Long-term monitoring of VOCs in the free troposphere above the UK

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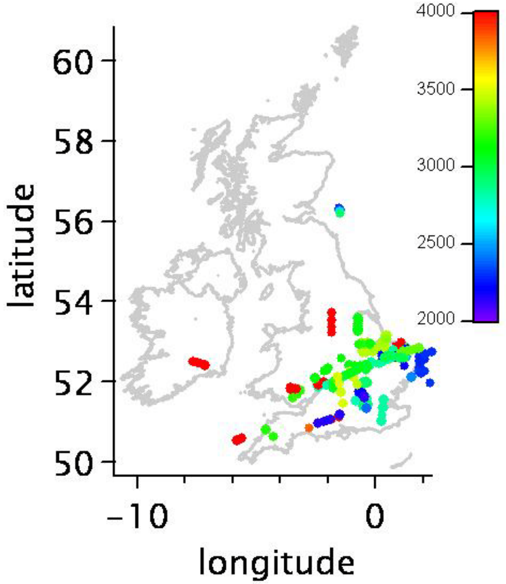

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VOC monitoring : Aims

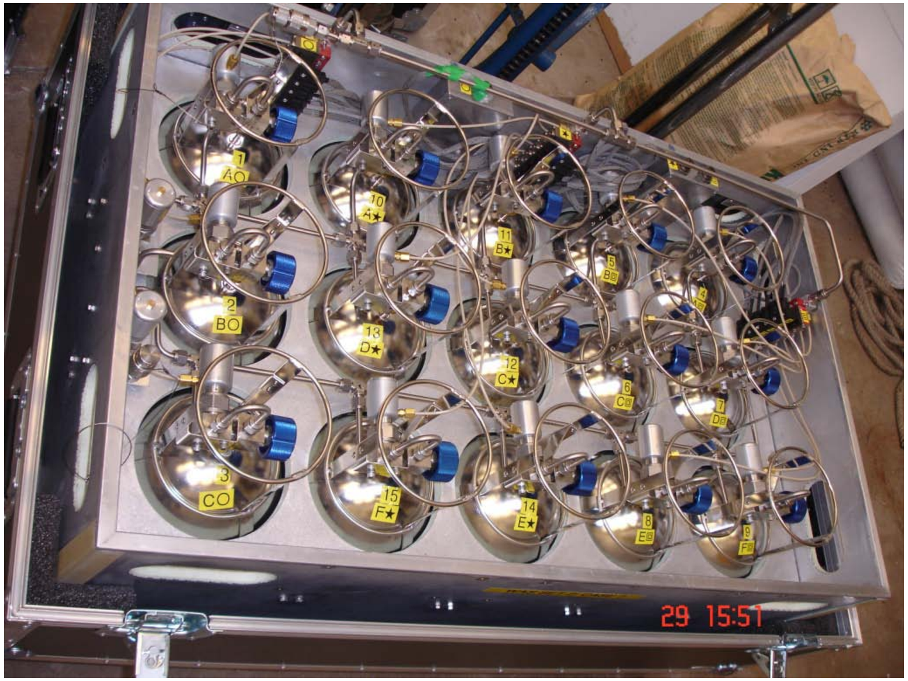
- To characterize seasonal and inter annual trends
- To capture important features related to transport, mixing and chemistry.
- To utilise UK based research aircraft's flying hours to the fullest for long-term study.

