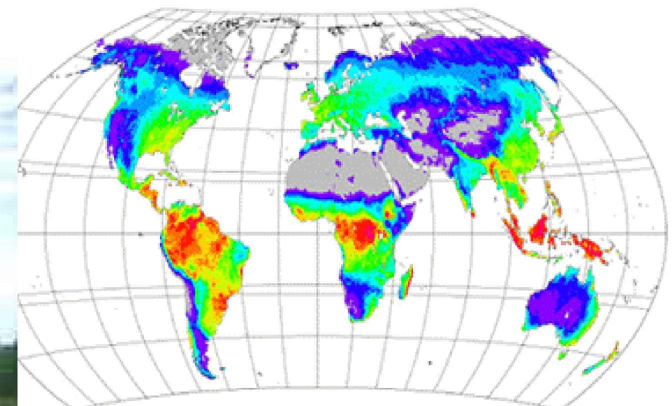
Emissions of volatile organic compounds from plants and their role in air quality



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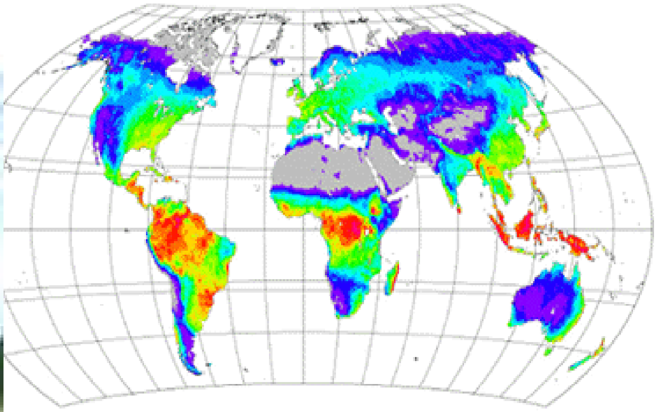
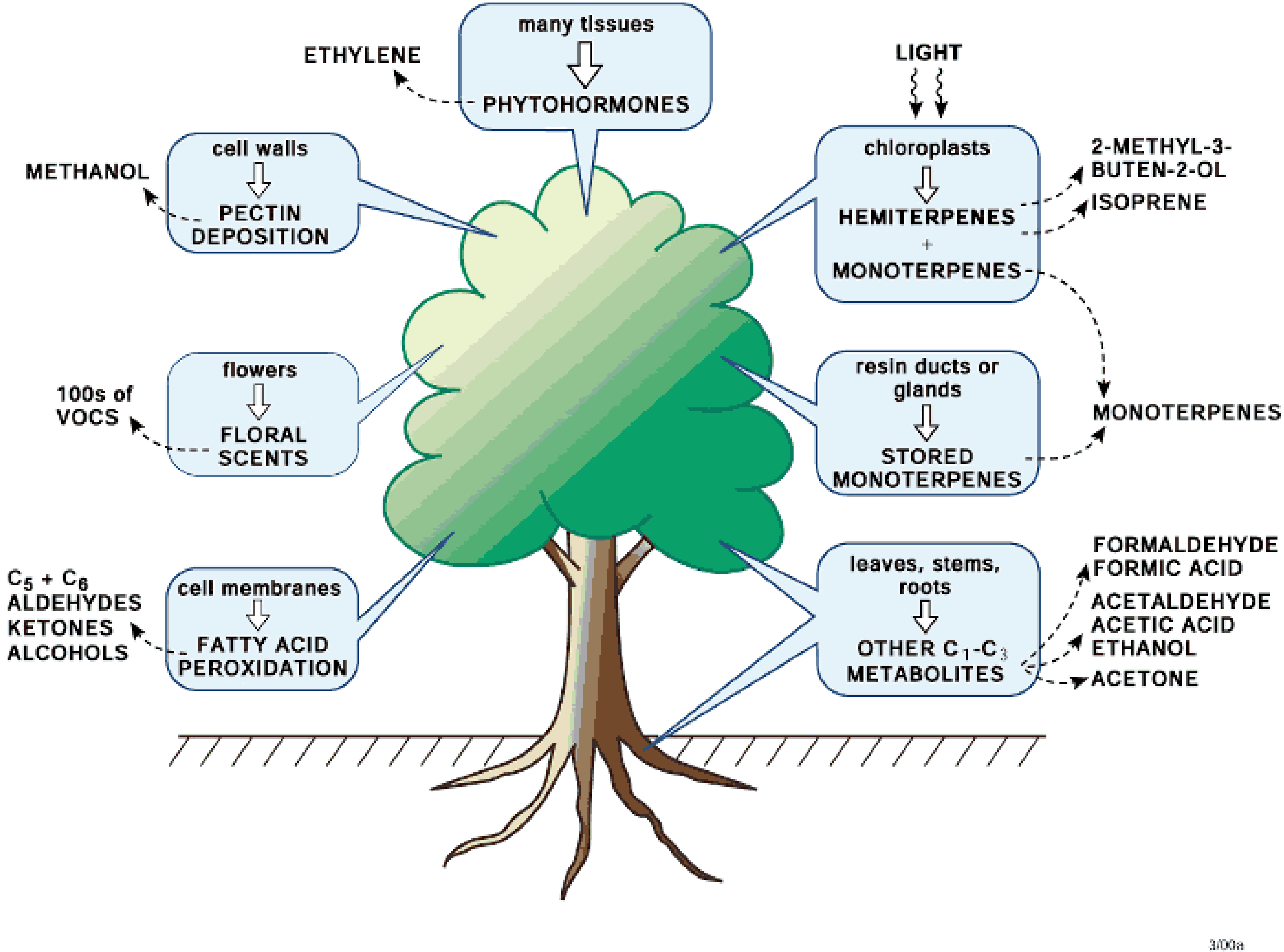
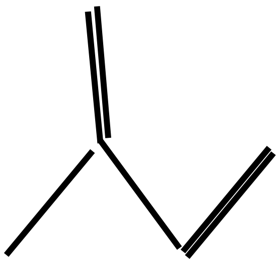
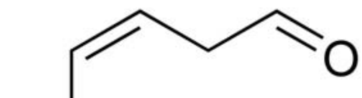


