) of the air en-route to Mace Head. Baseline mole fractions are defined as those which have not been influenced by significant emissions within the previous 12 days of travel en-route to Mace Head, i.e. those that are well mixed and representative of the mid-latitude Northern Hemisphere background mole fractions. European air masses are those which have travelled from mainland Europe, the UK and Ireland. Further details of this sorting method can be found in Manning et al. (2011).

### 3.1 Long term trends and elevations

Many studies have reported marked decreases in the mole fractions of NMHCs measured in mainland Europe and the UK between the 1990s and 2000 (Derwent et al., 2003; Dollard et al., 2007; Dore et al., 2007; Solberg et al., 2002). This decrease in observed mole fractions was brought about by a reduction in hydrocarbon emissions resulting from the implementation of the Geneva Protocol to the Convention on Long-Range Transboundary Air Pollution CLRTAP (UN ECE, 1991, [http://www.unece.org/env/lrtap/vola\\_h1.htm](http://www.unece.org/env/lrtap/vola_h1.htm)) with the aim of reducing emissions of ozone precursors. The Gothenburg multi-pollutant Protocol (UN ECE, 1999, [http://www.unece.org/env/lrtap/multi\\_h1.htm](http://www.unece.org/env/lrtap/multi_h1.htm)) was set-up eight years later with the same aim. Reductions were primarily made in the transport sector through improvements in engine systems and installation of 3-way catalysts, reducing emissions of both VOC and NO<sub>x</sub>. Solberg et al. (2002) reported decreases in VOC concentrations of 20–50% from 1993–2000 at two central European EMEP sites. However, in the same report an absence of trend was found at two rural Finnish sites, one of which (Pallas) is reported in Table 2 (Hakola et al., 2006).

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To estimate long-term variation in hydrocarbon data the non-parametric Mann-Kendall test for the existence of a trend was used (Gilbert, 1987; Salmi et al., 2002). The Mann-Kendall tests the null hypothesis of no trend against the alternative hypothesis that there is an increasing or decreasing monotonic trend as described by Salmi et al. (2002). Results of the Mann-Kendall test are shown in Table 2, where percentage change is the slope of the linear trend relative to the first year of measurements and is shown with other trend data from recent literature.

Benzene and toluene in Europe have been reported to be decreasing in the years up to 2000. Table 2 displays trend data from across the period we have studied and other non-comparable data which shows trends prior to 2005 (Dollard et al., 2007; Sauvage et al., 2009; Helmig et al., 2009). Results from Mace Head in both baseline and European air masses do not show significant downward trends for benzene or toluene. Benzene is emitted from petrol-engine motor vehicle exhaust with a small contribution from evaporation. On closer inspection benzene decreases reported in literature are much less significant after 2000. This is due to stricter regulations on car exhaust gas emissions and gasoline transport and distribution (1998/70/CE European directive). Dollard et al. (2007) reported a large decrease in benzene of 20% per year from rural UK sites between 1995 and 2001. Sauvage et al. (2009) reported a decrease of 3.5% per year from three rural French sites from 1997–2006 but highlighted that this trend was much more significant prior to 2000, as Derwent et al. (2000) reported a decreasing trend of 11.4% per year from 1990–2000. Results by Helmig et al. (2009) show a decrease of 7% per year from 1999–2009, although it is unclear how this trend was calculated. It appears that monthly mean values from daily flask samples were used with a sine curve superimposed on these data from which a linear trend was calculated. It is not clear whether the trend was constant throughout the period studied. Our data show insignificant benzene decreases of 1% per year in baseline and European air masses. Subarctic data from Hakola et al. (2006) also observes no significant trend from 1994–2003. Toluene is emitted from solvent use and is considered the fourth most important organic compound for peak ozone formation by mass emission in Europe (Derwent et

al., 2003). Our toluene data shows upward trends of 42% and 34% per year in baseline and European air masses respectively with the European increase having a 90% significance level. These results are contrary to those reported by other studies in Table 2 and unexpected as strict regulations on emissions due to solvent use were adopted by all EU countries in 1999 (1999/13 European directive). Our ethyl-benzene data also show a significant upwards trend, in line with toluene, and again we have no simple explanation for the observed trend.

