

Highlights of Non-Methane Hydrocarbon Measurements During EASE 96 & 97.

[Alastair C. Lewis^{1,2}](#), James B. McQuaid¹ & Michael J. Pilling¹

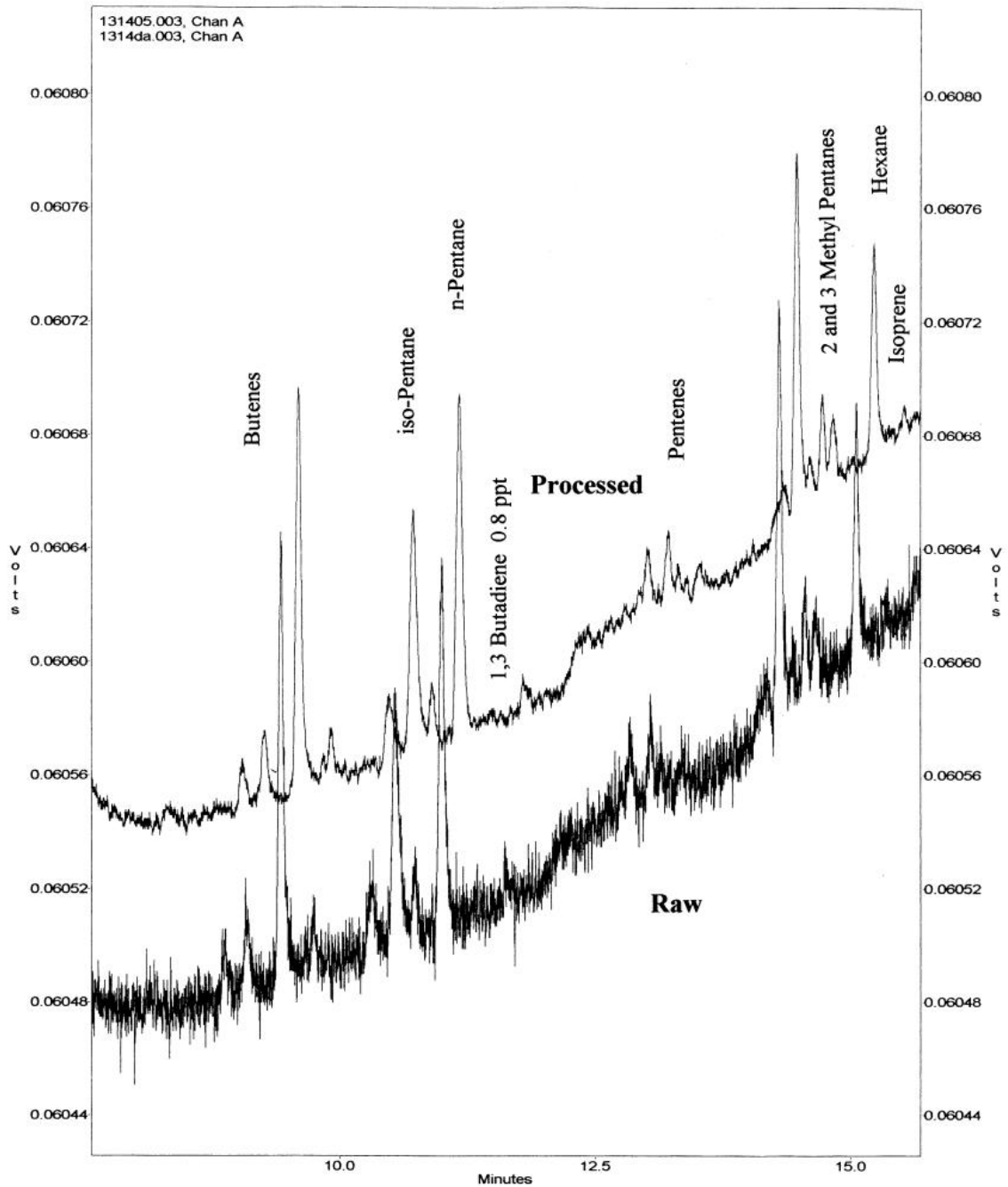
¹*School of Chemistry and* ²*Environment Centre, University of Leeds, Woodhouse Lane, Leeds, LS2 9JT.*

