

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

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10
11 **Abstract**

12 Continuous high-frequency *in situ* measurements of a range of non-methane hydrocarbons
13 have been made at Mace Head since January 2005. Mace Head is a background Northern
14 Hemispheric site situated on the eastern edge of the Atlantic. Five year measurements (2005-
15 2009) of six C₂-C₅ non-methane hydrocarbons have been separated into baseline Northern
16 Hemispheric and European polluted air masses, among other sectors. Seasonal cycles in
17 baseline Northern Hemispheric air masses and European polluted air masses arriving at Mace
18 Head have been studied. Baseline air masses show a broad summer minima between June
19 and September for shorter lived species, longer lived species show summer minima in
20 July/August. All species displayed a winter maxima in February. European air masses
21 showed baseline elevated mole fractions for all non-methane hydrocarbons. Largest
22 elevations (of up to 360 ppt for ethane maxima) from baseline data were observed in winter
23 maxima, with smaller elevations observed during the summer. Analysis of temporal trends
24 using the Mann-Kendall test showed small (< 6%/year) but statistically significant decreases
25 in the butanes and i-pentane between 2005 and 2009 in European air. No significant trends
26 were found for any species in baseline air.

27 **1 Introduction**

28 The role of non-methane hydrocarbons (NMHCs) in the production of tropospheric ozone
29 was first reported in 1956 by Haagen-Smit and Fox. NMHC as a classification includes
30 alkanes, alkenes, alkynes and aromatic species, all of which form ozone by reaction with the
31 hydroxyl radical (OH) in the presence of nitrogen oxides (NO_x where $\text{NO}_x = \text{NO} + \text{NO}_2$). NO_x ,
32 which is emitted mainly by fossil fuel combustion, is an essential component in the ozone
33 formation cycle, in the absence of NO_x ozone cannot be formed in the troposphere.
34 Tropospheric ozone is a harmful pollutant which has negative effects on human health and
35 vegetation. Background tropospheric ozone in the Northern Hemisphere has been reported to
36 be increasing by 0.49 ppb/year with a current background Northern Hemispheric mole
37 fraction of ~ 42 ppb (Simmonds et al., 2004). Oltmans et al., (2006) also reported an increase
38 of 13%/decade from 1987 to 2005 at Mace Head. To assess if recent increases in tropospheric
39 ozone can be linked to changes in NMHC mole fractions one needs to analyse a long-term
40 record of NMHC measurements. These measurements must be made at a background
41 location to minimise the effects of local pollution on data and enable effective analyses of
42 long-term trends and seasonal cycles. It is difficult to elucidate trends and seasonal cycles
43 from urban measurement records because of almost continually elevated NMHC mole
44 fractions from local pollution.

45 This paper reports on continuous high-frequency measurements of a range of NMHCs
46 conducted at Mace Head from January 2005 to December 2009. These measurements extend
47 those reported by Yates et al., (2010) from January 2005 to December 2006. This longer
48 dataset enables the assessment of long-term trends of NMHC species. NMHCs reported
49 include ethane, propane, i and n-butane, i and n-pentane. These data provide information on
50 long-term trends and seasonal cycles of NMHCs in background Northern Hemispheric air.
51 Individual measurements are sorted using a Lagrangian dispersion model to separate clean
52 background air from regionally polluted European air masses and those transported from
53 southerly latitudes. Yearly and seasonal trends are assessed and variations and anomalies in
54 baseline air masses accounted for. The aim of this paper is to report the long-term, high
55 frequency NMHC measurements made at Mace Head, further publications are in preparation
56 which will include detailed and comprehensive interpretation of the data presented here.

57

58 **2 Experimental**

59 **2.1 Measurement location**

60 The Mace Head atmospheric research station (53° 20' N, 9° 54' W) is situated on the west
61 coast of Ireland (Figure 1). At the station, numerous ambient air measurements are made as
62 part of the Advanced Global Atmospheric Gases Experiment (AGAGE) (Cunnold et al.,
63 1997; Prinn et al., 2000) and the Global Atmospheric Watch network (GAW). It is one of
64 only a few clean background western European stations, thus providing an essential baseline
65 input for inter-comparisons with continental Europe, whilst also acting as a baseline site
66 representative of Northern Hemispheric air. Prevailing winds from the west to southwest
67 sector bring clean background air to the site. Polluted European air masses as well as tropical
68 maritime air masses cross the site periodically. Mace Head is therefore uniquely positioned
69 for resolving these air masses and for comparative studies of their constitution. Galway is the
70 closest city, with a population of 72,000, sitting 50 km to the east whilst the area immediately
71 surrounding Mace Head is very sparsely populated providing very low local anthropogenic
72 emissions. The sample inlet is located 10 metres inland from the shoreline, sampling at 10
73 metres above sea level, through stainless steel lines attached to a meteorological tower. The
74 area surrounding Mace Head is generally wet and boggy with areas of exposed rock (Dimmer
75 et al., 2001).

