

Measurements and modeling of ambient concentrations of biogenics in summer episodes:
TORCH campaign 2003.

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- NERC Polluted Troposphere Programme

TORCH expt summer 2003 – Writtle College, Chelmsford





Aerial photos of 4.5 km upwind



Measurements

- O₃
- CO_x
- NO_x, NO₂
- C₂ – C₈ hydrocarbons (38 species)
- C₁ – C₄ oxygenated hydrocarbons (9 species)
- PAN
- Peroxides (Organic and Inorganic)
- Organic nitrates
- OH and HO₂ radicals
- Sum of RO₂ + HO₂ radicals
- OH chemical lifetime
- Photolysis frequencies (e.g. j(O¹D), j(NO₂), j (HCHO))
- Aerosol number and size distribution
- Aerosol composition
 - Nitrate, Ammonium, Sulphate, Organic
- Local meteorology
- 5 and 10 day back trajectories

METHODOLOGY FOR VOCS

Samples collected from 10m height.

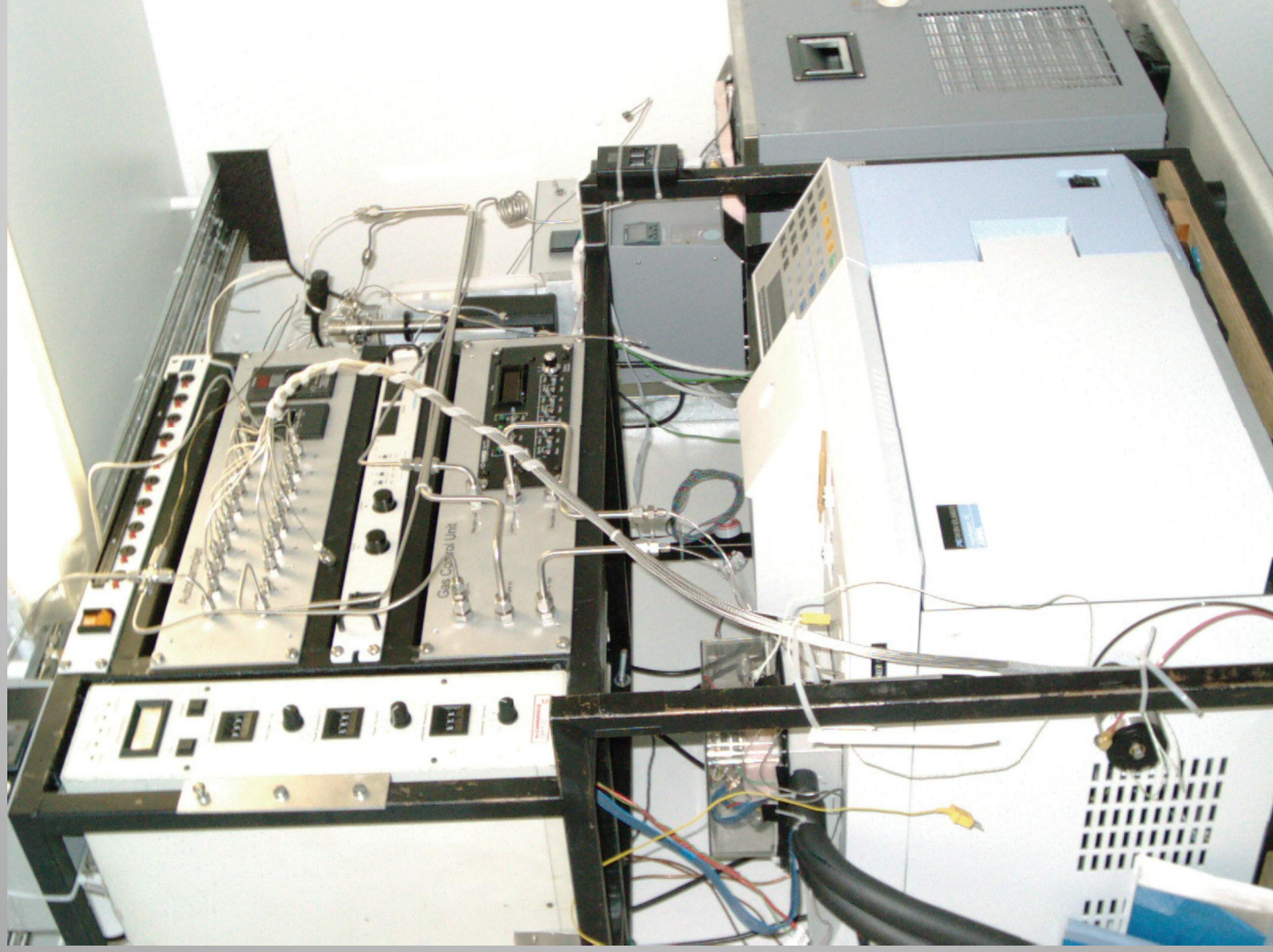
Analysis in situ with GC-2x2FID

NaSO₄ Al₂O₃ PLOT - NMHCs
LOWOX PLOT – O-VOCS

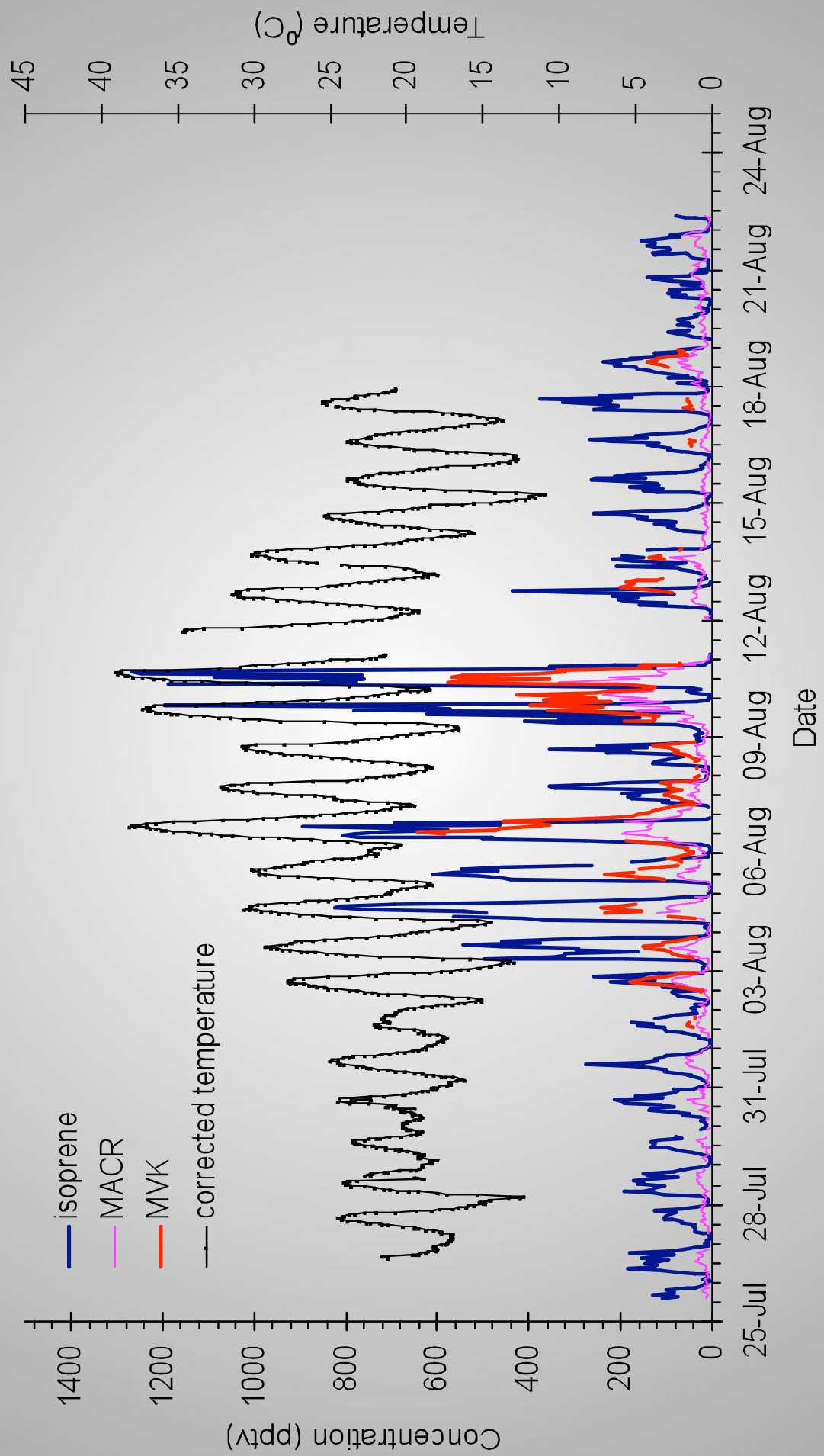
NIST and NPL NMHC standards.
WMO - GAW reference in UK.

Cal. 1/24 samples
Zero. 1/24 samples

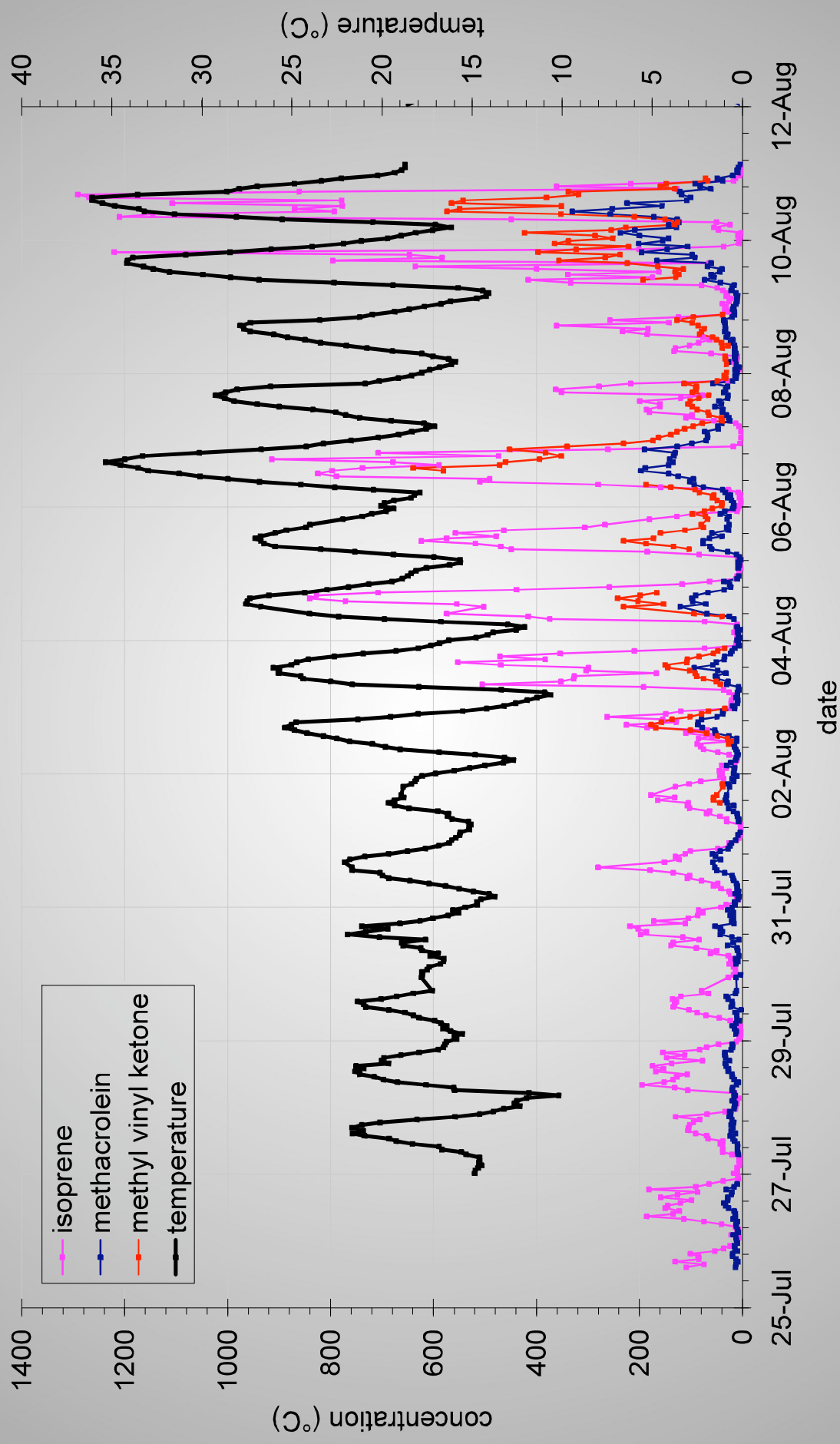
1 sample / hour.



