Launch of AQEG report: Ozone in the United Kingdom, 3rd March 2009

Measurements of isoprene at UK sites – anthropogenic and biogenic contributions

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Defra ambient hydrocarbon network

1993-2001: 24 hydrocarbons routinely monitored at 13 sites

2001 - present: 6 hydrocarbons routinely monitored at 5 sites

ethane
propane
n-butane
i-butane
n-pentane
i-pentane
n-hexane
methylpentane
n-heptane

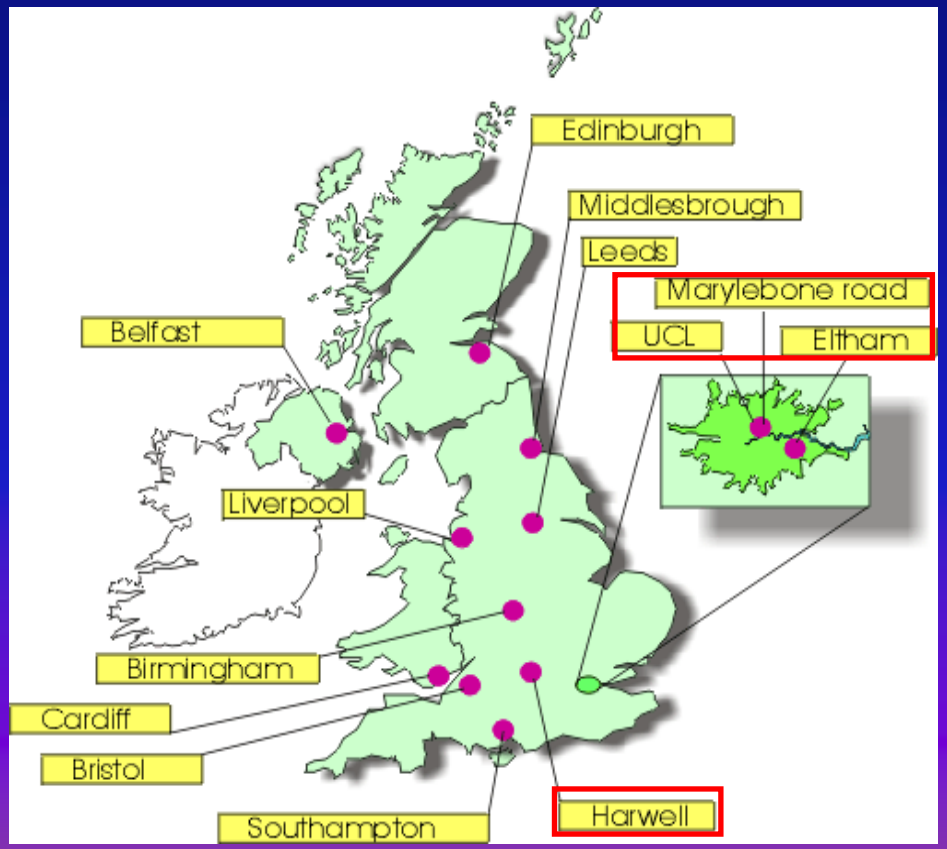
ethene
propene
1-butene
cis-2-butene
trans-2-butene