1. What controls VOC emission rates from plants
2. A BVOC emission inventory for GB
3. Uncertainties, a surprise and next steps


many tissues
PHYTOHORMONES
ETHYLENE
cell walls
PECTIN DEPOSITION
METHANOL
LIGHT
chloroplasts
HEMITERPENES
+
MONOTERPENES
2-METHYL-3-BUTEN-2-OL
ISOPRENE
flowers
FLORAL SCENTS
100s of VOCS
resin ducts or glands
STORED MONOTERPENES
MONOTERPENES
cell membranes
FATTY ACID PEROXIDATION
C_5 + C_6 ALDEHYDES KETONES ALCOHOLS
leaves, stems, roots
OTHER C_1-C_3 METABOLITES
FORMALDEHYDE
FORMIC ACID
ACETALDEHYDE
ACETIC ACID
ETHANOL
ACETONE
3/00a

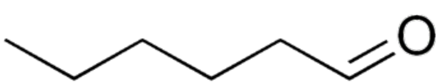


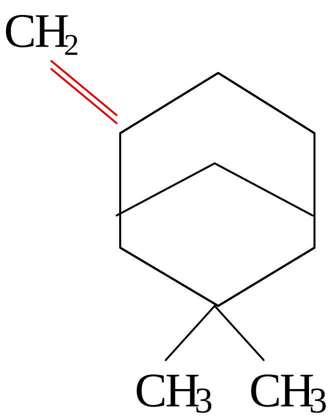
isoprene
C_5H_8



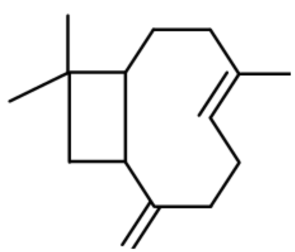
C_6 hexenal

C_6 hexanal





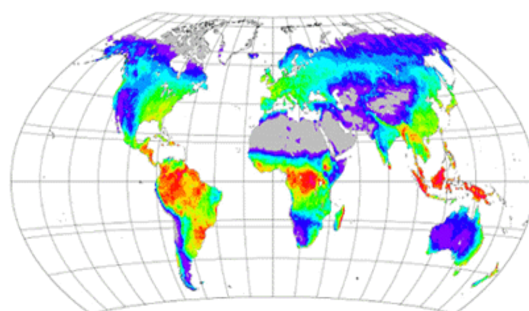
C_{10} β-pinene



C_{15} β-caryophyllene

Protection against biotic and abiotic stresses – T, ox, bugs

Communication - friends and neighbours



Effects -
oxidant budget,
particle formation,
methane lifetime

air quality
ozone
PM

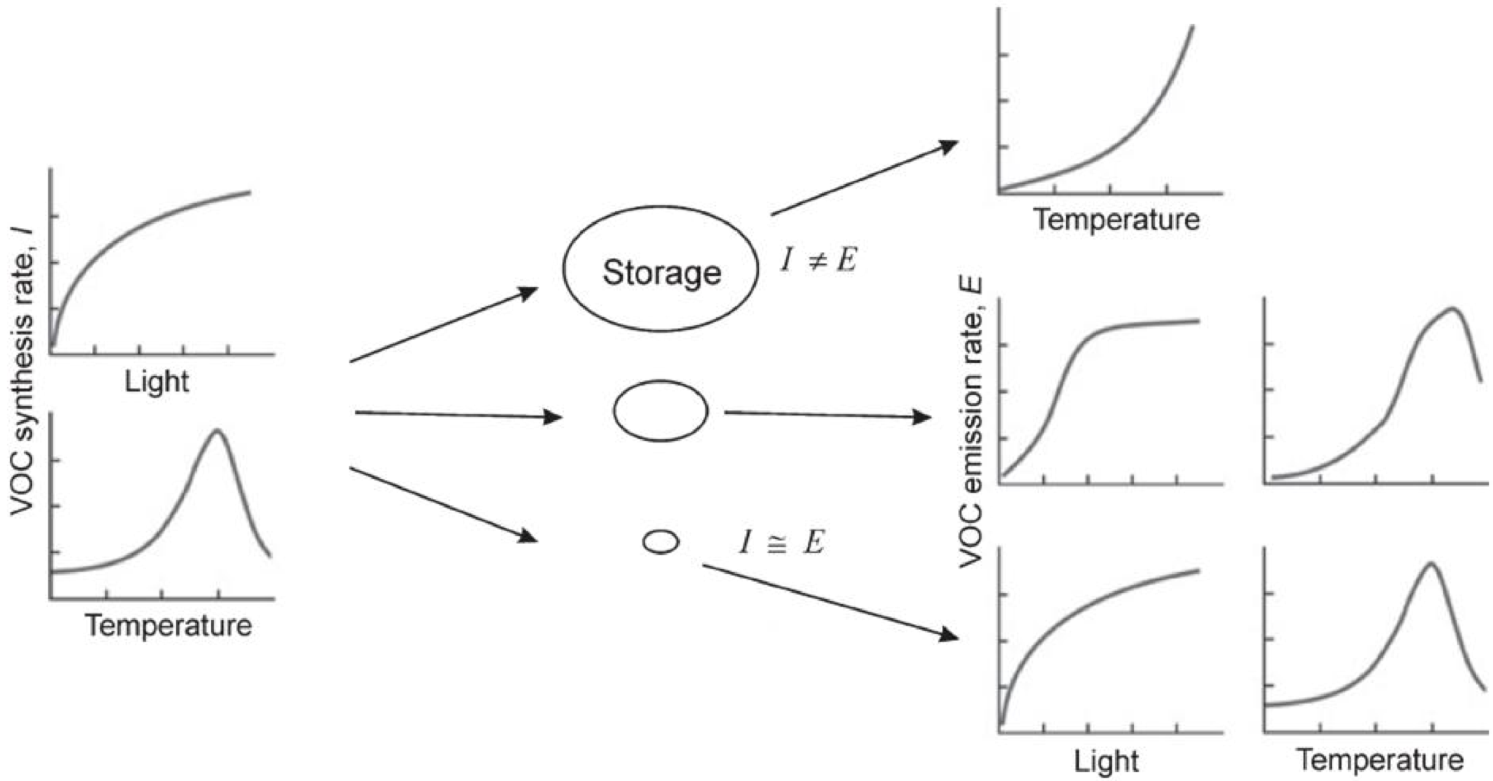
Which plants produce reactive VOCs?

Probably all, but only some in significant quantities

Which plants produce isoprene?	In the UK:
Some, but not all:	
Mosses	
Ferns	
Gymnosperms (conifers)	Spruce, especially Sitka spruce
Angiosperms (flowering plants)	Poplar, willow, oak

Other compounds	In the UK:
Monoterpene and sesquiterpenes	Spruce
Aldehydes, ketones (C_6), alcohols	Crop harvesting, grass cutting

What controls VOC emission rates?