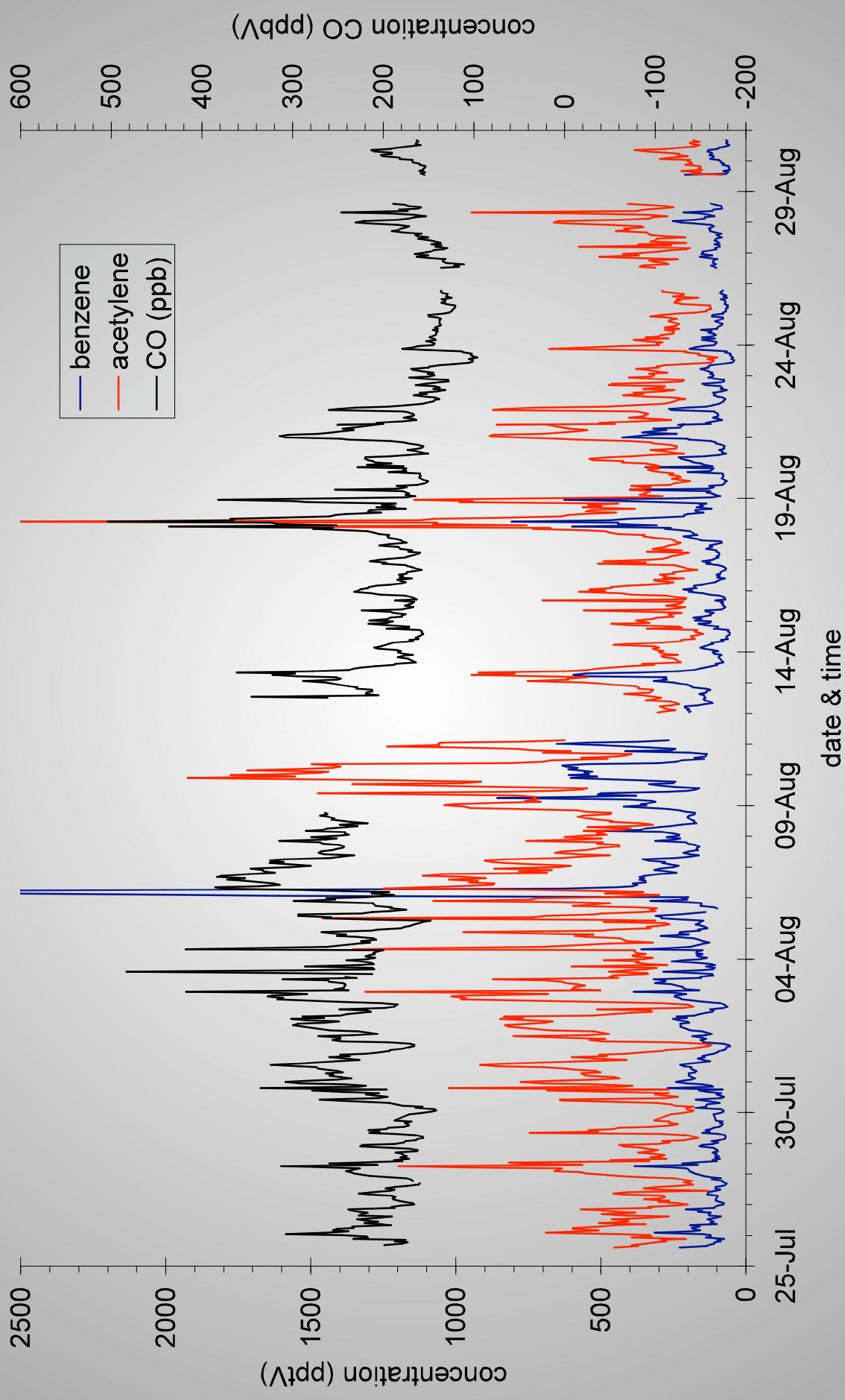
30 days July – August 2003



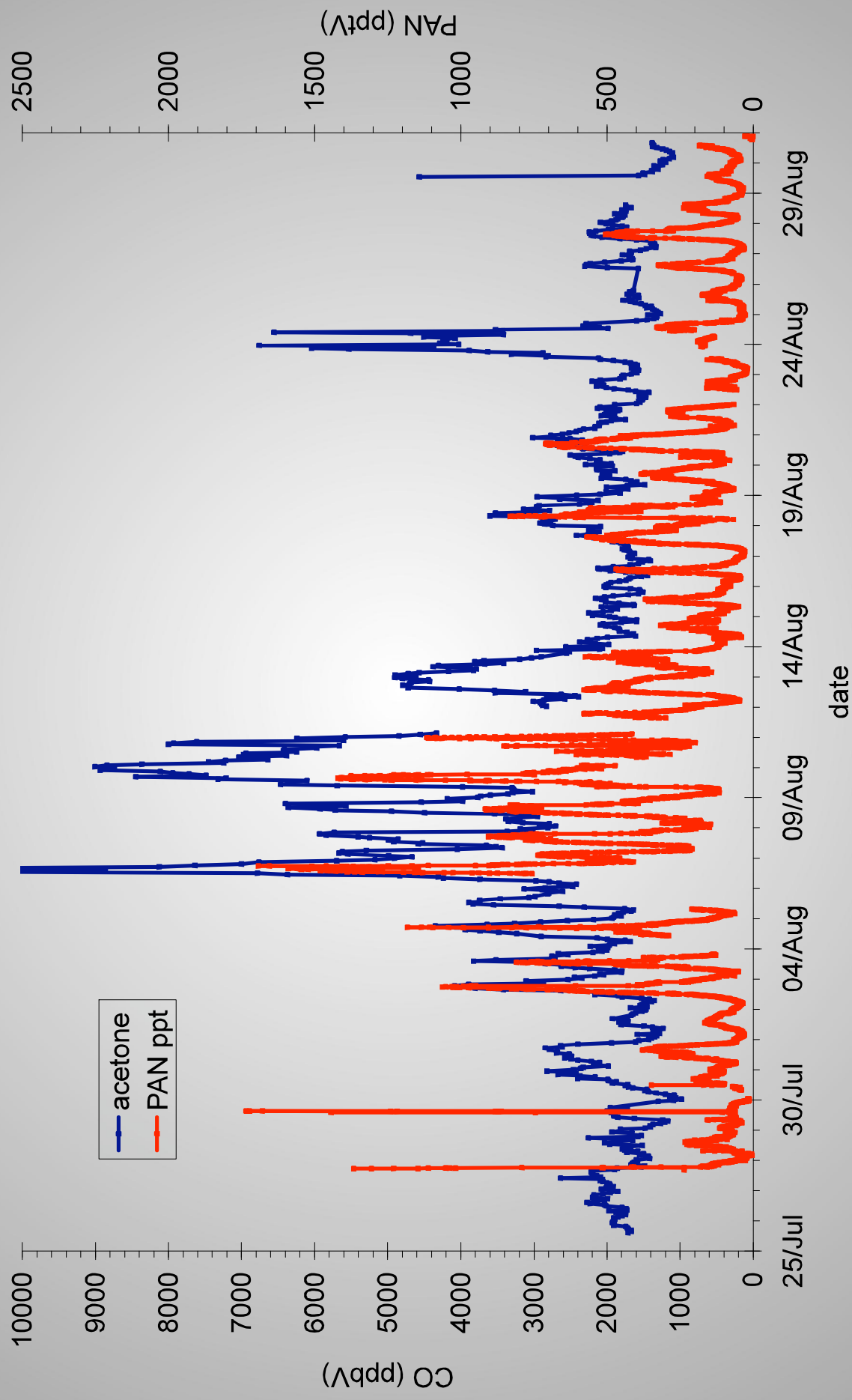
Isoprene and degradation products