cis-2-pentene
trans-2-pentene

1,3-butadiene
isoprene

acetylene

benzene
toluene
ethylbenzene
o-xylene
m+p-xylene



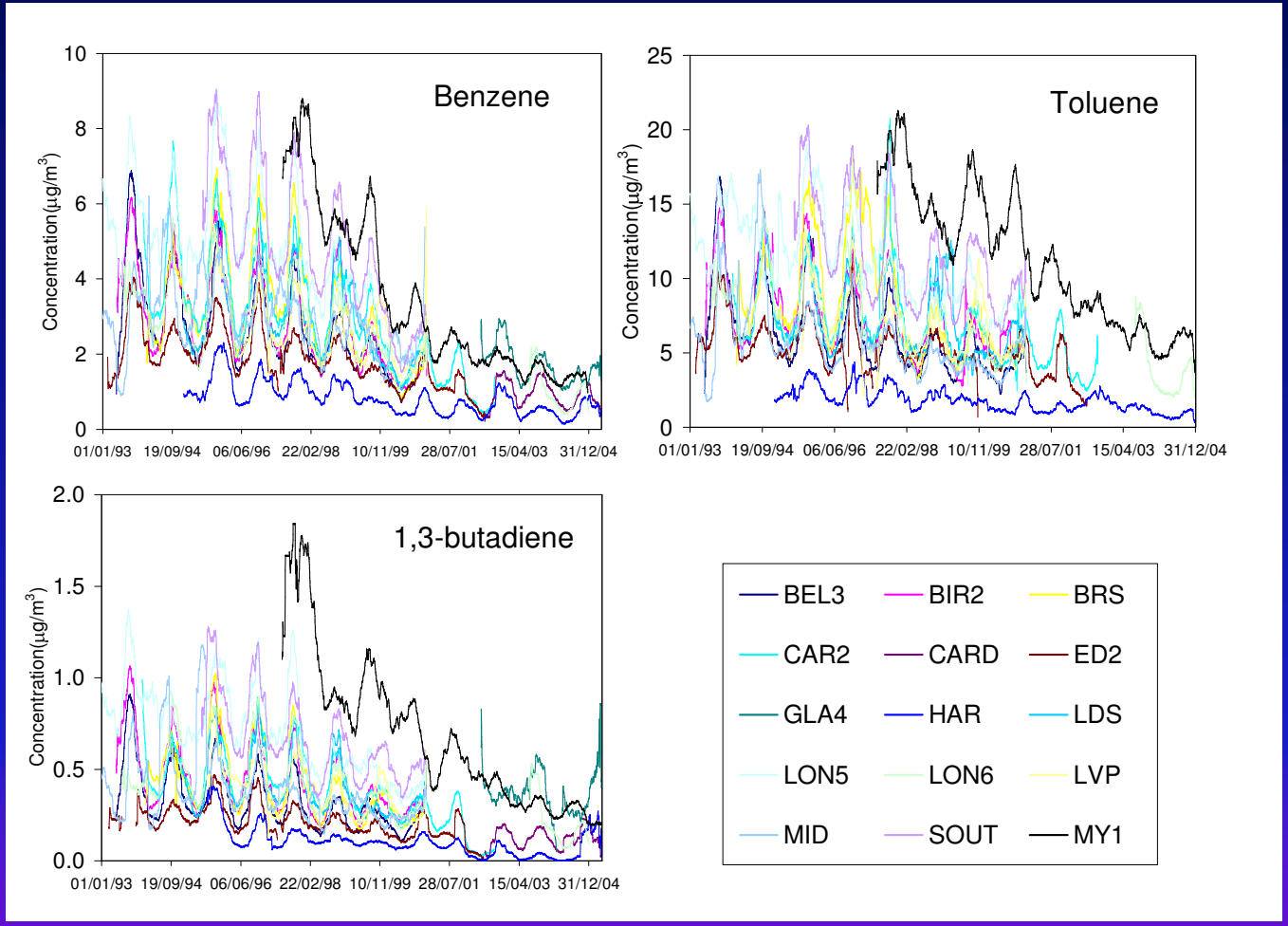
Defra ambient hydrocarbon network

- Operation, management and QA/QC by AEA Technology and/or National Physical Laboratory (NPL)
- Measurements made by automated GC-FID instrumentation:
  - Chrompack VOCAIR at most sites up to 2000-2001

  subsequently…
  - Perkin Elmer OPA at Marylebone Rd and Eltham
  - Environment VOC71M at other sites
- Data reported at hourly resolution at:

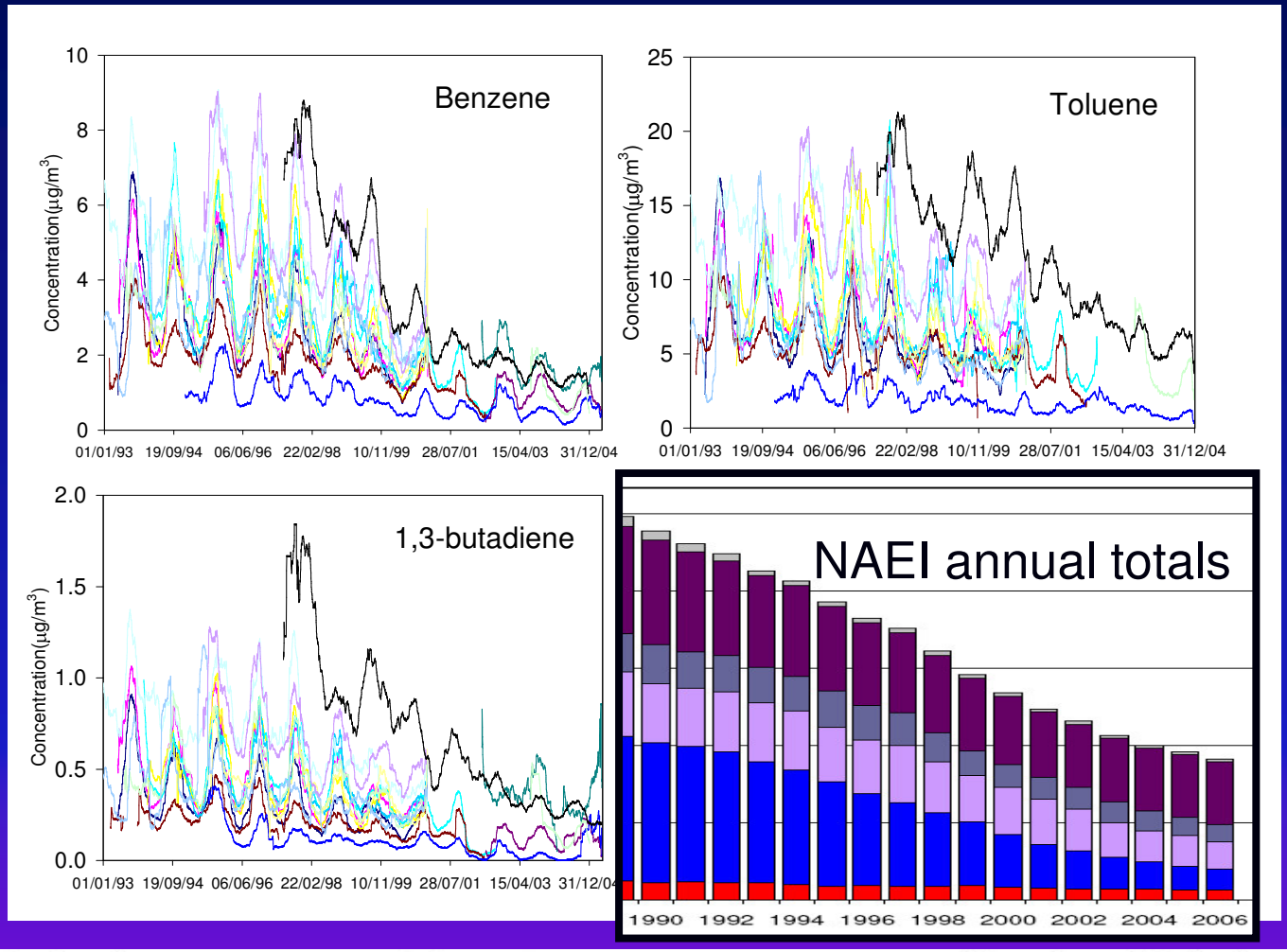
www.airquality.co.uk

Trends in anthropogenic hydrocarbon concentrations 1993-2004



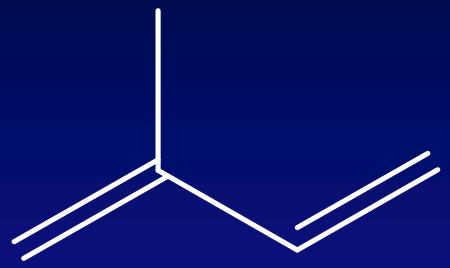
Data from Dick Derwent, as analysed in Dollard et al., Atmos. Env., 41, 2559 (2007)

Trends in anthropogenic hydrocarbon concentrations 1993-2004



1,3-butadiene and isoprene

1,3-butadiene



isoprene
(2-methyl-1,3-butadiene)

	1,3-butadiene	isoprene
k_{OH}	6.7×10^{-11} cm^3 $molecule^{-1}$ s^{-1}	1.0×10^{-10} cm^3 $molecule^{-1}$ s^{-1}
Lifetime (for [OH] = 2.4×10^6 molecule cm^{-3})	1.7 hours	1.2 hours