Sample collection

- Silico-treated stainless steel canisters

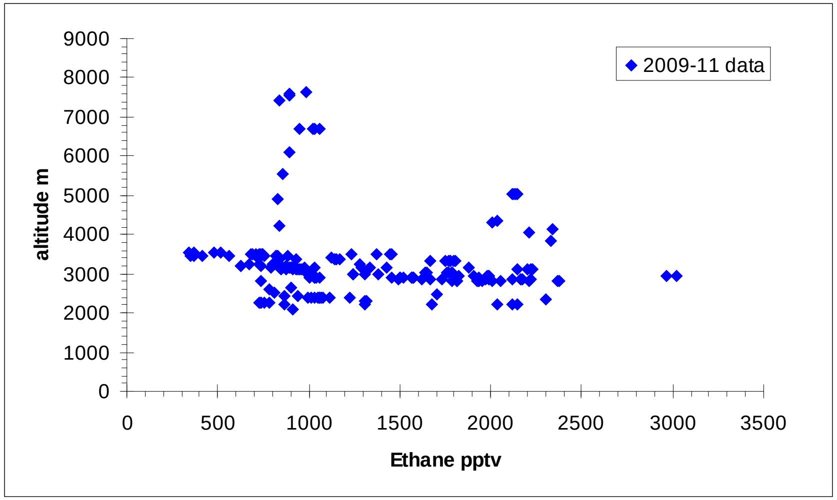
- Max. filling pressure 40psi

- Altitude preferably : 2000 - 5000m



The Whole Air Sampling System

•Sampling frequency : variable, typically once in a month

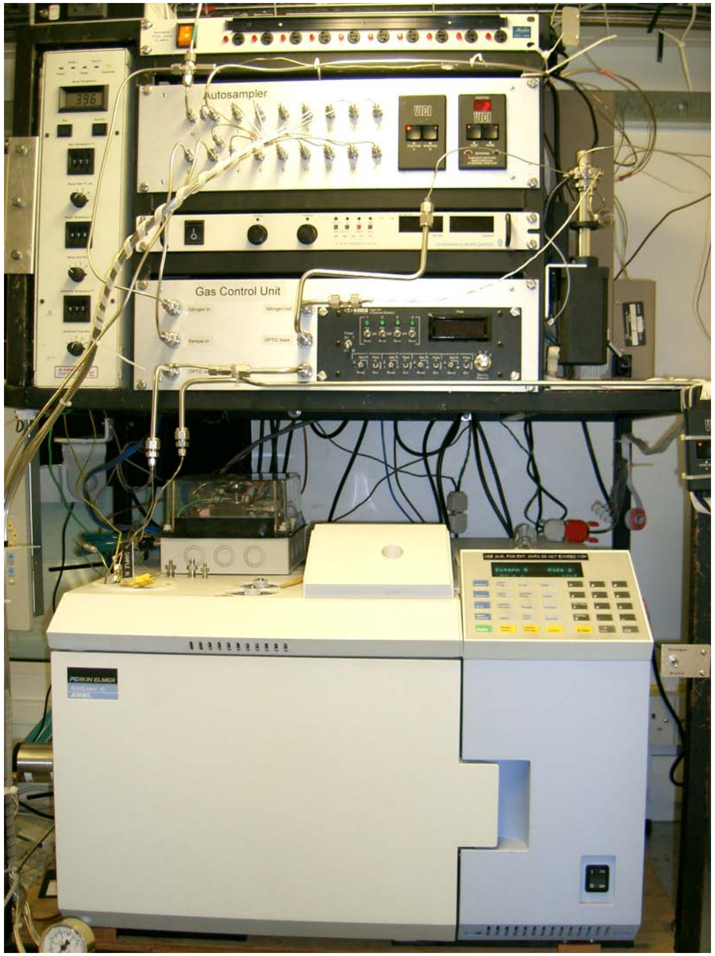


Technique and analytical configuration

York FGAM dc-gc-fid

Dual channel gas chromatograph

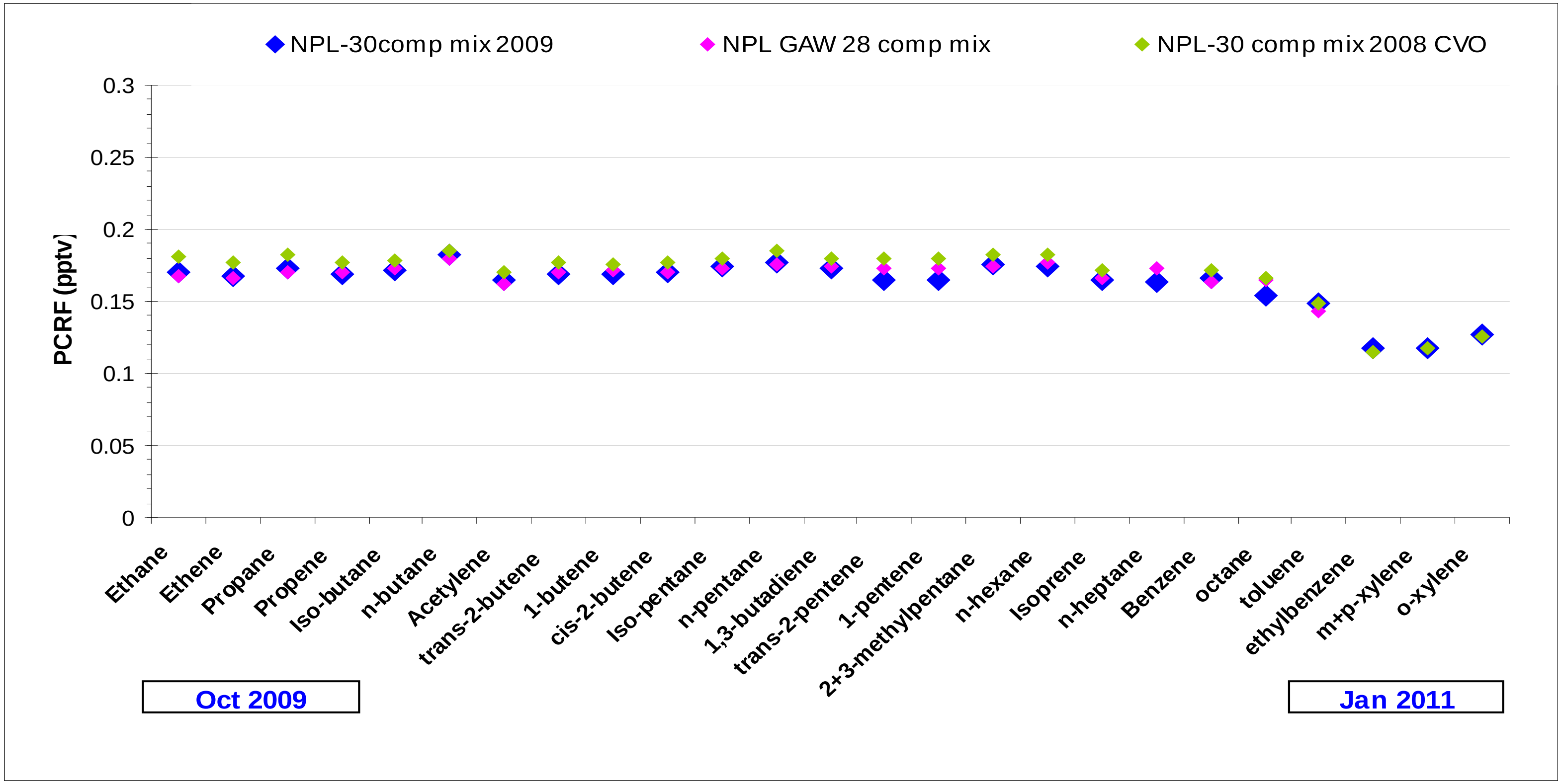
- Water removal
  - condensation trap maintained at -30^{o}C
- Preconcentration
  - Trapping temperature : Peltiers cooling -23^{o}C
  - Multi adsorbent bed: Carbopack B and carboxen 1000
- Thermal desorption
  - 320^{o}C with carrier flow (helium)
- Separation
  - Two capillary columns 50 m PLOT and 10 m LOWOX
- Detection
  - FID 1 and FID 2
- Calibration and standards:
  - National Physical Laboratory (NPL)- 30 component mix
  - GAW-VOC standards