Introduction

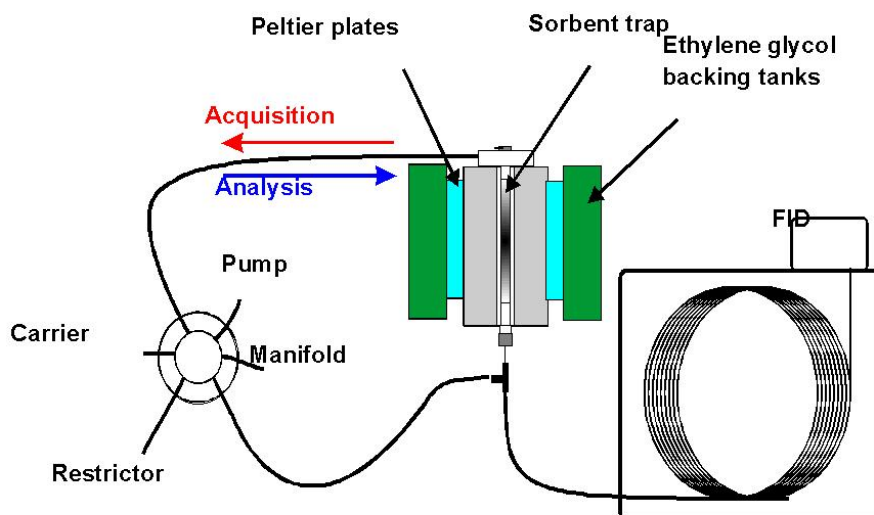
The role played by non-methane hydrocarbons (NMHC) in the atmosphere is now well established as central to the processes controlling the production and destruction of tropospheric ozone. An *in situ* PTV-GC-FID system was deployed at Mace Head during the ACSOE EASE 96 and 97 field campaigns. The instrument produced hourly data for a range of light molecular weight hydrocarbons (ethane - toluene) plus dimethyl sulphide (DMS) with detection limits approaching 1 part per trillion. Over 1200 discrete samples were automatically analysed during the two campaigns. NMHC data have been used to constrain the Leeds Box Model (LBM) simulations of boundary radical chemistry.

Figure 1 shows a section of a typical chromatogram obtained in 'clean' marine air and the PTV-GC assembly. The lower GC trace shows raw signal from FID, the upper, the results from unique digital signal processing electronics applied for the first time in GC atmospheric measurements as part of this project.

Figure 1. Typical Chromatogram In Westerly Air (select the image to enlarge)