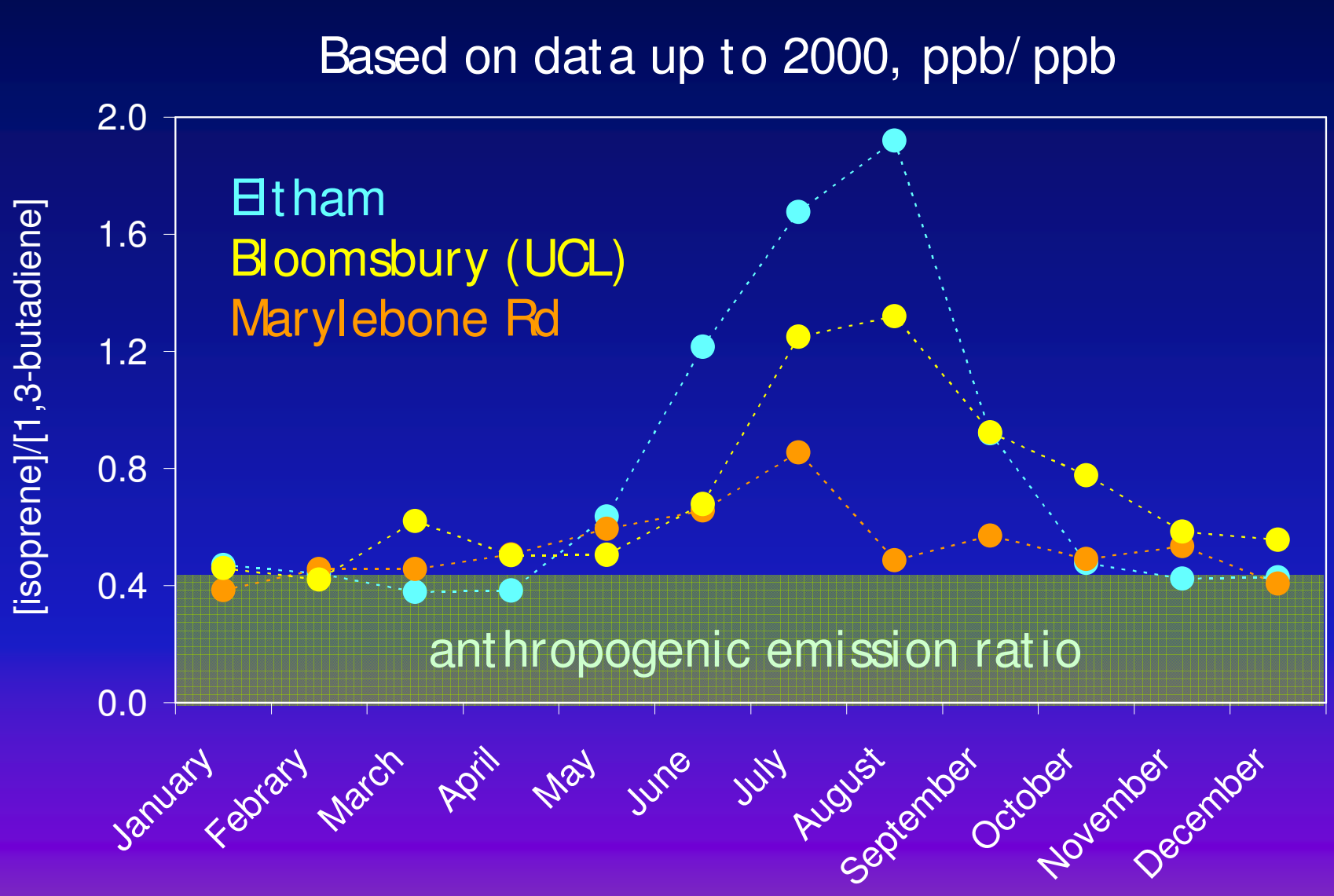
1,3-butadiene and isoprene

- Both 1,3-butadiene and isoprene are emitted in combustion, in particular in vehicle exhaust emissions
- Evidence for isoprene emissions obtained from ambient measurements in numerous studies, e.g.:
  - Burgess and Penkett (1993) – UK
  - Derwent et al. (1995) – UK
  - McLaren et al. (1996) – Canada
  - Reimann et al. (2000) – Switzerland
  - Borbon et al. (2001) – France
  - Duane et al. (2002) - Italy
- Reproducible [isoprene]/[1,3-butadiene] ratio reported for exhaust emissions source:

$$\approx 0.4 \text{ ppb/ ppb}$$

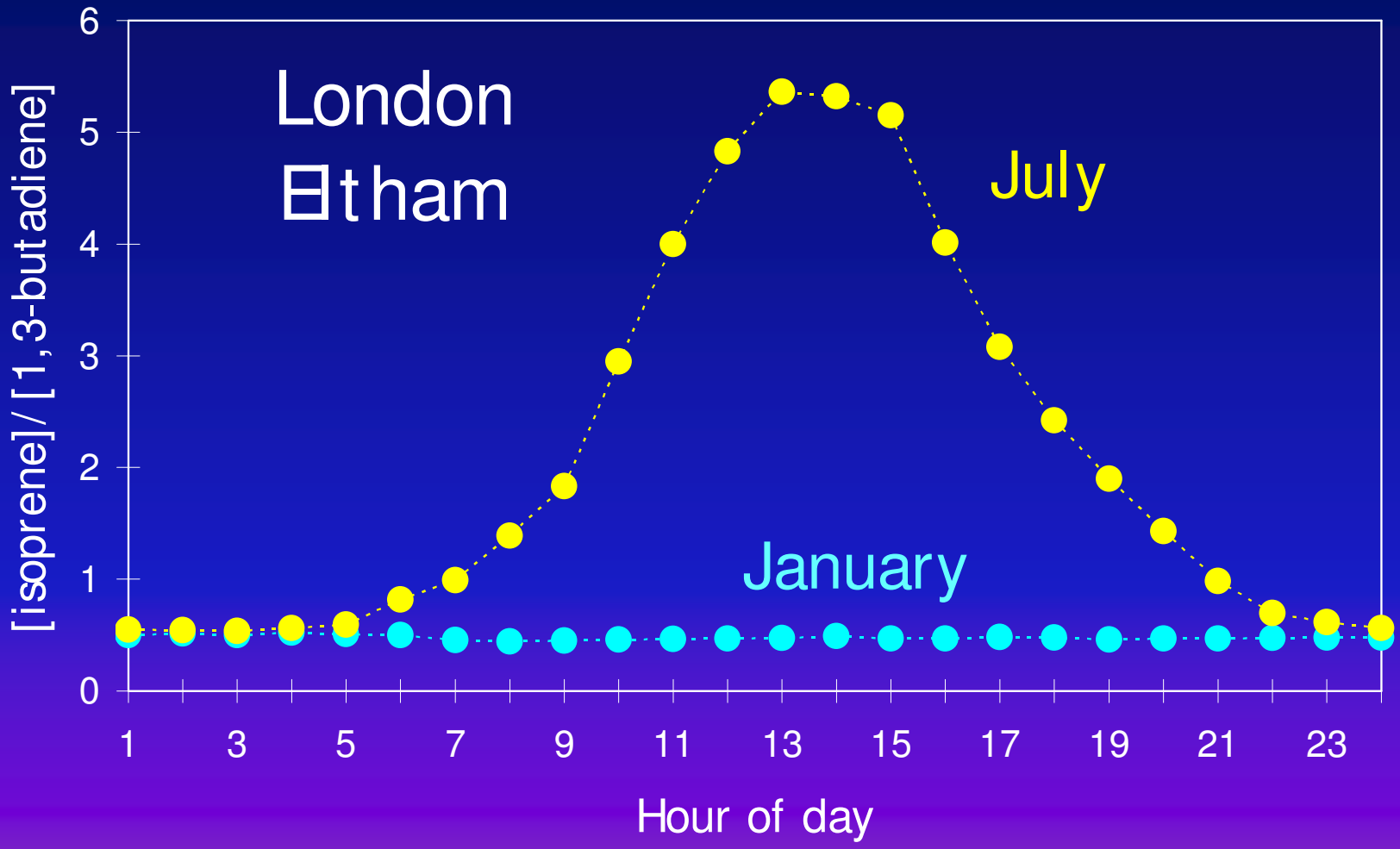
$$\approx 0.5 \ \mu g \ m^{-3} / \ \mu g \ m^{-3}$$

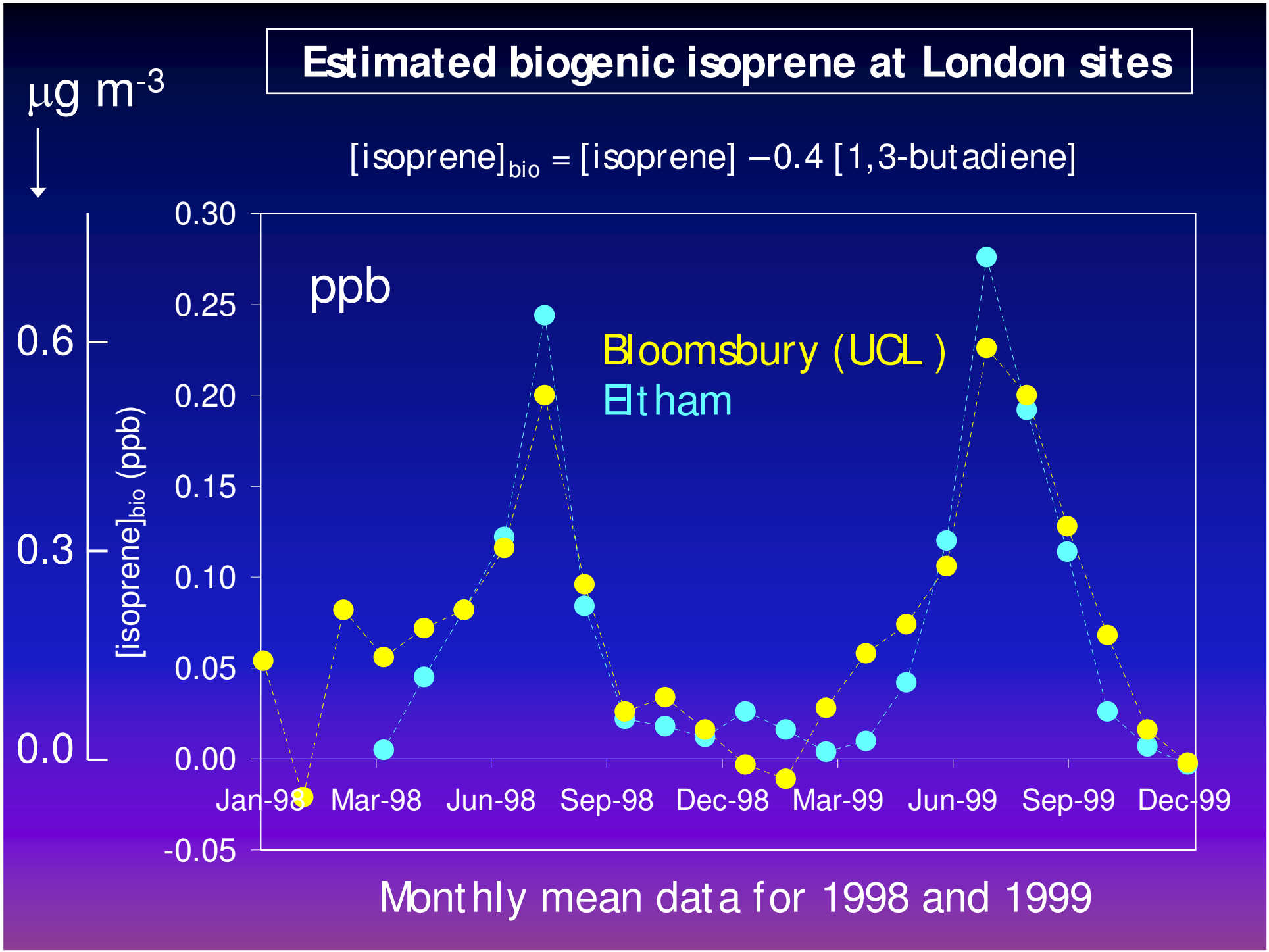
Monthly [isoprene]/[1,3-butadiene] at London sites