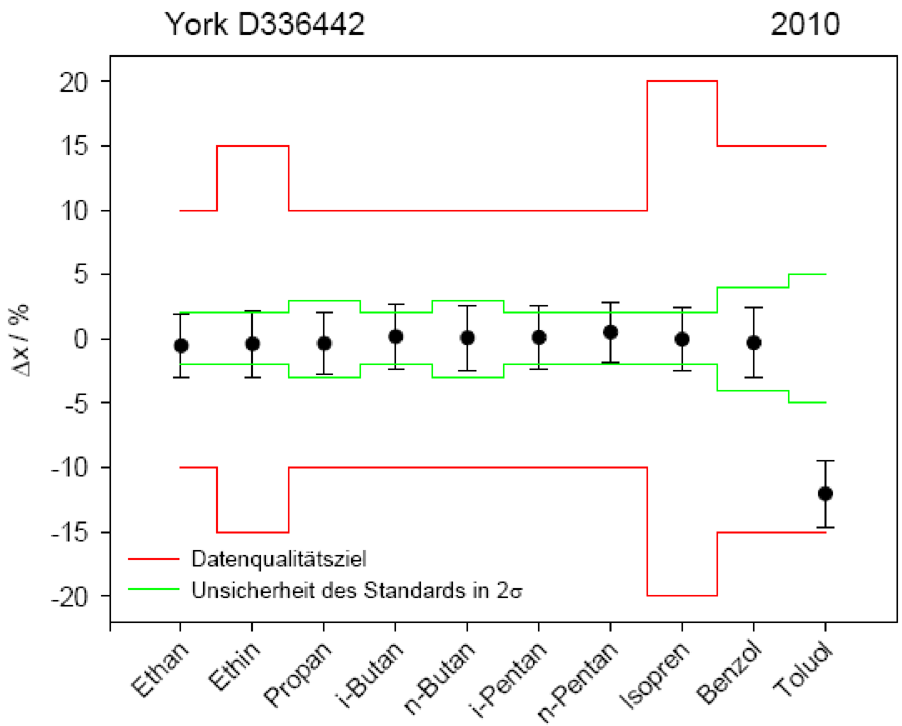
C_2-C_8 Alkanes,C_2-C_5 Alkenes
Aromatics (BTEX), Acetylene
C_2-C_4 Oxygenated VOCs

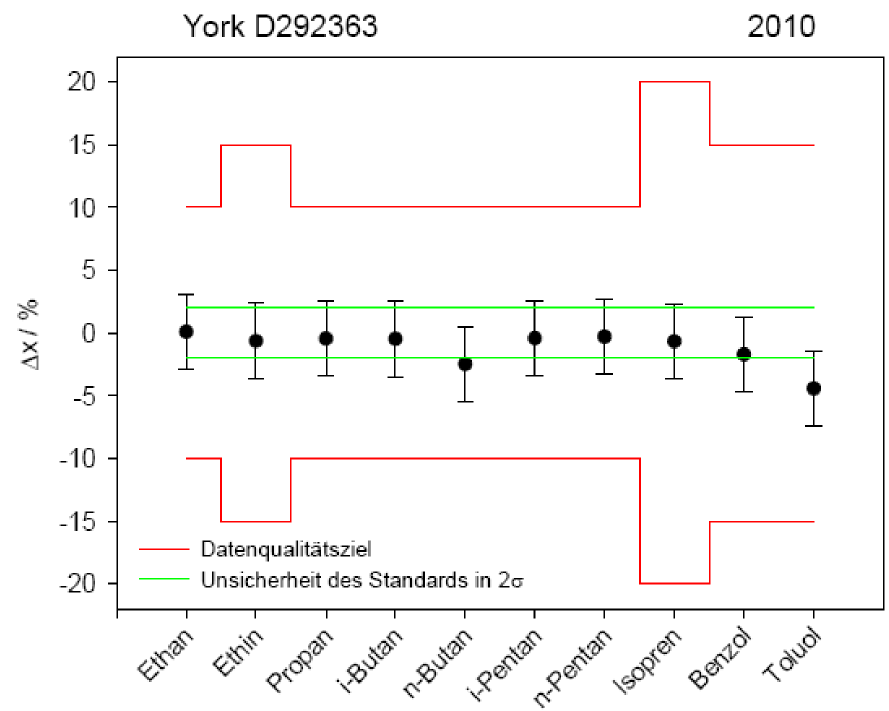
Hopkins, J.R., Lewis, A.C. & Read, K.A. (2003) , J. Environ. Monit., 5 (1), pp. 8-13.