76 **2.2 Instrumentation**

77 The measurement system couples an Agilent 6890 gas chromatograph (GC)/5973 mass
78 selective detector (MSD) with a low-temperature, cryogen-free pre-concentration system
79 (Medusa, (Miller et al., 2008)). This self-contained cryogenic technology is essential due to
80 the inaccessibility of field locations and difficulty of obtaining consumables such as liquid
81 nitrogen. The ambient air sample inlet is situated 10 metres up a 20 metre high tower.
82 Ambient air is flushed through an inlet line, made of ¼" instrument-grade stainless steel
83 tubing, a portion of this air is delivered to the Medusa inlet where a backpressure regulator
84 controls the sample pressure at 1.5 bar and vents at ~2 L/min (Miller et al., 2008). Analysis
85 of each 2 L sample of ambient air was alternated with analysis 2 L of reference gas (also
86 delivered to the Medusa at 1.5 bar) to determine and correct for short term instrumental drift,
87 resulting in 12 fully calibrated air samples per day. At the heart of the Medusa is a Polycold

88 “Cryotiger” (Polycold division of Brooks Automation, Petaluma, CA) cold end which
89 maintains a minimum trapping temperature of -175 °C. This cold end conductively cools a
90 copper baseplate which supports two traps to about -165 °C. By using aluminium standoffs
91 of limited thermal conductivity to connect the traps to the cold head, each trap can
92 independently be heated resistively to any temperature from -165 °C to +200 °C or more,
93 while the baseplate remains cold. The use of two traps with very wide programmable
94 temperatures ranges, coupled with the development of appropriate trap absorbents, permits
95 the desired analytes from 2 L air samples to be effectively separated from more-abundant
96 gases in the air matrix that would otherwise interfere with chromatographic separation or
97 mass spectrometric detection. A detailed description of Medusa sampling is presented in
98 Miller et al., (2008). NMHC measurements from another AGAGE Medusa GC-MS
99 instrument situated at the Scripps institution of Oceanography, USA have been reported by
100 Mühle et al. (2007).

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

107 In this study, hydrocarbon measurements carried out at Mace Head since 2005 are reported.
108 The Medusa-GCMS which measures NMHCs was originally developed to make high
109 frequency in situ measurements for the determination of atmospheric lifetimes and emissions
110 of various compounds related to the Montreal and Kyoto Protocols. The Medusa measures a
111 wide range of halocarbons, NMHCs and sulfur compounds involved in ozone depletion and
112 climate forcing (Miller et al., 2008). A network of five Medusa systems are located at remote
113 field stations around the world (Mace Head, Ireland; Ragged Point, Barbados; Cape Grim,
114 Tasmania; Cape Mataula, American Samoa; and Trinidad Head, California) operated by the
115 Advanced Global Atmospheric Gases Experiment (AGAGE) since 2003 providing 12 in situ
116 ambient measurements per day (<http://agage.eas.gatech.edu/>). The Medusa-GCMS at Mace
117 Head initially measured the NMHC ethane. The suite of NMHCs measured was extended in
118 2005 by Yates et al., (2010) to also include: propane, n-butane, i-butane, n-pentane and i-
119 pentane. Modifications made to the Medusa-GCMS to extend the number of compounds

120 measured are detailed in Yates et al., (2010). NMHC measurements are limited in number in
121 order to leave the Medusa-GCMS AGAGE measurements of CFCs, PFCs, HFCs, HCFCs and
122 SF₆ uncompromised. It is essential that any additional measurements do not interfere with
123 measurements of AGAGE core species. Alkene measurements are recorded using this
124 system, but research shows that there is production of alkene artefacts from the Nafion drier
125 (pentene and butenes) (Boudries et al., 1994). Since the Medusa-GCMS uses two Nafion
126 driers to dry air samples prior to pre-concentration alkene measurements have not been
127 attempted with this system.

128 Ethane was detected with the MSD in selected ion monitoring mode (SIM) using a target ion,
129 C₂H₂⁺ (m/z 26), propane C₃H₅⁺ (m/z 41), i-butane C₃H₆⁺ (m/z 42), n-butane, i-pentane and n-
130 pentane C₃H₇⁺ (m/z 43). Blanks and laboratory air were measured weekly to check for
131 contamination of the instruments working environment. Blank samples are carrier gas
132 trapped as a normal air or standard sample and run under standard instrument conditions.
133 Blanks were < 0.5 % of the average baseline peak size for ethane, propane and n-butane and
134 <2 % of the average peak size for i-butane and the pentanes. Instrument precision is an
135 indicator of the detectors response over a period of time. Precision was calculated from the
136 standard-standard ratios of concurrent standard analyses. Table 1 shows precisions and limits
137 of detection of the range of NMHCs measured where the limit of detection is calculated as
138 three times of the mean blank.