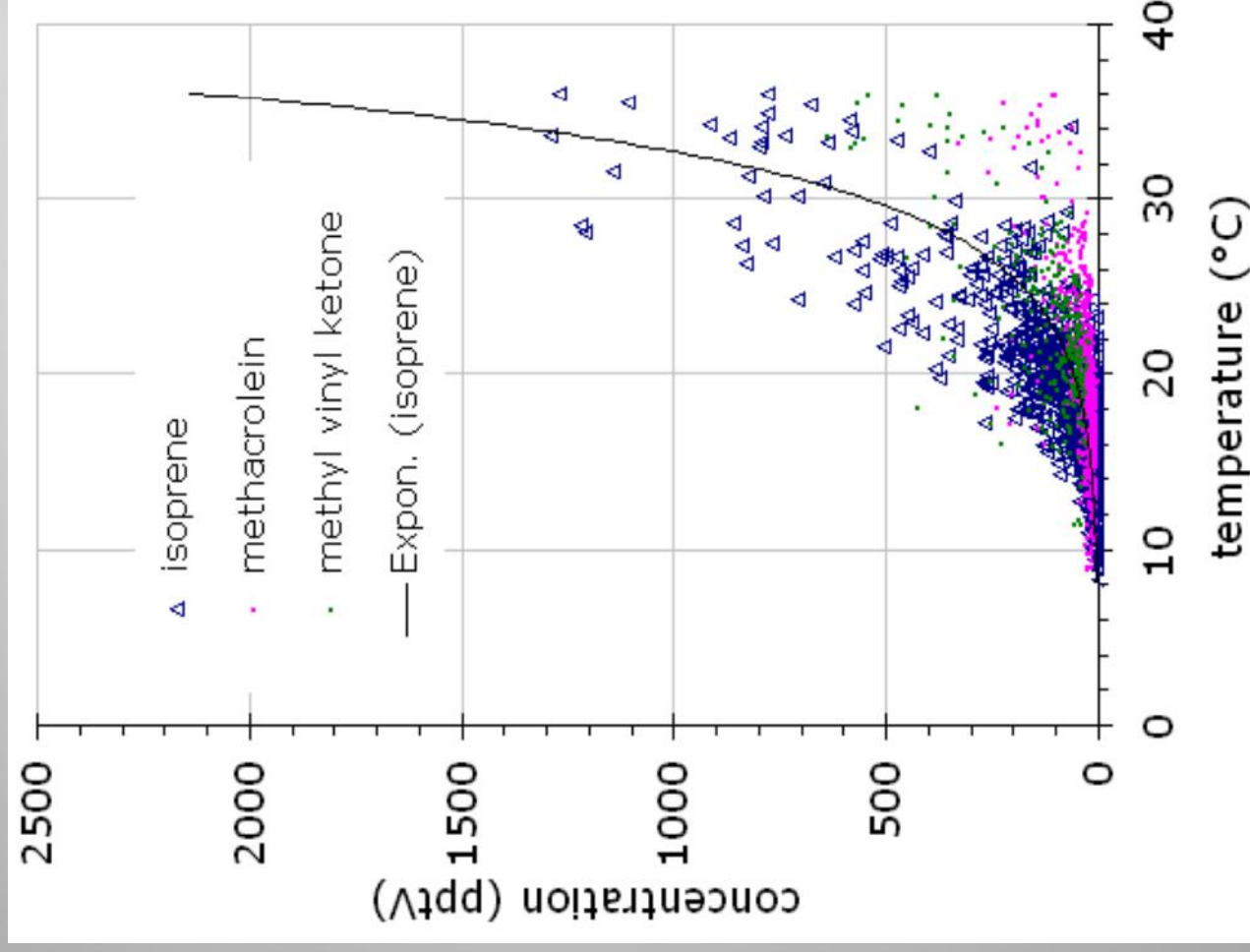
Other NMHCs and CO



Secondary products, acetone and PAN



Isoprene temperature dependence