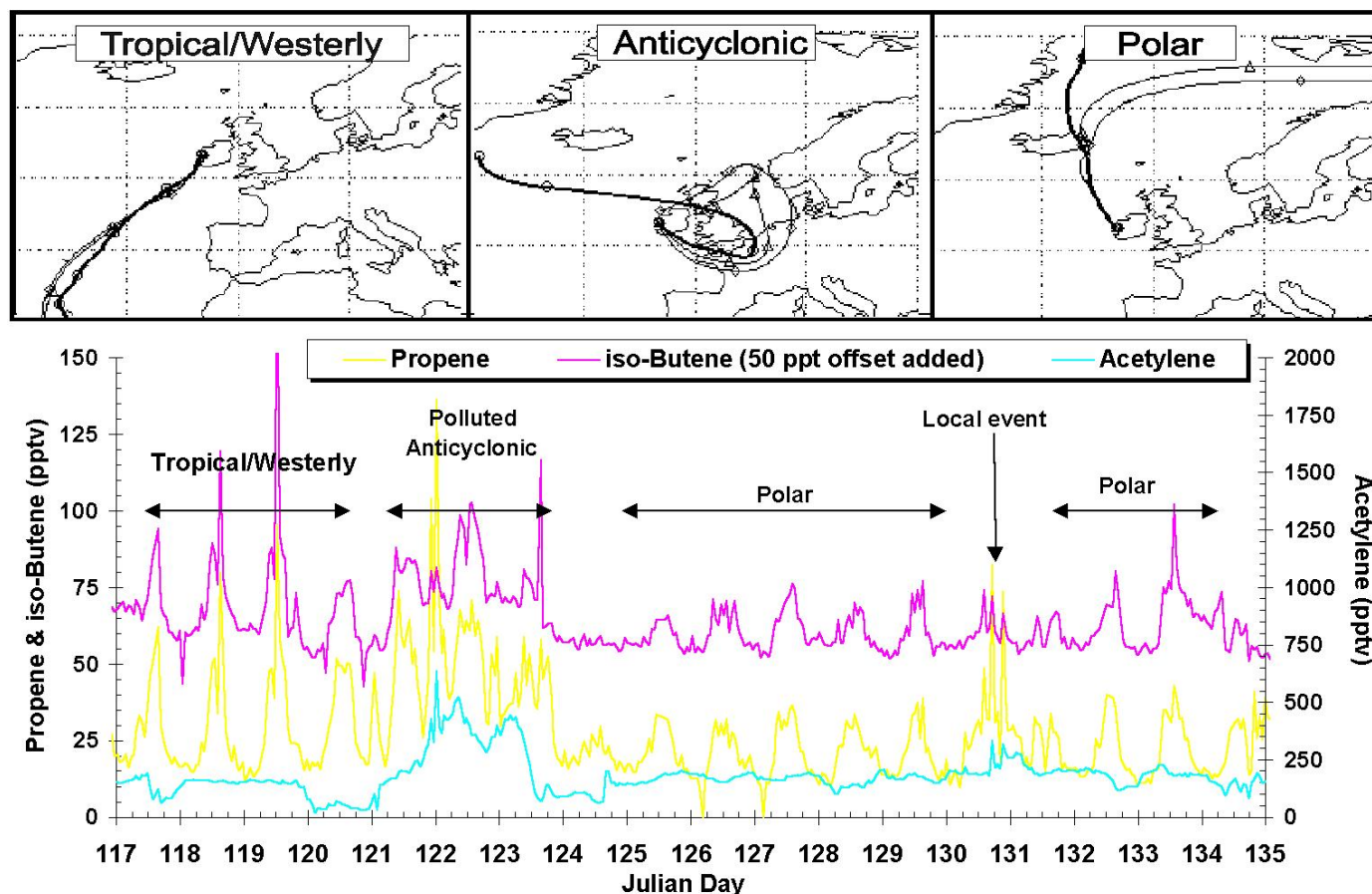
Peltier Cooled PTV injector developed specifically for continuous cryogen free NMHC measurements as part of this project (select the image to enlarge)



Strong diurnal cycles of some alkenes in marine air were observed during EASE 97, these can clearly be seen in Figure 2. The relatively short atmospheric lifetimes of these compounds (<12 hrs) indicates that the source region must lie within ~300 km of the site. The production of hydrocarbons by photochemical degradation of dissolved organic carbon has been recently reported from laboratory studies and these measurements support this mechanism. Alkenes from oceanic sources may therefore play an important role in tropospheric ozone production in the background atmosphere of the Northern Hemisphere.

Figure 2. Diurnal Cycles In Alkenes Observed In Clean Atlantic Air

Select the image to enlarge



The combination of NMHC data and back trajectory analysis allows for high resolution air mass classifications to be obtained. Figures 3 & 4 show the wide variety of different air mass types observed during the EASE 96 & 97 campaigns when classified using wind field back trajectories and NMHC abundance. Different species show clearly differing source regions, highlighted by plots of alkanes, DMS and isoprene with respect to time. During EASE 96 a strong covariance between DMS and CH3I was observed and has been reported in Bassford et al 1999.

(Select the image to enlarge)