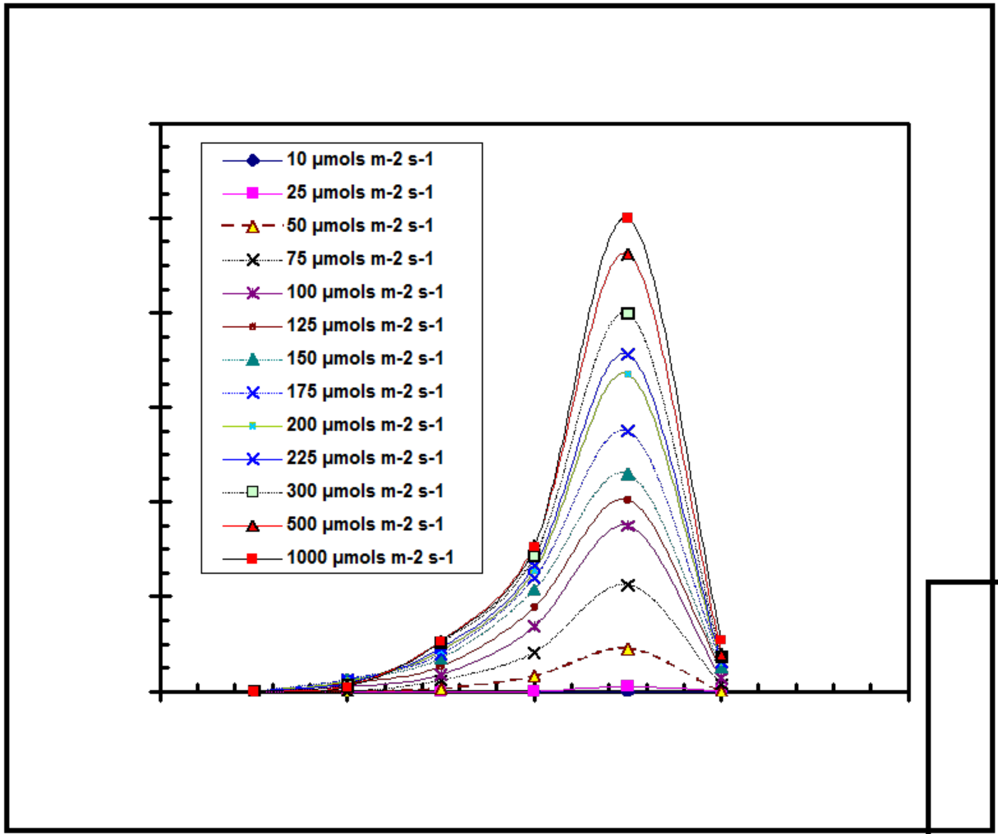


e.g. most MTs

e.g. isoprene

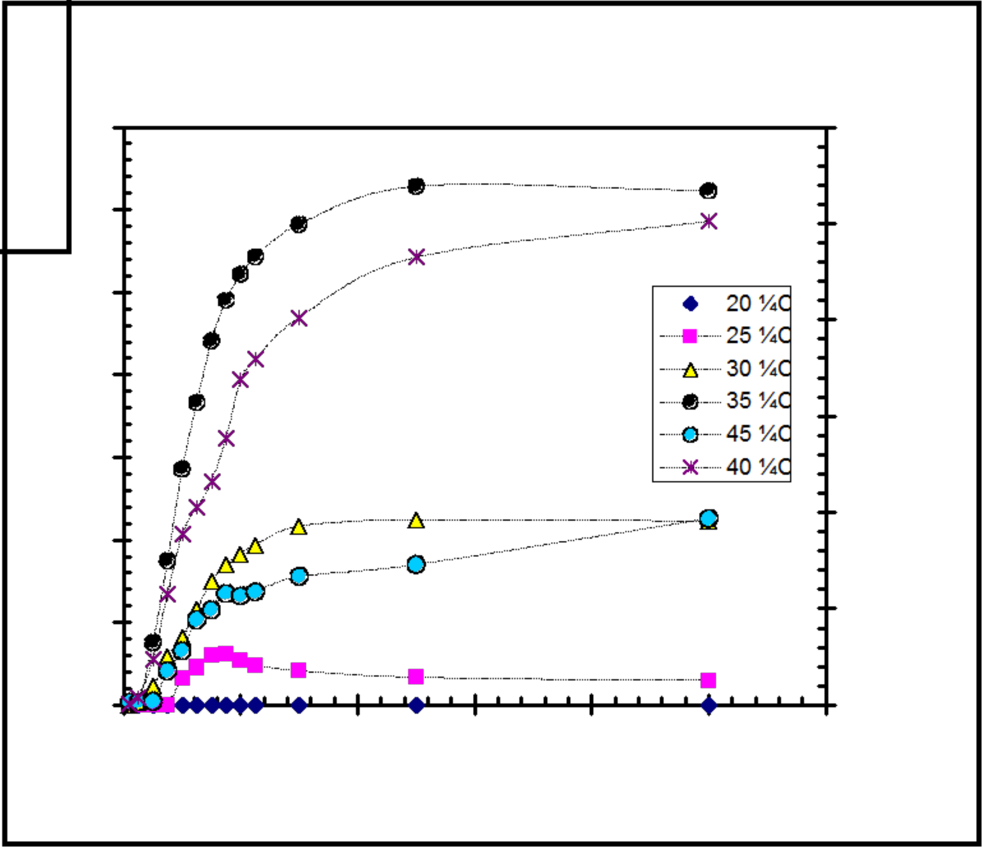
Grote & Niinemets, Plant Biology, 2008

Isoprene from oil palm



temperature dependent

light dependent



What controls isoprene emissions?

Leaf T
Incident PAR

Circadian control
Leaf age
Leaf growth T

$[CO_2]$	increasing $[CO_2]$ decreases IE
$[O_3]$	increasing $[O_3]$ *decreases* IE

What does not control isoprene emissions?

Water stress

What controls other BVOC emissions?