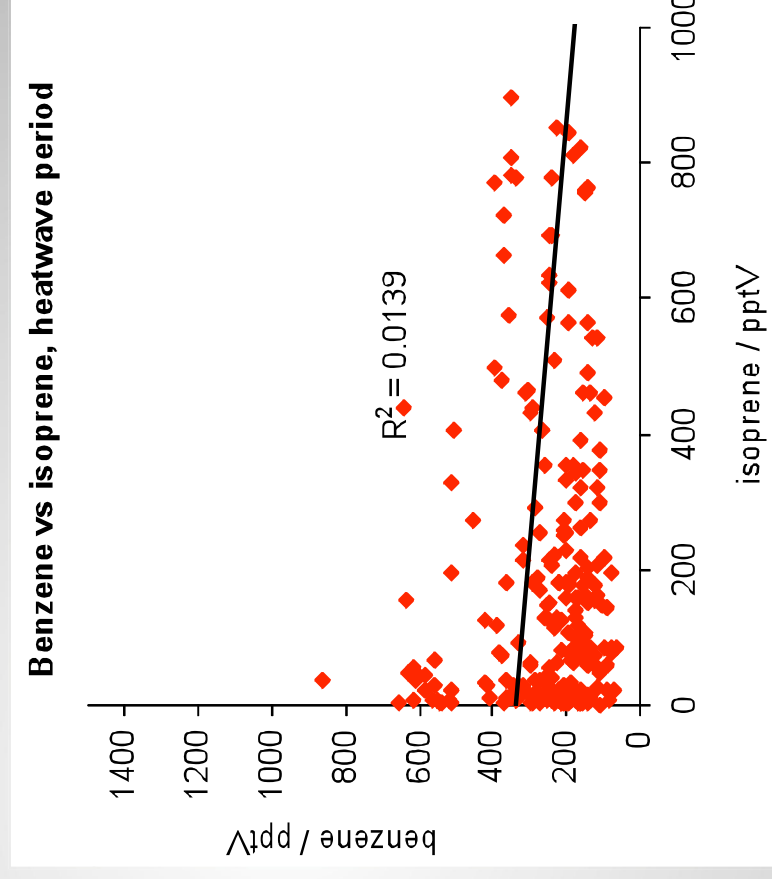
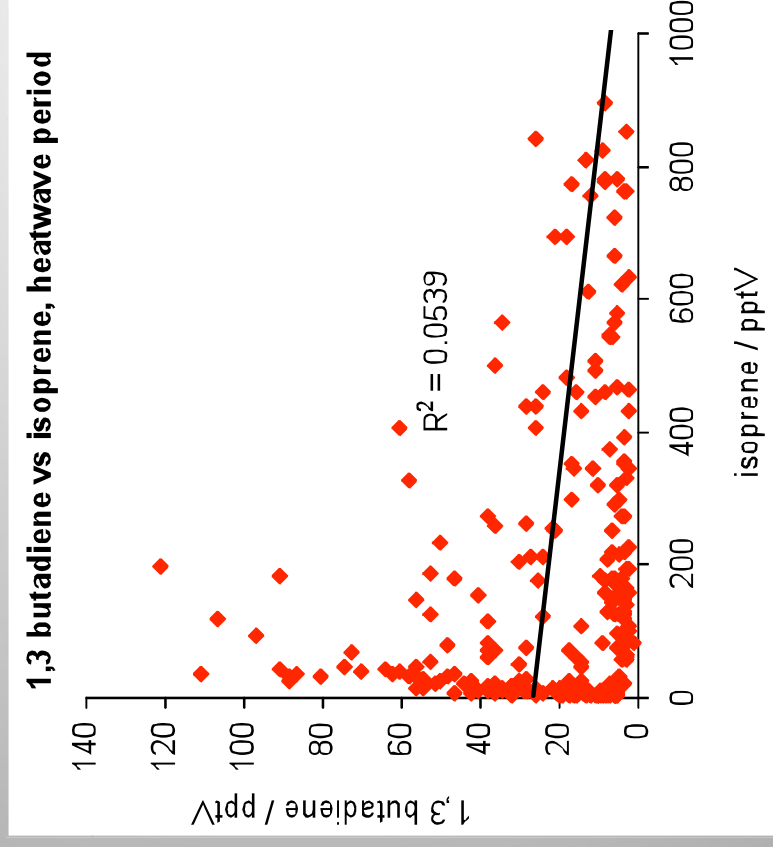


Good agreement with Guenther algorithms for isoprene release from vegetation.