Figure 3. EASE 96 Time Series

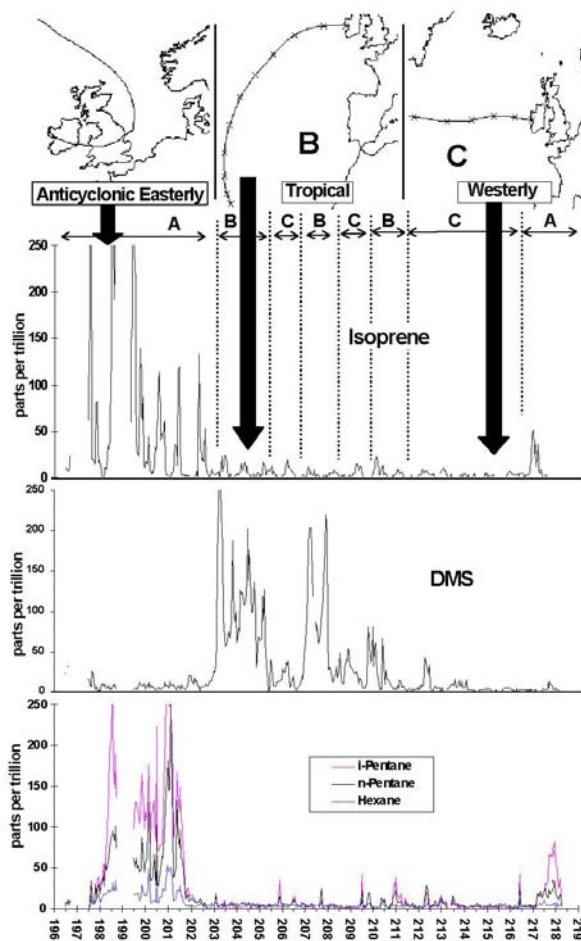
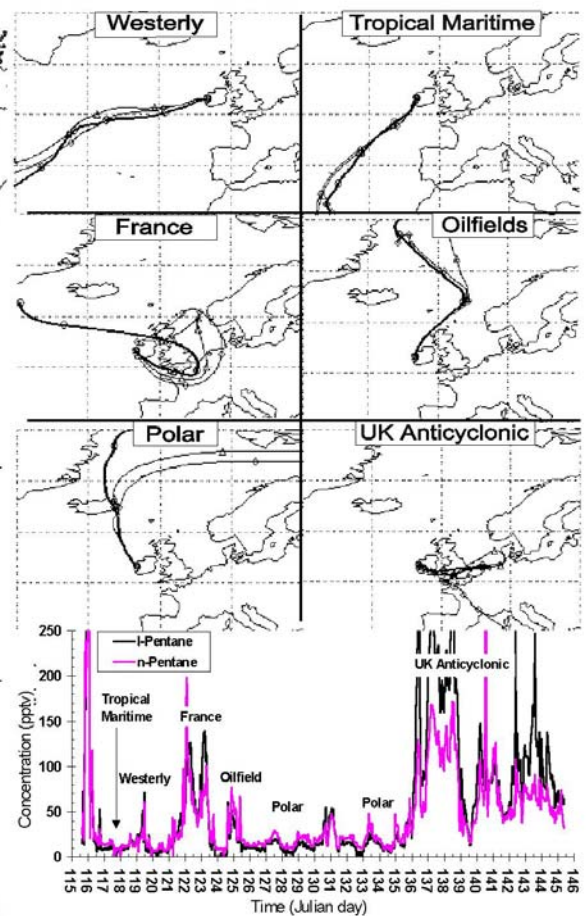
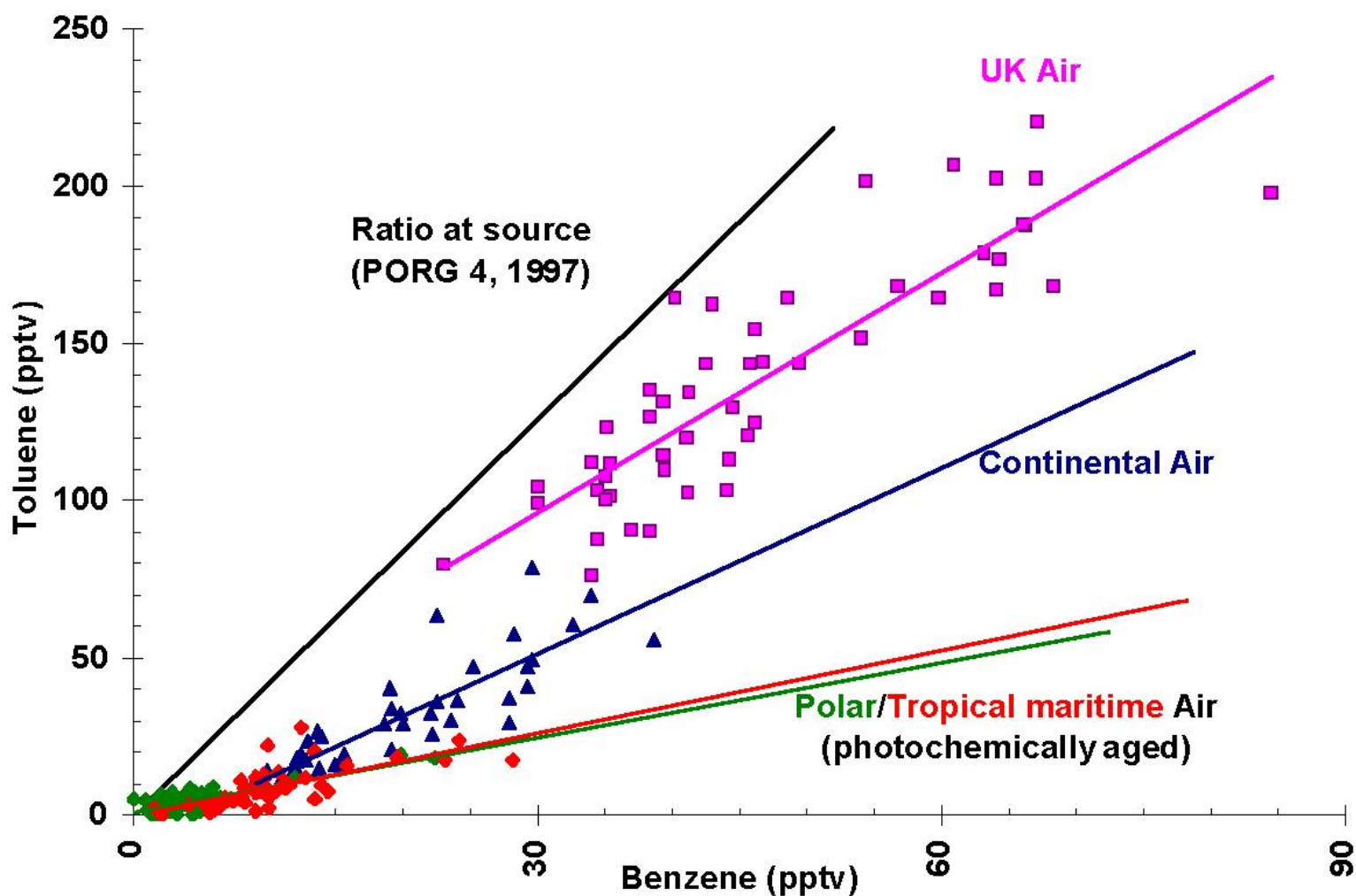