Wounding, including harvesting and herbivory

Modelling BVOC emission rates

light- and temperature-dependent emissions (isoprene and some monoterpenes):

$$I = I_s C_L C_T$$

I	isoprene emission rate at temp T and PAR flux L
I_s	isoprene emission rate at standard T and PAR
C_L	light response function
C_T	temp response function

temperature-dependent (light-independent) emissions (most monoterpenes):

$$M = M_s \exp(\beta(T - T_s))$$

M	MT emission rate at temp T
M_s	MT emission rate at standard T
β	empirical coefficient (K^{-1})

T is leaf T, normally assumed to be surface air T

A BVOC emissions inventory for Great Britain
(Stewart et al, JGR, 2003)

1: Geographically referenced species data – area and biomass
(Stewart et al, Biomass and Bioenergy, 2008)

- ITE land classification – each 1 x 1 km assigned to one of 32 land classes based on 56 land cover types
- Countryside Survey: quantitative mapping of 1100 most prevalent plant and tree species on 1 km x 1 km grid
- Mean species cover area and foliar biomass calculated
- Annual growth cycle (monthly biomass) simulated, incl crop harvesting

Largest area coverage

Moss	27,000 km^2
Rye grass	25,000
Wheat	25,000
Heather	14,000
…..	
Sitka	5,000

Largest biomass – summer

Rye grass	25 Mt
Wheat	19 Mt
Barley	16 Mt
Sitka spruce	7 Mt

– winter

Sitka spruce
Heather

2: Species-specific emission potentials

www.es.lancs.ac.uk/cnhgroup/iso-emissions.pdf

I and MT emission potentials at 30^{o}C/1000 μE PAR assigned to each 1100 species

- Measurements – 9% (I) and 7% (MT)
- Taxonomic assignment method – 70% (informed guess…)
- Default - ~20%

	Isoprene	MT
	μg g^{-1} h^{-1}	
e.g. Rye grass	0	0
Sitka spruce	3.3	3.3
Oak	38	1

3: Meteorology

MM5 used to generate hourly T, PAR etc at 12 x 12 km (1998)

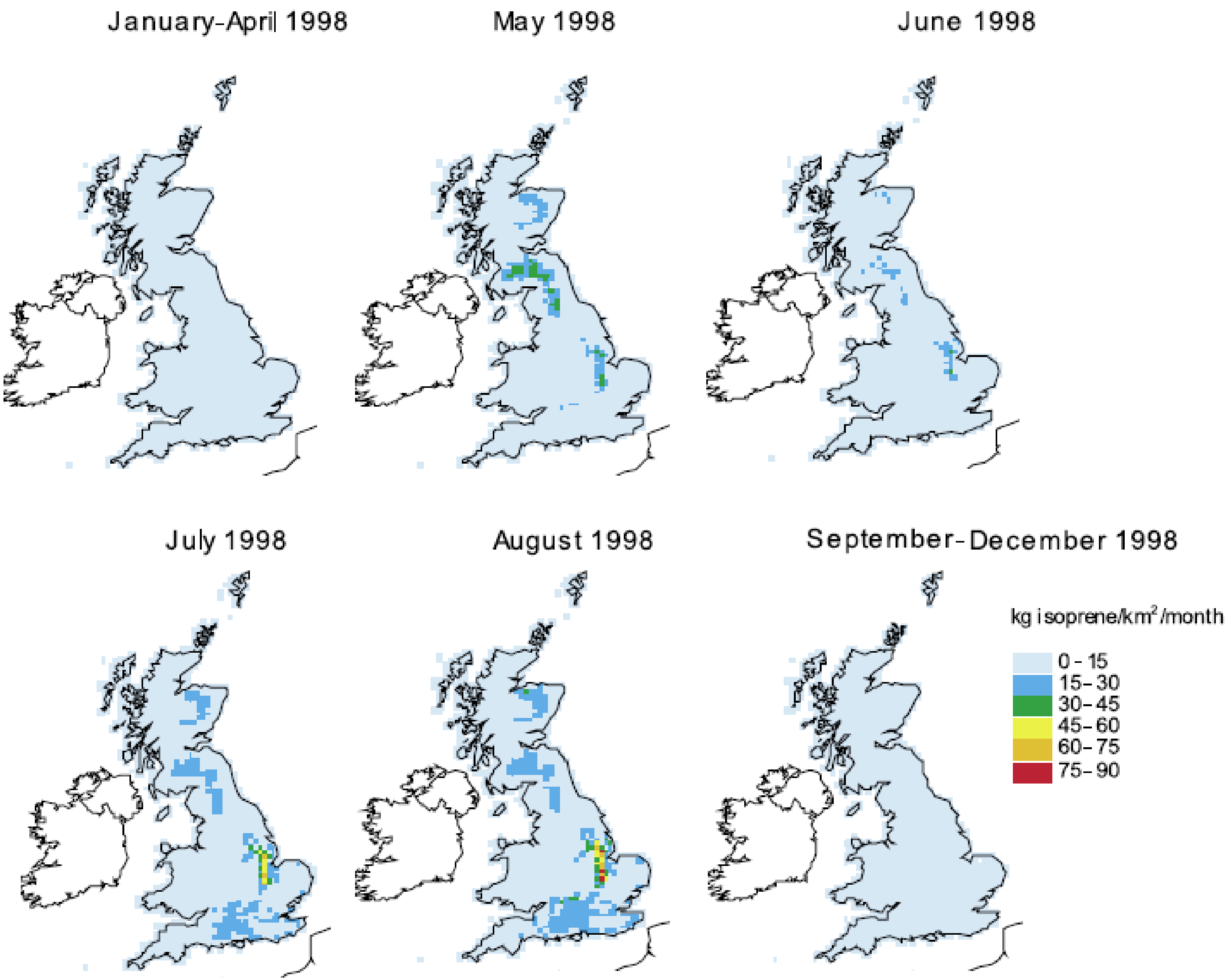
- Output compared with data and analysis of Parker and Horton (1999)
- Warmer than 30 year annual mean
- Cooler cloudier June than 30 year mean