Can we rule out any other sources?

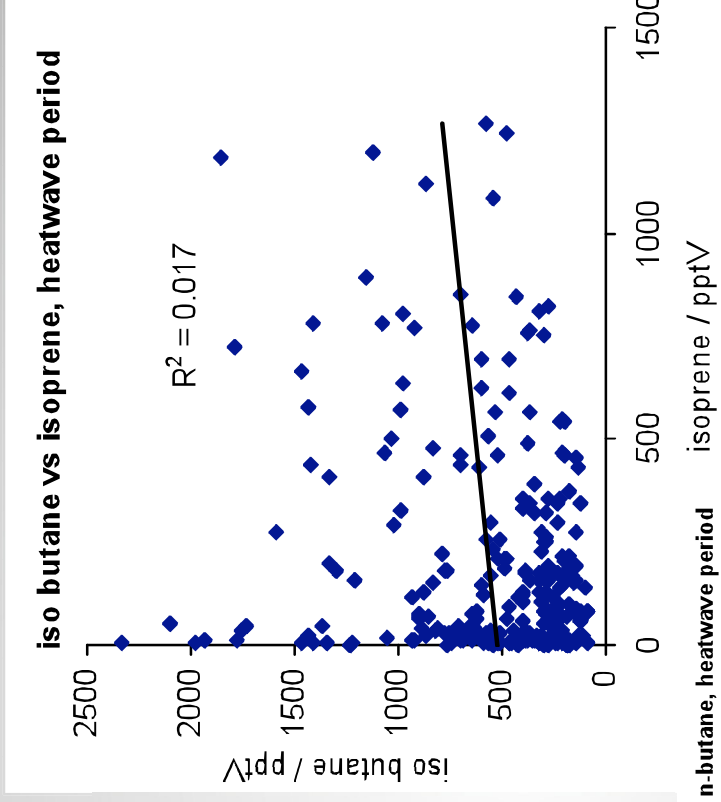
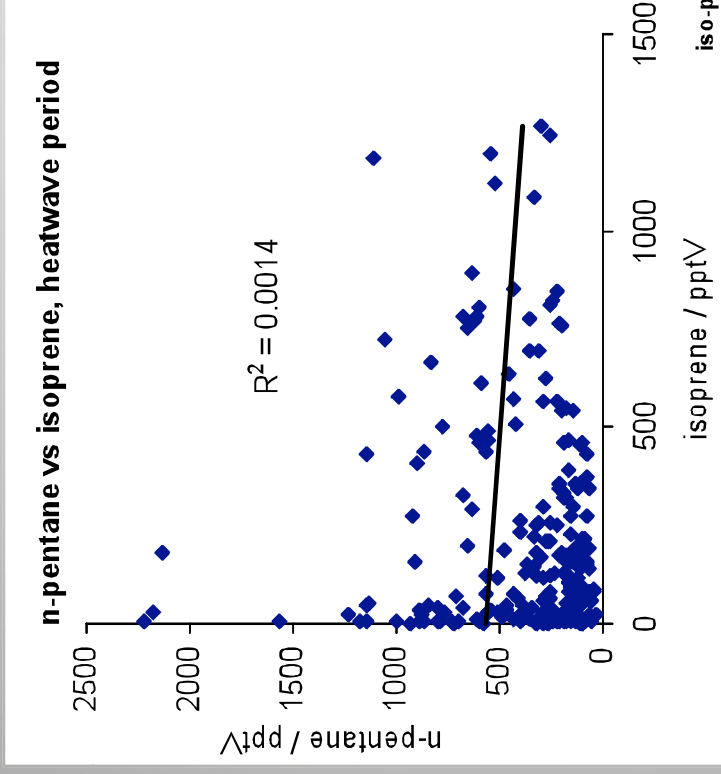
Is heatwave isoprene from an anthropogenic source?

- Urban source seen in heavily trafficked locations like Marylebone Road.
- This has been shown *via* correlations between isoprene and other trace gases associated with vehicle tailpipe such as benzene and 1,3 butadiene

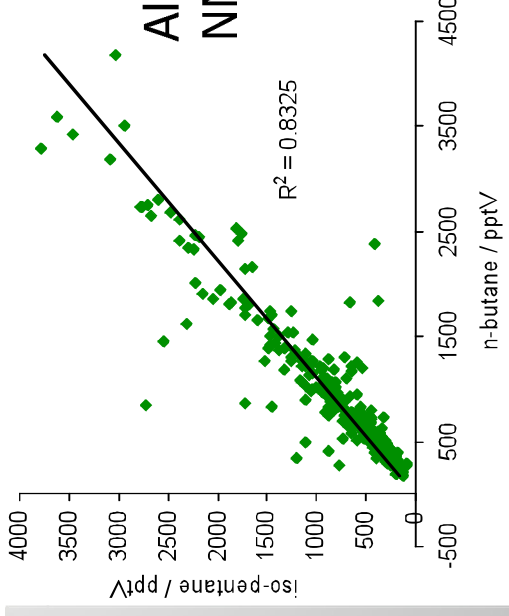


No correlation between isoprene and tailpipe NMHCs during heat wave

Diffuse evaporative emission of isoprene from nearby petrochemical sources, including individual vehicles?