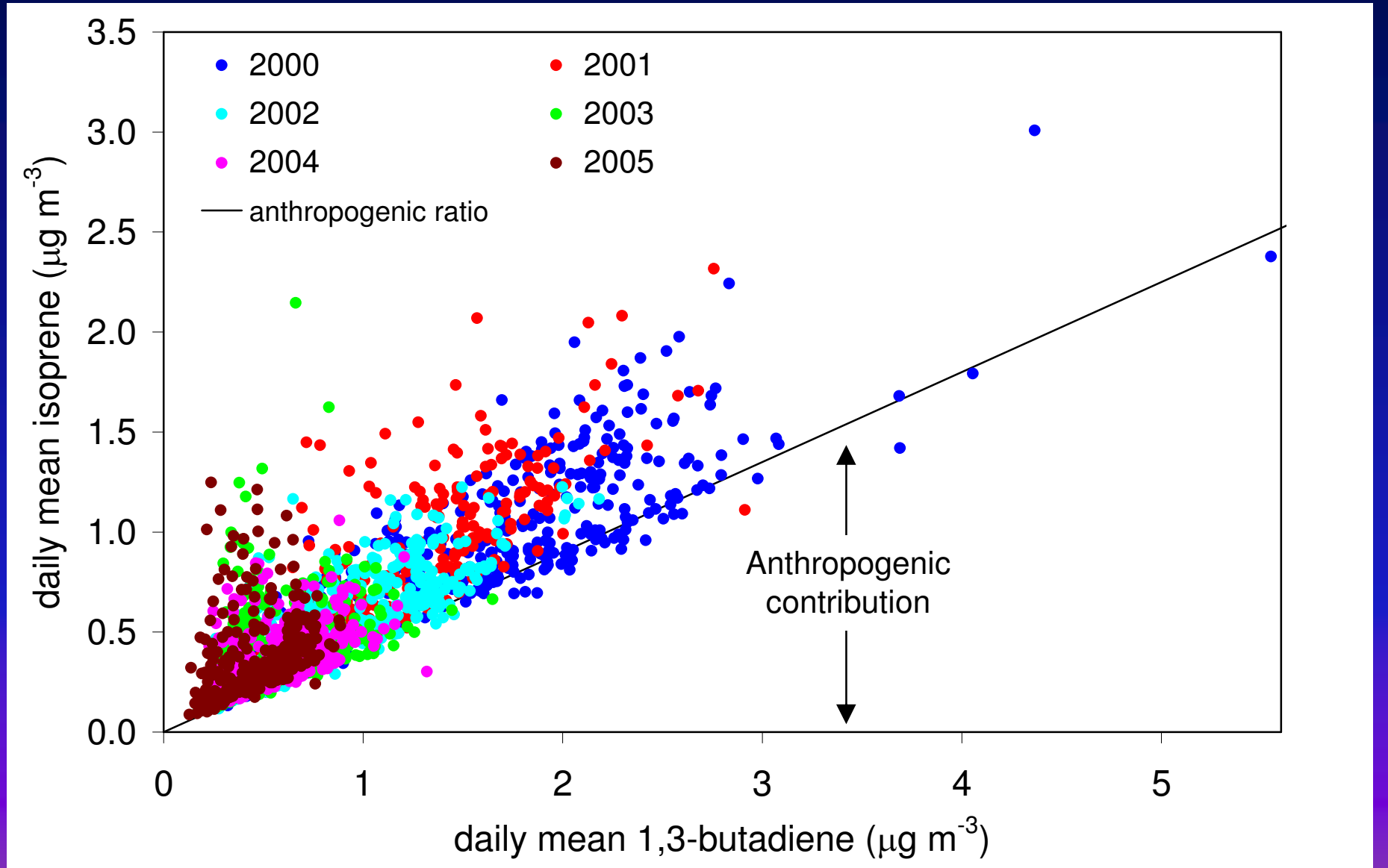
Hourly [isoprene]/[1,3-butadiene] at London Eltham

