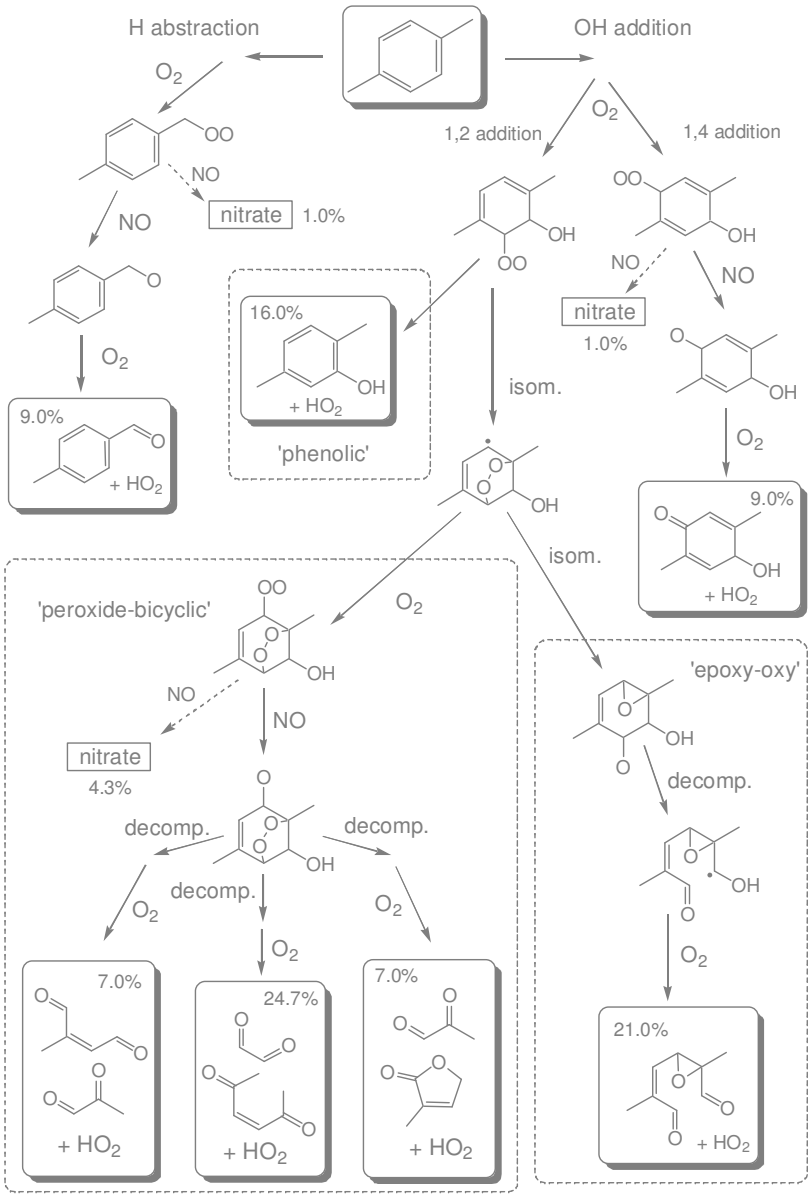


# Comparison of Photochemical Mechanisms used in Mesoscale Models


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# Scope of Presentation

- Introduction and Background
- VOC Speciation
- Photolysis Rates
- Comparison of Mechanisms
- Improvements to Mechanisms


# Acknowledgements

- EMEP
- David Simpson and Robert Bergström
- Mike Jenkin
- Dick Derwent
- Neil Passant and Tim Murrells

# Project Background and Objectives

- *EMEP unified model widely used for air pollution policy development in UN ECE and EU*
- *EMEP unified model available to the community*
- *Single photochemical mechanism currently used in the EMEP unified model*
- *Opportunity to update the chemistry in the model*
- *Project Objectives*
  - *to implement a number of other mechanisms into the EMEP unified model*
  - *to compare the performance of the different photochemical mechanisms*
  - *to submit a paper on the comparison*

# Related activities

- Ozone in the UK (AQEG, 2009)☑
  - *Many of the photochemical mechanisms currently used in ozone policy models have not been compared to environmental chamber data*
- Defra Review of Ozone Modelling (2007) – Recommendations on Chemical Mechansims:
  - *to support models which use chemical schemes, tested for ozone, such as the MCM or CBM-IV (R2.1)☑*
  - *to explore the use of surrogate schemes which have a firm basis in explicit chemistry such as CRI and which have been tested by comparison with experimental data (R2.1)☑*
  - *to use models with chemical schemes that allow robust coupling between the speciation in the emission inventories and the chemical scheme (R2.2)☑*

