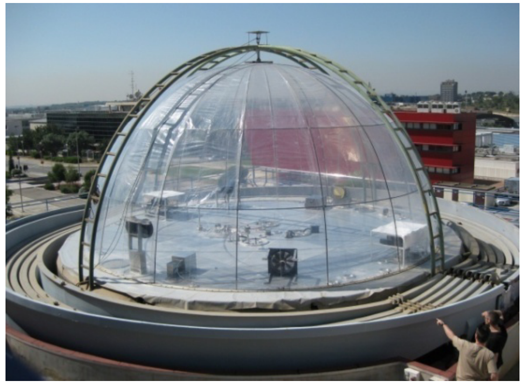
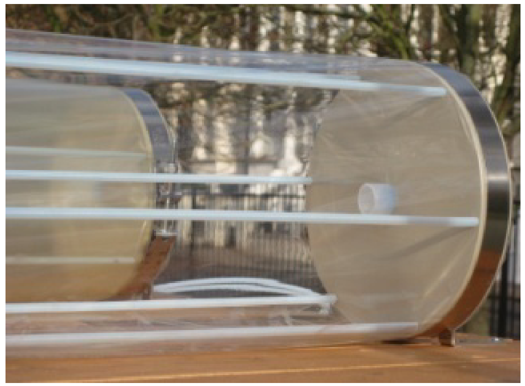
Understanding local ozone formation

New research tools to support AQ policy

Dr William Bloss

University of Birmingham





Overview

- **Ozone Trends: Recent UK experience**

Key questions for effective Air Quality policy :

1 How can we identify which VOCs are the most important ?

2 What do we do about “new” VOCs ?

3 Separating transport vs processing of local precursors

- **Other Uncertainties**

Tropospheric chemistry

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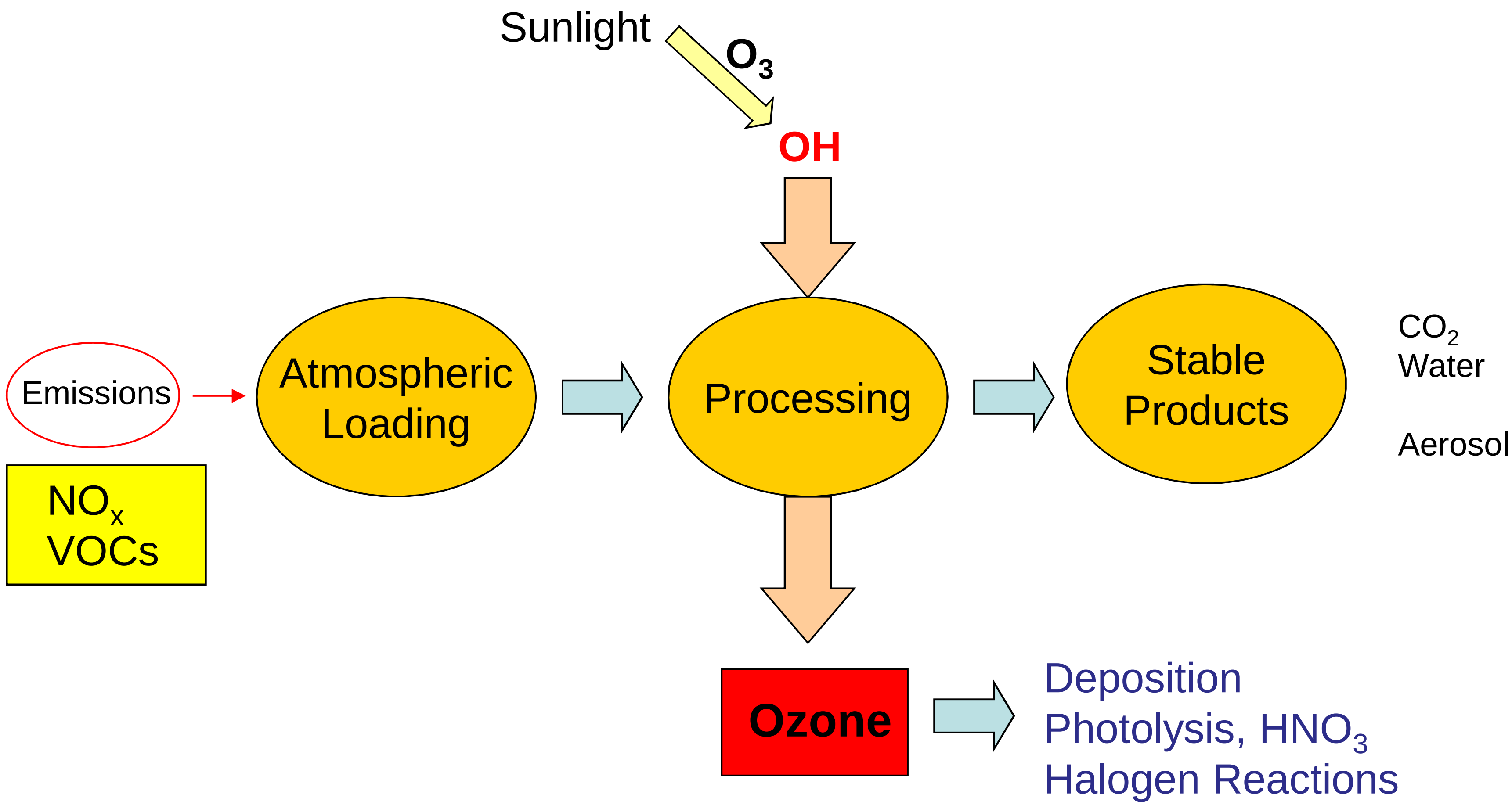
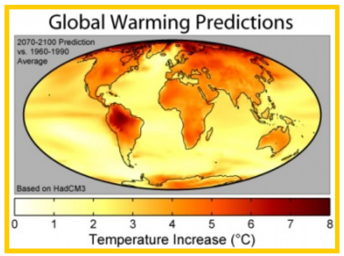
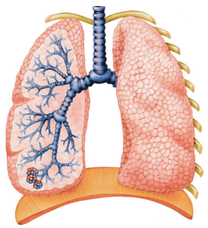
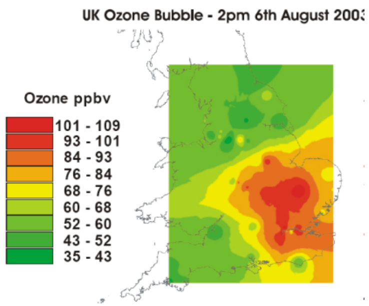
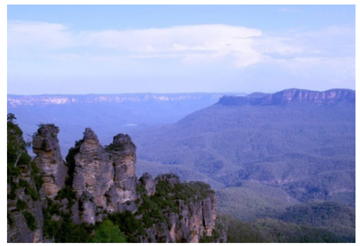






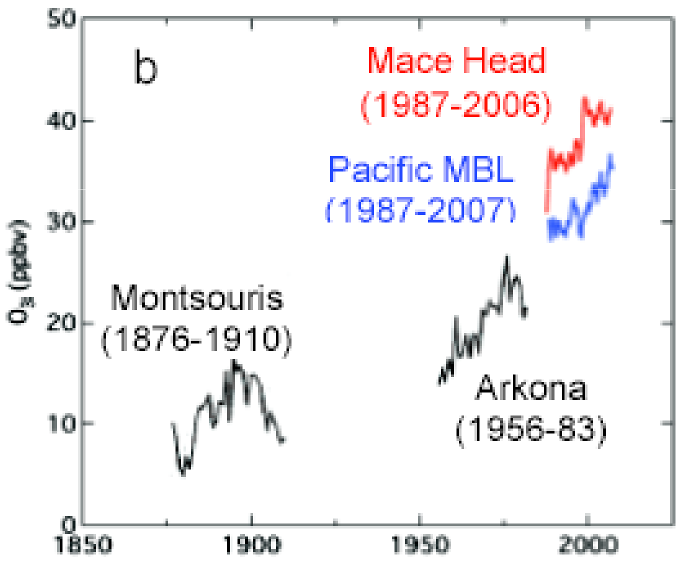




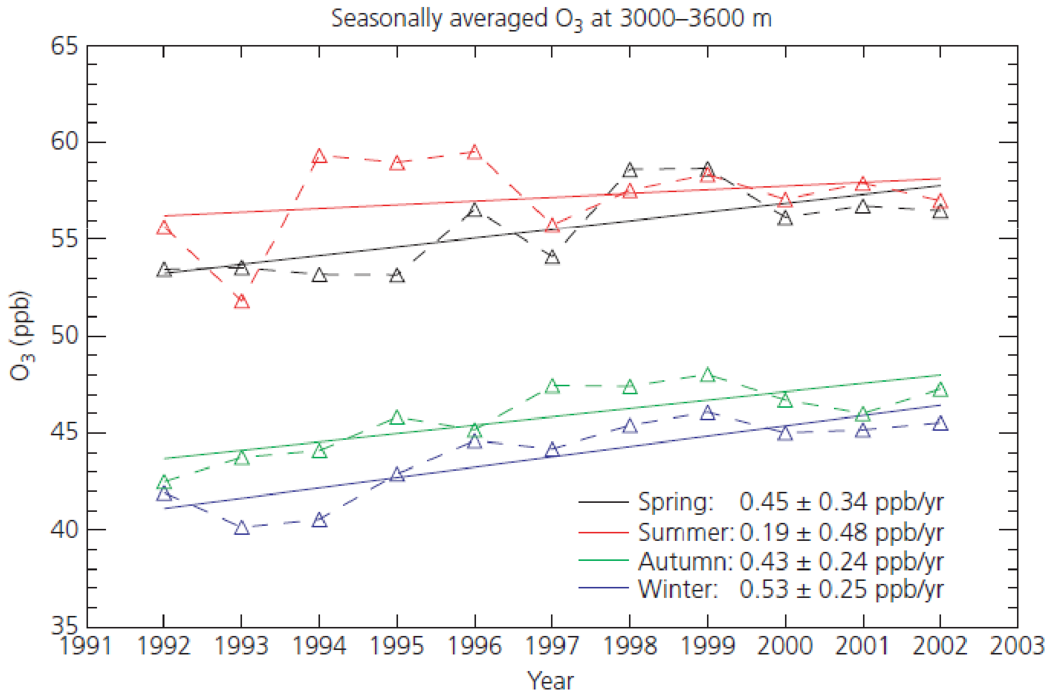
Ground-Level Background Ozone Trends

- ≈ Factor of 2 increase in boundary layer ozone since ≈ 1900
- Continuing increase in background ozone

Marine boundary layer sites



European Mountain sites



From Parrish *et al*., ACP 9, 1303, 2009

From Ordonez *et al*., 2006 cited in Fowler et al., Royal Society,, 2009

Inflow to the UK: Mace Head, Ireland data

- Limited increase 2000 – 2014…

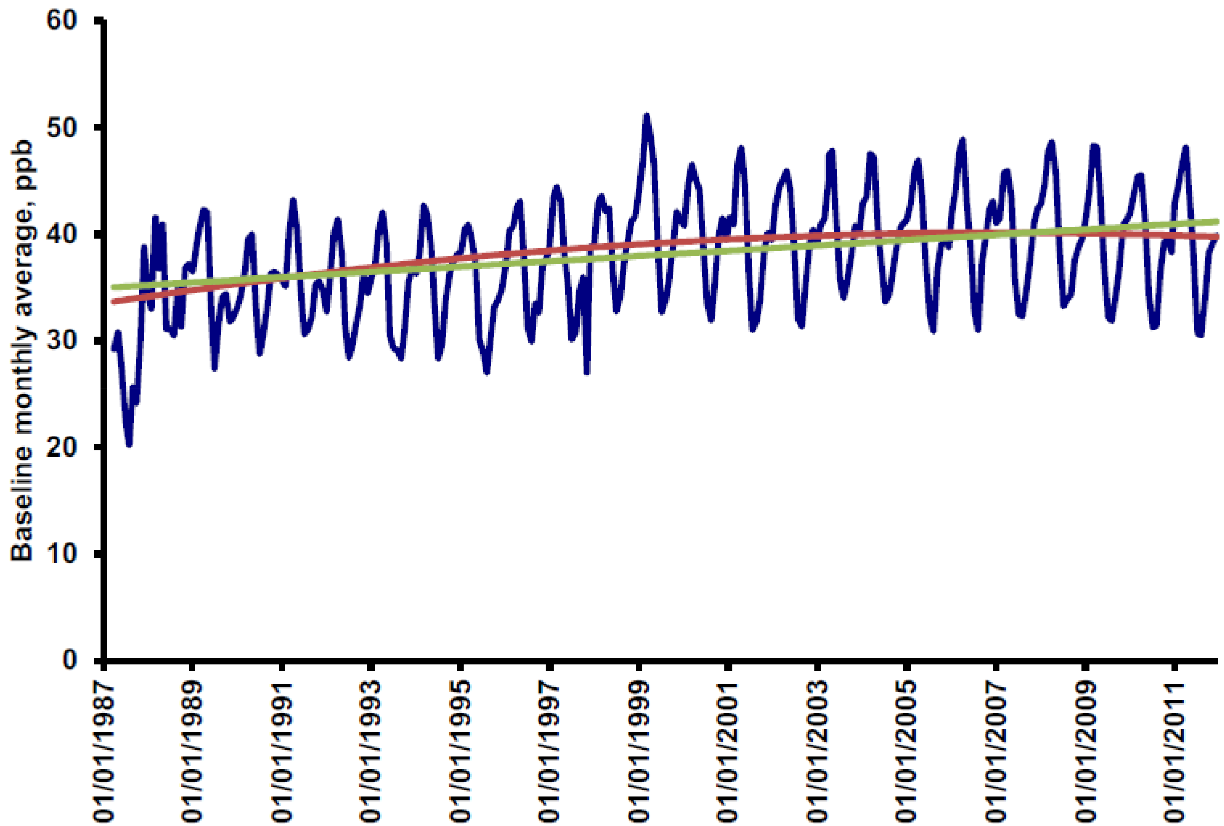
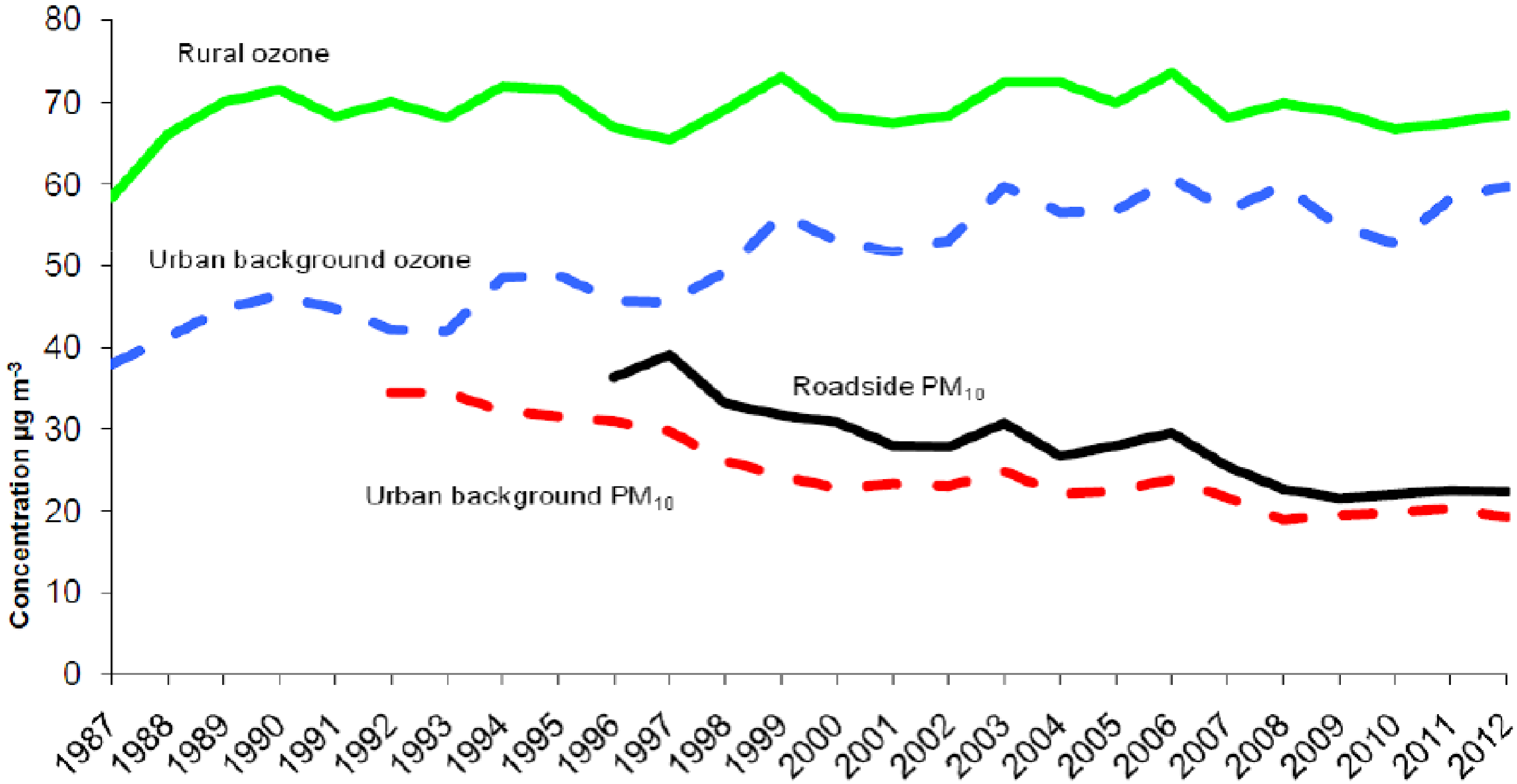


Fig. 2. Baseline monthly average O_3 mixing ratios at the Mace Head Atmospheric Research Station over the period from April 1987 to December 2012, shown as a blue