Based on data up to 2000, ppb/ppb



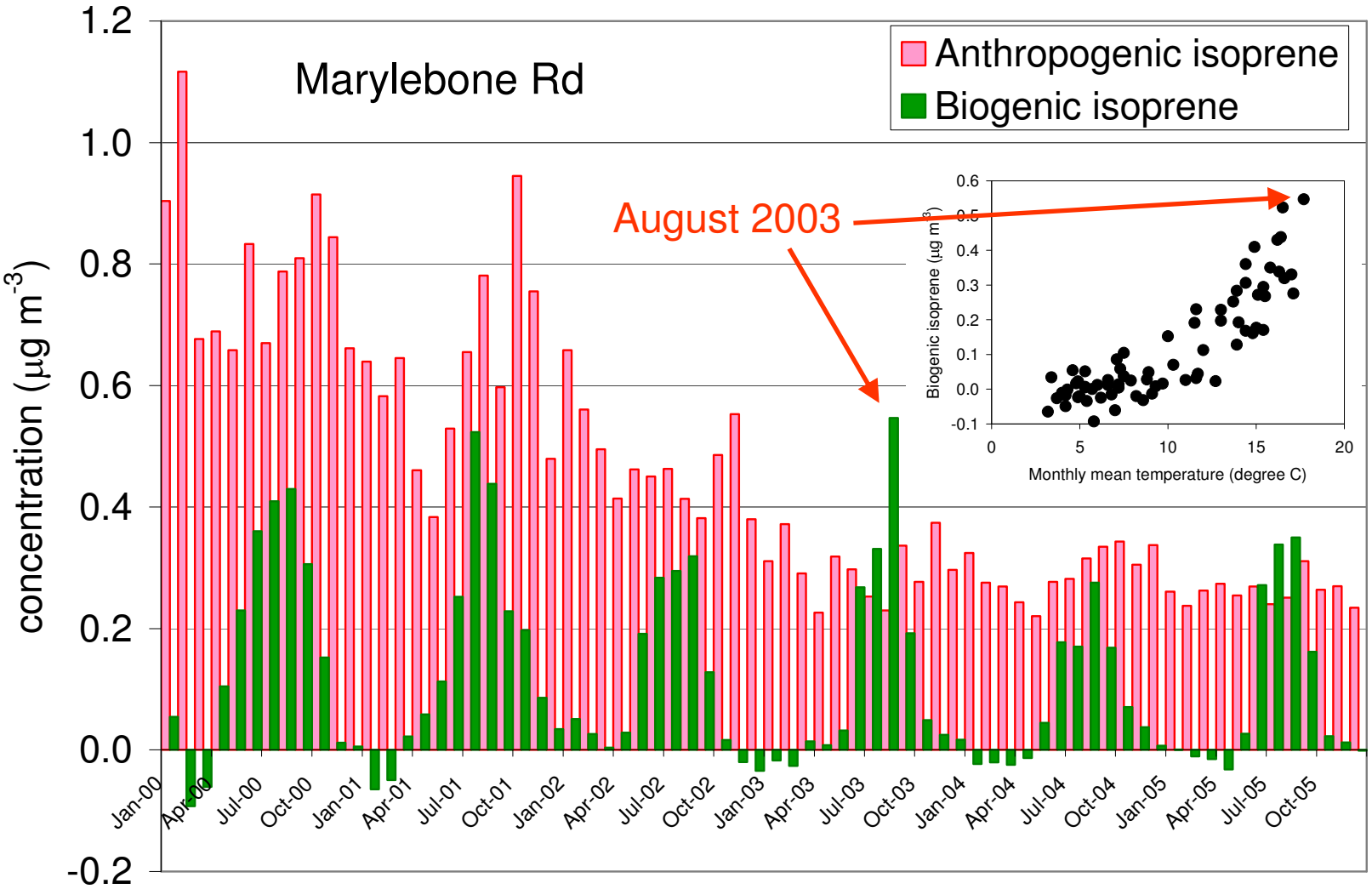

Estimated biogenic isoprene at London sites
µg m-3
[isoprene]bio = [isoprene] −0.4 [1,3-butadiene]
0.6
0.3
0.0
[isoprene]bio (ppb)
0.30
0.25
0.20
0.15
0.10
0.05
0.00
-0.05
ppb
Bloomsbury (UCL)
Eltham
Jan-98
Mar-98
Jun-98
Sep-98
Dec-98
Mar-99
Jun-99
Sep-99
Dec-99
Monthly mean data for 1998 and 1999

Isoprene vs. 1,3-butadiene, Marylebone Rd, 2000-2005



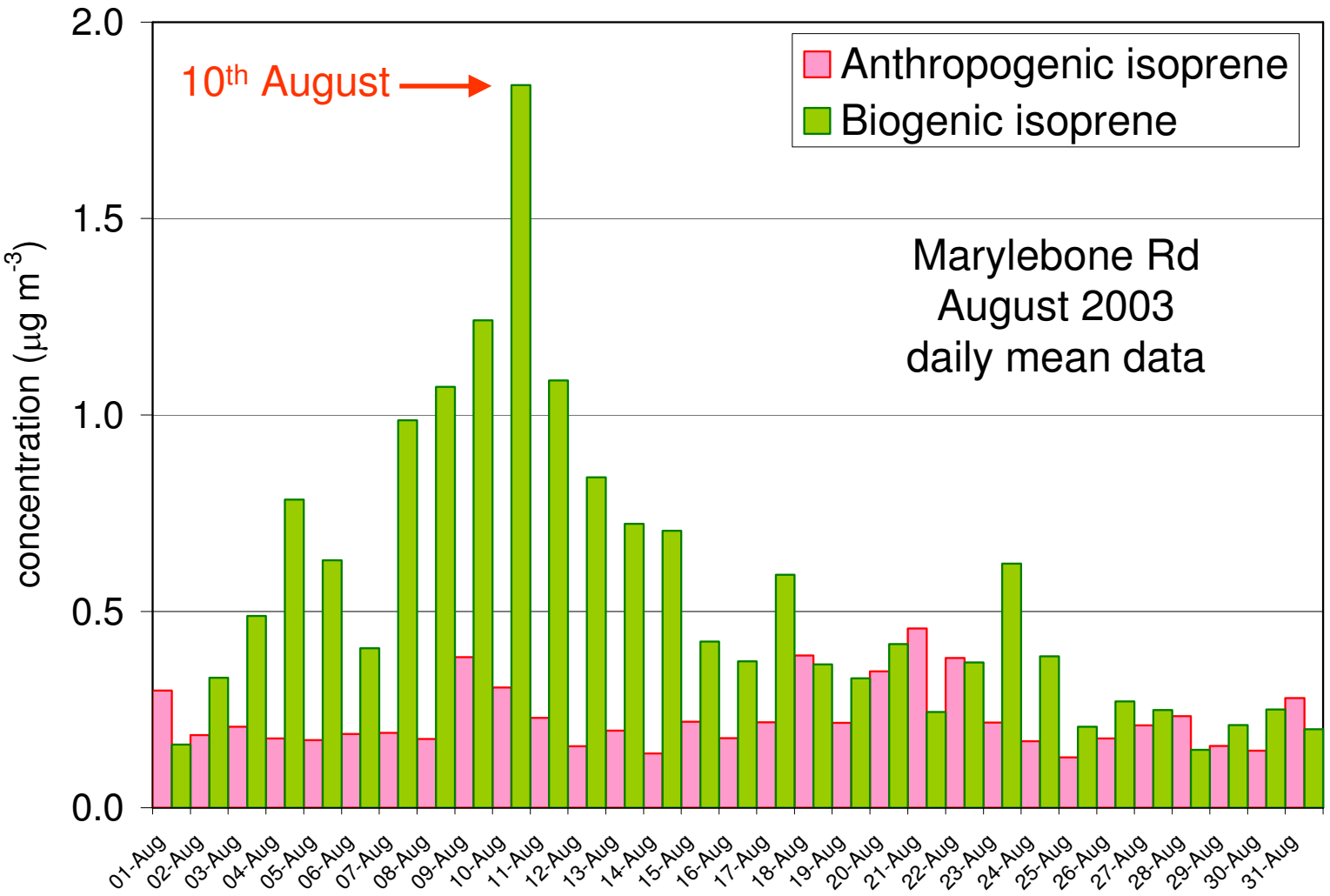
Monthly mean isoprene, Marylebone Rd, 2000-2005

$$[\text{isoprene}]_{bio} = [\text{isoprene}] - F.[1,3\text{-butadiene}], \quad 0.45 < F < 0.55$$