Other significant trends are seen for i-butane and n-butane in European air masses with decreases of 5 and 2% per year respectively with 90 and 95% levels of significance. The pentanes both show decreases of 4% per year. These results are in agreement with regulations as the principle source of butanes and pentanes is from the evaporation of motor spirit which has been reduced in recent years due to the introduction of more efficient fuel canisters in motor vehicles (Dollard et al., 2007). As expected no significant trends are seen for ethane and propane which are primarily emitted from natural gas leakage and not from motor vehicles.

We note that monthly averaged baseline data showed elevations of ethane, propane, the butanes and the pentanes from January until June of 2008. However, these elevations were not found to be statistically significant thus further work was not carried out into the source of this anomaly.

### 3.2 Seasonal cycles

Seasonal cycles of alkane and aromatic species can be seen in Fig. 3. Maximum concentrations are observed in January and February and minima for slowly reacting compounds in July. More reactive compounds (butanes, pentanes, toluene and the xylenes) show a much broader summer minima from June right through to September in many cases. Ethane shows the most pronounced seasonal cycle followed by propane, n-butane and i-butane. From visual inspection of the aromatic species benzene displays the most pronounced seasonal cycle followed by toluene and then the substituted aromatics (ethyl-benzene, m+p-xylene and o-xylene). Variation in the amplitude of seasonal cycles occurs due to differing reactivity of hydrocarbon species.

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Hydrocarbon data from other remote Northern Hemispheric background sites are sparse. A Finnish study reported measurements of a range of NMHCs from a maritime site, Pallas, in the subarctic (Hakola et al., 2006). This site primarily receives clean air from the north and west where winter maxima and summer minima values are used for comparison in Table 4. Winter maxima values are always lower at Mace Head than at Pallas. The higher latitude of Pallas means it consequently receives many less hours of sunlight in winter months thus reducing removal by OH oxidation and photolysis compared with Mace Head. Summer minima show significant variation between baseline and European air masses as well as other European stations. Other data included in Table 4 comes from a maritime cruise which took place in the Arctic in August, 1999 (Hopkins et al., 2002). These data have been filtered to include only air masses which have not passed over land for at least 5 days prior to sampling. Hydrocarbon measurements made at Mace Head during a summer campaign in 1996 included in Table 4 have been filtered to only include measurements from the baseline south-westerly sector (Lewis et al., 1997). For the same site measurements made by Lewis et al. (1997) show reasonable similarity for the aromatics and pentanes with differences of < 4 ppt. Large differences are seen between summer minimum propane at Mace Head (6.5 ppt) and the summer minimum values recorded at other stations. Propane measurements of 143 ppt are reported by Lewis et al. in August 1996, summer minimum propane of 56 ppt is reported from the Arctic cruise and 100 ppt propane is reported by the clean maritime subarctic site, Pallas. Unusually all summer minima values reported from Pallas (at 67°58' N) in northern Finland are higher than the same species at Mace Head (at 53°20' N). One would expect the Pallas site to have lower summer minima due to the higher OH radical concentration arising from longer sunlight hours at higher latitudes compared to sites of lower latitude (Hakola et al., 2003). Interestingly the Arctic cruise shows lower ethane values but higher mole fractions of all other NMHCs measured. The difference in propane values measured at other sites during earlier time periods may be explained if one takes into account changes in motor vehicle emissions. Dollard et al., (2007) highlighted that propane emissions from motor

vehicles was being steadily reduced due to the large scale implementation of catalytic converters, which now exist on the majority of the motor vehicle fleet. This could explain why baseline Mace Head summer minima are lower than all other European propane measurements made in years prior to 2005.

Hydrocarbon mole fractions measured at Mace Head in European air masses were found to be elevated significantly from baseline air masses. Annual averages showed minimum elevations of 10 ppt for ethyl-benzene and maximum elevations of 200 ppt for ethane (Table 5). Seasonal variations were found to be much higher where European winter maxima were elevated compared to baseline seasonal cycles by >300 ppt for ethane and propane, and by >100 ppt for the butanes, benzene, toluene and m+p-xylene (Table 4). Differences between European and baseline summer minima were much smaller. This is due to increased species loss in the summer months due to elevated levels of The OH radical. Largest differences between baseline and European summer minima were seen for propane (73 ppt), followed by ethane (49 ppt) with i-butane and the aromatics showing differences of <20 ppt.