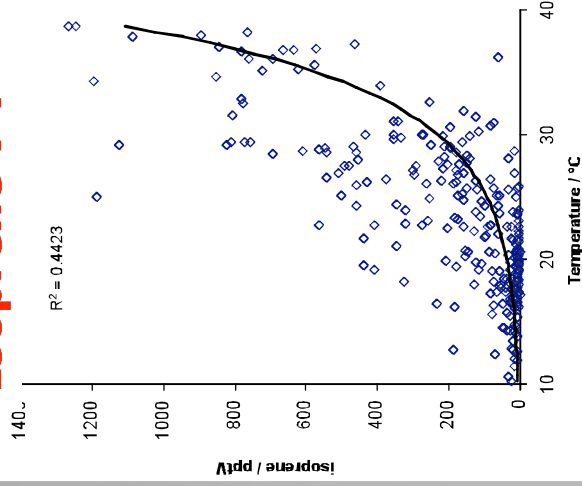
No correlation or covariance with evaporative type NMHCs and isoprene



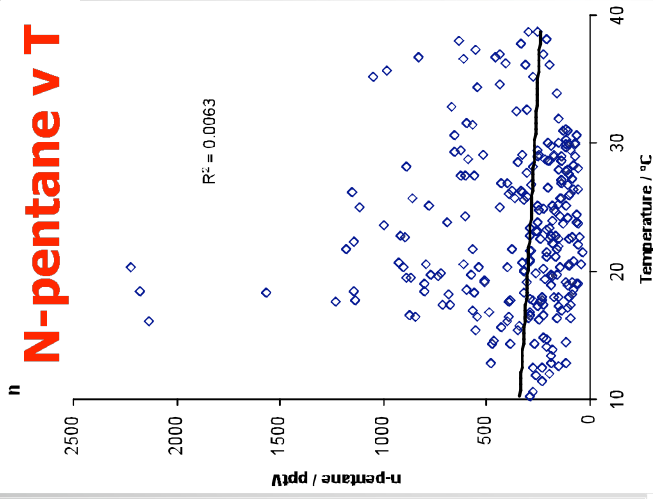
All other evaporative source NMHCs show tight correlation

Temperature dependencies during heat wave.