From Derwent *et al*., *Atmos. Env.*, 2013

UK trends: O_3 and PM_{10}, urban vs rural

- Annual levels of PM_{10} and Ozone in the UK 1987 – 2012 (DEFRA, 2013)



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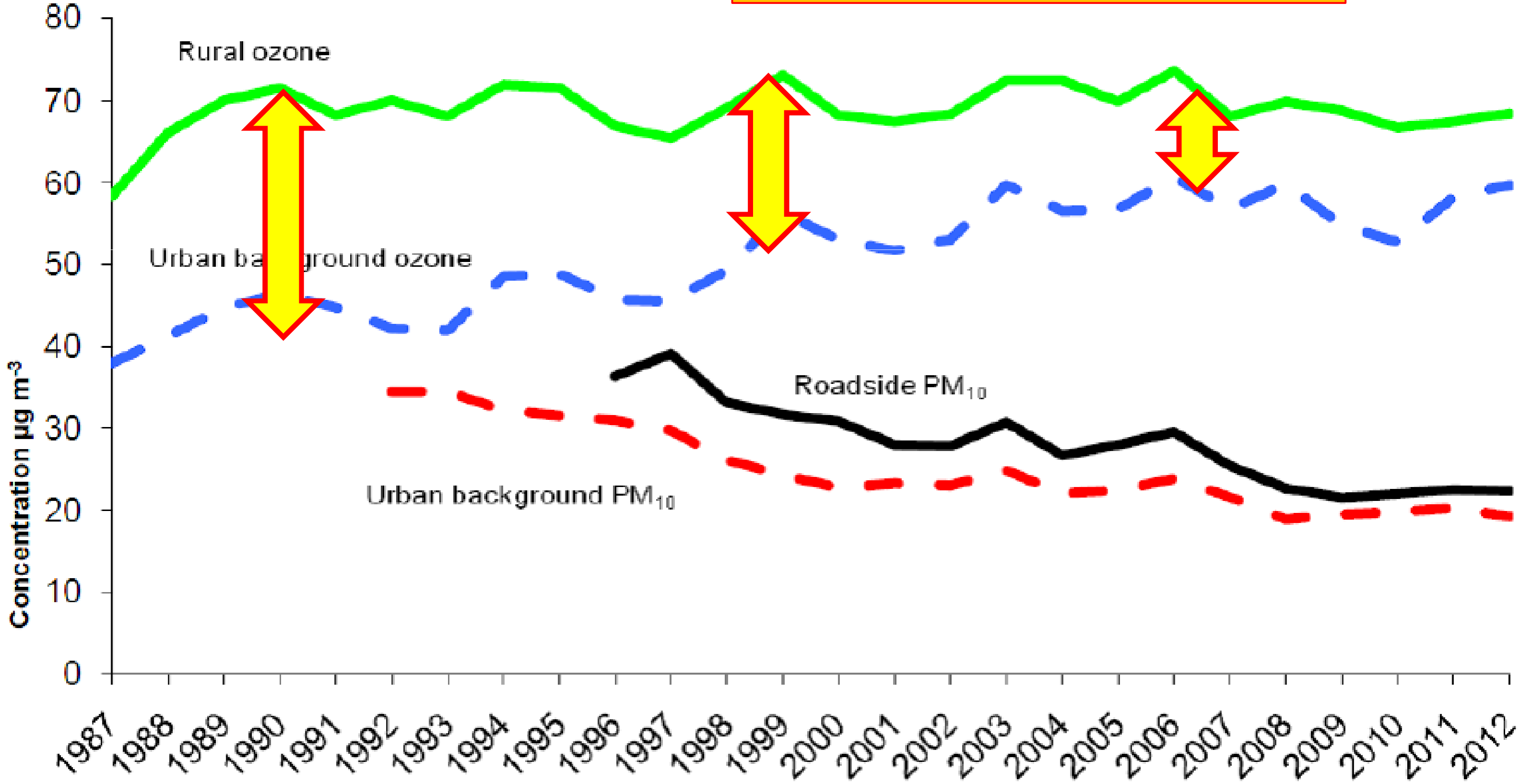
Reducing Urban Decrement
$NO + O_3 \rightarrow NO_2 + O_2$



Figures from Ozone in the UK, AQEG, 2009

Reduction in Urban Decrement

- Traffic NOx emissions are mostly in form NO

$$NO + O_3 \rightarrow NO_2 + O_2$$

- Reduction in traffic NOx emissions

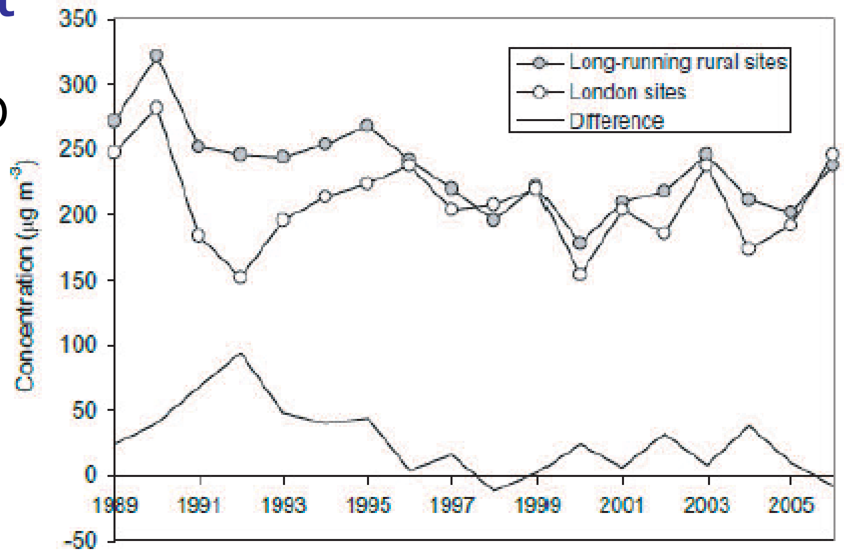
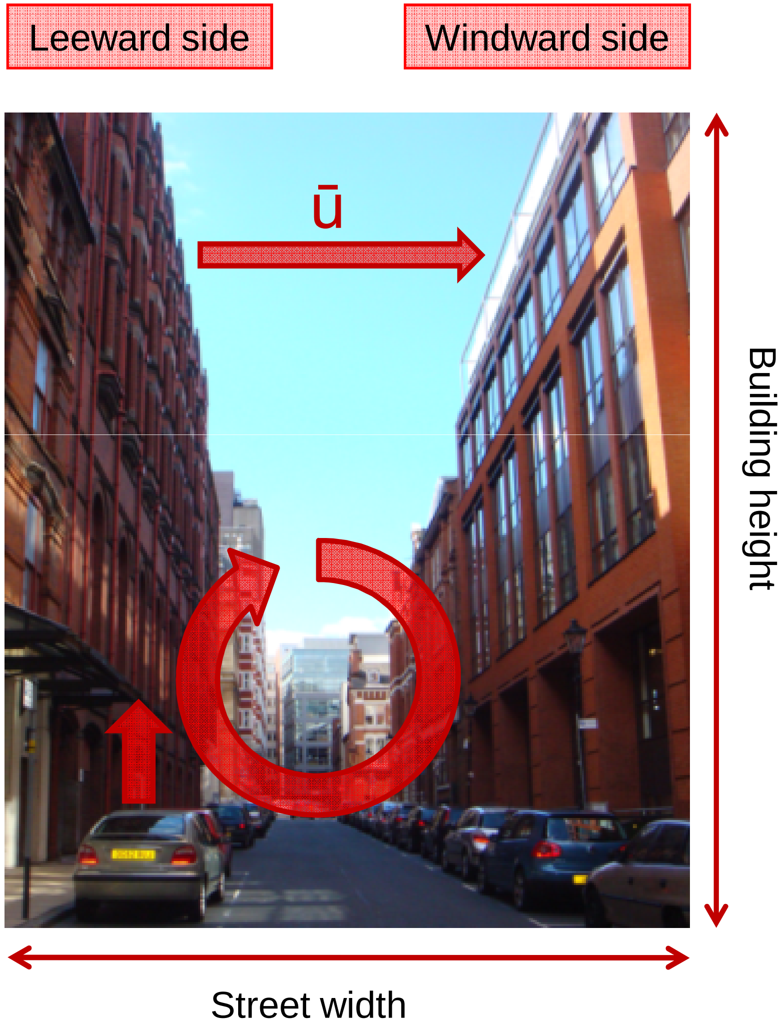


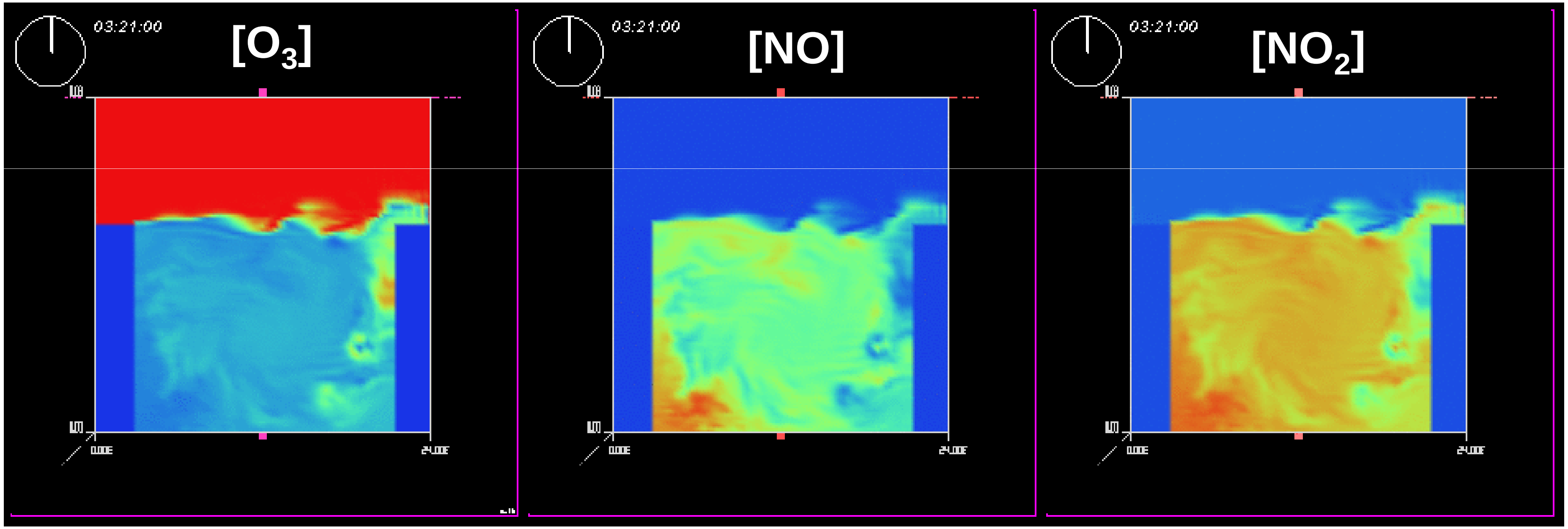
Figure 2.19 Maximum hourly mean ozone concentrations in each year at the long-running rural sites identified in Figure 2.3 and at London sites over the period 1989-2006. The difference between the rural and London sites for the given ozone metric is termed the "urban decrement".

“Street Canyon” chemistry



Street Canyon LES Simulations

$$NO + O_3 \rightarrow NO_2 + O_2$$



- **Low-resolution models *underestimate* canyon O_3 levels**

- From Bright et al., 2012; Zhong et al., 2014

Figures from Ozone in the UK, AQEG, 2009

Reduction in Urban Decrement

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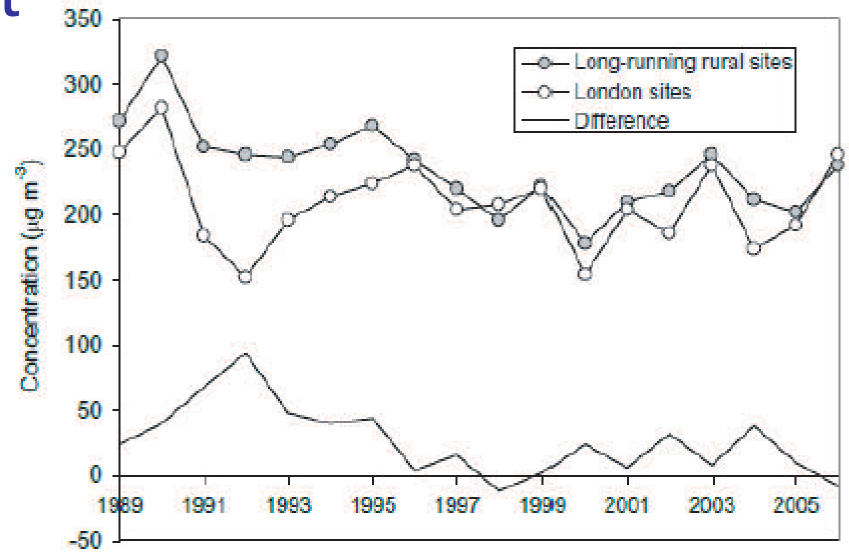
$$NO + O_3 \rightarrow NO_2 + O_2$$

- **Reduction in traffic NOx emissions**

…but…



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Reduction in Urban Decrement

- Traffic NOx emissions mostly in form NO

$$NO + O_3 \rightarrow NO_2 + O_2$$

- **Reduction in traffic NOx emissions**

…but…

- **Increase in primary (direct emission) NO_2**

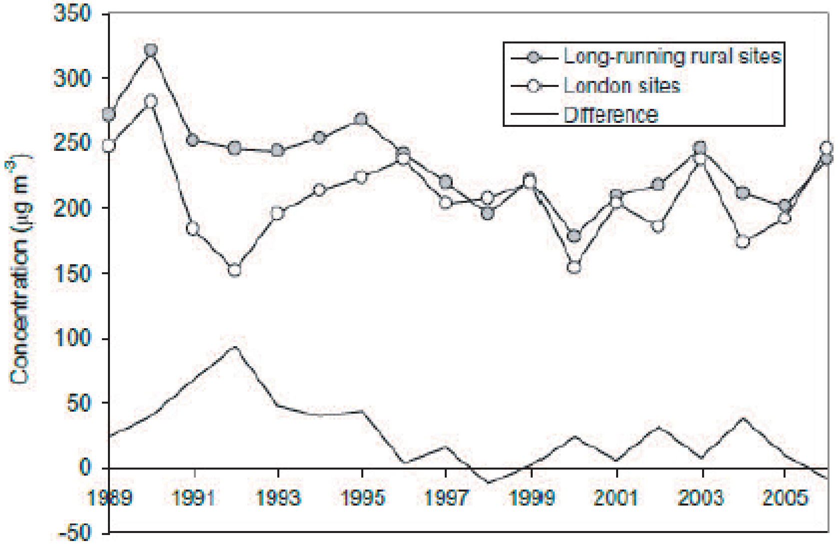
  -Diesel vehicle fleet penetration

  -Reality of EURO standards

$\Rightarrow$ *Lower urban decrement in O_3*

$\Rightarrow$ *Increased total O_x*

$$NO_2 + h\nu \rightarrow NO + O$$
$$O + O_2 + M \rightarrow O_3 + M$$



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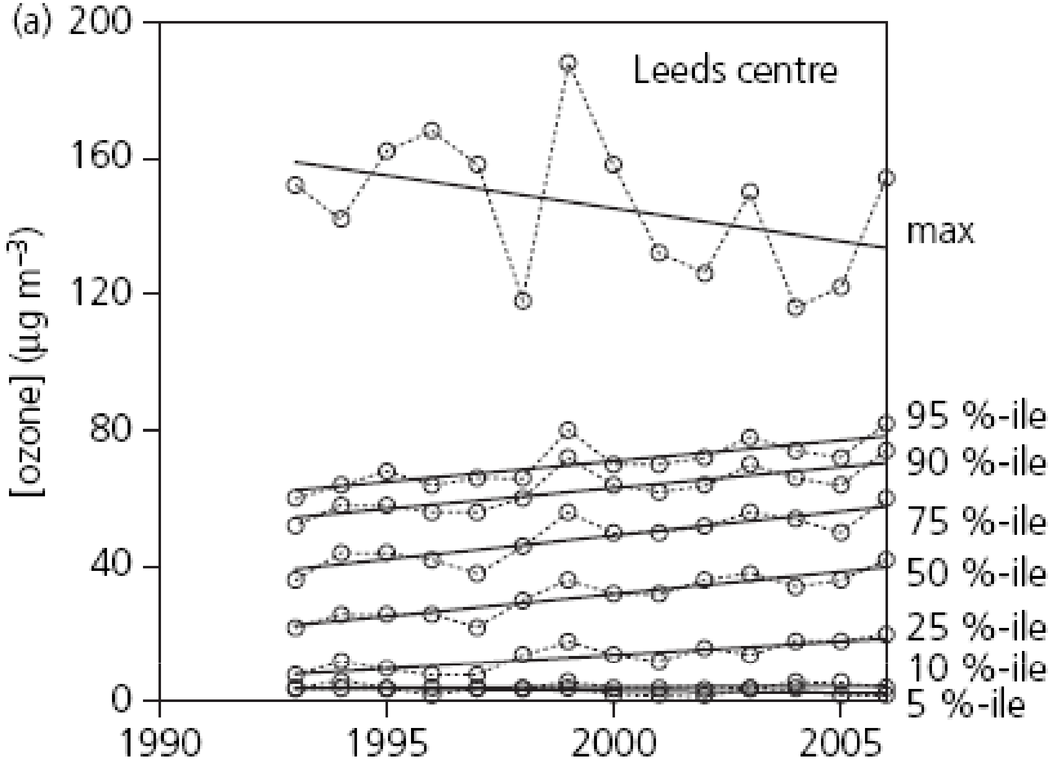
UK ozone trends :