System performance with time

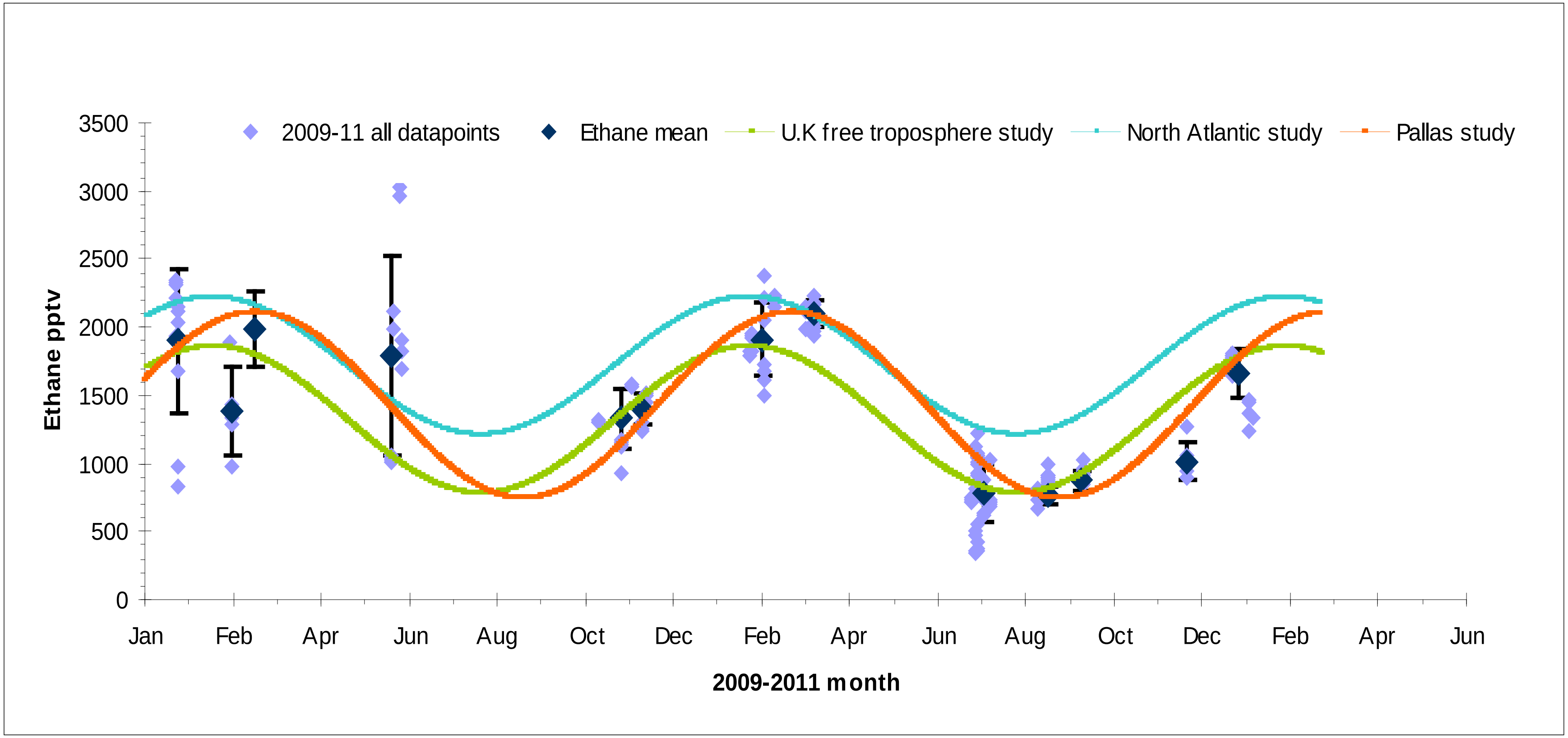


WCC-VOC intercomparison





Seasonal trends : Ethane



U.K free troposphere,2009-11 **y=1318.32 + 539.34(2π/365(day+46.25)**

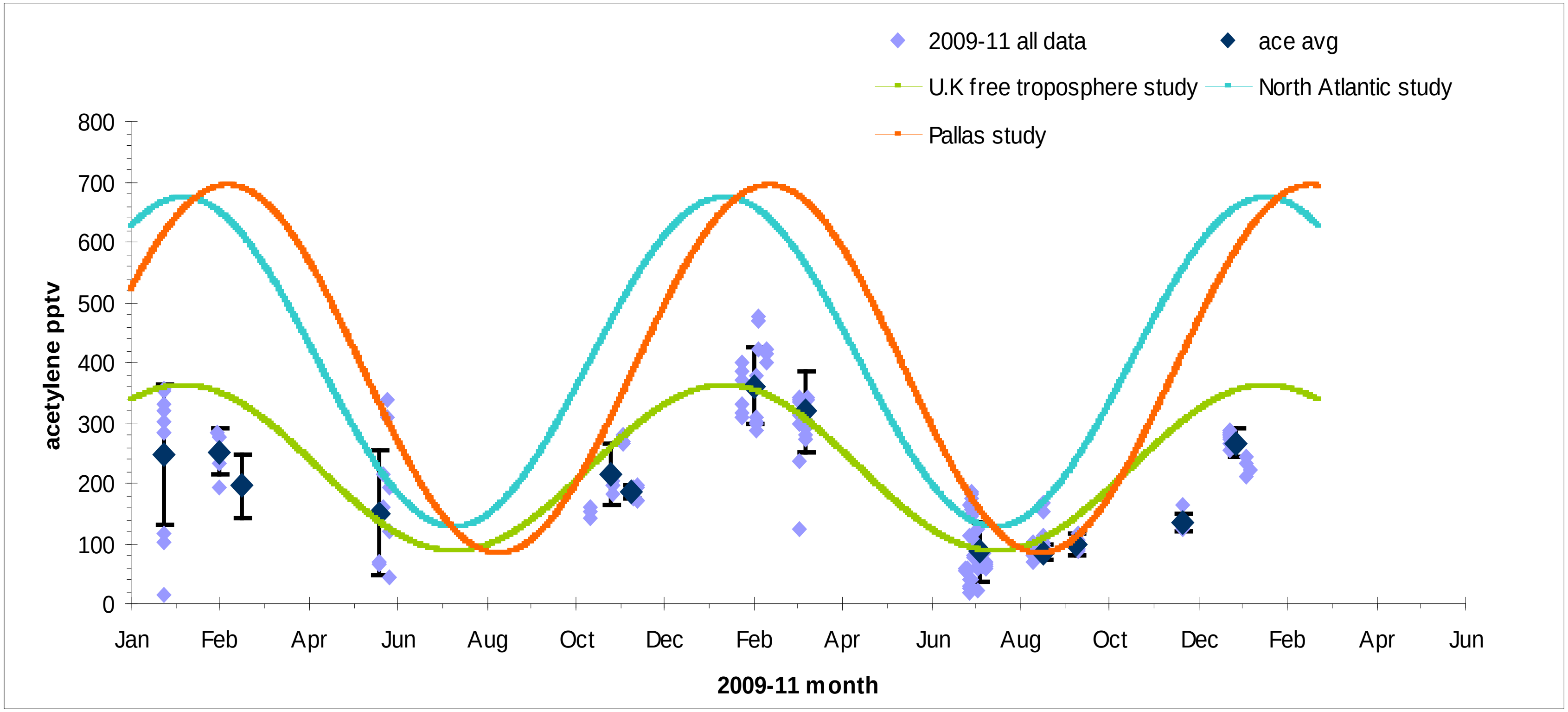
North Atlantic study,1989 **y =1715 + 505(2π/365(day+46.25)**

Pallas ,Baltic sea ,1994 **y=1425.00 + 683.34(2π/365(day+16.25)**

Laurila, T. and Hakola, H., 1996 ,Atmospheric Environment 30, pp. 1597–1607

S.A. Penkett, N.J. Blake, P. Lightman, A.R.W. Marsh and P. Anwyl, Journal of Geophysical Research 98 (1993), pp. 2865–2885