139

140 2.2.1 Calibration

141 Working standards (quaternary standards) are prepared by compressing background ambient
142 air at Mace Head, into 35 L electropolished stainless steel canisters (Essex Cryogenics,
143 Missouri, USA) using a modified oil-free compressor (SA-3, RIX California, USA). This
144 ensures that NMHC mole fractions in quaternary standards are close in concentration to air
145 sample values at Mace Head minimising sample matrix non-linearities. The quaternary
146 standards are used to bracket each air measurement in an attempt to minimise detector
147 response non-linearities. In addition tertiary standards (air filled at Trinidad Head, California
148 and calibrated for halocarbons at Scripps Institution of Oceanography (SIO) against their
149 primary calibration scales) are analysed weekly against the quaternary standards. The
150 quaternary working gases are calibrated over the course of their use in the field by analyses
151 against the tertiary standards. The NMHC quaternary calibration is linked by analysis of

152 tertiary standards against an NMHC primary standard (O'Doherty et al., 2004). The NMHC
153 primary standard was made by accurate volumetric dilution of a ppb mole fraction synthetic
154 standard (Apel Reimer USA, cylinder CC144868) to ppt mole fractions, to mimic ambient
155 NMHC mole fractions observed at this background site. The Apel-Reimer standard was
156 diluted by a ratio of 12.9 as detailed in Yates et al., (2010). The NMHC primary calibration
157 standard has concentrations of C₂-C₅ alkanes in ppt of 908 for ethane, 813 for propane, 736
158 for n-butane, 372 for i-butane 591 for n-pentane and 556 for i-pentane. Analysis of this
159 NMHC primary standard against each new tertiary standard from SIO enabled application of
160 NMHC mole fractions measured on the Medusa. This primary standard was assigned values
161 based on a comparison made against the NPL-scale, standard D45 7238. This found our
162 primary standard to be higher by 3 %, 5 %, 5%, 20 % and 25% for ethane, propane, n-butane,
163 i-pentane and n-pentane respectively, whilst i-butane was 2% lower than the NPL-scale in our
164 primary standard.

165

166 **3 Results**

167 NMHC species measured by the Medusa-GCMS include; ethane, propane, i-butane, n-butane,
168 i-pentane and n-pentane. NMHC data from January 2005 to December 2009 is shown in
169 Figure 2. These data were sorted into air mass origins using the NAME Lagrangian
170 atmospheric dispersion model (Jones et al., 2007; Ryall and Maryon, 1998) using the
171 technique described in Manning et al. (2003). This classified measurements into different
172 sector types: baseline (westerly or north westerly airflow shown in Fig. 3), European
173 polluted, southerly transport, mixed (when air was from a variety of sectors), and local (times
174 when there were low wind speeds and stable air so sources and sinks in the local region
175 would significantly impact the observations). Only air masses classified as baseline,
176 European and southerly transported will be discussed in detail in this paper. These three air
177 masses display distinctly different concentration patterns and baseline and European data
178 form the large majority (>70%) of air masses measured at Mace Head.

179 To calculate air mass sectors the NAME dispersion model is run backwards to estimate the
180 recent history (12 days) of the air en-route to Mace Head. Baseline mole fractions are
181 defined as those which have not been influenced by significant emissions within the previous
182 12 days of travel en-route to Mace Head, i.e. those that are well mixed and representative of
183 the mid-latitude Northern Hemisphere background mole fractions. European air masses are

184 those which have travelled from mainland Europe, the UK and Ireland. Further details of this
185 sorting method can be found in Manning et al. (2011).

186 **3.1 Long term trends and elevations**

187 Many studies have reported marked decreases in the mole fractions of NMHCs measured in
188 mainland Europe and the UK between the 1990s and 2000 (Derwent et al., 2003;Dollard et
189 al., 2007;Dore et al., 2007;Solberg et al., 2002). This decrease in observed mole fractions
190 was brought about by a reduction in hydrocarbon emissions resulting from the
191 implementation of the Geneva Protocol to the Convention on Long-Range Transboundary Air
192 Pollution CLRTAP (UN ECE, 1991, http://www.unece.org/env/lrtap/vola_h1.htm) with the
193 aim of reducing emissions of ozone precursors. The Gothenburg multi-pollutant Protocol
194 (UN ECE, 1999, http://www.unece.org/env/lrtap/multi_h1.htm) was set-up eight years later
195 with the same aim. Reductions were primarily made in the transport sector through
196 improvements in engine systems and installation of 3-way catalysts, reducing emissions of
197 both VOC and NO_x. Solberg et al. (2002) reported decreases in VOC concentrations of 20-
198 50% from 1993-2000 at two central European EMEP sites. However, in the same report an
199 absence of trend was found at two rural Finnish sites, one of which (Pallas) is reported in
200 Table 2 (Hakola et al., 2006).