Table 5 shows yearly average mole fractions in baseline and European air masses of the range of compounds measured at Mace Head compared with other measurements made at Mace Head and in Europe. All species reported in the rural UK site by Dollard et al. (2007) are higher than Mace Head averages due to the influence of anthropogenic emissions in the UK. Data from a maritime site on the west coast of France (Sauvage et al., 2009) are always higher than Mace Head data and lower than rural UK data.

## 4 Summary

A five year record of high-frequency in situ measurements of NMHCs measured at Mace Head, a background Northern Hemispheric station, was analysed. These data were separated into their air mass origins of baseline, European polluted and southerly transported using a Lagrangian dispersion model. Hydrocarbon mole fractions were elevated in European air masses for all species. Baseline air masses which have been

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transported across the north Atlantic showed the most stable mole fractions. Southerly transported air masses showed significant depletions in  $C_2$ – $C_4$  alkanes resulting from high OH at low latitudes. Summer minima occurred in July/August and winter maxima in February for all species. Shorter lived species, like the substituted aromatics, showed a prolonged summer minima which sometimes lasted for four months. Although summer minima in baseline air masses showed low mole fractions (<5 ppt) of certain species (e.g. the butanes, pentanes, ethyl-benzene and the xylenes), mole fractions did not reach zero. As baseline air masses have not been in contact with any major pollution sources as they crossed the Atlantic for ~3 days one would expect none of these species to be present. Emissions from local and trans-Atlantic shipping is suggested as a source of these low, non-zero mole fractions of short lived species in baseline air.

Long-term trends in Northern Hemispheric baseline air were assessed by use of the Mann-Kendall test. No statistically significant trends were observed in baseline air masses over the five year period (2005–2009). European air masses were found to have statistically significant downward trends of i and n-butane and i-pentane of 5, 2 and 4% per year, respectively. Contrary to many other studies in European benzene was not found to be decreasing with any statistically significant trend. Toluene in European air masses was found to have an upward trend of 34% per year with a 90% significance level. Baseline air masses in early 2008 were found to have elevated levels of  $C_2$ – $C_5$  alkanes, however this elevation was found to be statistically insignificant.

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**Table 1.** Measurement parameters including limit of detection, sample precision and blank size.

Species	Precision %	Limit of Detection ppt	Average Blank ppt
ethane	1–2	2.8	0.9
propane	0.6–2	1.2	0.4
i-butane	2–5	3.0	1.0
n-butane	3	0.9	0.3
i-pentane	3–10	1.2	0.4
n-pentane	3–6	1.0	0.3
benzene	0.6–2.5	1.2	0.4
toluene	0.5–5	1.8	0.6
ethyl-benzene	2–8	1.0	0.3
m+p-Xylene	4–8	2.5	0.8
o-Xylene	4–10	1.0	0.3

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**Table 2.** Trends of hydrocarbons (%/year) measured at Mace Head in baseline and European air masses from 2005–2009 calculated using the Mann-Kendall test.

% / year	Comparable Data			Other Data		
	Our Work NH Baseline 2005–2009	European 2005–2009	Helmig et al. Rural Germany 1999–2009	Sauvage et al. Rural France 1997–2006	Dollard et al. Rural UK 1995–2001	Hakola et al. Subarctic 1994–2003
Ethane	< 1	< -1	-1	< 1	-7	1.6
Propane	6	-1	-2		-12	< 1
i-butane	1	-5 <sup>d</sup>			-21	4 <sup>c</sup>
n-butane	< 1	-2 <sup>c</sup>			-24	2 <sup>c</sup>
i-pentane	< 1	-4 <sup>d</sup>		-4 <sup>c</sup>	-19	< -1
n-pentane	< 1	-4			-27	-4
Benzene	-1	-1	-6	-4 <sup>d</sup>	-20	2
Toluene	42	34 <sup>d</sup>	-7	-6 <sup>b</sup>	-18	
ethyl-benzene	26	6				
o-xylene	5	-6 <sup>d</sup>				
m+p-xylene	9	-6	-6			

<sup>a</sup> 0.001, <sup>b</sup> 0.01, <sup>c</sup> 0.05, <sup>d</sup> 0.1 level of significance.

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**Table 3.** Rate coefficients and atmospheric lifetimes with respect to OH reactivity for a range of NMHCs.