Seasonal trends: Acetylene



U.K free troposphere study ,2009-11 **y = 223.67 + 137.47 (2π/365(day+56.25)**

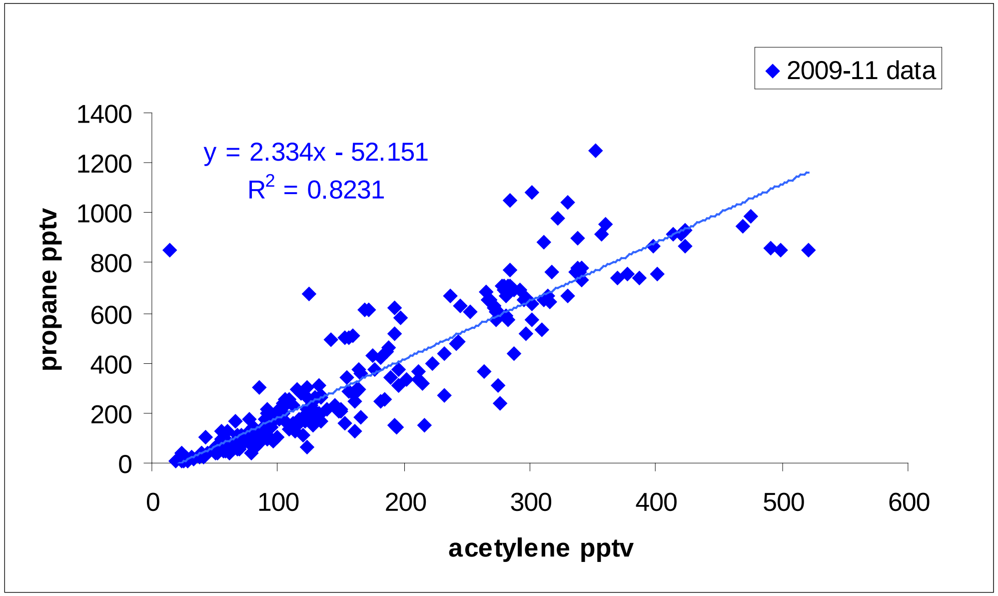
North Atlantic study ,1989 **y = 399.5 + 273.5 (2π/365(day+56.25)**

Pallas study ,1994 **y = 388 + 305.33.5 (2π/365(day+26.25)**

Laurila, T. and Hakola, H., 1996 ,Atmospheric Environment 30, pp. 1597–1607

S.A. Penkett, N.J. Blake, P. Lightman, A.R.W. Marsh and P. Anwyl, Journal of Geophysical Research 98 (1993), pp. 2865–2885