201 To estimate long-term variation in hydrocarbon data the non-parametric Mann-Kendall test
202 was used to test for the existence of a trend (Gilbert, 1987;Salmi et al., 2002). The Mann-
203 Kendall tests the null hypothesis of no trend against the alternative hypothesis that there is an
204 increasing or decreasing monotonic trend as described by Salmi et al. (2002). Results of the
205 Mann-Kendall test are shown in Table 2 and Figure 4, where percentage change is the slope
206 of the linear trend relative to the first year of measurements and is shown with other trend
207 data from recent literature. We would like to note that this five year record is a rather short
208 dataset from which to estimate long-term atmospheric trends however we have included these
209 to enable initial comparison to other available datasets. Other studies have calculated long-
210 term trends using ten year datasets and propose this to be the minimum length dataset over
211 which one can verify a 'long-term' trend (for example von Schneidmesser et al.,
212 2010;Dollard et al., 2007;Hakola et al., 2006;Helmig et al., 2009).

213 Trends are compared with other data from literature in Table 2. Short term trends in Mace
214 Head data from 2005 to 2009 are seen for i-butane and n-butane in European air masses with

215 decreases of 5 and 2% per year respectively with 90 and 95% levels of significance. The
216 pentanes both show decreases of 4% per year. These results are in agreement with
217 regulations as the principle source of butanes and pentanes is from the evaporation of motor
218 spirit which has been reduced in recent years due to the introduction of more efficient fuel
219 canisters in motor vehicles (Dollard et al., 2007). As expected no significant trends are seen
220 for ethane and propane which are primarily emitted from natural gas leakage and not from
221 motor vehicles. A large reduction in the magnitude of downward trends for the hydrocarbons
222 can be seen in the Mace Head dataset and also in other longer datasets (von Schneidmesser
223 et al., 2010) from ~2000 onwards. Data from von Schneidmesser et al., show reductions in
224 NMHC mixing ratios from rural European sites of 2-8 %/year from 1998 to 2008. These data
225 act to verify to small downward trend seen from Mace Head data taken during European
226 pollution events from 2005 to 2009.

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

231 **3.2 Seasonal Cycles**

232 Seasonal cycles of C₂-C₅ alkanes can be seen in Figures 3 and 5. Maximum concentrations
233 are observed in January and February and minima for slowly reacting compounds in July.
234 More reactive compounds (butanes and pentanes) show a much broader summer minima
235 from June right through to September in many cases. Ethane shows the most pronounced
236 seasonal cycle followed by propane, n-butane and i-butane. Variation in the amplitude of
237 seasonal cycles occurs due to differing reactivity of hydrocarbon species. Table 3 displays the
238 rates of reaction and atmospheric lifetimes (τ) of a range of VOCs in relation to the hydroxyl
239 (OH) radical. NMHC's reaction with OH acts as the primary controller of seasonal cycles,
240 determining both their amplitude and distribution (Derwent et al., 2000). High OH levels in
241 the summer results in increased removal of these compounds by OH oxidation. The
242 prevailing westerly winds at Mace Head bring clean background air which has not
243 encountered anthropogenic emissions in the previous 12 days, accounting for baseline
244 Northern Hemispheric mole fractions. Air from southerly latitudes is depleted in ethane and
245 propane due to increased mole fractions of the OH radical (from increased photolysis) at

246 southerly latitudes which removes hydrocarbon species. European pollution events are
247 marked by a sharp rise in hydrocarbon mole fractions from baseline values due to
248 anthropogenic emissions.

249 **3.3 Literature comparison**

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

278 from motor vehicles was being steadily reduced due to the large scale implementation of
279 catalytic converters, which now exist in the large majority of motor vehicles. The main
280 source of propane is from natural gas leakage. However, this source is relatively constant and
281 therefore the reduction or removal of propane emissions from motor vehicles would explain
282 why baseline Mace Head summer minima measured from 2005 to 2009 are lower than all
283 other European propane measurements which were made before 2005 prior to reductions in
284 motor vehicle propane emissions.

285 Hydrocarbon mole fractions measured at Mace Head in European air masses were found to
286 be elevated significantly from baseline air masses. Annual averages showed minimum
287 elevations of 36 ppt for n-pentane and maximum elevations of 200 ppt for ethane (Table 5).
288 Seasonal variations were found to be much higher where European winter maxima were
289 elevated compared to baseline seasonal cycles by > 300 ppt for ethane and propane, and by >
290 100 ppt for the butanes (Table 4). Differences between European and baseline summer
291 minima were much smaller. This is due to increased species loss in the summer months due
292 to elevated levels of The OH radical. Largest differences between baseline and European
293 summer minima were seen for propane (73 ppt), followed by ethane (49 ppt) with i-butane
294 and showing differences of < 20 ppt.

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

301

302 **4 Summary**

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

309 significant depletions in C₂-C₄ alkanes resulting from high OH at low latitudes. Summer
310 minima occurred in July and winter maxima in January/February for all species. Shorter lived
311 species, showed a prolonged summer minima which sometimes lasted for four months.