Figure 4. EASE 97 Time Series



The changes in ratio between a pair of hydrocarbon species is commonly used as an indicator of the extent of photochemical processing between source region and monitoring location. For example 'new' anthropogenic pollution contains considerably higher levels of toluene than benzene (~4:1) a result of emission profiles at source. The reaction with the hydroxyl radical is the major loss process of both species, and toluene reacts considerably faster (~ x4) than benzene. Hence, as the time since emission into the air mass increases, the ratio of the two species decreases - a result of photochemical action. Dispersion and dilution processes also occurring during transport affect both species equally, having no impact on the change in ratios observed. Figure 5 shows benzene and toluene ratios observed in different air masses during the EASE 97 campaign.

Figure 5. Variation In Benzene / Toluene Ratios As Function Of Airmass Age. (Select the image to enlarge)



Continuous measurements at the Mace Head Observatory in Westerly and South Westerly airflow, in conjunction with more recent studies at Cape Grim, Tasmania, has allowed for a comparison between Northern and Southern Hemisphere background hydrocarbon values. Table 1 demonstrates the significantly higher levels of most alkane species in Northern Hemisphere Atlantic background air.

Table 1. Comparison Of Northern And Southern Hemisphere Background NMHCs (Select the table to enlarge)

Ethane		Propane		<i>Iso</i> -butane		<i>n</i> -Butane		<i>Iso</i> -Pentane		<i>n</i> -Pentane		Hexane	
<i>CG</i>	<i>MH</i>	<i>CG</i>	<i>MH</i>	<i>CG</i>	<i>MH</i>	<i>CG</i>	<i>MH</i>	<i>CG</i>	<i>MH</i>	<i>CG</i>	<i>MH</i>	<i>CG</i>	<i>MH</i>
142.05	557.9	8.80	27.3	5.6	5.4	3.15	11.2	2.28	2.9	3.19	7.3	1.69	6.5
11.92	130.1	1.74	12.32	0.87	2.1	1.54	6.7	0.50	2.1	0.62	4.1	1.42	5.9
8.39	23.3	19.8	45.1	27.5	38.8	27.35	59.8	22.19	138	19.56	56.1	84.12	90.8

* *CG* – Cape Grim, *MH* – Mace Head.