	$k_{\text{OH}}$ $\text{cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$	$\tau_{\text{OH}}$ hours	$\tau_{\text{OH}}$ days
ethane	$2.40 \times 10^{-13\text{a}}$	771.6	32.2
propane	$1.10 \times 10^{-12\text{a}}$	168.4	7.0
i-butane	$2.12 \times 10^{-12\text{b}}$	87.4	3.6
n-butane	$2.30 \times 10^{-12\text{a}}$	80.5	3.4
i-pentane	$3.60 \times 10^{-12\text{b}}$	51.4	2.1
n-pentane	$3.80 \times 10^{-12\text{b}}$	48.7	2.0
benzene	$1.32 \times 10^{-12\text{c}}$	140.3	5.8
toluene	$5.96 \times 10^{-12\text{c}}$	31.1	1.3
ethyl-benzene	$7.10 \times 10^{-12\text{c}}$	26.1	1.1
m+p-xylene	$1.90 \times 10^{-11\text{c}}$	9.7	0.4
o-xylene	$1.37 \times 10^{-11\text{c}}$	13.5	0.6

<sup>a</sup> Atkinson et al. (2006); <sup>b</sup> Atkinson (2003); <sup>c</sup> PORG (1997).

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**Table 4.** Winter maxima and summer minima VOC mole fractions (in ppt) at Mace Head during the arrival of baseline northern hemispheric air masses with VOC measurements from other remote northern hemispheric stations.

	Winter Maximum (ppt)			Summer Minimum (ppt)				
	This study 2005–2009 Baseline NH	Hakola et al. 1994–2003 Pallas Subarctic	This study 2005–2009 European NH	This study 2005–2009 Baseline NH	Lewis et al. 1996 Baseline cruise	Hopkins et al. 1999 Arctic Subarctic	Hakola et al. 1994–2003 Pallas European	This study 2005–2009
Ethane	1928	2500	2289	604	558	442	750	729
Propane	635	1300	962	6.5	143	56	100	86
i-Butane	123	300	238	3.5	23.6	13	8	20
n-Butane	246	590	429	3.0		10	100	43
i-Pentane	71	220	158	3.0	2.9		20	17
n-Pentane	69	150	125	2.0	5.3		20	14
Benzene	129	240	231	13	11.0	50	40	29
Toluene	52		209	4.7	4.6			20
ethyl-benzene	7.1		28	1.5	2.3			4.4
m+p-Xylene	16		142	4.8	3.2			18
o-Xylene	8.1		42	1.8	2.2			7.1

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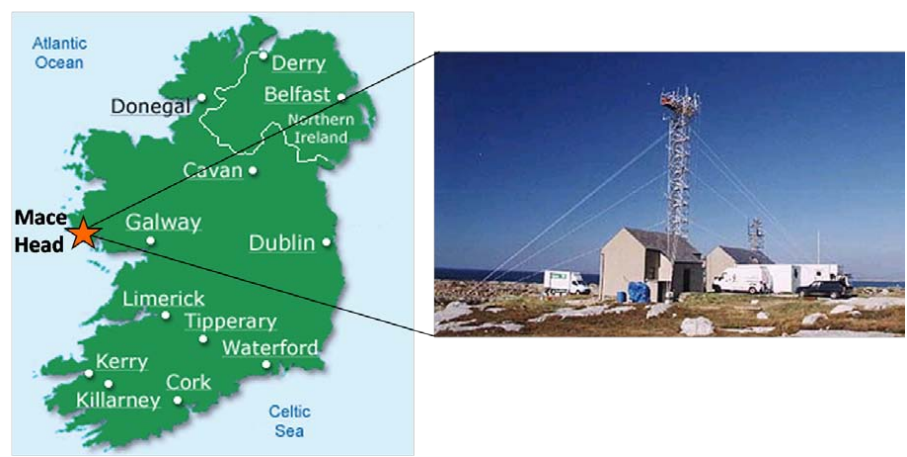
**Table 5.** Yearly and overall averages of hydrocarbon data (in ppt) split into sectors of baseline air, European and southerly transported air masses.