4: Biogenic emissions model

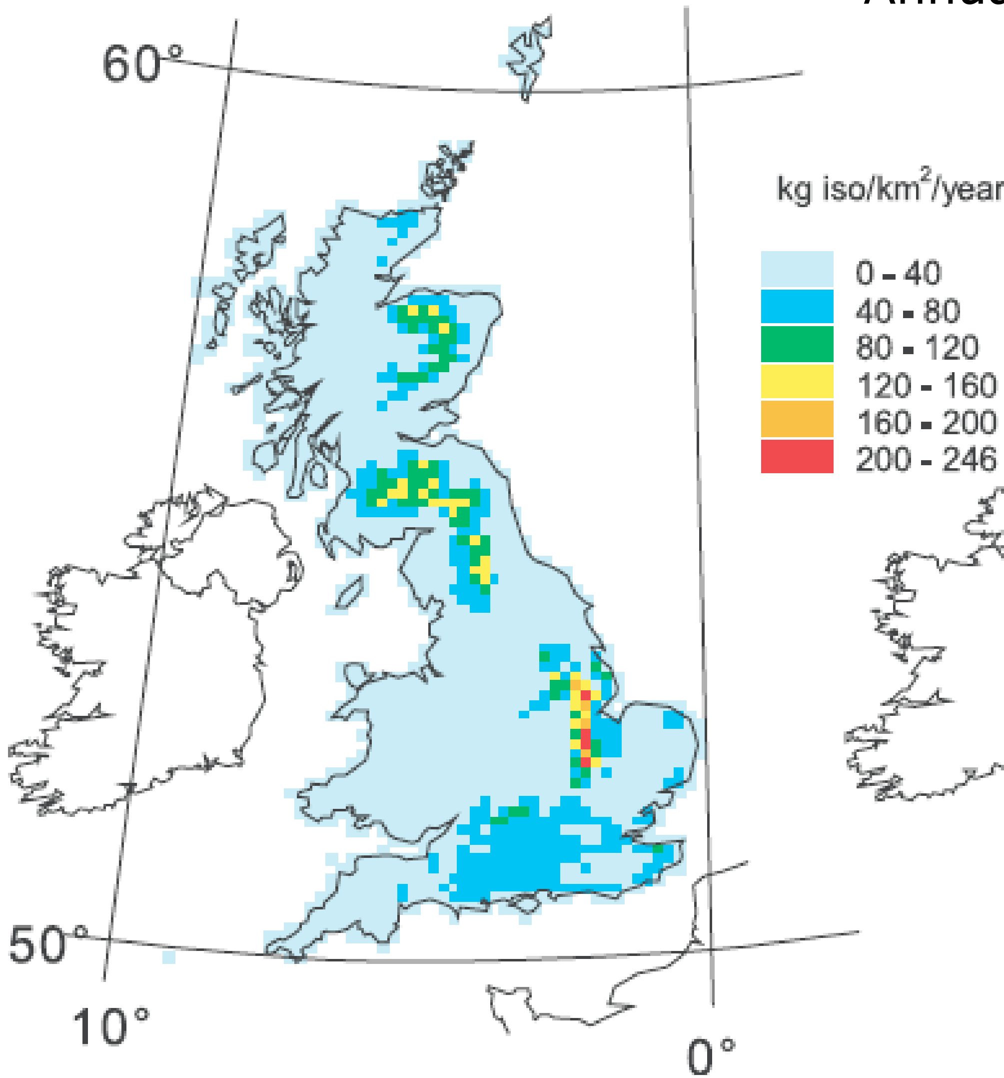
$$\text{Flux} = f(\text{area}_{sp} . \text{biomass}_{sp} . \text{Ep}_{sp} . \text{ECF}_{CL.CT})$$

Species area and biomass – monthly
T, PAR – hourly
12 x 12 km
MT emissions – T dependent only
Leaf T assumed to equal air T
PAR estimated from surface radiation

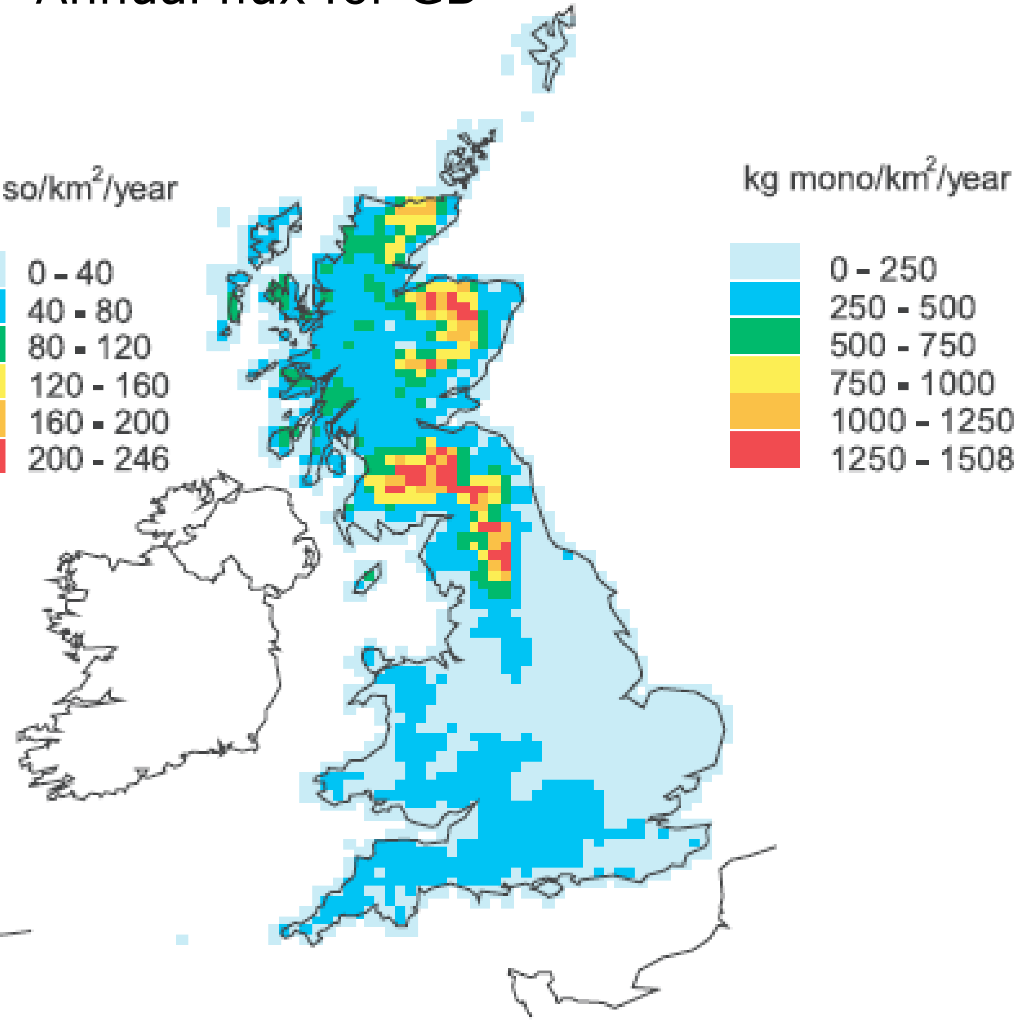
Monthly isoprene (kg km^{-2} month^{-1})