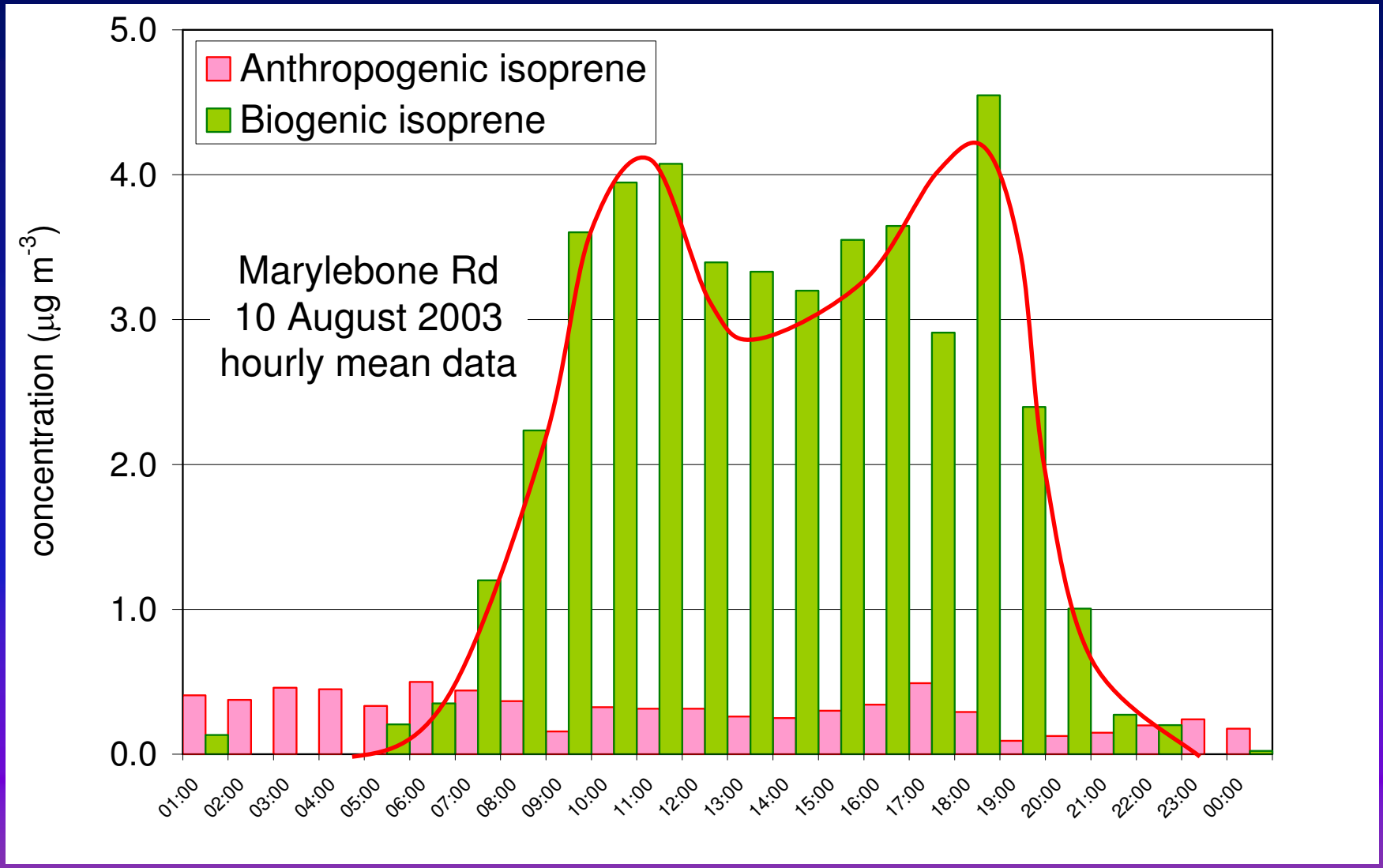
Daily mean isoprene, Marylebone Rd, August 2003

$$[\text{isoprene}]_{bio} = [\text{isoprene}] - F.[\text{1,3-butadiene}],\ F = 0.463$$



Hourly mean isoprene, Marylebone Rd, 10 August 2003

$$[\text{isoprene}]_{bio} = [\text{isoprene}] - F.[1,3\text{-butadiene}],\ F = 0.463$$



PERGAMON

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ATMOSPHERIC ENVIRONMENT

www.elsevier.com/locate/atmosenv

Developing receptor-oriented methods for non-methane hydrocarbon characterisation in urban air—Part I: source identification

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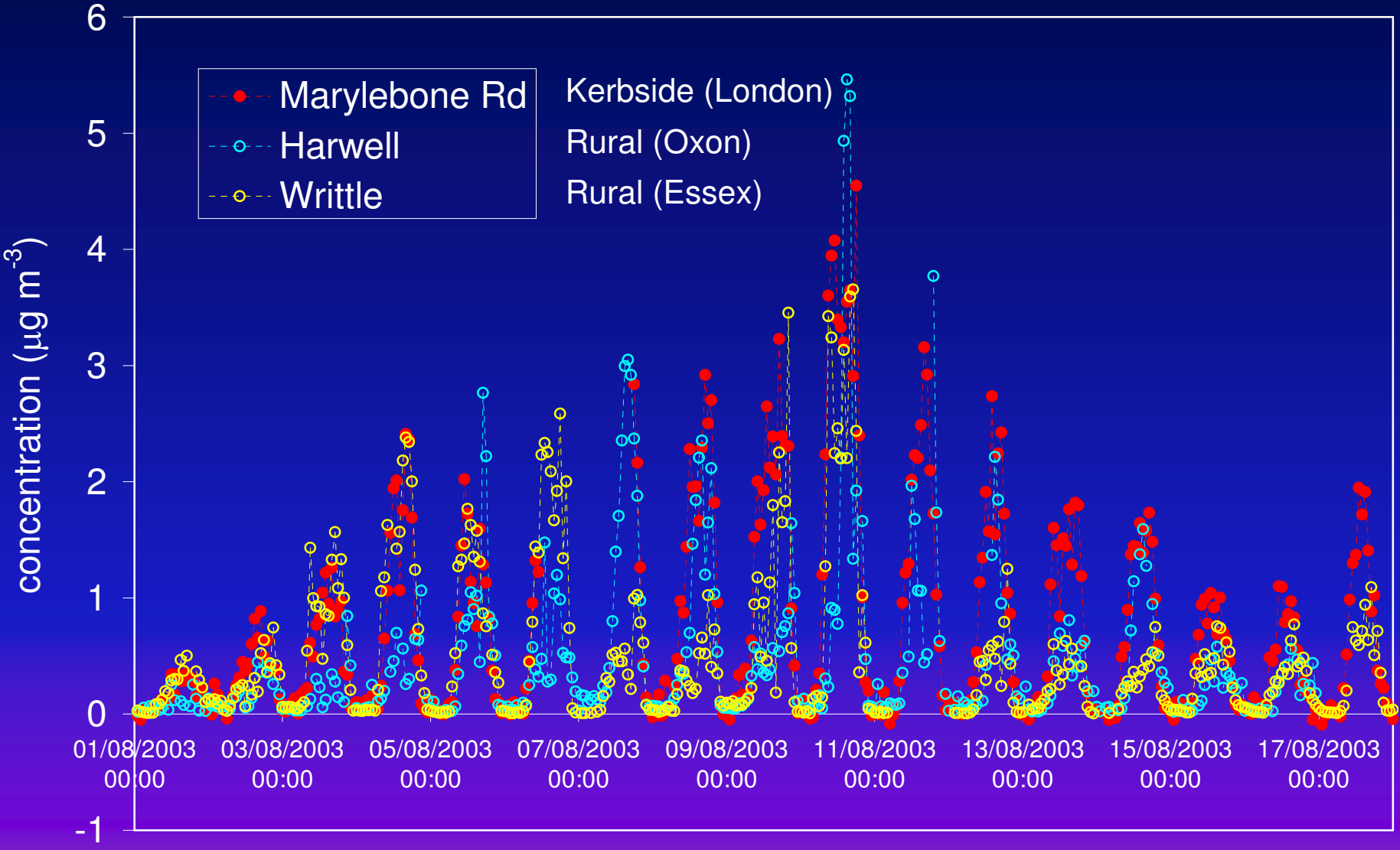
Based on Principal Component Analysis (PCA) of 4-year continuous hourly measurements of nearly 40 C_2–C_9 ambient NMHC at two urban sites in Lille, northern France.