- **Increasing baseline** ozone leve
- **Reduction** in **peak** episodes



(f) Number of days with maximum 8-hour running mean ozone concentration greater than 120 $\mu g\ m^{-3}$

From *Ozone in the UK*, AQEG, 2009

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Insight into emissions controls: POCP Values

- POCP = **Photochemical Ozone Creation Potentials**
- Trajectory model (highly comprehensive chemically)

- Emissions inventory
- Add additional emission of VOC_i
- Assess resulting ΔO_3 after some time t

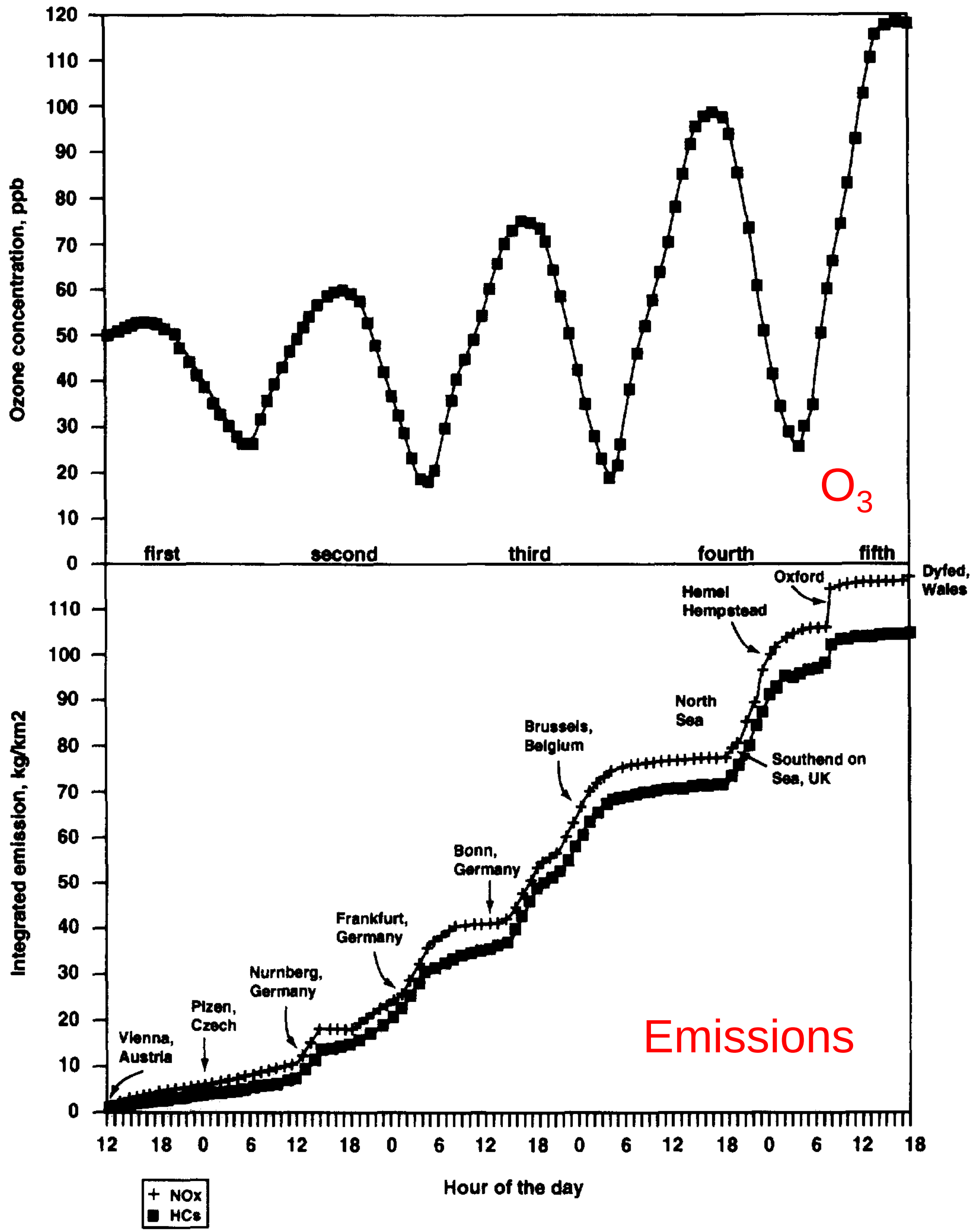
$$\mathrm{POCP}_i = 100 \times \frac{\text{ozone increment with the } i\text{th VOC}}{\text{ozone increment with ethene}}$$

- t = 1 – 5 days

- A metric to assess impacts of local emissions (and hypothetical controls) on top of trans-boundary components

Europe → UK POCP trajectories

- Modelled [O_3] and cumulative NOx and VOC emissions along Trajectory Austria → UK



POCP Values

- 5-day trajectory POCP values (subset of species)

Species	POCP
Methane	3.4
Ethane	14
Propane	41.1
Cyclohexane	59.5
Ethene	100
Propene	107.9
Acetylene	28
Benzene	33.4
Toluene	77.1
m-Xylene	108.8
Formaldehyde	55.4

Apply total emissions ⇒ cumulative contribution to net ozone production

Rank	Common name	Emission	POCP	POCP weighted emission ($t\,yr^{-1}$)	Cumulative percentage of weighted emission (%)
1	Toluene	138574	77	106841	8
2	*n*-Butane	128743	60	77117	15
3	Ethylene	75308	100	75308	22
4	*m*-Xylene	60585	109	65917	27
5	*p*-Xylene	60464	95	57320	33
6	*o*-Xylene	52433	83	43572	37
7	*i*-Pentane	67855	60	40577	40
8	Ethyl alcohol	84923	45	37876	44

POCP Caveats

- Trajectory dependent, Emissions Dependent
- Defined NOx scenario: most suited for VOC dependencies
- Outcomes dependent upon simulation duration
  (fast vs. slow reacting VOCs)

Other Metrics also available:

Maximum Incremental Reactivity…etc

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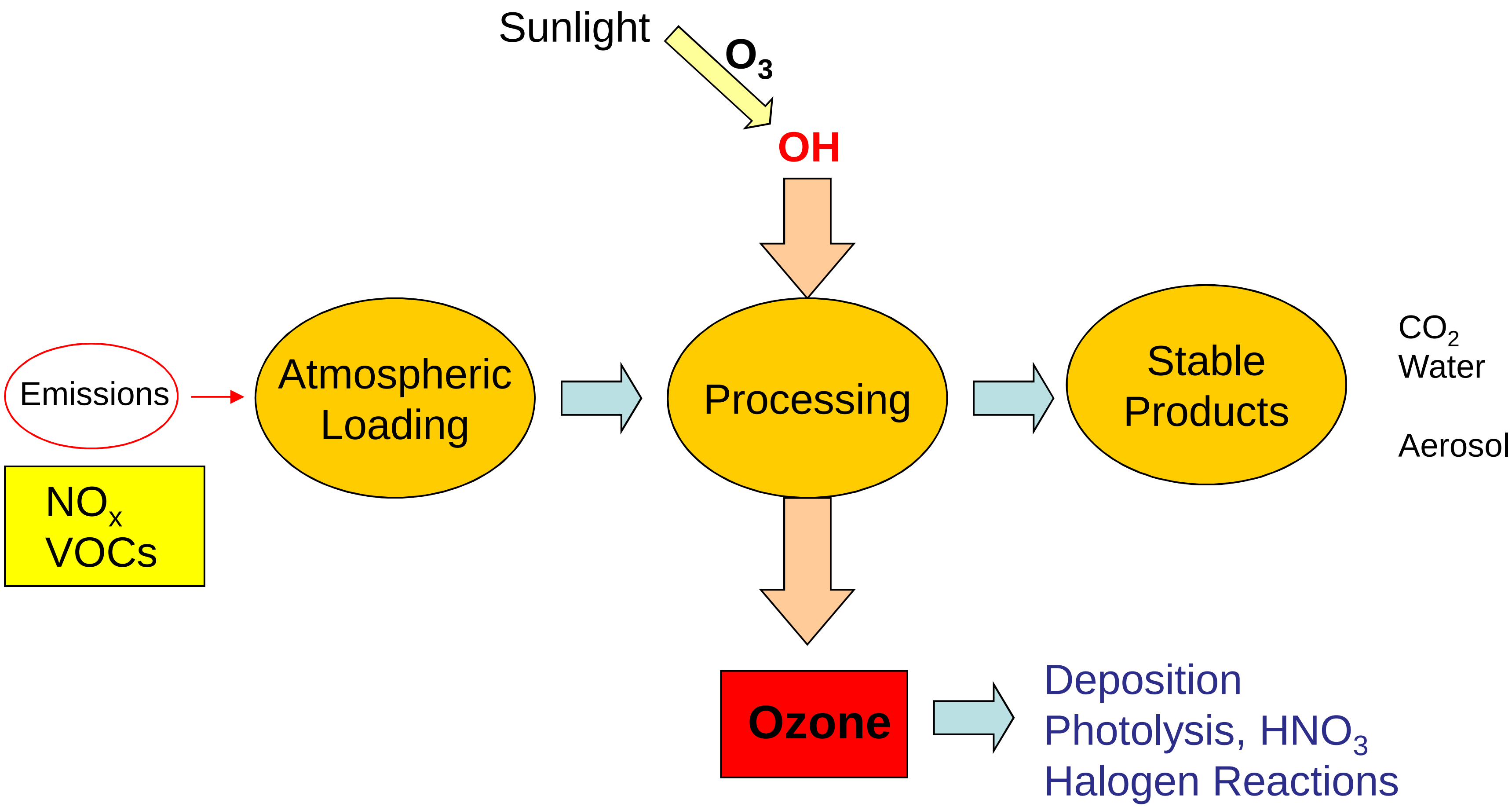
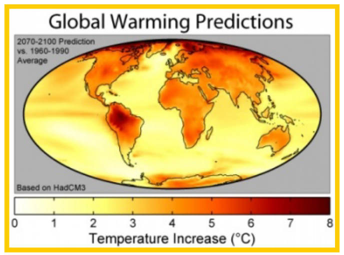
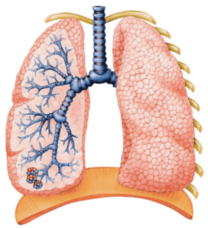
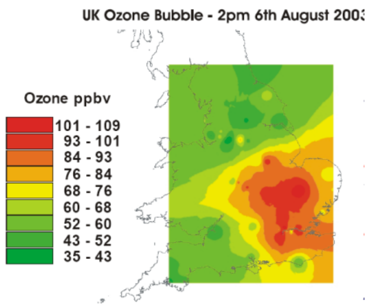
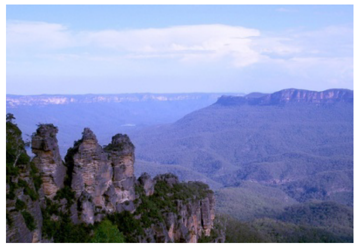










“Bottom-up” mechanism approach...

- Laboratory studies of individual reactions

JPL Publication 06-2

Chemical Kinetics and Photochemical Data for Use in Atmospheric Studies

				f(298 K)[b]	g	Notes
						B11
				1.15	+160 −80	B12
				1.2	200	B13
				1.2	200	B13
NO_x Reactions						
$O + NO \xrightarrow{M} NO_2$	(See Table 2-1)					
$O + NO_2 \rightarrow NO + O_2$	5.1×10^{-12}	-210	1.04×10^{-11}	1.1	20	C 1
$O + NO_2 \xrightarrow{M} NO_3$	(See Table 2-1)					
$O + NO_3 \rightarrow O_2 + NO_2$	1.0×10^{-11}	0	1.0×10^{-11}	1.5	150	C 2
$O + N_2O_5 \rightarrow$ products			$<3.0\times10^{-16}$			C 3
$O + HNO_3 \rightarrow OH + NO_3$			$<3.0\times10^{-17}$			C 4
$O + HO_2NO_2 \rightarrow$ products	7.8×10^{-11}	3400	8.6×10^{-16}	3.0	750	C 5
$H + NO_2 \rightarrow OH + NO$	4.0×10^{-10}	340	1.3×10^{-10}	1.3	300	C 6
$OH + NO \xrightarrow{M} HONO$	(See Table 2-1)					
$OH + NO_2 \xrightarrow{M} HNO_3$	(See Table 2-1)					
$OH + NO_3 \rightarrow$ products			2.2×10^{-11}	1.5		C 7
					+200	

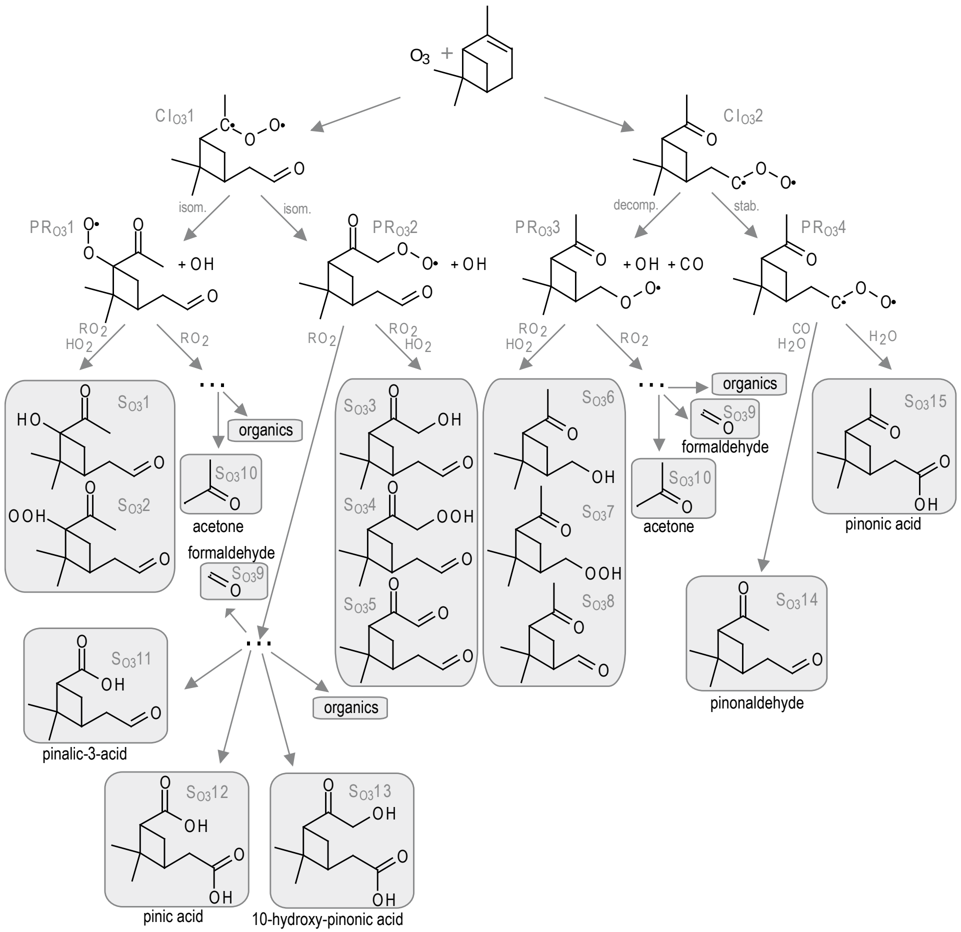
- CH_4
- C_2H_4 ….

“Bottom-up” mechanism approach...