Annual flux for GB

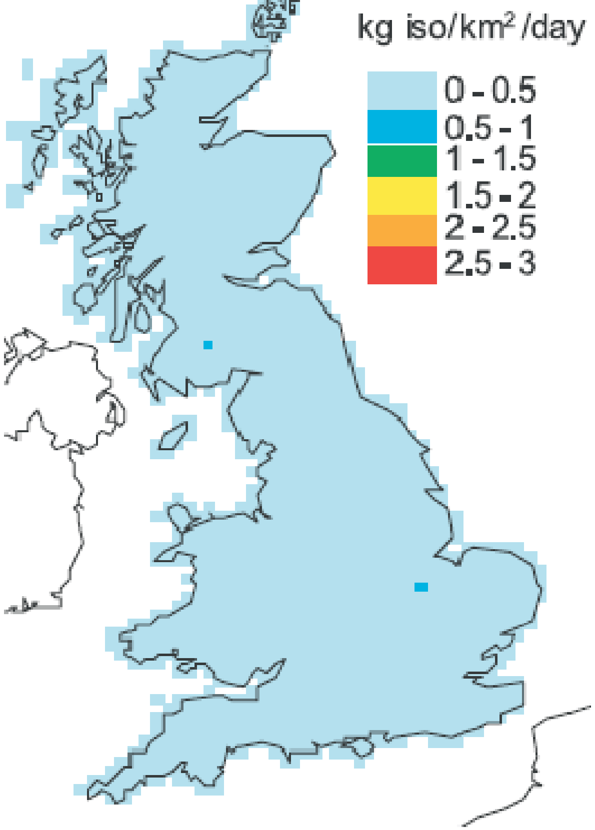


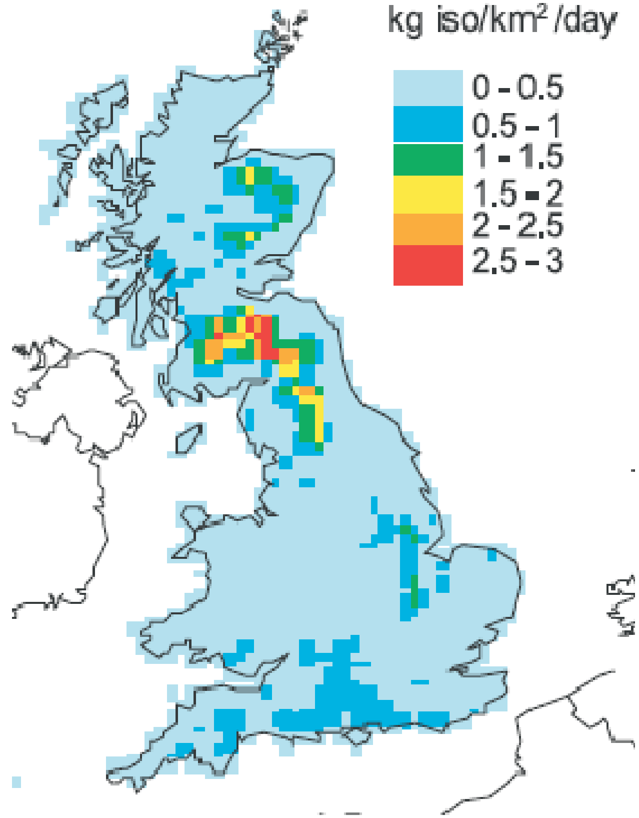
Isoprene 8 kt y^{-1}



Total monoterpenes 83 kt y^{-1}

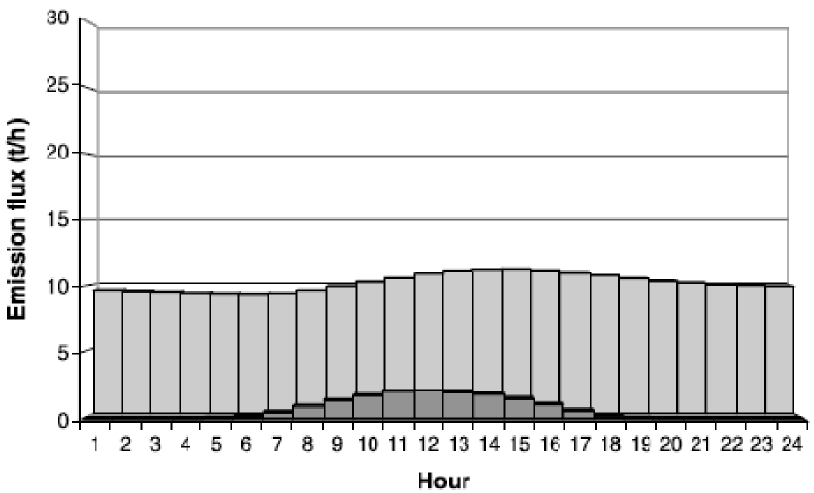
c.f. anthrop VOC flux 1800 kt y^{-1}

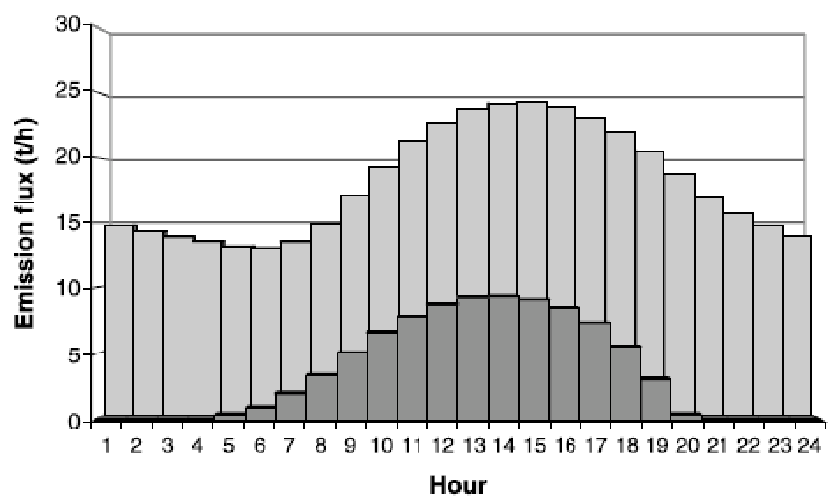




6 May 1998 cloudy/cool

16 May 1998 sunny/warm





Comparison with previous BVOC flux estimates for GB

	Iso	MT (kt y^{-1})	
G95	110	145	56 x 27 km
S99	58	31	150 x 150 km
S03	8	83	12 x 12 km