Species	2005		2006		2007		2008		2009		Overall (2005–2009)			Sauvage et al. (2009)	Dollard et al. (2007)
	Baseline	European	Base	Euro	Base	Euro	Base	Euro	Base	Euro	Base	Euro	South	West France	Rural UK
Ethane	1306 ±125	1576 ±297	1310 ±118	1567 ±257	1338 ±115	1548 ±318	1383 ±124	1549 ±307	1075 ±867	1332 ±231	1282	1490	1092	1756	1871
Propane	249.2 ±69.0	488.2 ±213.8	263.6 ±72.4	470.1 ±176.6	279.3 ±56.9	458.9 ±183.2	296.4 ±70.5	475.7 ±226.6	227.4 ±57.9	430.6 ±182.7	263	452	223	731	832
i-Butane	–	–	44.2 ±12.3	123.8 ±62.4	43.9 ±11.3	119.6 ±64.2	48.7 ±14.4	113.6 ±72.0	40.1 ±7.8	82.1 ±48.0	44	113	42	–	376
n-Butane	95.8 ±30.7	240.6 ±134.2	96.4 ±25.1	222.6 ±102.8	97.4 ±24.8	221.1 ±112.2	104.4 ±30.5	215.4 ±121.0	80.3 ±24.7	204.1 ±105.8	95	215	90	294	505
i-Pentane	26.9 ±10.8	91.8 ±66.4	27.2 ±8.8	87.0 ±47.1	27.2 ±8.6	82.1 ±50.3	29.2 ±11.8	80.4 ±52.7	22.1 ±8.1	73.9 ±43.5	26	81	34	205	407
n-Pentane	26.6 ±9.9	71.2 ±44.9	26.5 ±8.1	65.2 ±33.3	26.7 ±7.8	67.1 ±35.0	28.6 ±10.0	61.1 ±35.4	20.9 ±7.4	54.8 ±29.0	26	62	26	177	102
Benzene	68.6 ±12.6	120.8 ±45.8	64.9 ±12.0	118.9 ±44.8	62.9 ±11.3	118.8 ±47.6	68.7 ±11.6	115.3 ±48.1	63.6 ±11.0	118.1 ±46.0	66	115	63	151	153
Toluene	17.2 ±7.3	80.0 ±47.6	15.1 ±6.6	70.0 ±39.8	15.4 ±5.6	87.2 ±59.3	24.2 ±11.1	107.7 ±69.3	32.9 ±13.3	149.4 ±85.7	21	96	38	272	345
ethyl-Benzene	3.1 ±1.4	12.8 ±7.3	2.7 ±0.8	10.2 ±6.4	3.2 ±1.0	14.8 ±10.5	4.1 ±1.7	14.7 ±9.1	3.7 ±1.3	14.4 ±8.0	3	13	5	42	–
m+p-Xylene	9.5 ±6.9	69.2 ±44.8	7.3 ±4.9	56.9 ±44.1	7.8 ±4.2	85.2 ±71.2	9.5 ±7.4	56.1 ±44.5	9.3 ±5.9	48.7 ±34.1	9	62	23	132	–
o-Xylene	4.4 ±2.9	30.7 ±21.1	3.4 ±1.9	22.4 ±16.5	3.3 ±1.6	22.6 ±16.7	4.4 ±2.8	21.9 ±16.2	3.7 ±2.3	21.0 ±13.7	4	23	10	47	–

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**Fig. 1.** Location of the Mace Head research station on the west coast of Ireland.