CG: Number of samples: 149.

MH: Number of samples: <200

The measurements show that very significant inter-hemispheric differences exist in the background boundary layer concentrations of all alkanes measured with the exception of *iso* pentane and *iso* butane. Most striking is the differences observed in C2 and C3 alkanes where concentrations in background Northern Hemisphere boundary layer air are up to a factor of 4 higher than in those measured over the Southern Ocean. The two alkanes that differ from the trend of elevated concentrations in Northern Hemisphere background air, are those of *iso* butane and *iso* pentane. Whilst both species have been seen previously to have oceanic sources, they are predominantly released from anthropogenic sources. A possible explanation for the low branched chain isomer concentrations may lie in the significantly higher abundance of NO₃ radical in the Northern Hemisphere background when compared to the boundary layer of the Southern Ocean. However individual case studies of *iso/n* ratio variability using back trajectory analysis often produce unrealistic simulations of nitrate radical concentrations, and considerable further long term study is required to explain the deviations found in these branched chain hydrocarbons.

The value of long term continuous NMHC measurements has been demonstrated during the ACSOE Mace Head projects. High temporal resolution from in situ measurements allows for accurate airmass classification subsequently yielding valuable information on emission sources and chemical processing within an airmass. In the maritime air of the North Atlantic it is clear that trace levels of NMHCs may play a central role controlling *in situ* ozone production, a combination of long range transport of anthropogenic pollution including odd nitrogen species and oceanic emissions. The variations in NMHC abundance are a key input in constraining computational models of tropospheric processes used to simulate radical chemistry.

Acknowledgements:

We would like to thank NERC-ACSOE for financial support, John Methven and Paul Berrisford (Reading/BADC/ECMWF) who provided the back trajectory analyses.

<http://chem.leeds.ac.uk/Atmospheric/Field/ease.html>

References:

Atmospheric Monitoring Of Volatile Organic Compounds Using Programmed Temperature Vaporisation Injection. (1996) A.C Lewis, J.B McQuaid, P.W Seakins, M.J Pilling, K.D Bartle, And P Ridgeon. *J. High Res. Chromatogr.* **19**, 686-690.

In Situ Diurnal GC Measurements Of NMHC And DMS At A Remote Coastal Location (Mace Head, Eire) July/August 1996. (1997) A.C Lewis, K.D Bartle, J.B McQuaid, D.E Heard, M.J Pilling And P.W Seakins. *J. Chem. Soc. Faraday Trans.* **93**, 2921-2927.

Studies Of Tropospheric Chemistry In Urban And Remote Areas. (1999) J.B McQuaid, *PhD Thesis*, University of Leeds U.K.

Sub-ppt Atmospheric Measurements Using PTV-GC-FID And Real-Time Digital Signal Processing. (1998) J.B McQuaid, A.C Lewis, K.D Bartle And S.J Walton. *J. High Resol. Chromatogr.* **21**, 181-184.

Observation of Diurnal Cycles in Short-lived Tropospheric Alkenes At A North Atlantic Coastal Site. A. C Lewis, J.B McQuaid, N Carslaw And M.J Pilling. (1999) *Atmos. Environ.* **33**, 2417-2421.

Photochemical Alkene Formation In Sea Water From Dissolved Organic Carbon: Results From Laboratory Experiments. (1998) M Ratte, O Bujok, A Spitzzy, J Rudolph, *J. Geophys. Res.* **103**, 5707-5717.

Concurrent Observations Of Alkyl Halides And Dimethyl Sulphide In Marine Air - Implications For Sources Of Atmospheric Methyl Iodide. M.R Bassford, G Nickless, P.G Simmonds, A.C Lewis, M.J Pilling, And M.J Evans. (1999) *Atmos. Environ.* **33**, 2373-2383.