- Laboratory studies of individual reactions

Biogenic VOCs, e.g. α-Pinene

Chemistry is too complex for (many) models



ata

	f(298 K)b	g	Notes
			B11
	1.15	+160 –80	B12
	1.2	200	B13
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10−11	1.1	20	C 1
10−11	1.5	150	C 2
10−16			C 3
10−17			C 4
10−16	3.0	750	C 5
10−10	1.3	300	C 6
10−11	1.5		C 7
		+200	

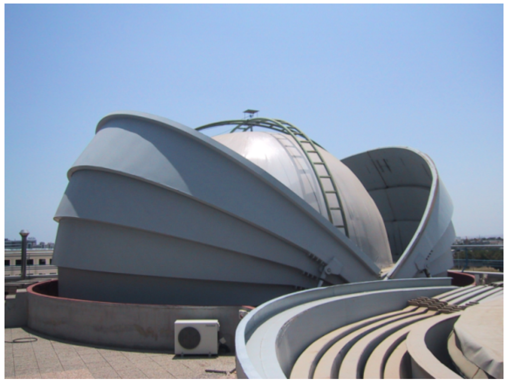
- C
- C

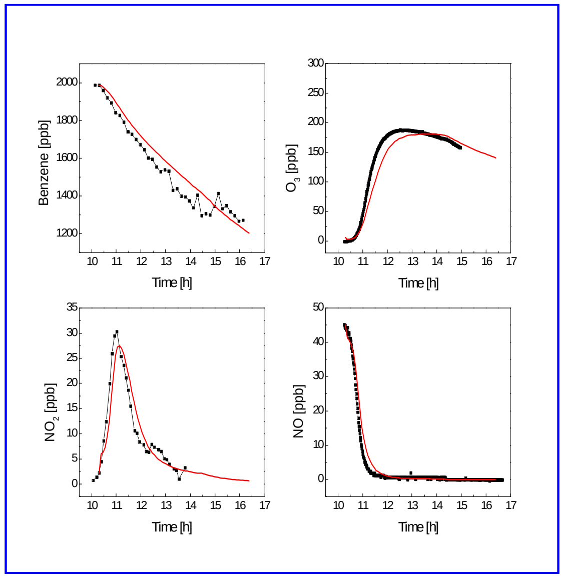
Simuation Chamber Approach

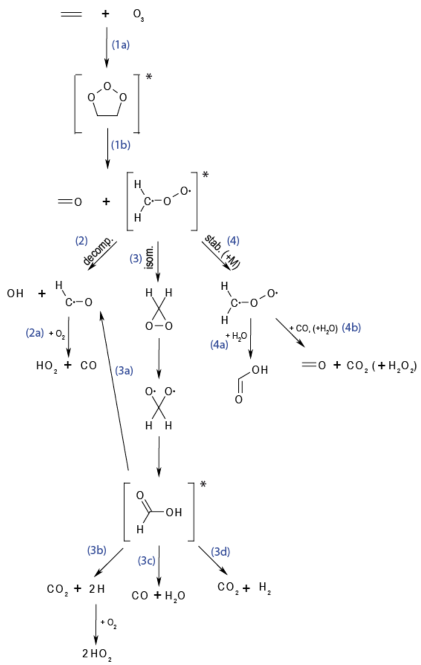
- Study Ozone and SOA formation from “new” VOCs
- Develop chemical mechanisms
- Test and evaluate existing models

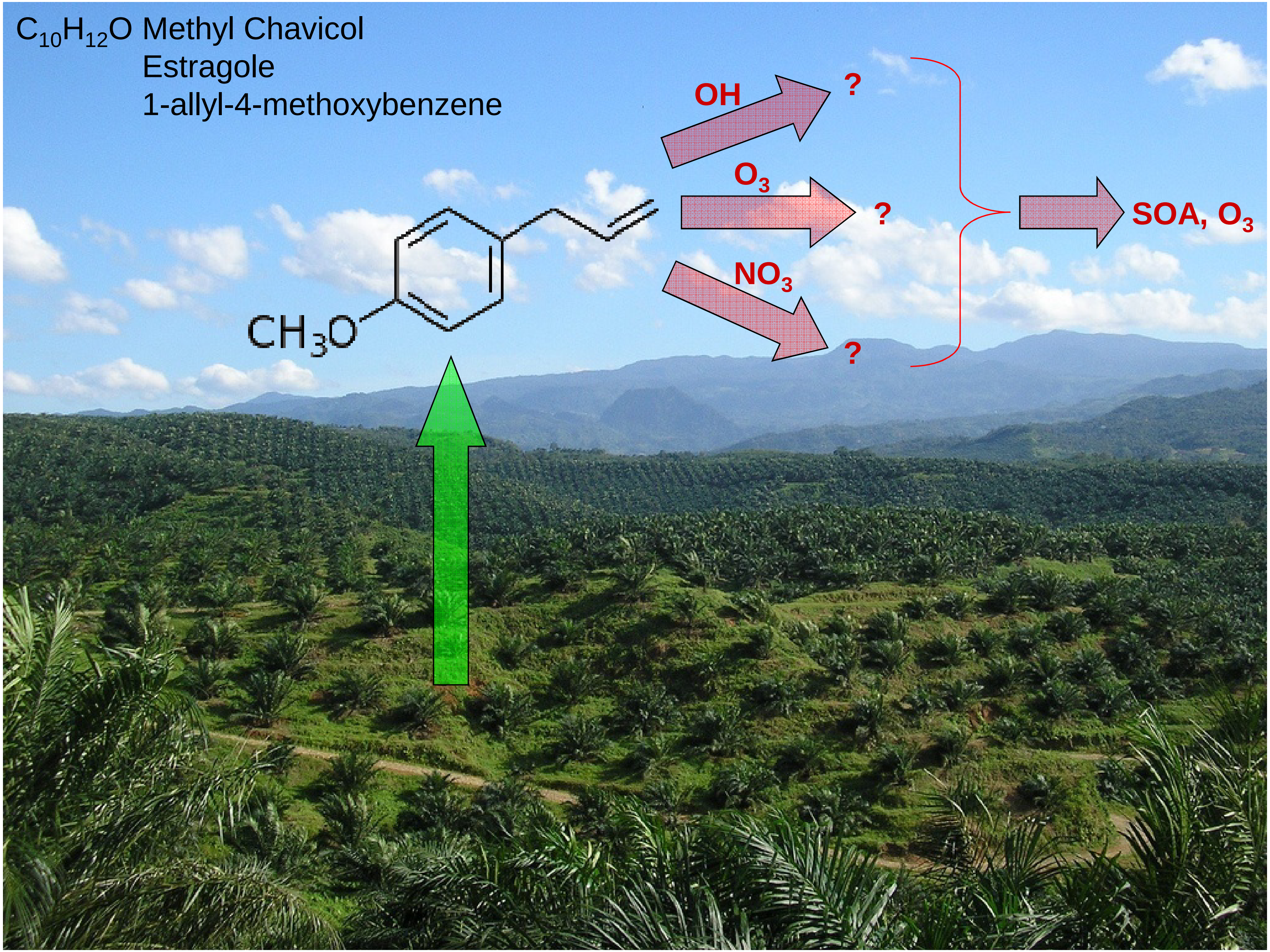
$\Rightarrow$ improved accuracy and quantified uncertainty in model predictions

$\Rightarrow$ more efficient air quality policy









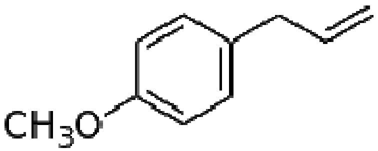
$C_{10}H_{12}O$ Methyl Chavicol
Estragole
1-allyl-4-methoxybenzene
CH_3O
OH
?
O_3
?
NO_3
?
SOA, O_3

EUPHORE simulation chamber, Valencia

Ozone production from MC oxidation

- To predict full ozone, other chemical impacts need full degradation mechanism

$C_{10}H_{12}O$



$\Rightarrow \Rightarrow \Rightarrow$ $CO_2 + H_2O$

…this would be rather complex to develop

Ozone production from MC oxidation

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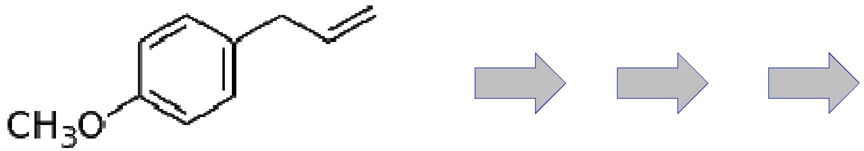
$C_{10}H_{12}O$



$CO_2 + H_2O$

…this would be rather complex to develop

$\Rightarrow$ **Surrogate mechanism, based on well-understood species, with a small number of "informed modifications"**

-Initial kinetics, product channels

-Enhanced yields to account for difference in molar mass

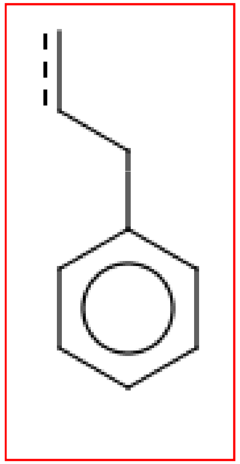
-Build upon existing MCM (v3.2) mechanisms

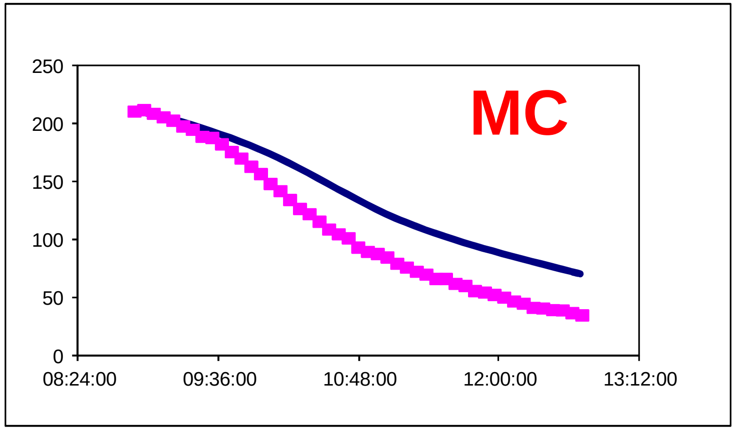
Propylbenzene mechanism base...

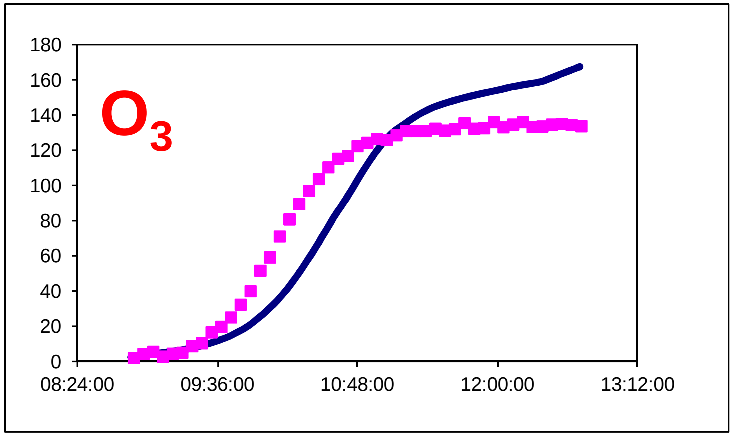
- Constrained to initial MC/NO, and to H_2O, T, *j*, HONO source only

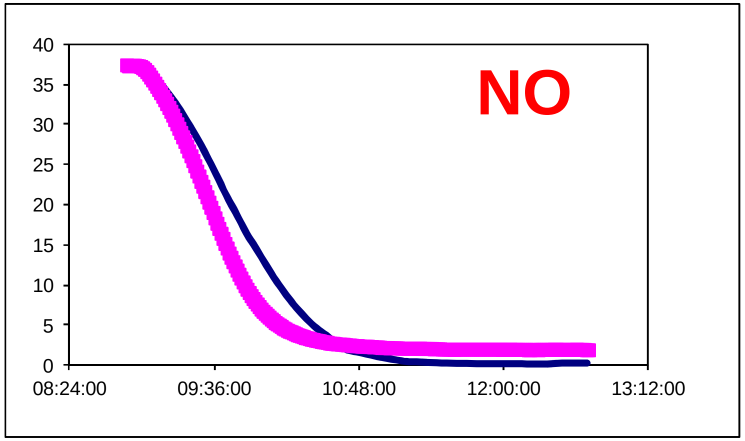
Model

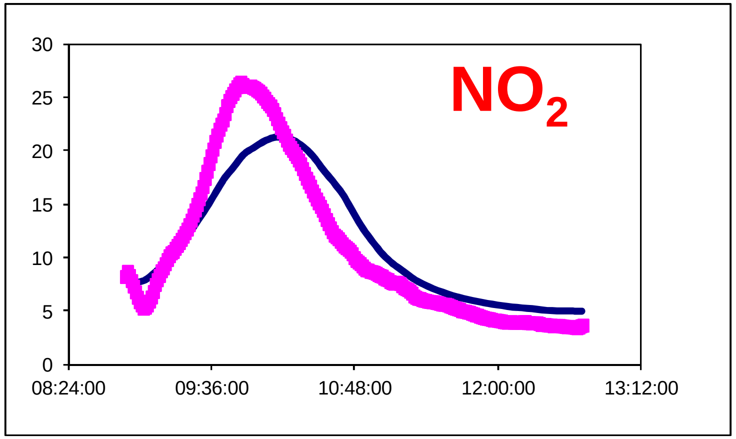
Measurement

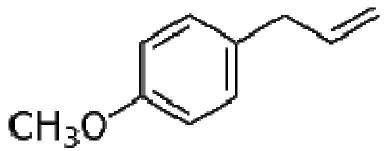












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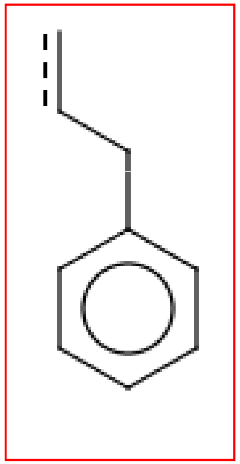
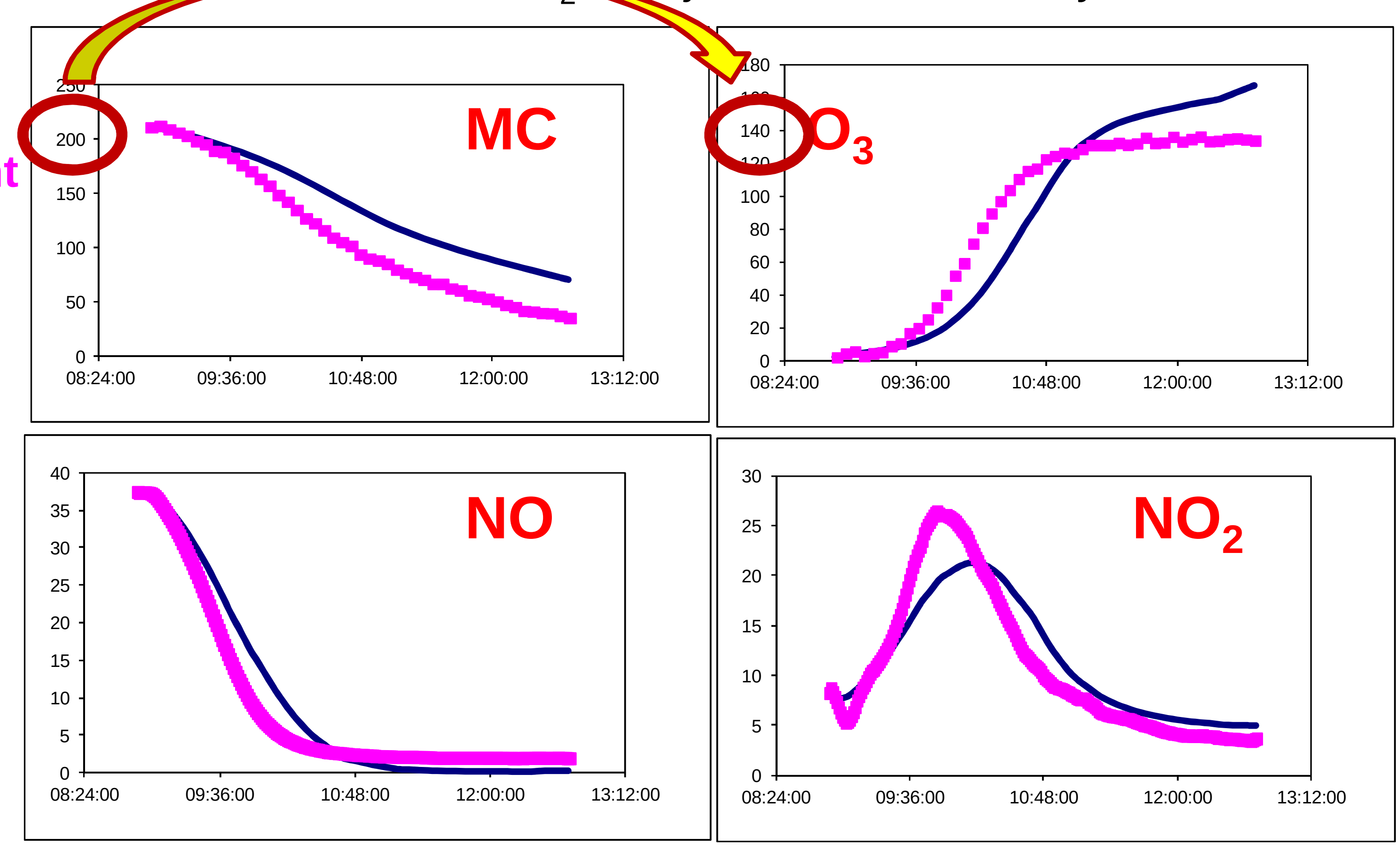
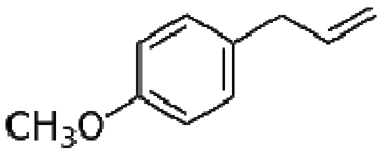




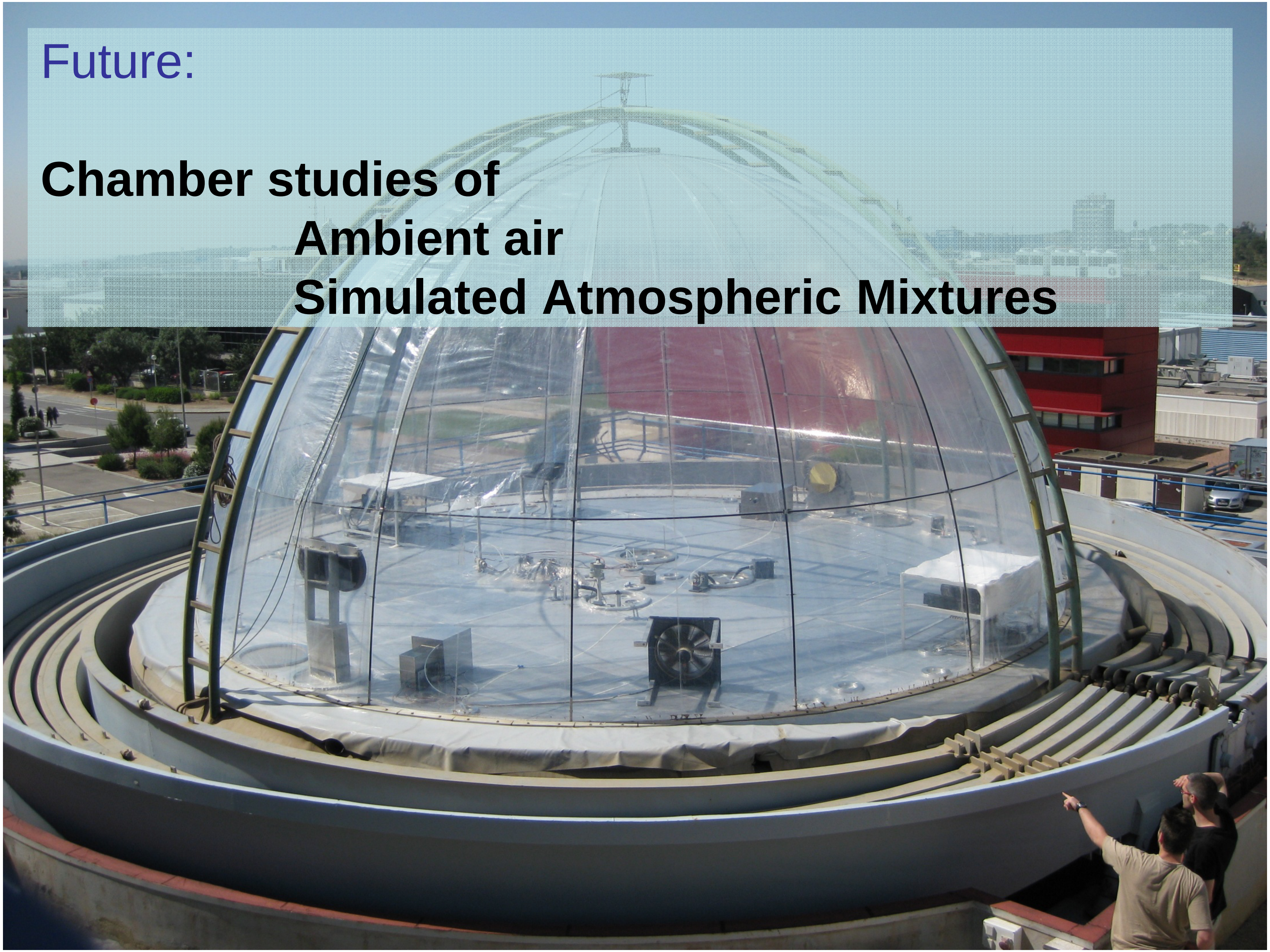


Future:

Chamber studies of

Ambient air

Simulated Atmospheric Mixtures



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Integrated Chemistry of Ozone in the Atmosphere

$$\frac{\partial[\mathrm{O_3}]}{\partial t} = \underbrace{p_{\mathrm{O_3}} - l_{\mathrm{O_3}}}_{P(\mathrm{O_3})} \underbrace{- \frac{v}{H}[\mathrm{O_3}]}_{SD} \underbrace{+ u_i \frac{\partial[\mathrm{O_3}]}{\partial x_i}}_{A}$$

Chemistry *Deposition* *Transport*

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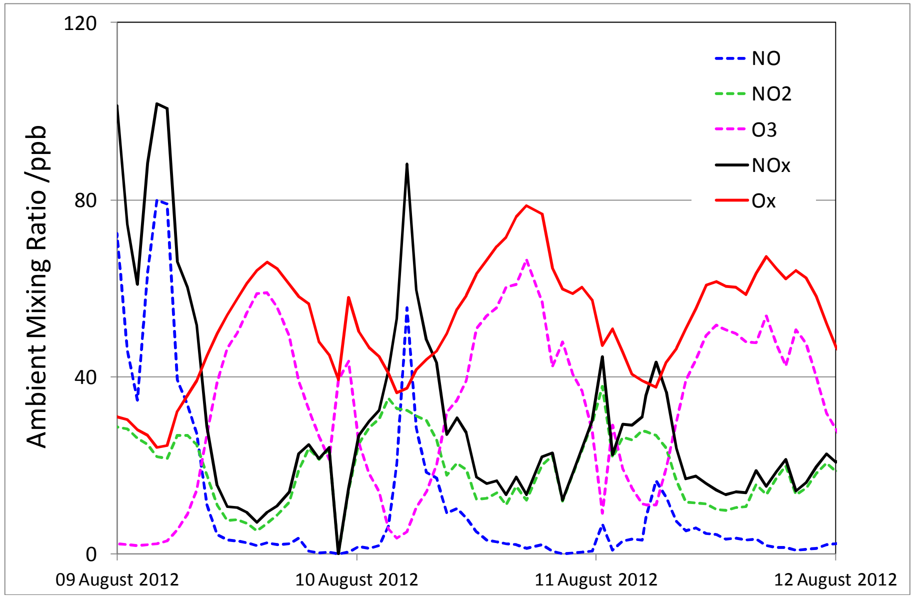
Chemistry *Deposition* *Transport*

- Directly measure *in situ* chemical ozone production rate $P(O_3)$
- Sidestep uncertainties in chemistry, emissions, observations
- Provide new metric with which to challenge [local] models

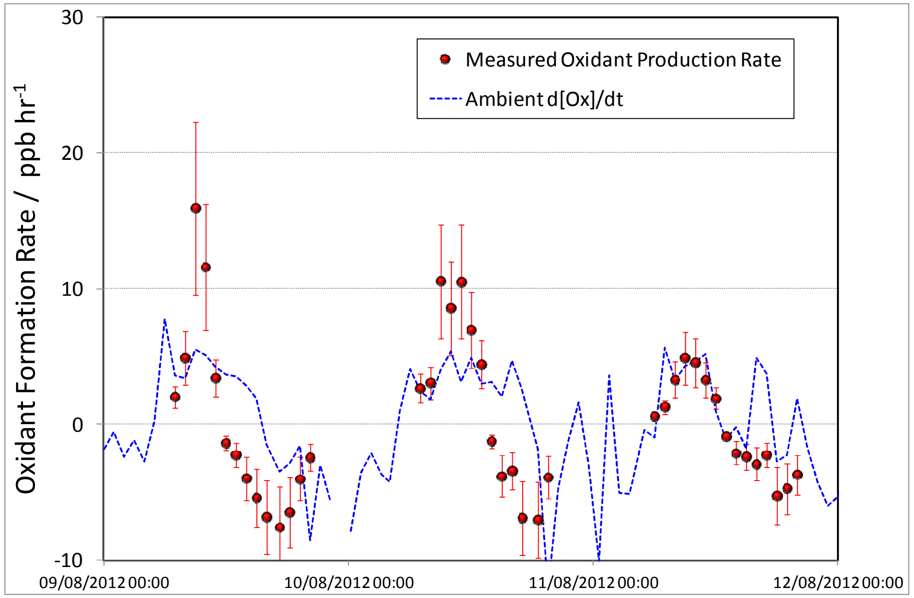
Chemical oxidant production / loss

- North Kensington

Urban Background Location



Ambient Levels



O_X Prod^n Rate: Total & Chemical

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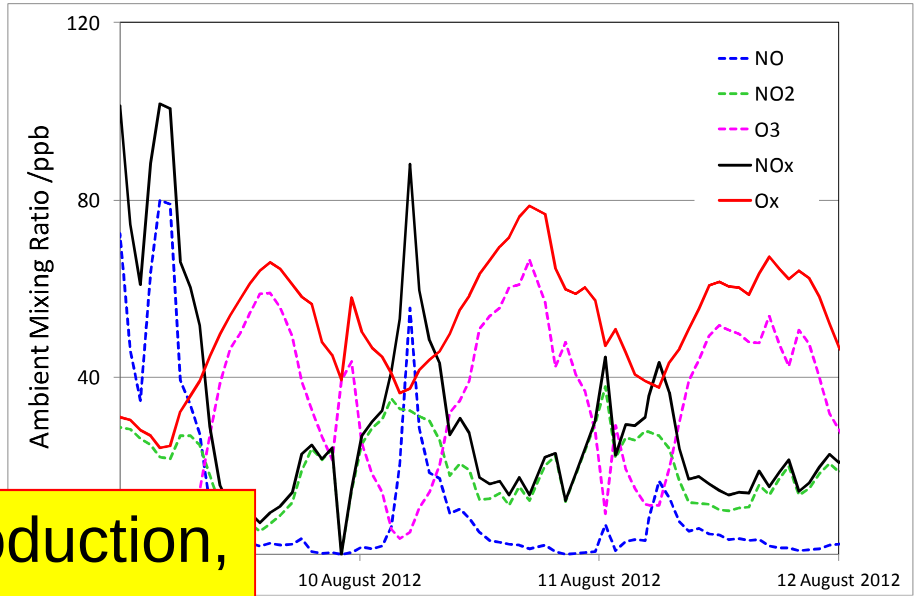
Chemical oxidant production / loss

- North Kensington

Urban Background Location

Local chemical ozone production, offset by dynamics



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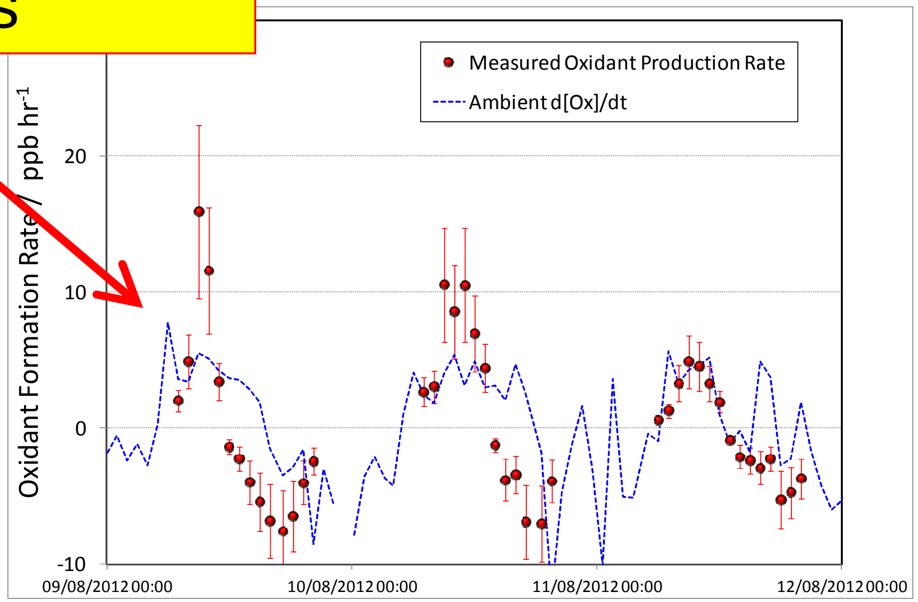

O_X Prod^n Rate: Total & Chemical

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Current Field Measurements – Weybourne, UK

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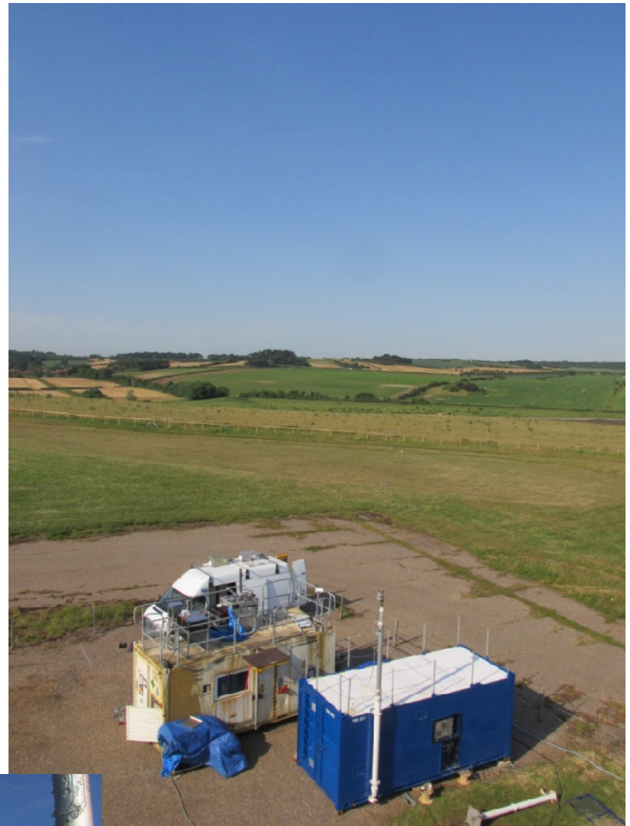
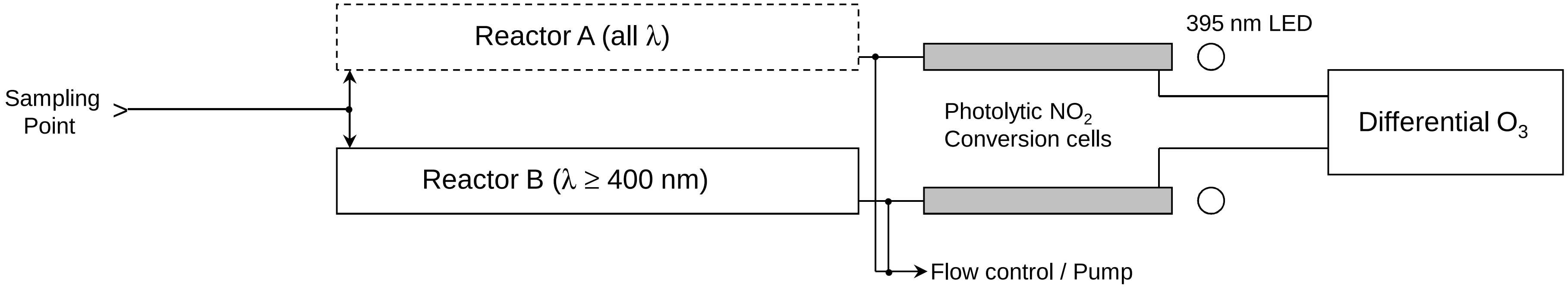
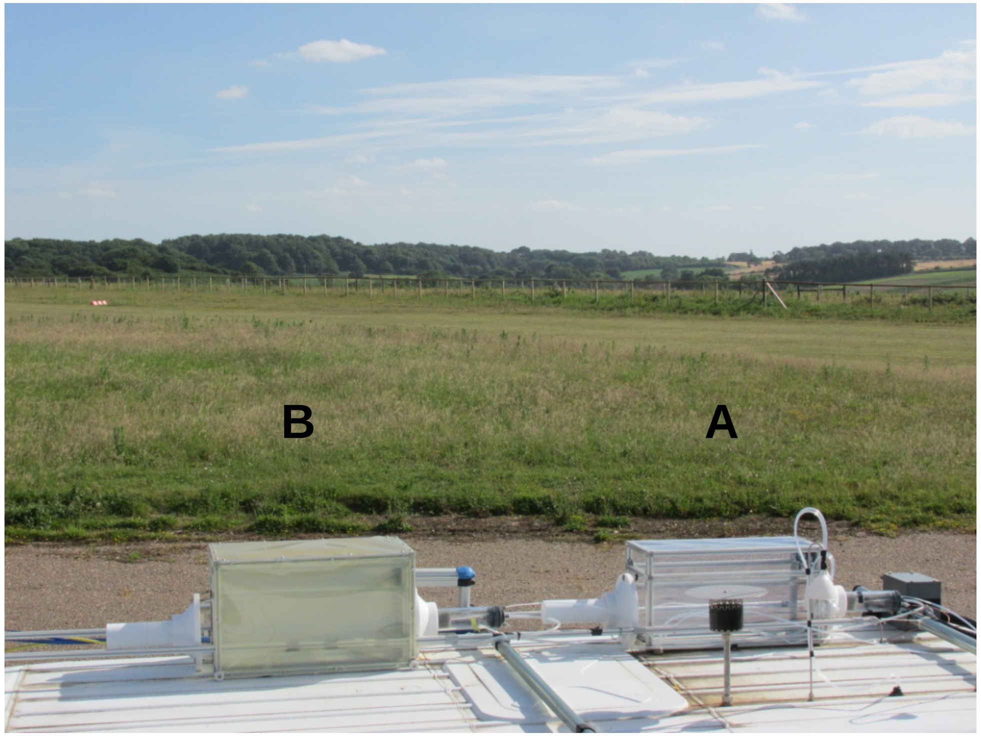