Ratios and source profile variation



$$\ln[P]/\{A] = (k_P - k_A/k_P)\ \ln[P] + C$$

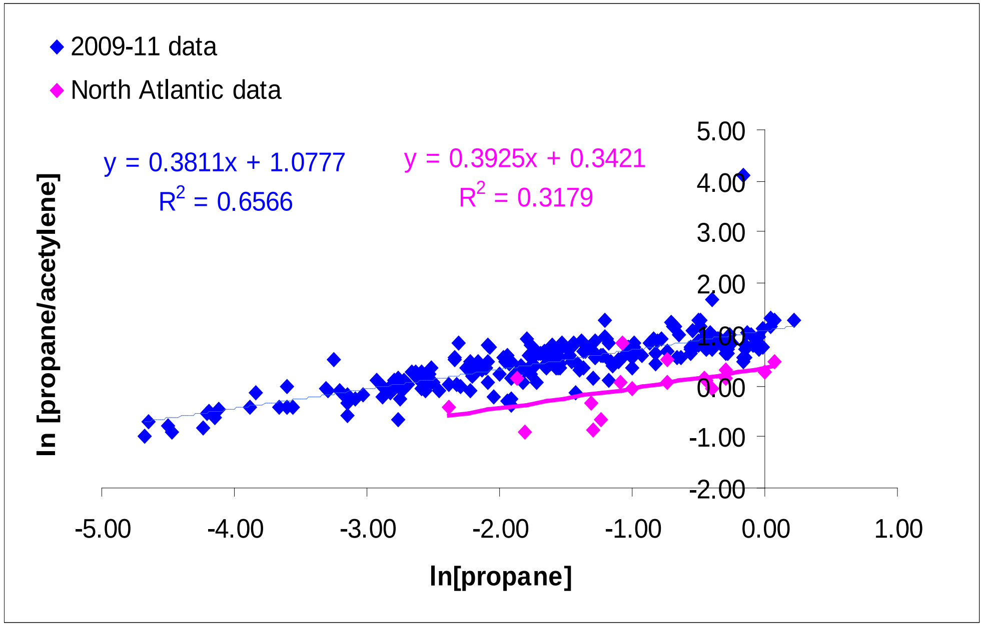
slope=rate constants

Where $C = \ln [P]_0 / [A]_0 - (k_p - k_a/k_p) \ln[P]_0$

intercept= source profile

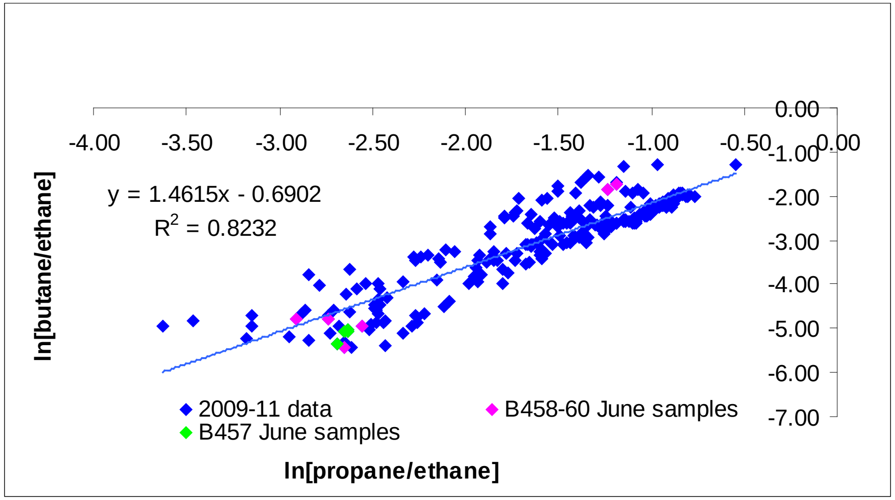
Our study and intercept =1.07

North Atlantic study and intercept =0.34

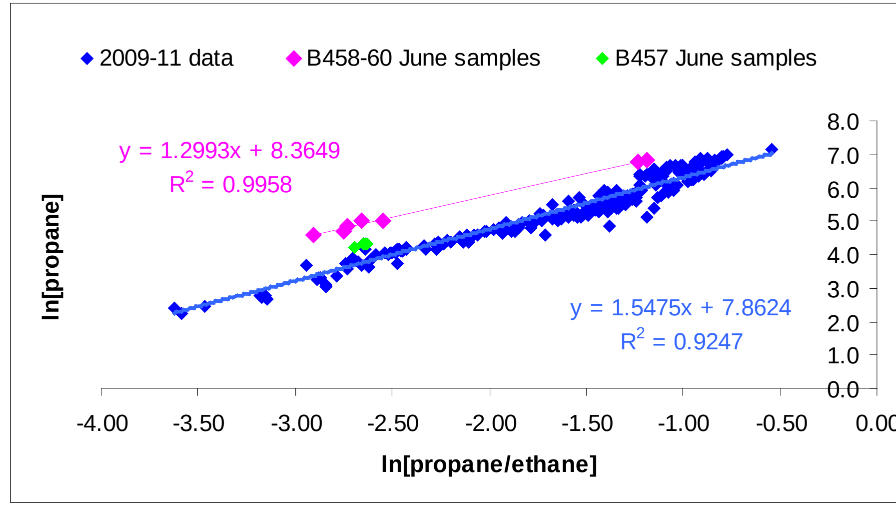


Goldan, P. D., D. D. Parrish, W. C. Kuster, M. Trainer, S. A. McKeen, J. Holloway, B. T. Jobson, D. T. Sueper, and F. C. Fehsenfeld (2000), *J. Geophys. Res.*, 105(D7), 9091–9105, doi:10.1029/1999JD900429.
Gong, Q., and K. Demerjian (1997), J. Geophys. Res., 102(D23), 28059-28069.