S03:

- lower EP for oak
- higher resolution for T
- better (surveyed) species distribution
    - less sitka area

- Note: 40% of total IE from sitka spruce

Sensitivity analysis	GB isoprene flux - July
+ 100% willow biomass	+ 10%
+ 100% sitka EP	+ 28
+ 1^{o}C	+ 14%
+ 2^{o}C	+ 31
+ 3^{o}C	+ 50
- 1^{o}C	- 13%
- 2^{o}C	- 24
- 3^{o}C	- 34

Uncertainty analysis

Annual flux +/- 200%

Emission potentials – use of defaults/”best-guess”
Species-specific biomass
Temperature

Seasonality in EP
Leaf T
PAR-dependent MT emissions
Canopy PAR and T profiles
Species distribution

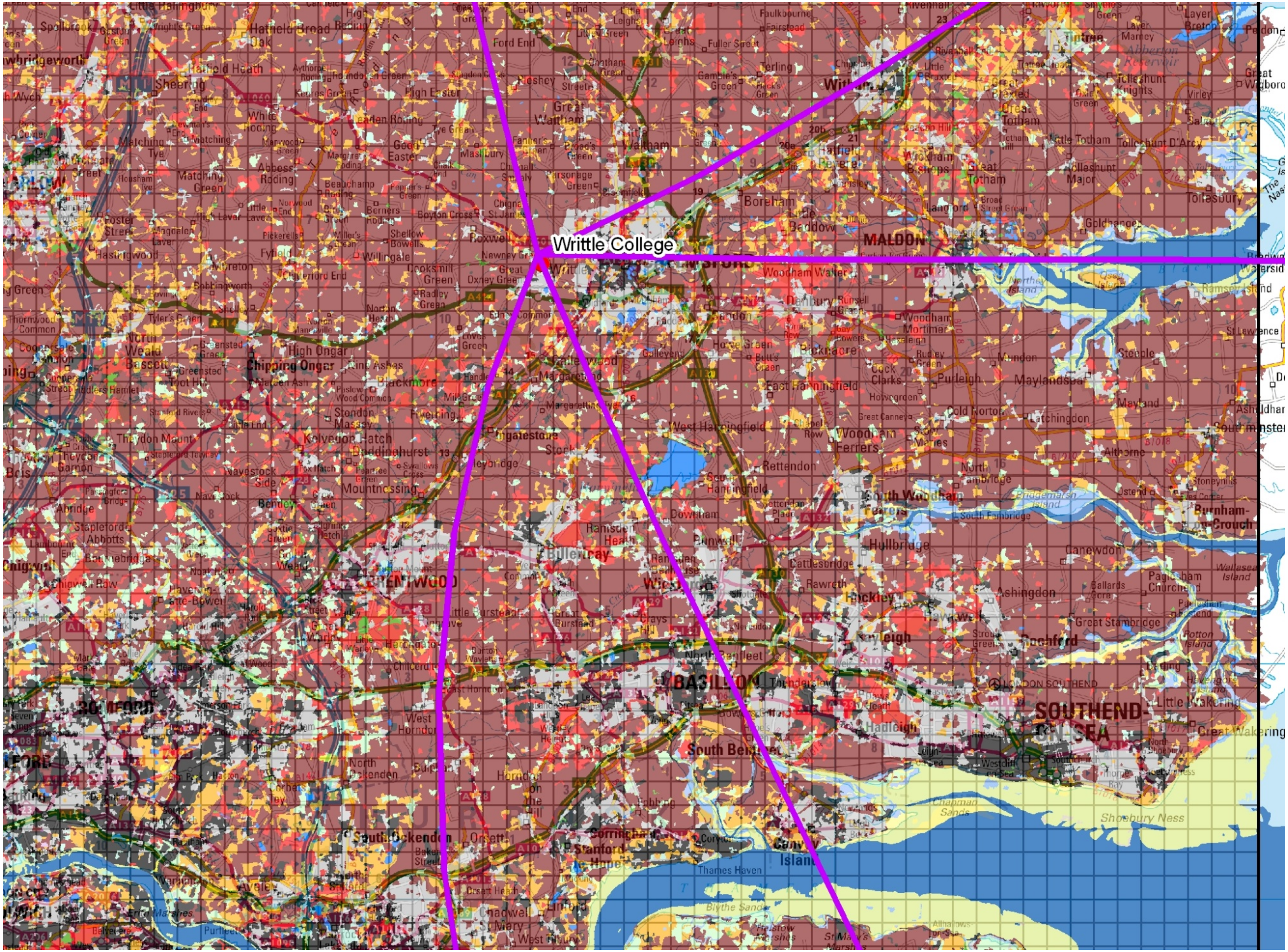
Other compounds

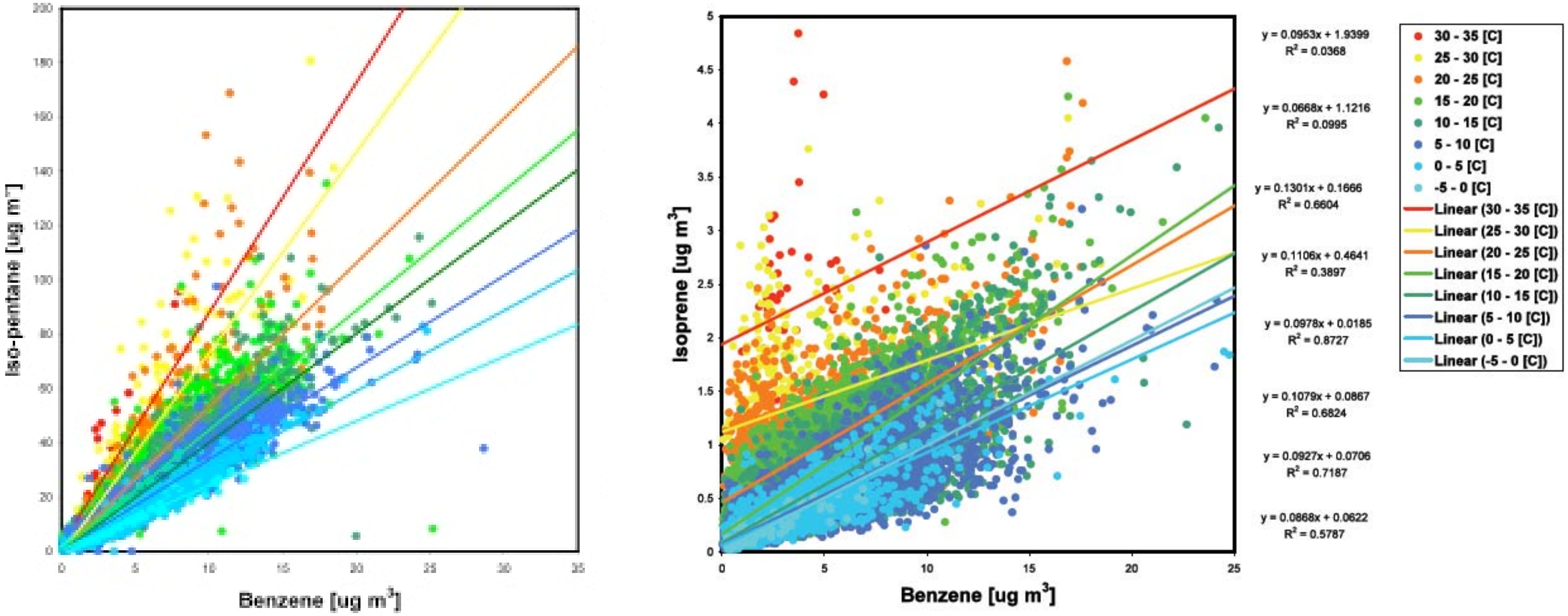
Oxygenated compounds after crop harvesting

Karl et al, 2000 – grass - for about 48 hours after cutting
Davison et al, 2008

methanol	1.0 – 8 mg m^{-2} h^{-1} > IE (x 10 - 10^2)
acetaldehyde	0.5 – 3
hexenal	0.1– 2
acetone	0.1– 2

UK arable crops ~60,000 km^2 (50% cereals)


Writtle College
MALDON
BASILDON
SOUTHEND-ON-SEA
Billericay
Chipping Ongar
Witham
Tiptree
Burnham-on-Crouch
South Benfleet
Canvey Island



Marylebone Rd (5 y) iso-pentane v benzene and isoprene v benzene, sorted by temperature (Langford et al., 2009)