PC1: Motor vehicle exhaust
PC2: Stationary combustion
PC3: Fuel/solvent evaporative
PC4: Biogenic

Table 4
Summertime PCA of hourly log-transformed data at Liberté. The reported values represent the VARIMAX rotated principal component loadings, which indicate the degree of correlation between the variables and each principal component. PC loadings <0.40 do not appear

Variables	PC1	PC2	PC3	PC4
Ethane	—	—	0.78	—
Propane	—	—	0.87	—
Butane	0.66	—	0.60	—
Isopentane	0.81	—	—	—
Hexane	0.68	—	0.51	—
Octane	0.85	—	—	—
Ethylene	0.84	—	—	—
1-Butene	0.76	0.47	—	—
1-Pentene	0.81	—	—	—
1-Hexene	0.67	0.46	—	—
1,3-Butadiene	0.84	0.40	—	—
Isoprene	0.66	—	—	0.62
Acetylene	0.83	0.41	—	—
Benzene	0.81	0.41	—	—
Toluene	0.83	—	—	—
$m+p$-xylene	0.87	—	—	—
1,3,5-Trimethylbenzene	0.88	—	—	—
Insolation	—	—	—	0.88
Temperature	—	—	—	0.81
NO_x	0.40	0.82	—	—
CO	0.49	0.75	—	—
Eigenvalues	27.25	2.21	0.95	0.77
% of variance explained	80.14	6.49	2.79	2.26

(Biogenic) isoprene observations in the southern UK, August 2003



Writtle data courtesy of University of York

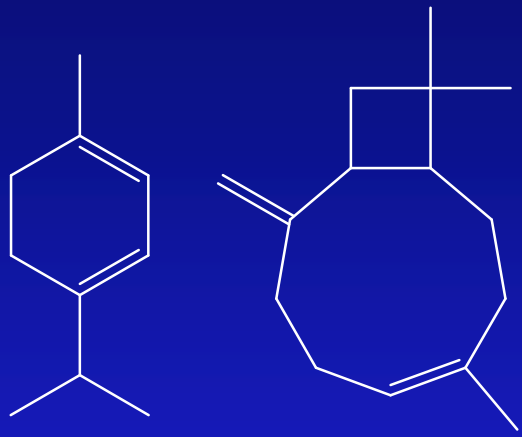
Summarising remarks

- Observations at UK sites are consistent with isoprene being emitted from both anthropogenic and biogenic sources.
- Anthropogenic and biogenic contributions appear to be separated reliably using 1,3-butadiene as a marker for the anthropogenic isoprene source.
- Following reductions in anthropogenic VOC emissions, even urban isoprene concentrations are dominated by the biogenic source during summertime, particularly during heat-waves.
- Based on observations at London sites, Harwell (Oxon) and Writtle (Essex), the "background" biogenic source appears to be comparable over a widespread area.
- UK measurements of other biogenic VOCs (e.g., monoterpenes and sesquiterpenes) would be valuable.

Other biogenic VOC (BVOC)

emission → BVOC

Typically up to ca. 20 species observed to make notable contributions



α–terpinene
β-caryophyllene

lifetime
≈ 1 minute

α–pinene

lifetime
≈ 2 hours

camphor

lifetime
≈ 2 days

BVOC reactivity and structure categories

Category	Compounds (possible representative highlighted)	OH reaction lifetime of representative[a,c]	O_3 reaction lifetime of representative[b,c]
Bicyclic monoterpene - endocyclic double bond	**α–pinene**, 2-carene, 3-carene	2.1 hours	4.3 hours
Bicyclic monoterpene - exocyclic double bond	**β–pinene**, camphene, sabinene	1.5 hours	1.0 days
Monocyclic diene monoterpene	**limonene**, terpinolene, β–phellandrene, γ–terpinene	40 minutes	1.9 hours
Monocyclic conjugated diene monoterpene	**α–terpinene**, α–phellandrene	20 minutes	1.1 minutes
Acyclic triene monoterpene	**ocimene**, myrcene	25 minutes	41 minutes
Reactive sesquiterpene	**β–caryophyllene**, α–humulene	30 minutes	1.9 minutes
Unreactive sesequiterpene	**α–cedrene**, α–copaene, longifolene	1.8 hours	13.2 hours
Reactive C_{10} oxygenates	**linalool**	45 minutes	51 minutes
Unreactive C_{10} oxygenates	**camphor**, 1,8-cineole	2.1 days	> 220 days

a: $[OH] = 2.4 \times 10^6$ cm^{-3} ; b: $[O_3] = 7.5 \times 10^{11}$ molec. cm^{-3} (ca. 30 ppb); c: Based on data from Calvert et al. (2000)