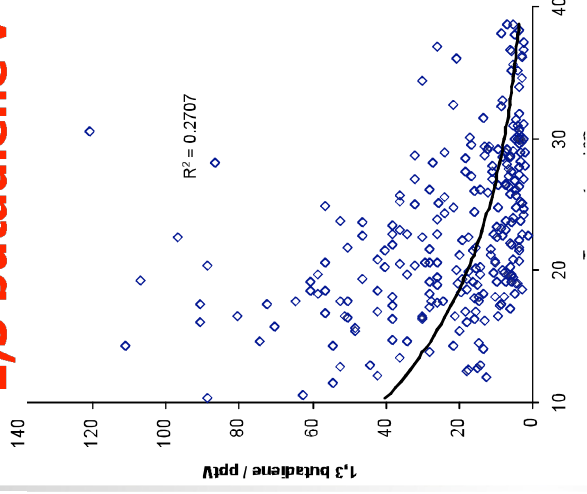
Isoprene v T



N-pentane v T

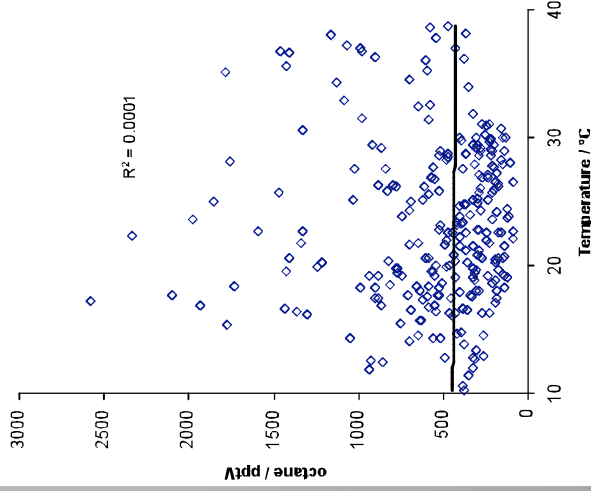


1,3 butadiene v T

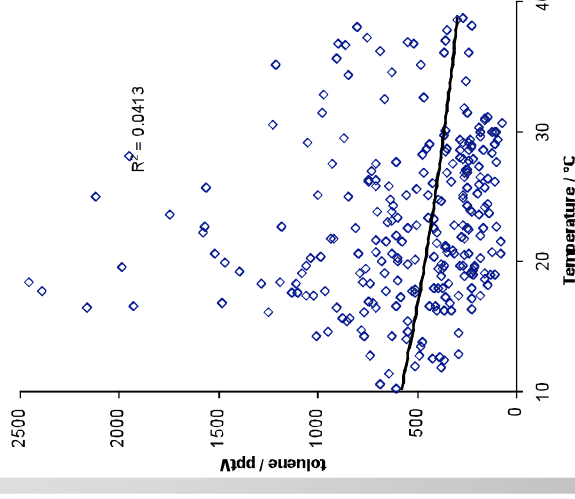


More reactive NMHCs tend towards anticorrelation

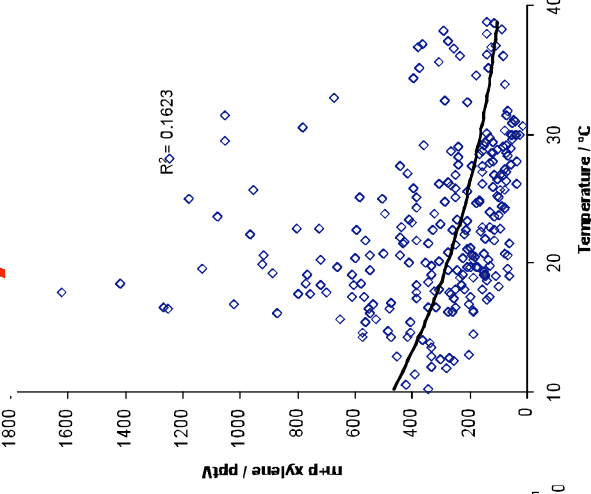
N-butane v T



Toluene v T



M-xylene v T



High OH/O₃ during periods of highest T

Only isoprene has +ve slope

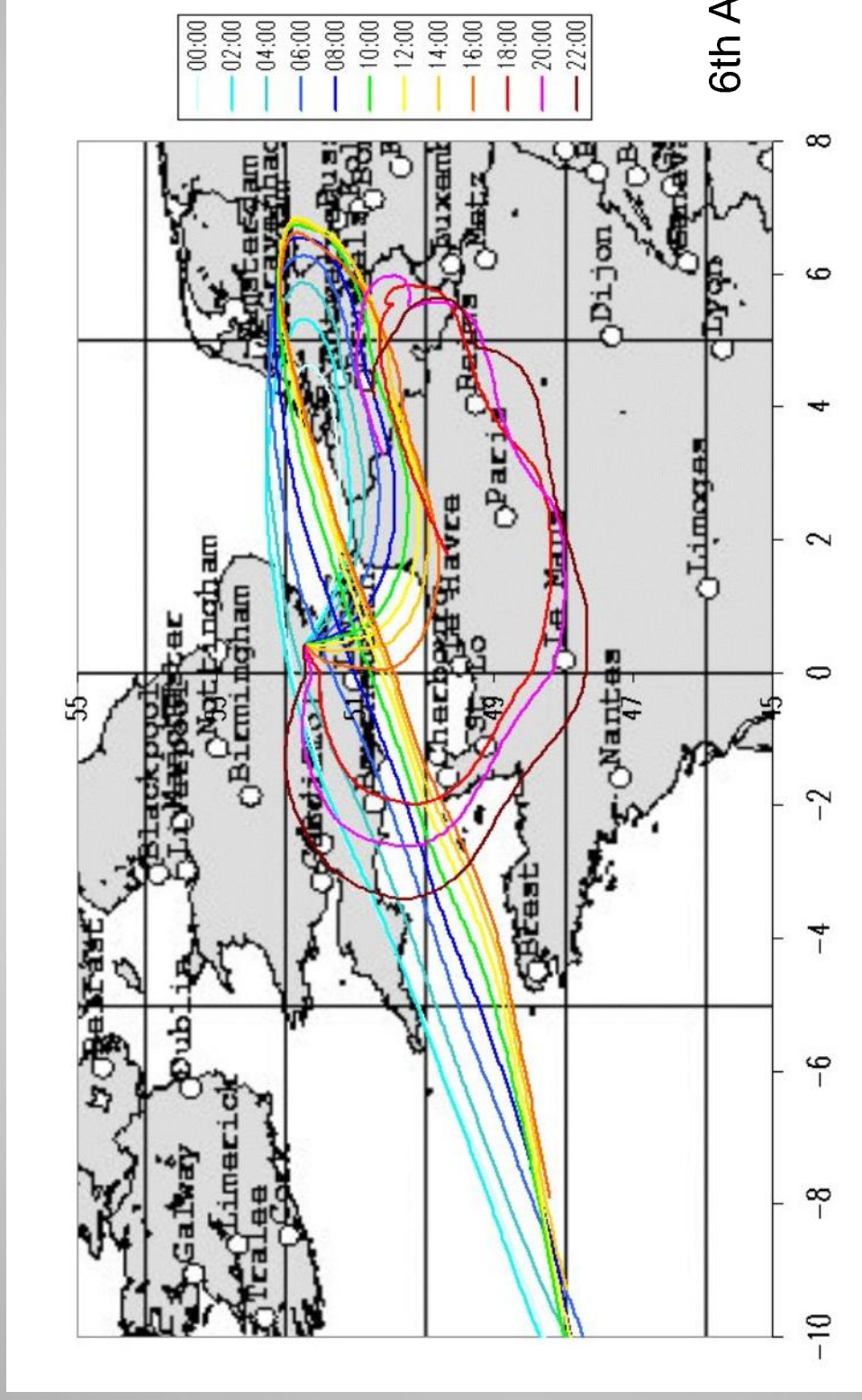
Is there Isoprene in UK gasoline?

No relationship between isoprene and any other anthropogenic NMHC in either temporal behaviour or temperature dependence at Writtle

- Diolefin content of gasoline in the UK is regulated by law to a total of less than 1% w/w.
- Majority are linear and cyclic C6 and C7 di-enes, residuals from aromatic ring opening.
- At Writtle, daytime, $[\text{isoprene}]_{\text{air}} = [\text{n pentane}]_{\text{air}}$ however content in typical gasoline 1:400.

(Hamilton and Lewis, Atmos. Env. 2003).

Rogue point sources?



6th Aug 2003

- No single approach trajectory direction
- Trajectories have up to a 'spread' in origin of ~100km, two hours before arrival even on anticyclonic days.

Conclusions.

1. During heat wave isoprene in rural UK background reached daytime maxima ~ 1.2 ppb.

Contrast:

'Normal' UK summertime rural ~ 0.2 ppb
Mediterranean forest $\sim 3-5$ ppb
Natural rainforest (Borneo) $\sim 2-4$ ppb
Oil Palm plantation (~ 10 ppb)

2. Unique behaviour. No covariance or correlation with any other NMHC, either temporal or temperature.
3. Fully consistent behaviour with a light and temperature dependant biogenic model of emissions
4. No evidence of major tailpipe exhaust source during heat wave when compared to other known emissions.
5. Very low trace levels in UK gasoline, around $1/400^{\text{th}}$ of pentane .