312 Long-term trends in Northern Hemispheric baseline air were assessed by use of the Mann-
313 Kendall test. No statistically significant trends were observed in baseline air masses over the
314 five year period (2005-2009). European air masses were found to have statistically significant
315 downward trends of i and n-butane and i-pentane of 5, 2 and 4 % per year, respectively.
316 Baseline air masses in early 2008 were found to have elevated levels of C₂-C₅ alkanes,
317 however this elevation was found to be statistically insignificant.

318

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328

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426

427 Table 1. Measurement parameters of sample precision and limit of detection.

Species	Precision	Limit of Detection
	%	ppt
ethane	1 - 2	2.8
propane	0.6 - 2	1.2
i-butane	2 - 5	3.0
n-butane	3	0.9
i-pentane	3 - 10	1.2
n-pentane	3 - 6	1.0

428

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

Comparable Data					Other Data		
	Our Work		von Schneidemesser et al	von Schneidemesser et al	Sauvage et al.	Dollard et al.	Hakola et al.
	NH Baseline	European	Rural UK	Rural Germany	Rural France	Rural UK	Subarctic
%/year	2005-2009	2005-2009	1998 - 2008	1998-2008	1997-2006	1995-2001	1994-2003
Ethane	<1	<-1	0	0	<1	-7	1.6
Propane	6	-1	-3 ⁺	-2 ⁺		-12	<1
i-butane	1	-5 ⁺	0	-4 ^{**}		-21	4 [*]
n-butane	<1	-2 [*]	-6 ^{***}	-4 [*]		-24	2 [*]
i-pentane	<1	-4 ⁺	-8 ^{***}	-5 ^{***}	-4 [*]	-19	<-1
n-pentane	<1	-4	-2 ⁺	0		-27	-4

***0.001, **0.01, *0.05, +0.1 level of significance

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

	k_{OH} $\text{cm}^3 \text{ molec}^{-1} \cdot \text{s}^{-1}$	τ_{OH} hours	τ_{OH} days
ethane	$2.40 \times 10^{-13} \text{ }^{\text{a}}$	771.6	32.2
propane	$1.10 \times 10^{-12} \text{ }^{\text{a}}$	168.4	7.0
i-butane	$2.12 \times 10^{-12} \text{ }^{\text{b}}$	87.4	3.6
n-butane	$2.30 \times 10^{-12} \text{ }^{\text{a}}$	80.5	3.4
i-pentane	$3.60 \times 10^{-12} \text{ }^{\text{b}}$	51.4	2.1
n-pentane	$3.80 \times 10^{-12} \text{ }^{\text{b}}$	48.7	2.0

433 ^a Atkinson et al. (2006); ^b Atkinson,(2003); ^c PORG, (1997)

434

Table 4. Monthly average NMHC mole fractions for yearly maxima and yearly minima (in ppt) at Mace Head during the arrival of baseline northern hemispheric air masses with NMHC measurements from other remote northern hemispheric stations.

	Winter Maximum (ppt)			Summer Minimum (ppt)				
	This study	Hakola et al.	This study	This study	Lewis et al.	Hopkins et al.	Hakola et al.	This study
	2005-2009	1994-2003	2005-2009	2005-2009	1996	1999	1994-2003	2005-2009
	Baseline NH	Pallas Subarctic	European	Baseline NH	Baseline NH	Arctic cruise	Pallas Subarctic	European
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