Measurement of *in situ* Oxidant Production Rate

- *Leigh Crilley; Louisa Kramer*

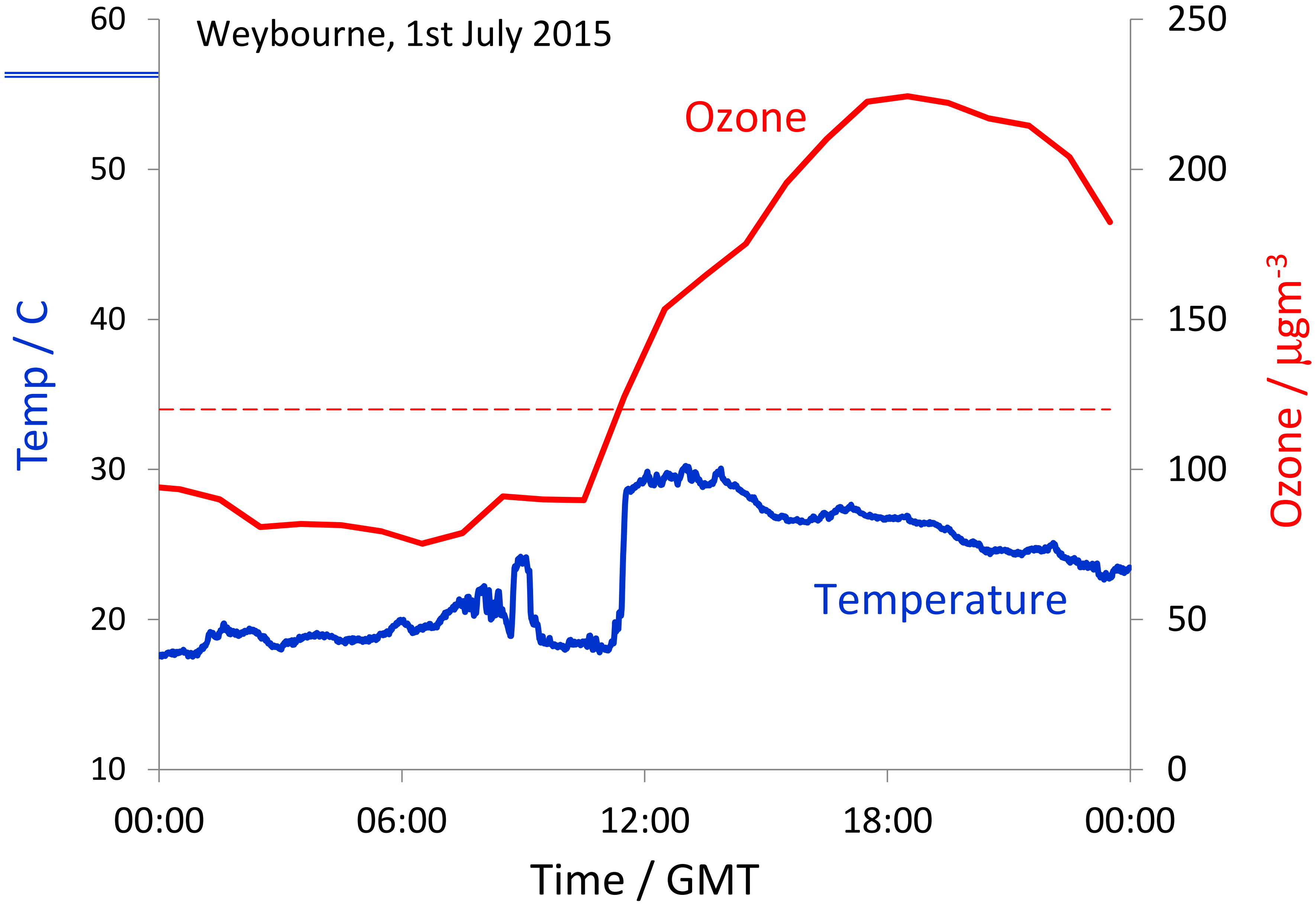




$$NO + O_3 \rightarrow NO_2 + O_2$$
$$NO_2 + hv \rightarrow NO + O$$
$$O + O_2 + M \rightarrow O_3 + M$$

$$NO_x = NO + NO_2$$
$$O_X = NO_2 + O_3$$

We measure ***d[O$_x$]/dt***



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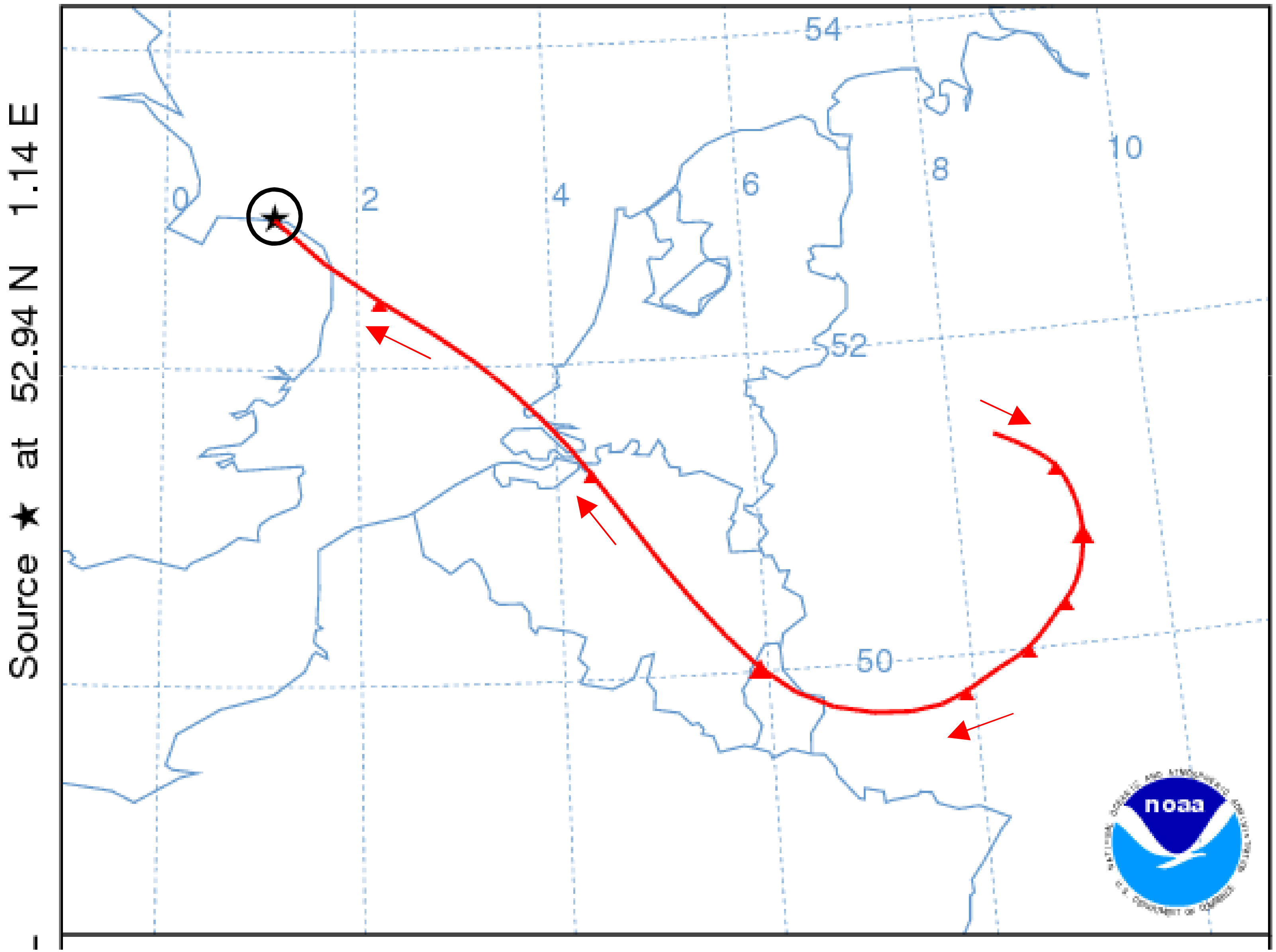
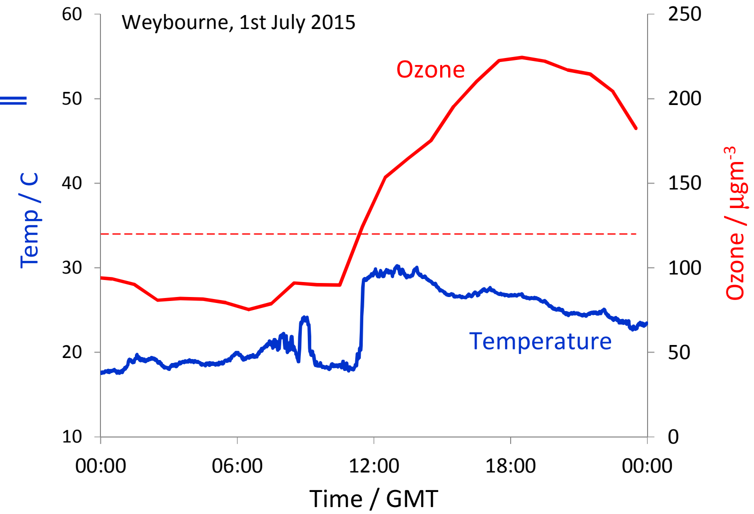
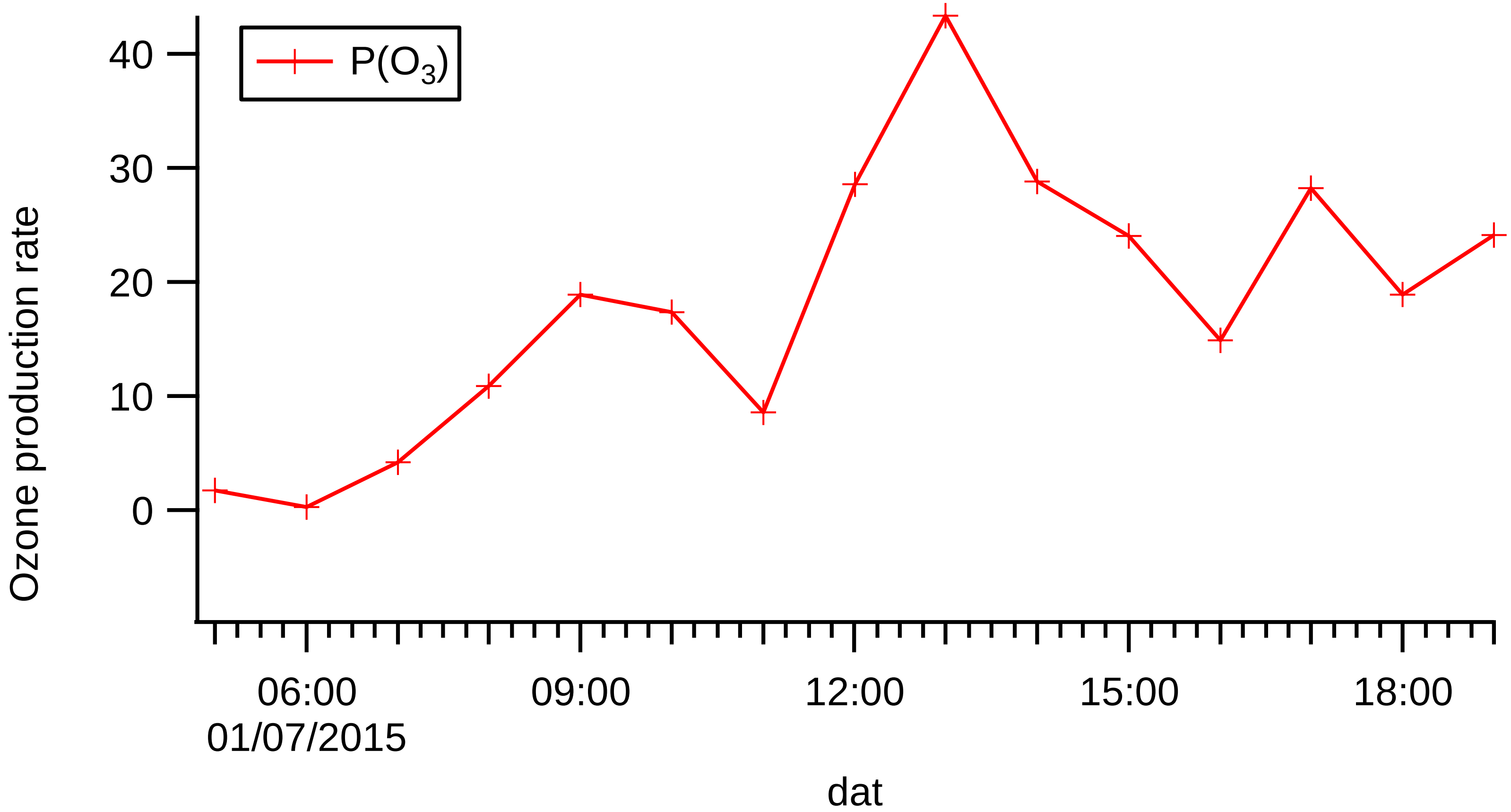
NOAA HYSPLIT MODEL
Backward trajectory ending at 1400 UTC 01 Jul 15
GDAS Meteorological Data

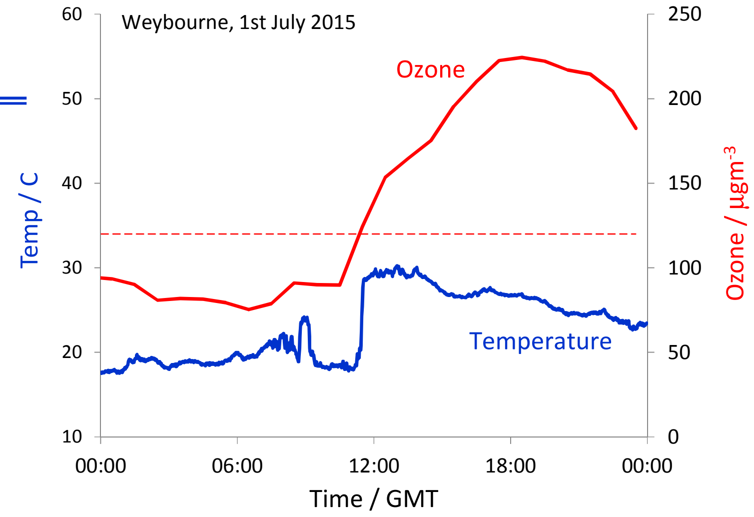


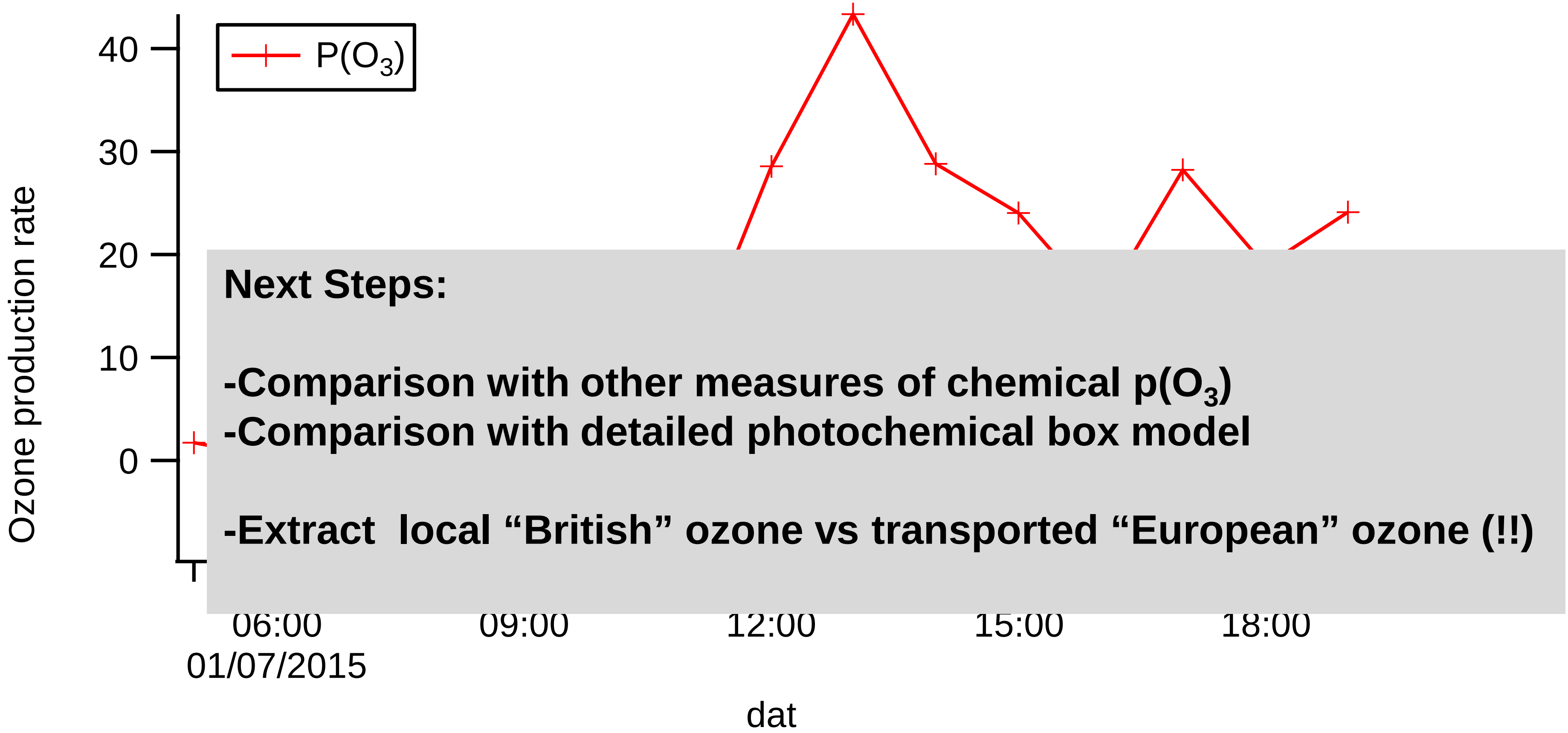
Local Chemical O_3 Production





Local Chemical O_3 Production





Next Steps:

-Comparison with other measures of chemical p(O_3)
-Comparison with detailed photochemical box model

-Extract local “British” ozone vs transported “European” ozone (!!)

Conclusions

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- **Ozone Trends: Recent UK experience**

    Rising (regional) background levels

    Falling frequency and intensity of severe ozone episodes

    Increasing primary NO_2 emission

Key questions for effective Air Quality policy :

1 How can we identify which VOCs are the most important ?

Model tools: POCP as an option to assess impact of local emissions superimposed upon trans-boundary input

2 What do we do about "new" VOCs ?

Use of simulation chambers to develop and test chemical mechanisms

3 Separating transport vs processing of local precursors

New field measurements to assess local emissions vs transport

Other Science Uncertainties

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- **Role of other radical sources**

  "traditional" OH sources – well known

  HONO

  ClNO2

- **"Unmeasured" VOCs**

  >C_{10} alkanes (diesel vehicles)

  Biogenic benzenoids

- **Ozone and temperature: "Climate Penalty"**

- **Will real world emissions follow Euro (and national) policy ?**

Acknowledgements

Leigh Crilley, Louisa Kramer, Salim Alam, Juan Najera, Hao Huang (Birmingham)

Andrew Rickard (York)

Marie Camredon (Paris-Est), EUPHORE Team

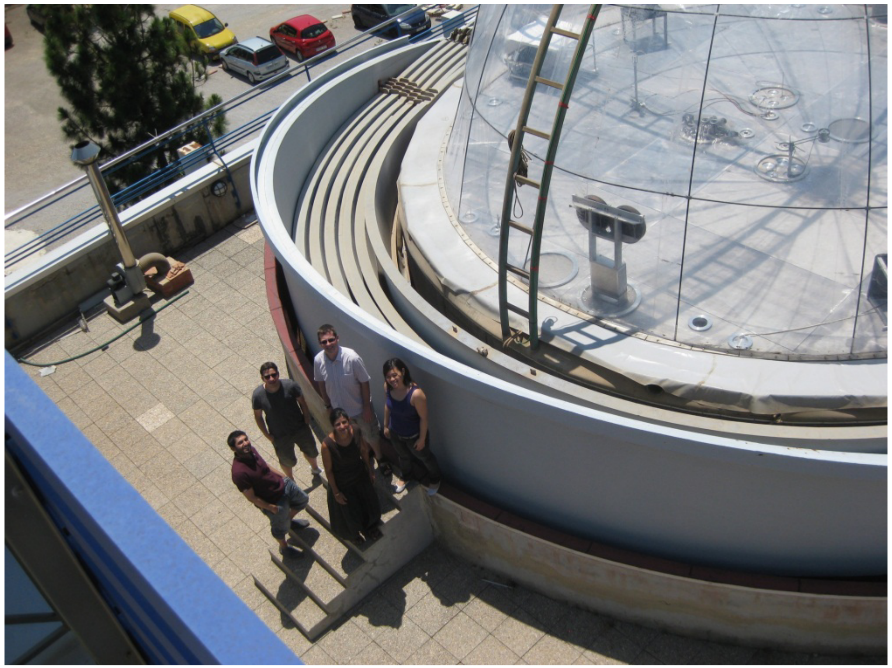
Funding:

UK NERC,

NCAS,

EU FP7

EUROCHAMP-2



Latest Mace Head O_3 trends...