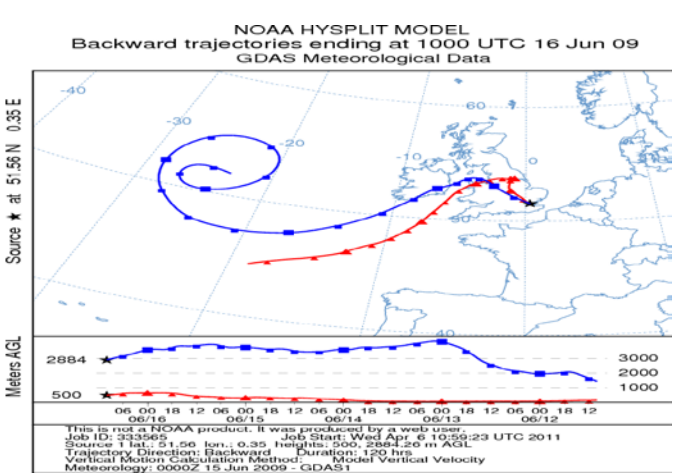
Ratios and aging pattern: another source



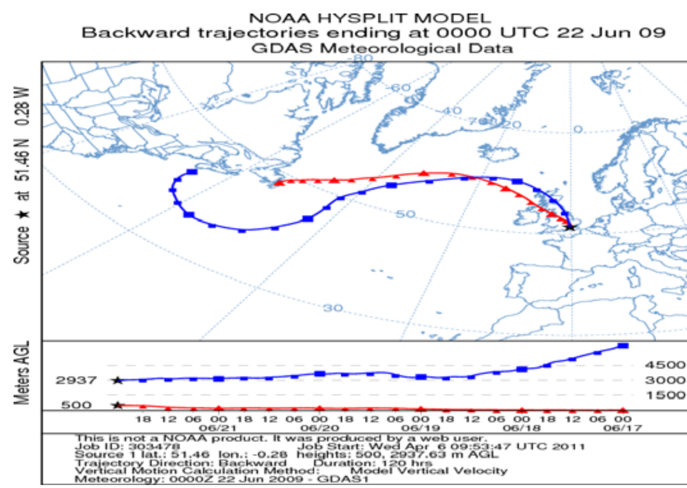
In [butane/ethane] vs In[propane/ethane]



In [propane/ethane] vs In [propane]