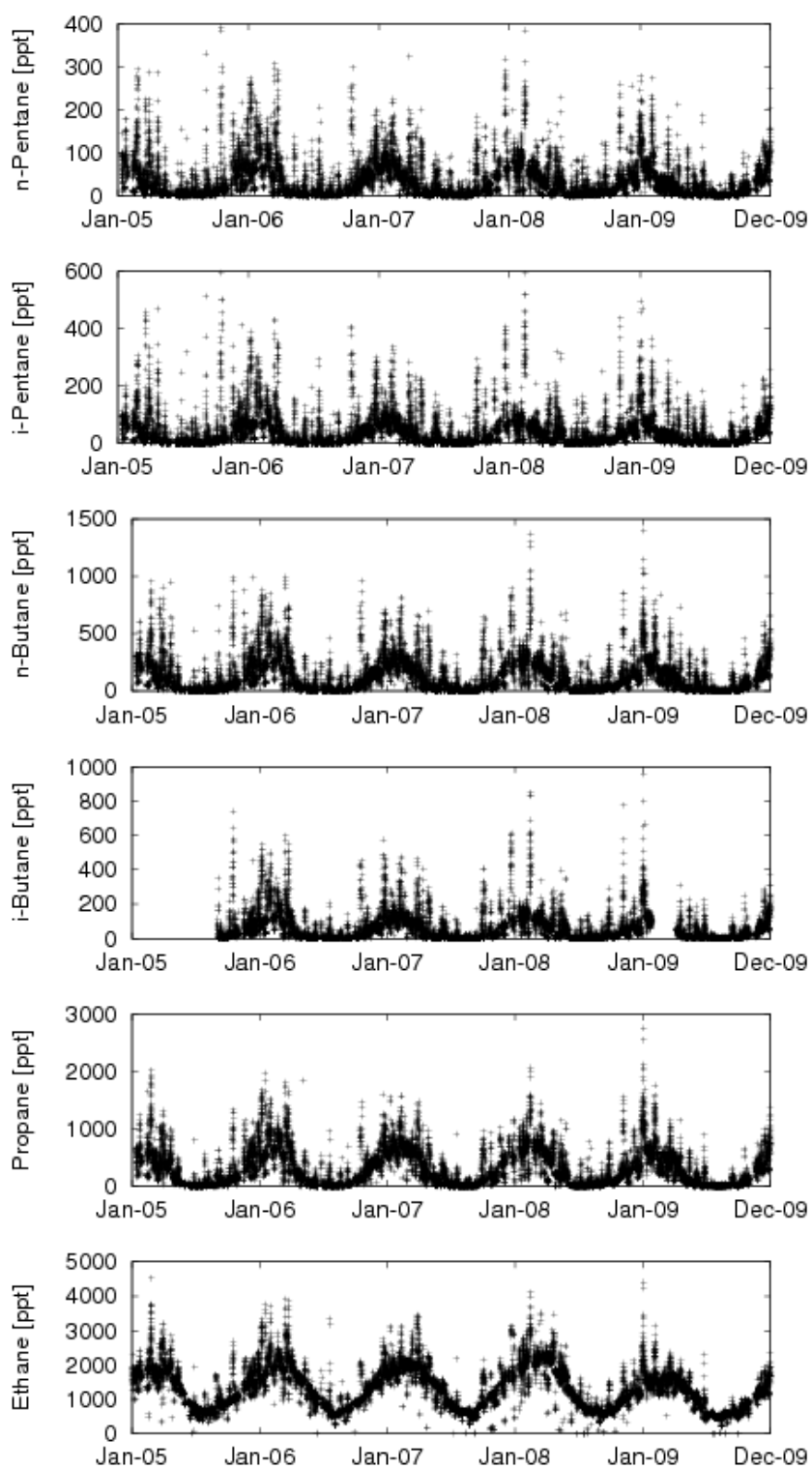
Table 5. Yearly and overall averages of hydrocarbon data (in ppt) split into sectors of baseline air, European and southerly transported air masses.

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 Coast 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