Scatter plots showing the relationship between isoprene and benzene concentrations over a range of temperatures for Marylebone Rd (5 years of data). The y intercept shows the amount of isoprene present not attributable to traffic sources. We use this value, expressed as a percentage of the total isoprene observed at each temperature band (e.g. range) to estimate the biogenic isoprene contribution. To avoid outliers we used the 5th and 95th percentiles for the range.

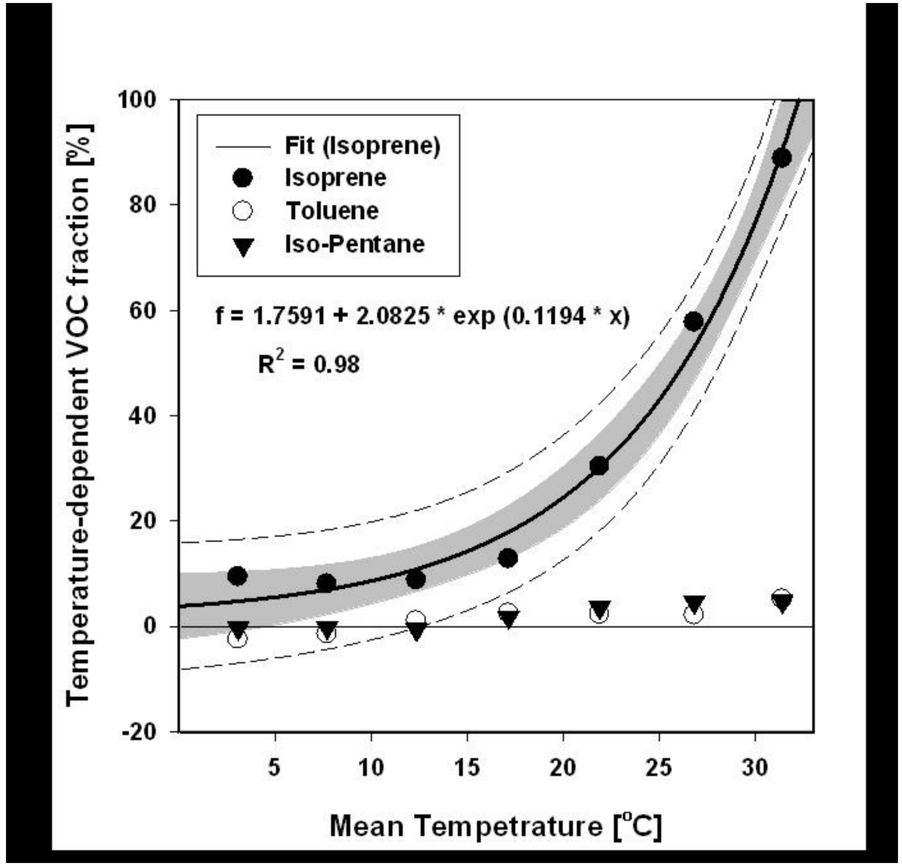


Figure 8. Plot showing the temperature dependency of isoprene (circles), toluene (diamonds) and iso-pentane (triangles) concentrations, calculated using 5 years of hydrocarbon data collected at the Marylebone Road automatic monitoring station and temperature data from the London weather centre. Temperature bands -5 – 0 ^oC, n = 114; 0-5 ^oC, n = 3405; 5-10 ^oC, n = 9539; 10-15 ^oC, n = 12176; 15-20 ^oC, n = 9340; 20-25 ^oC, n = 3171; 25-30 ^oC, n = 673; 30-35 ^oC, n = 73.

(Langford et al., 2009)

Requirements for air quality modelling and assessment

Better resolved BVOC emissions inventory (hourly 1 km x 1 km)

- Better understanding of other BVOC emissions (including after crop harvesting
- Better controlled-environment measurements
- Better T, species distributions, biomass fields

Focus on short duration, high T episodes

Validation by eddy covariance flux measurements