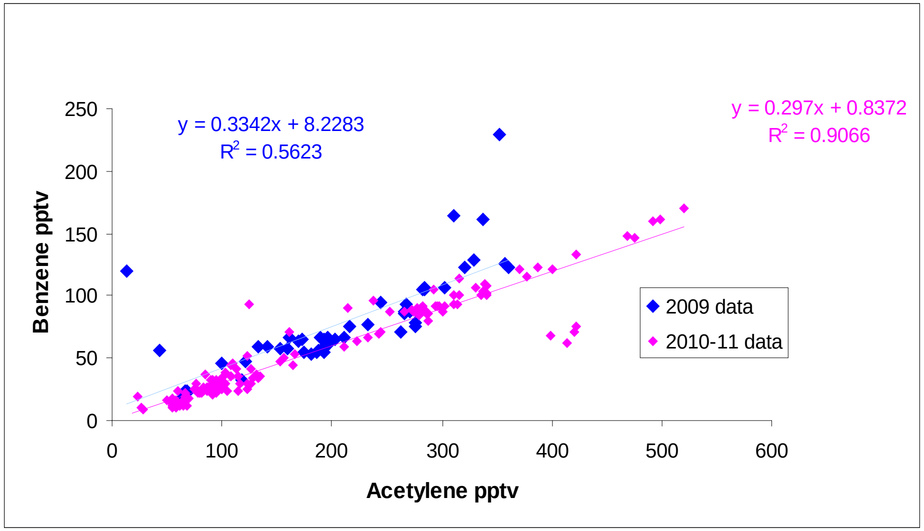
Flight B457 Atlantic ocean



Flight B458 continental influence

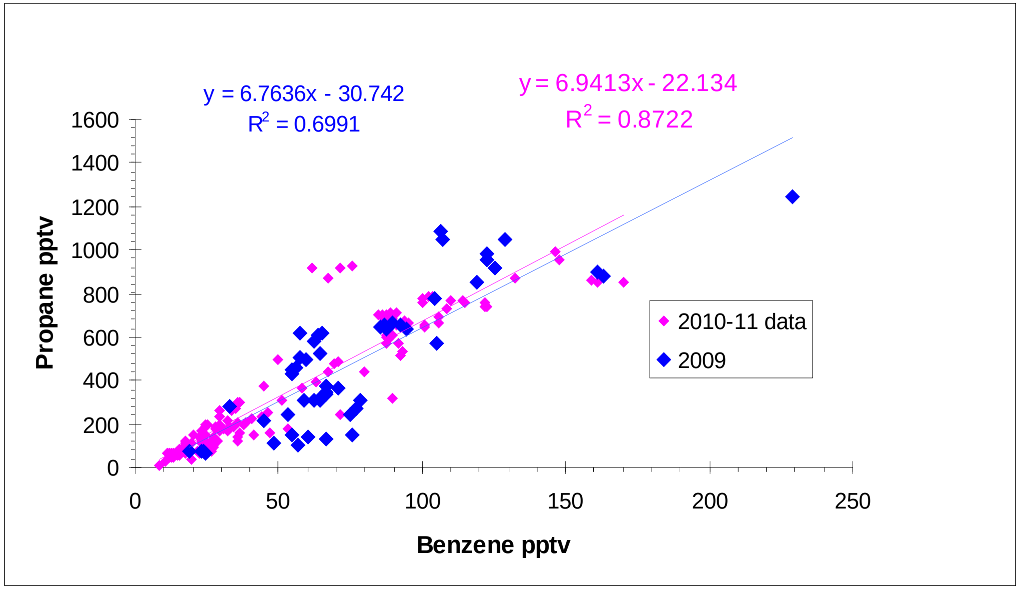
Parrish, D. D., et al. (2004), *J. Geophys. Res.*, 109, D23S18, doi:10.1029/2004JD004978

Ratios : source characterization



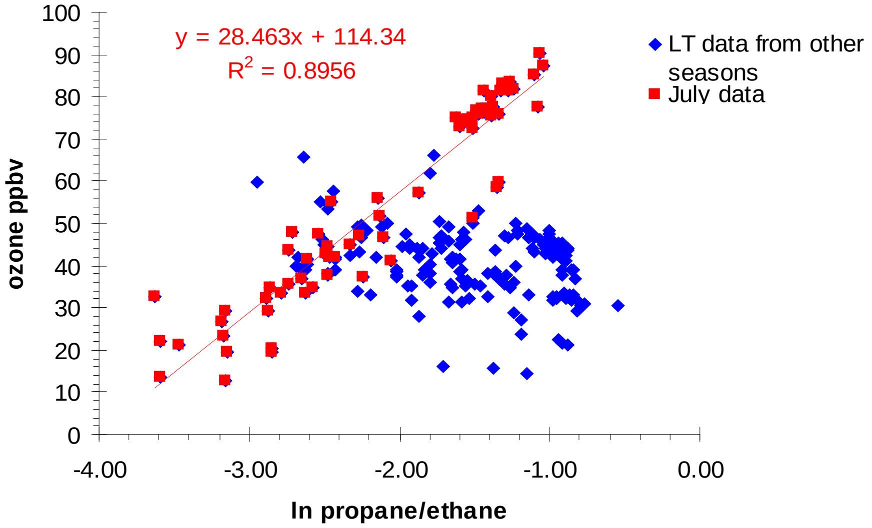
Vehicular exhaust responsible for benzene and acetylene emissions.

Natural gas as a main source for propane emission

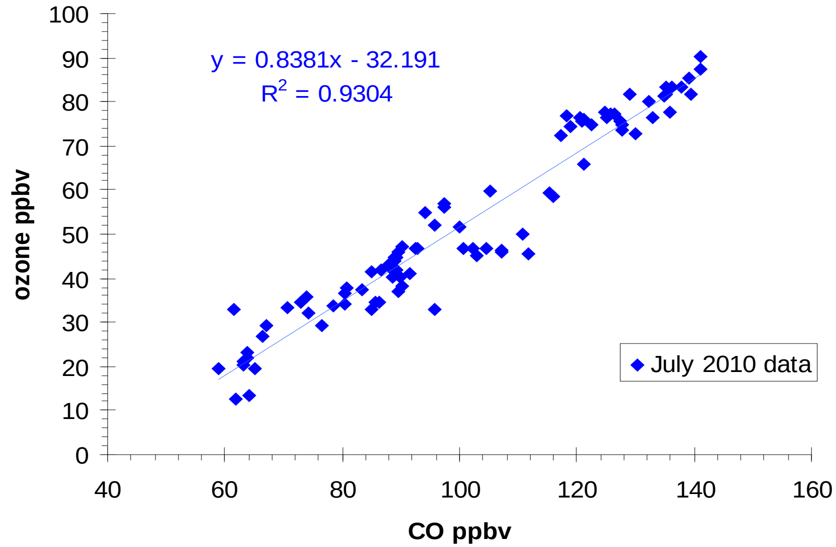


Russo, R. S.; Zhou, Y.; White, M. L.; Mao, H.; Talbot, R.; Sive, B. C. Volume 10, Issue 1, 2010, pp.1083-1134

Hydrocarbon Processing and ozone



Low NO levels or mixing of polluted air with clean marine air could be the reasons for ozone destruction.



Helmig, D., D. M. Tanner, R. E. Honrath, R. C. Owen, and D. D. Parrish (2008), *J. Geophys. Res.* , 113 , D20S91, doi:10.1029/2007JD008930.

Summary and further plans

- Hydrocarbon ratios as a tracer
- Free tropospheric study provides useful information on transport, mixing and chemistry
- Continue to collect data over longer timescales and monitor instrument performance
- Improve data coverage by collecting and analysing more samples.

Acknowledgements

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Research group people

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THE UNIVERSITY *of York*

Facility for Ground based Atmospheric Measurements
NATURAL ENVIRONMENT RESEARCH COUNCIL