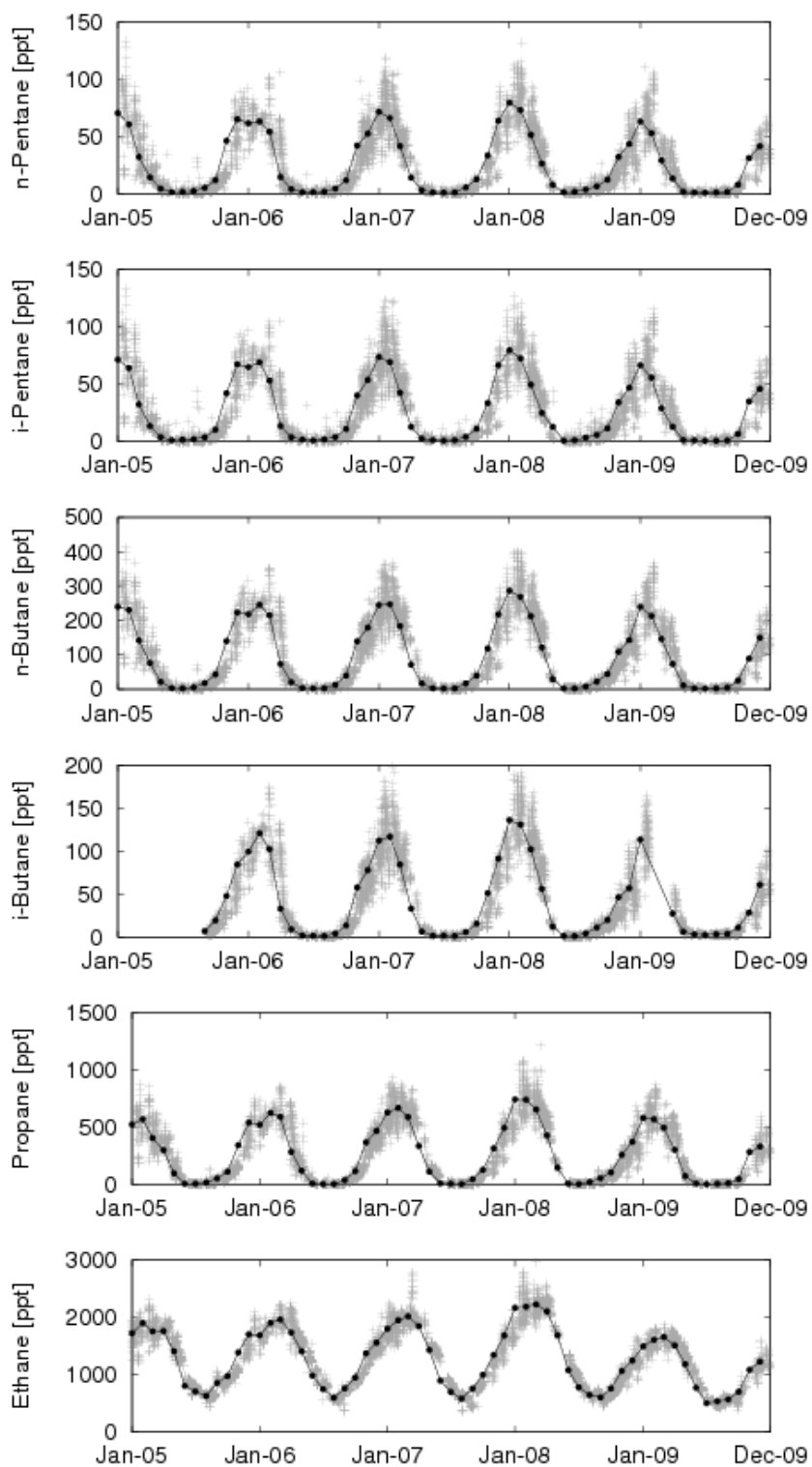


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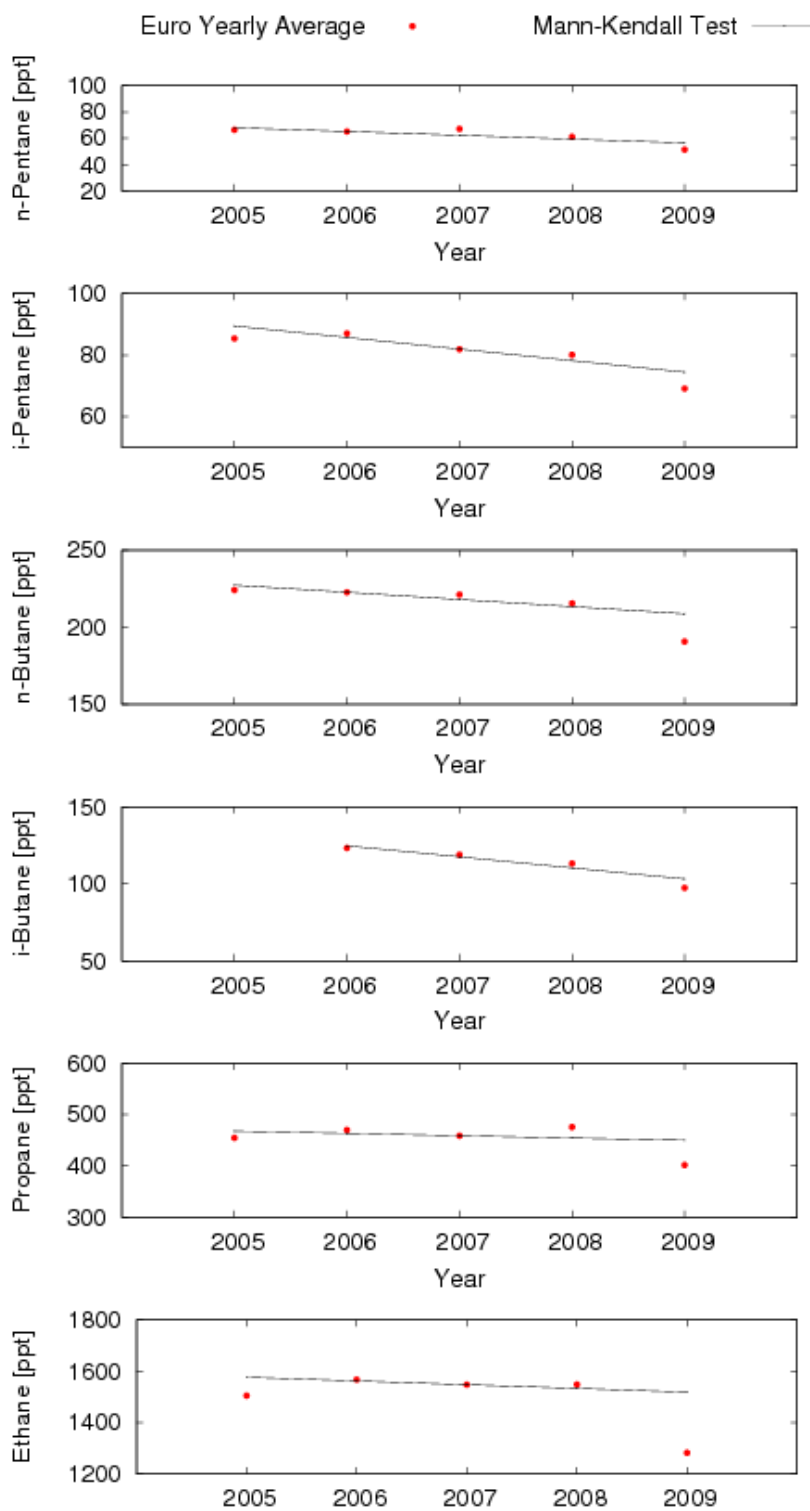
2 Figure 1. Location of the Mace Head research station on the west coast of Ireland.