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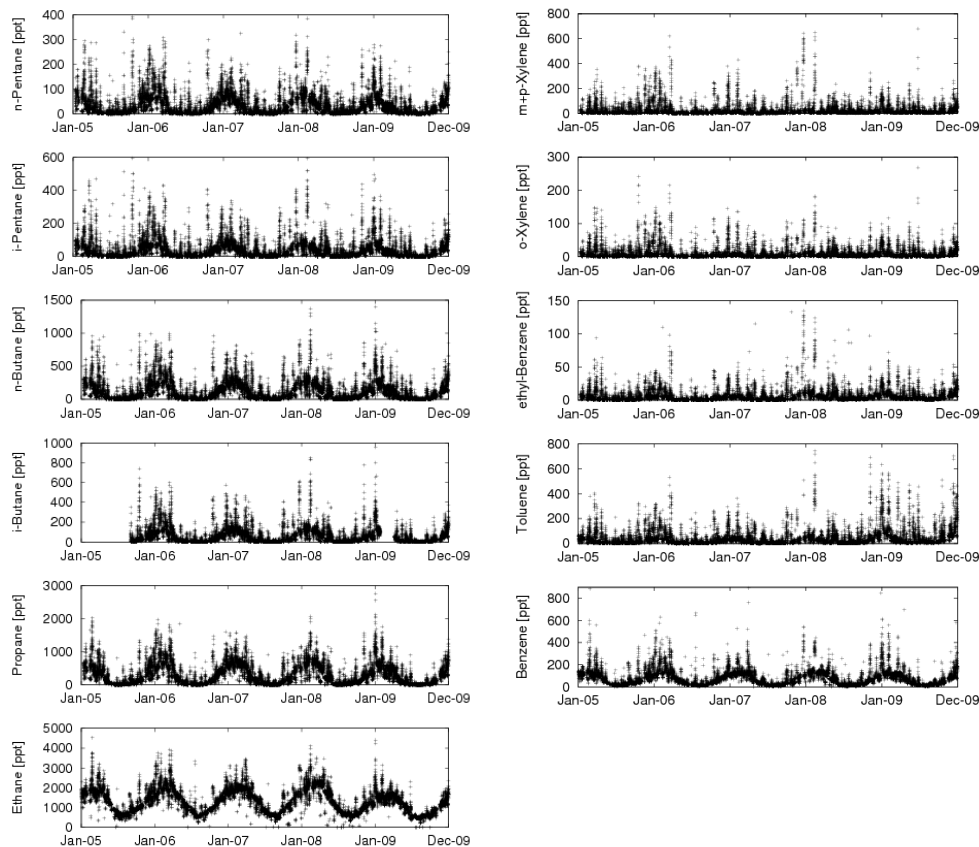
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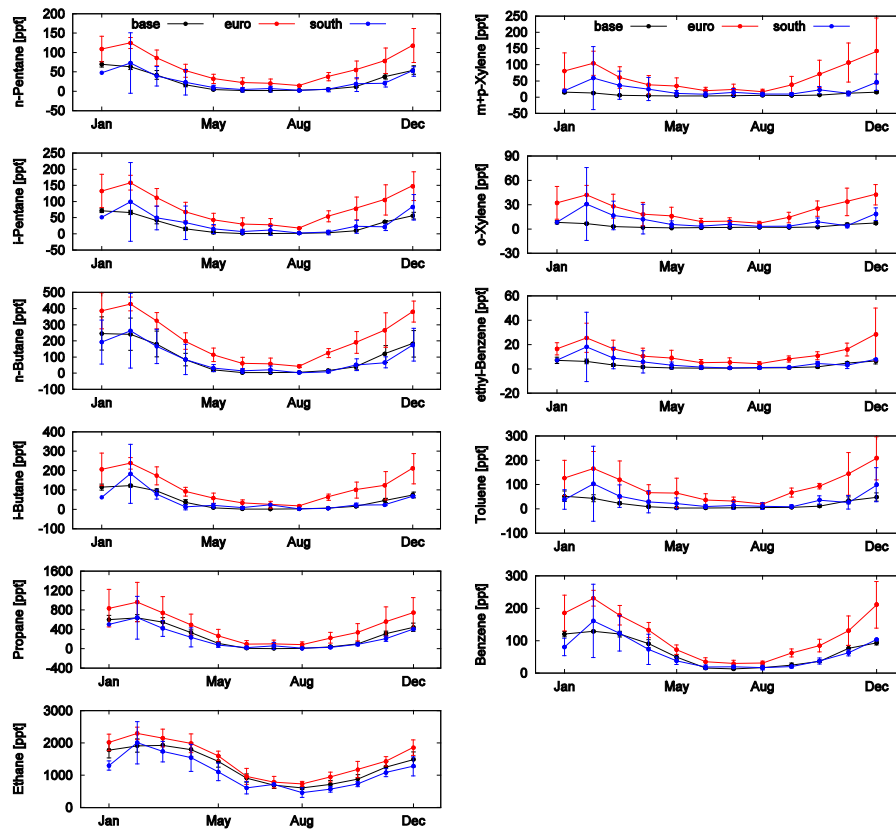
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**Fig. 2.** All data for  $C_2$ – $C_5$  alkanes and aromatic species from January 2005 until December 2009.

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**Fig. 3.** Monthly averaged data over the five year period from 2005–2009 separated into baseline (black), European (red) and southerly transported (blue) air masses with error bars as  $1\sigma$ .

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