- Derwent et al., Atmos Env 2013

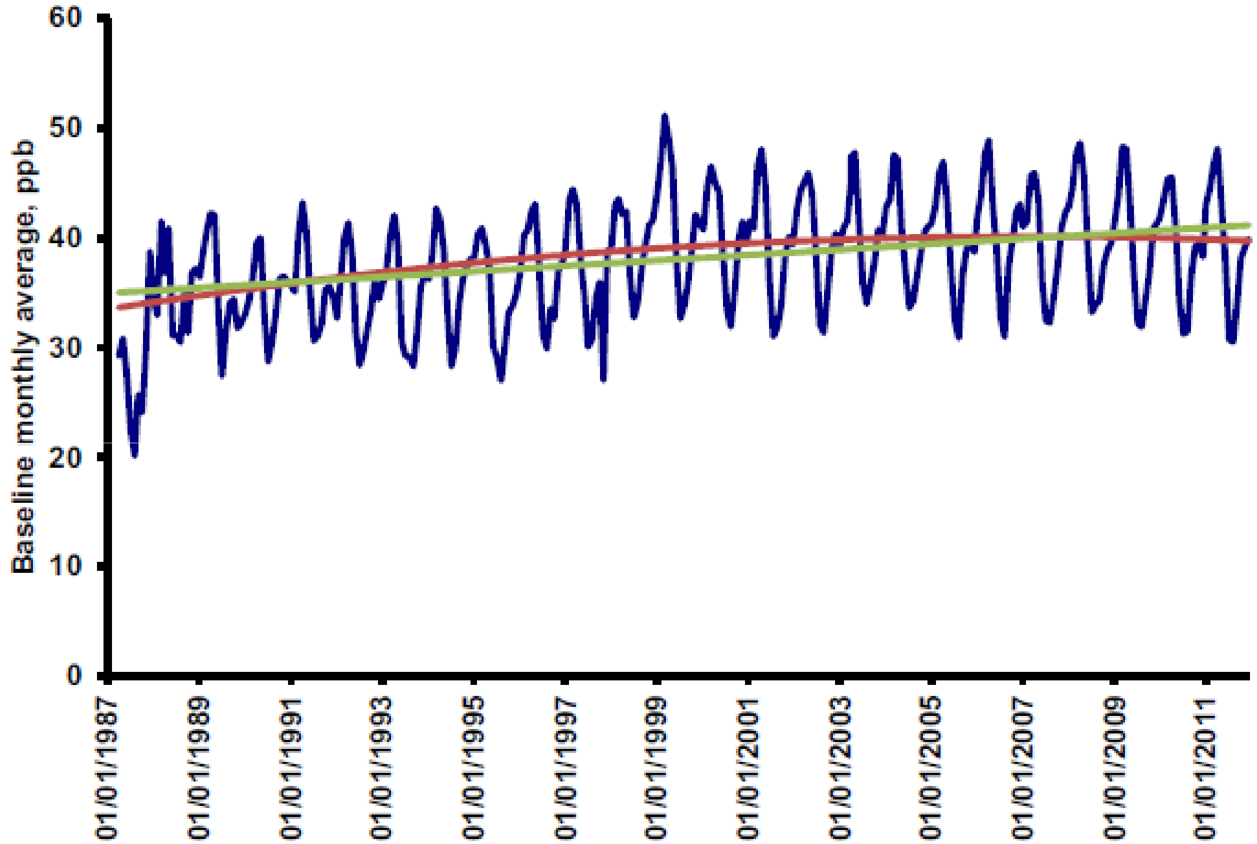
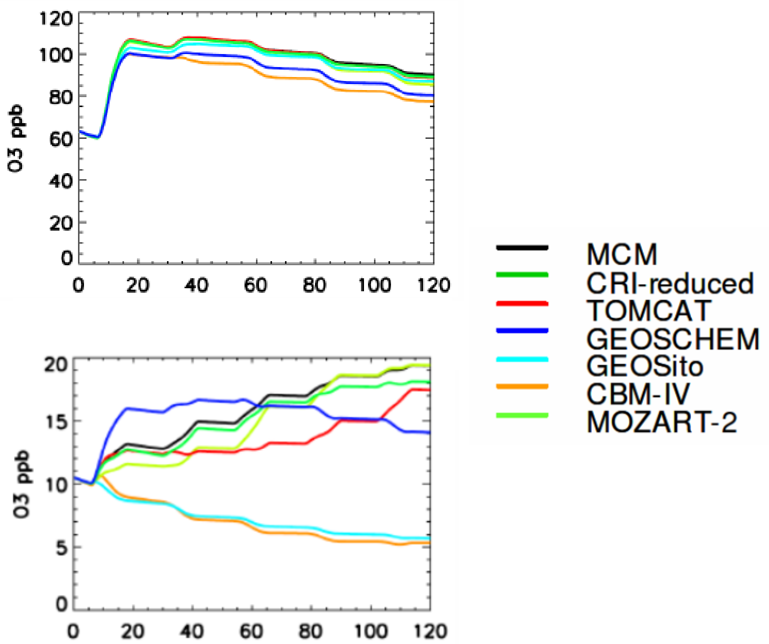


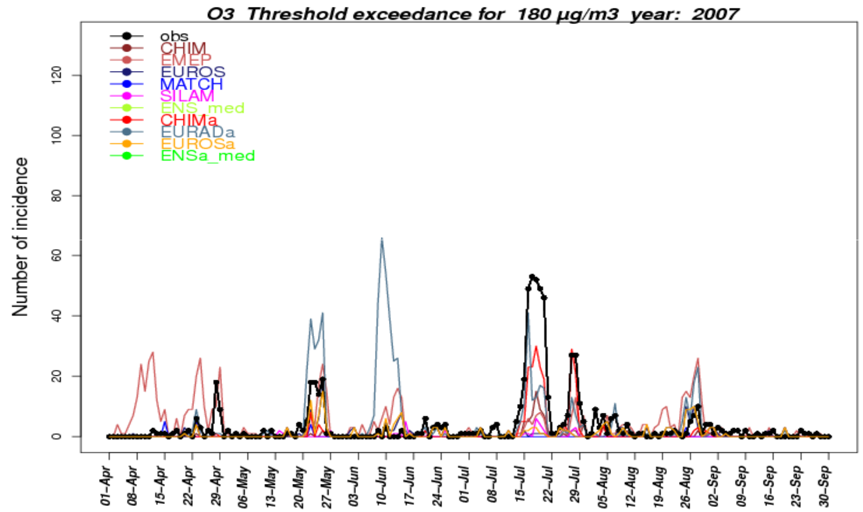
Fig. 2. Baseline monthly average O_3 mixing ratios at the Mace Head Atmospheric Research Station over the period from April 1987 to December 2012, shown as a blue line, with a linear fit to the annual average mixing ratios shown as green line and a quadratic fit shown as a red line. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Model performance

- Major uncertainties shown by model-model and model-observation comparisons



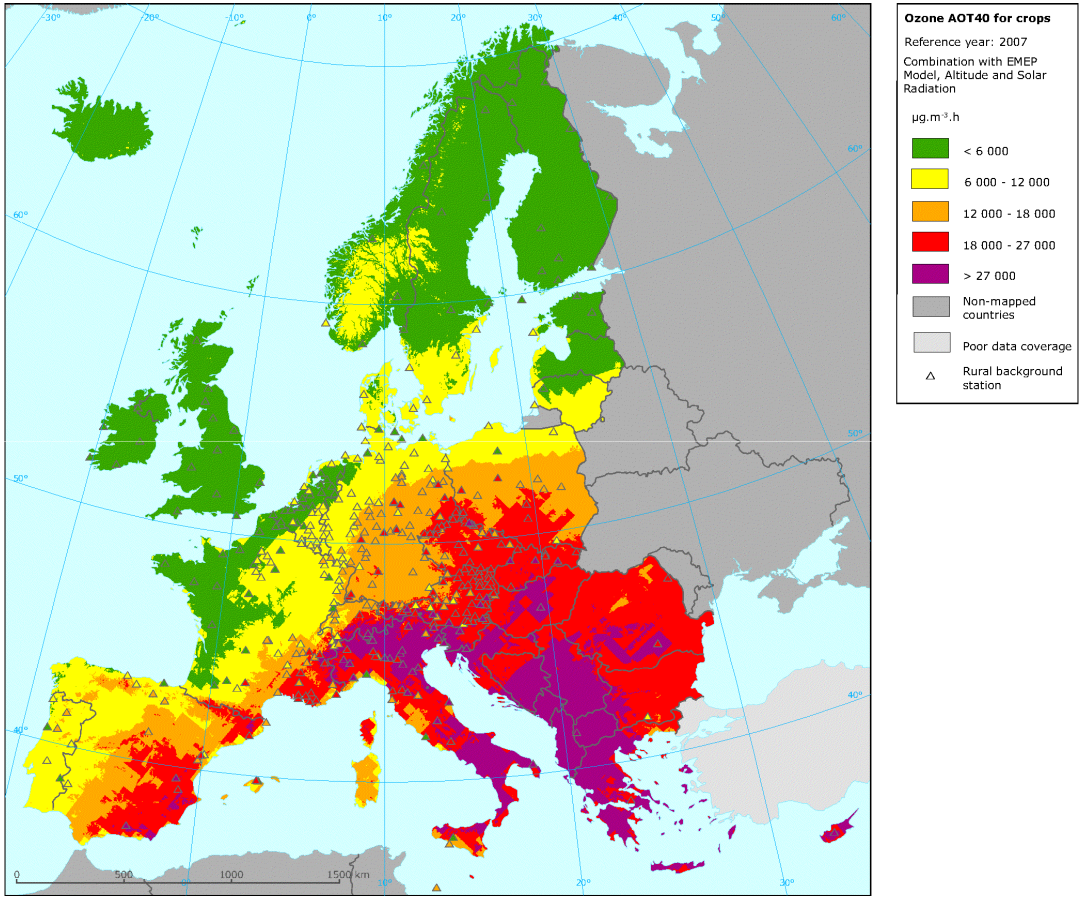
Effect of model chemical schemes upon predicted $[O_3]$ (Emmerson & Evans, 2009)

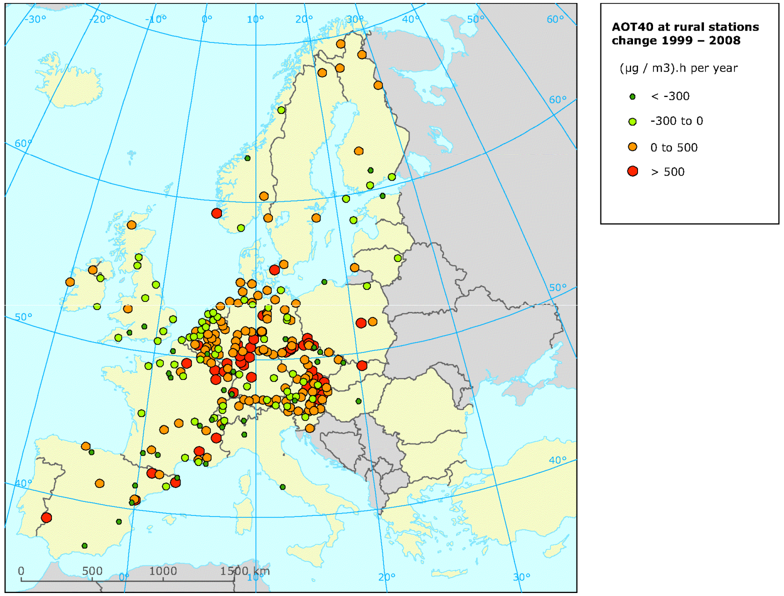


MACC European surface ozone exceedances – 2007 observations (black) vs. all (regional) models (colours)

European AOT-40 cumulative ozone exposure

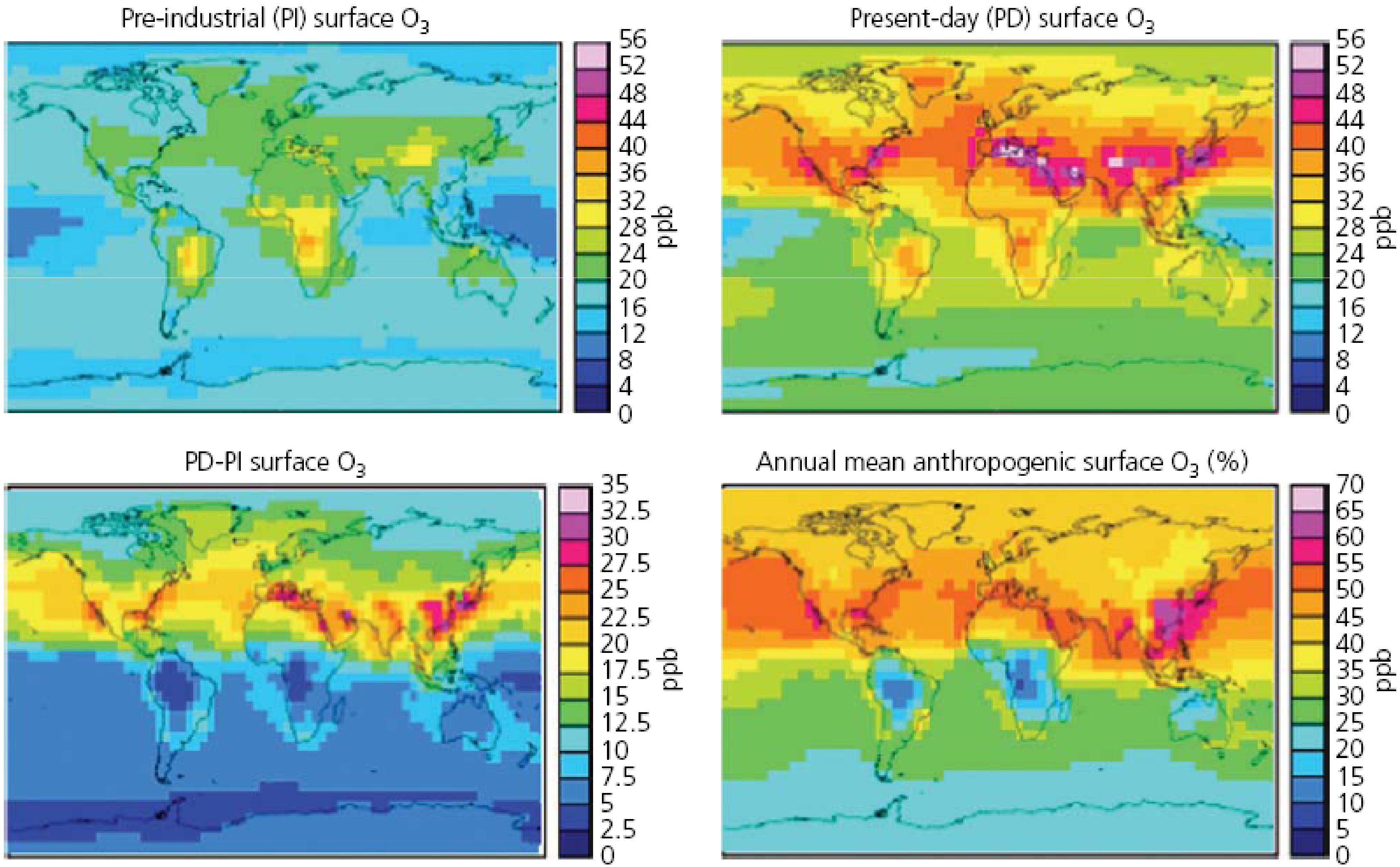
- Crop yield losses across EU = € 6.7 bn yr^{-1} (Holland *et al*., CEH, 2006)





Man-made Ozone

Figure 1.1 Modelled global changes in surface O_3 concentrations between pre-industrial times and the present day. Multi-model mean surface layer annual mean O_3 (ppb) is presented for pre-industrial (PI) times in the top left, and for the present day (PD) in the top right. The modelled increase in O_3 (PD–PI) is presented in the lower left figure and the percentage of annual mean O_3 attributable to anthropogenic sources in the lower right.