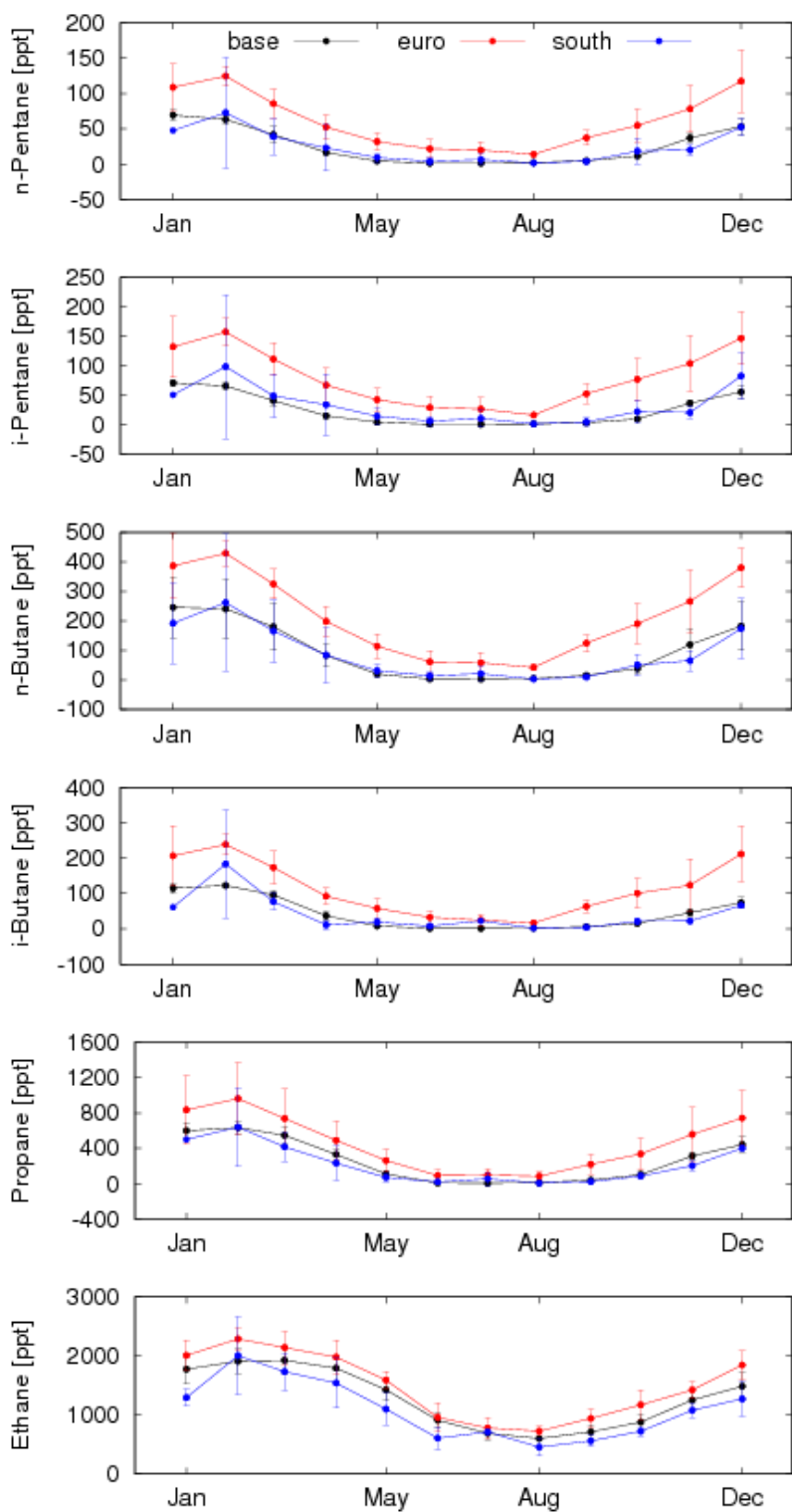
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2 Figure 2: All data for C₂-C₅ alkanes from January 2005 until December 2009.



1
 2 Figure 3: Baseline data for C₂-C₅ alkanes from January 2005 until December 2009 with
 3 monthly averaged data overlaid in grey.



1
 2 Figure 4: Yearly averaged data from European air masses arriving at Mace Head (circles)
 3 with the line computed from use of the Mann-Kendall test for the presence of significant
 4 trend.



1
 2 Figure 5: Monthly averaged data over the five year period from 2005-2009 separated into
 3 baseline (black), European (red) and southerly transported (blue) air masses with error bars as
 4 1σ .