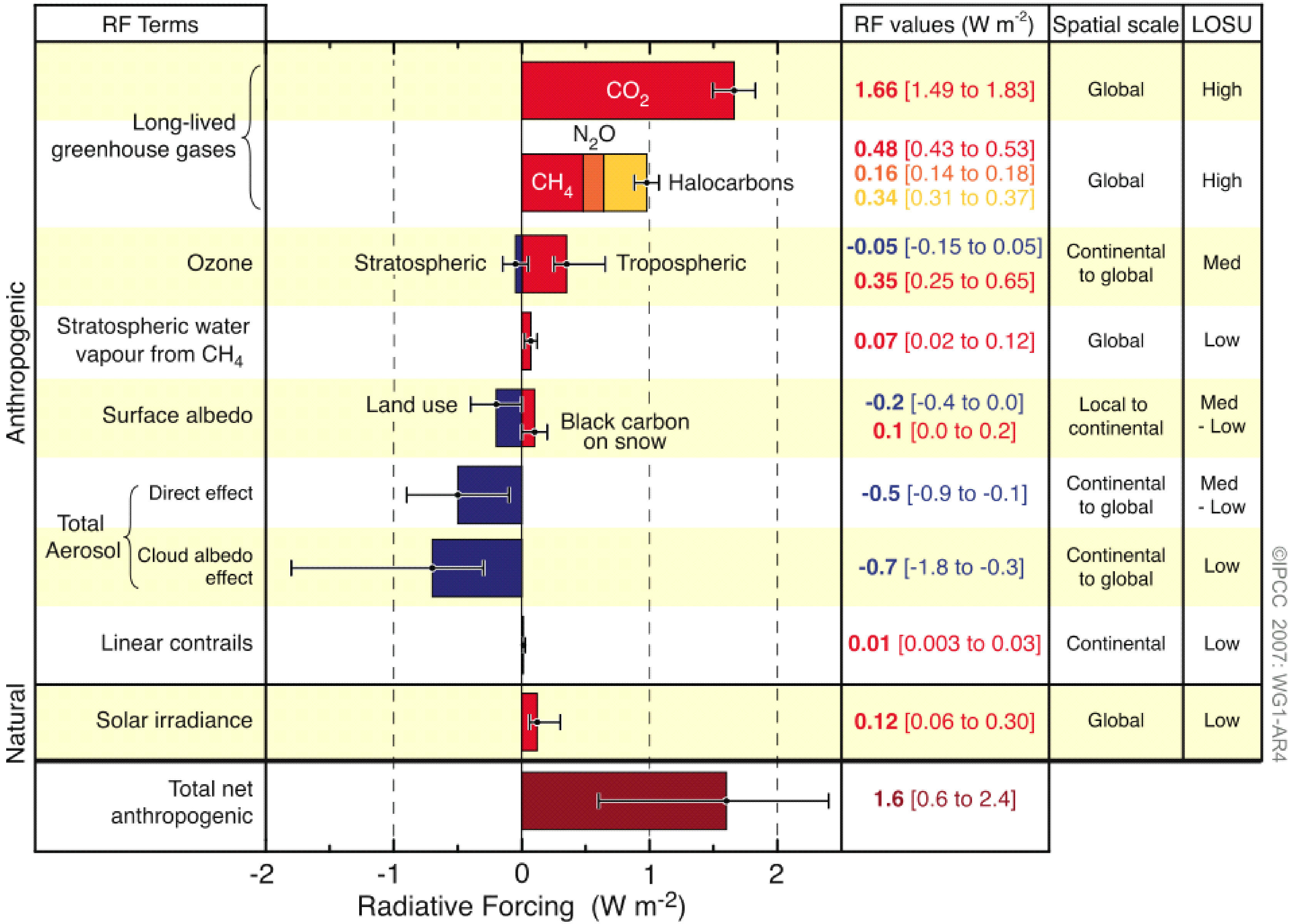
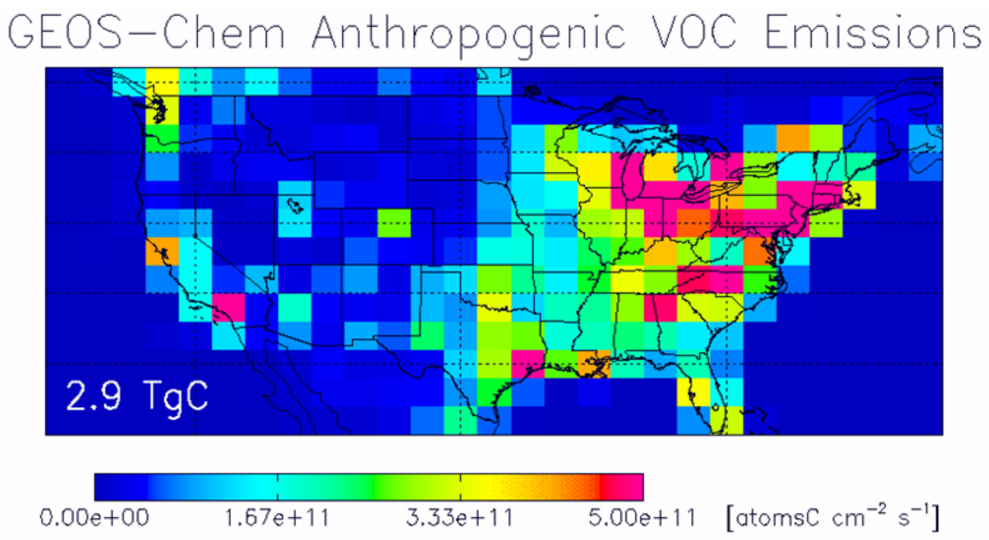
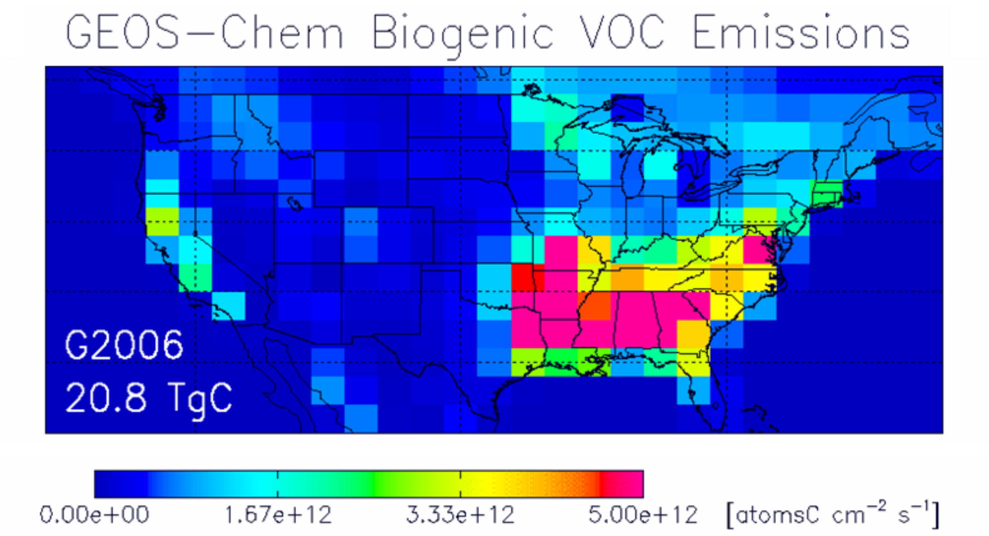

RF Terms
RF values (W m-2)
Spatial scale
LOSU
Long-lived greenhouse gases
CO2
1.66 [1.49 to 1.83]
Global
High
N2O
CH4
Halocarbons
0.48 [0.43 to 0.53]
0.16 [0.14 to 0.18]
0.34 [0.31 to 0.37]
Global
High
Ozone
Stratospheric
Tropospheric
-0.05 [-0.15 to 0.05]
0.35 [0.25 to 0.65]
Continental to global
Med
Stratospheric water vapour from CH4
0.07 [0.02 to 0.12]
Global
Low
Surface albedo
Land use
Black carbon on snow
-0.2 [-0.4 to 0.0]
0.1 [0.0 to 0.2]
Local to continental
Med - Low
Total Aerosol
Direct effect
-0.5 [-0.9 to -0.1]
Continental to global
Med - Low
Cloud albedo effect
-0.7 [-1.8 to -0.3]
Continental to global
Low
Linear contrails
0.01 [0.003 to 0.03]
Continental
Low
Solar irradiance
0.12 [0.06 to 0.30]
Global
Low
Total net anthropogenic
1.6 [0.6 to 2.4]
Anthropogenic
Natural
-2
-1
0
1
2
Radiative Forcing (W m-2)
©IPCC 2007: WG1-AR4

Figure SPM.2

Sources of Alkenes

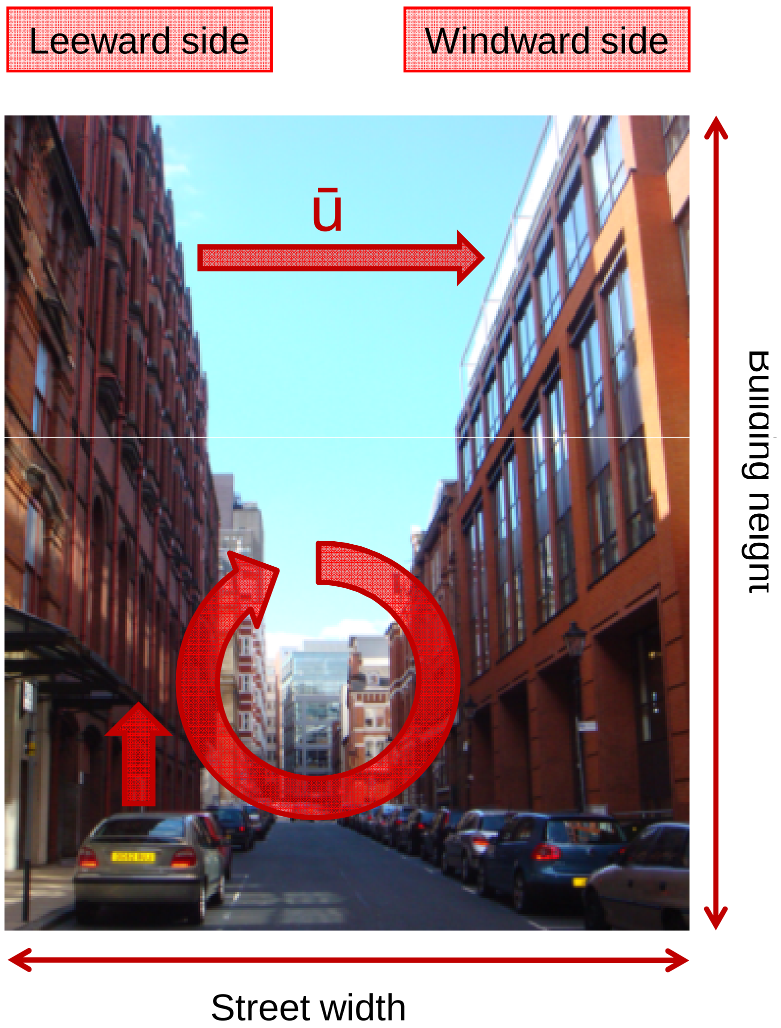
- Biogenic vs anthropogenic VOC emissions; future temperature response

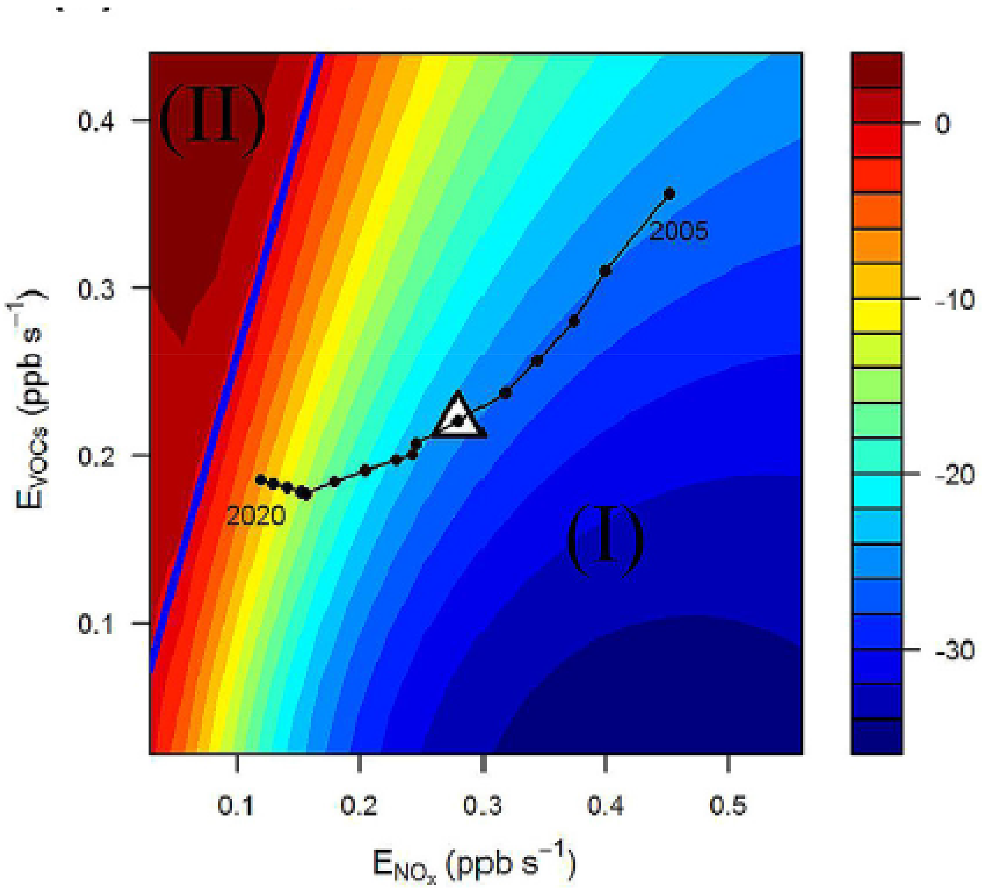




Millet et al (2007)

“Street Canyon” chemistry





Error in modelled $[O_3]$ using a single-box treatment

Increasing Primary NO_2 emissions

- Increasing primary NO_2 emissions
  - -Increased diesel useage
  - -Effects of some emissions controls (DPF) (?)

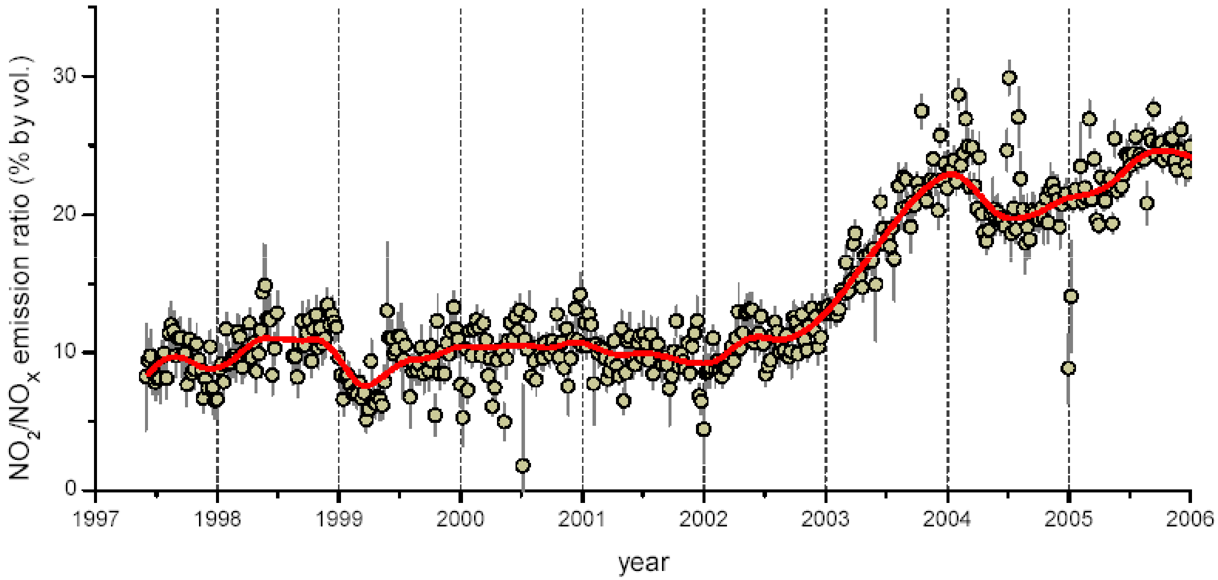


Figure 3.15: Estimated weekly NO_2/NO_X emission ratio (f-NO_2) at Marylebone Road derived using the method of Carslaw and Beevers (2005). Error bars are shown at 2σ.

From: Trends in Primary Nitrogen Dioxide in the UK, AQEG, 2007

- Will lead to increased urban NO_2, increased urban and regional O_3, increased nitrate aerosol

Ozone Production in the Atmosphere

- Chemical ozone production displays a complex dependence upon prevailing composition, NO_x and VOC abundance

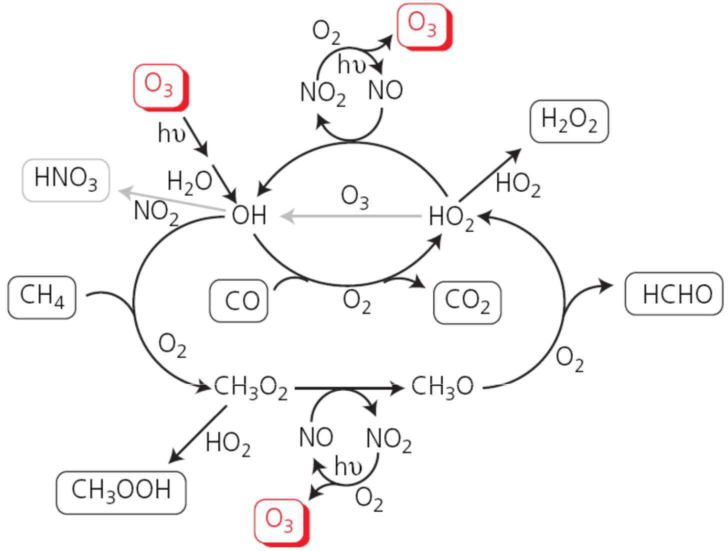


Figure from Fowler et al. (2008)

Challenges in predicting ozone production (and developing mitigation strategies) :

- Emissions inventories
- Composition measurements
- Chemical processes

Inherent limitations to "bottom up" approach to date $\Rightarrow$ solution: integrated approach…