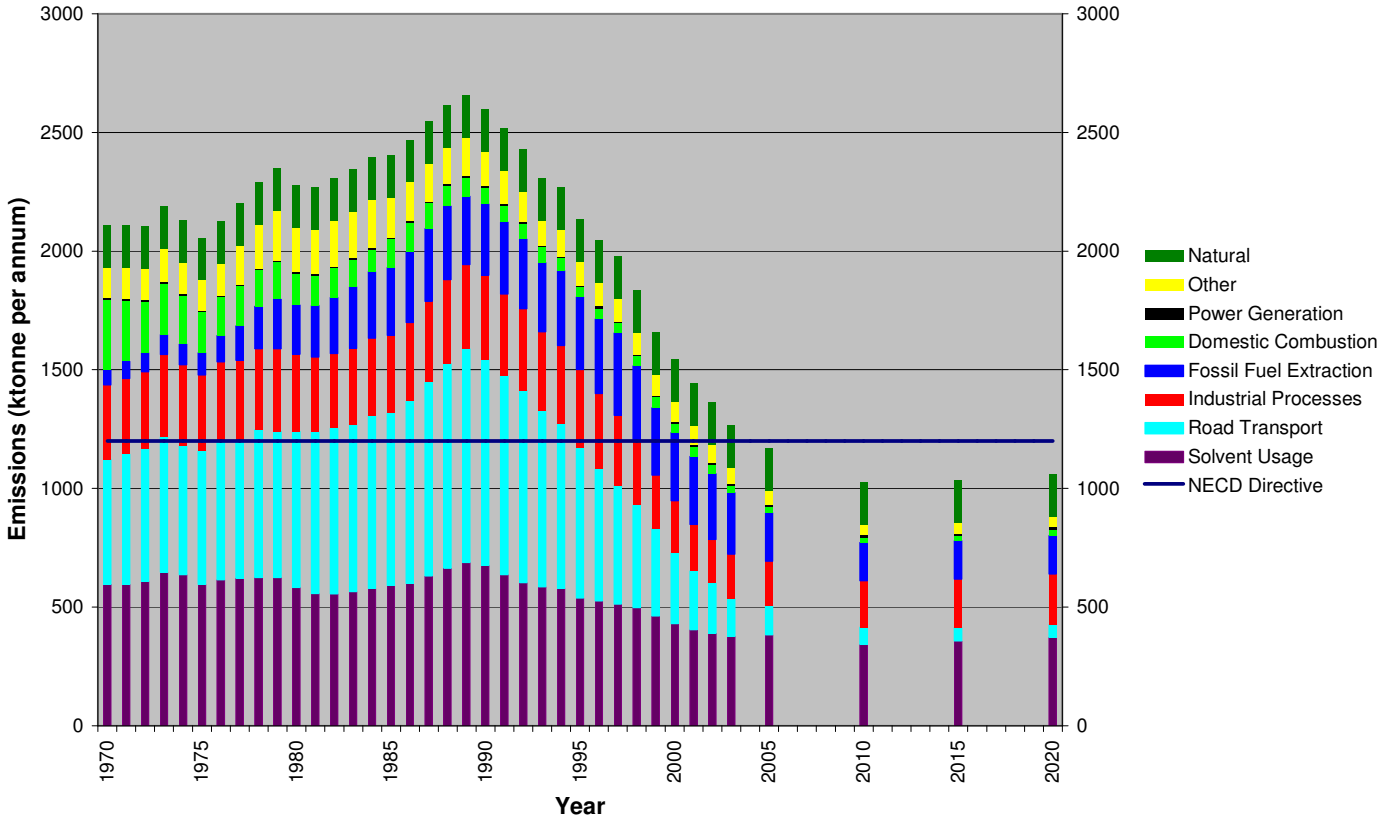
# Photochemical Mechanisms

- Some of the photochemical mechanisms currently used in mesoscale chemical-transport models

| | Total VOC | Biogenic VOC | Chamber |
|---|---|---|---|
| CBM-IV | 10* | 1 | ✓ |
| CB05 | 16* | 2 | ✓ |
| EMEP | 10 | 1 | |
| CHIMERE-MELCHIOR | 13 | 1 | |
| OSRM | 15 | 1 | |
| SAPRC | - | - | ✓ |
| CRI v2.0 | 116 | 3 | ✓ |
| MCM v3.1 | 135 | 3 | ✓ |

(*) including non-reactive

# VOC Speciation

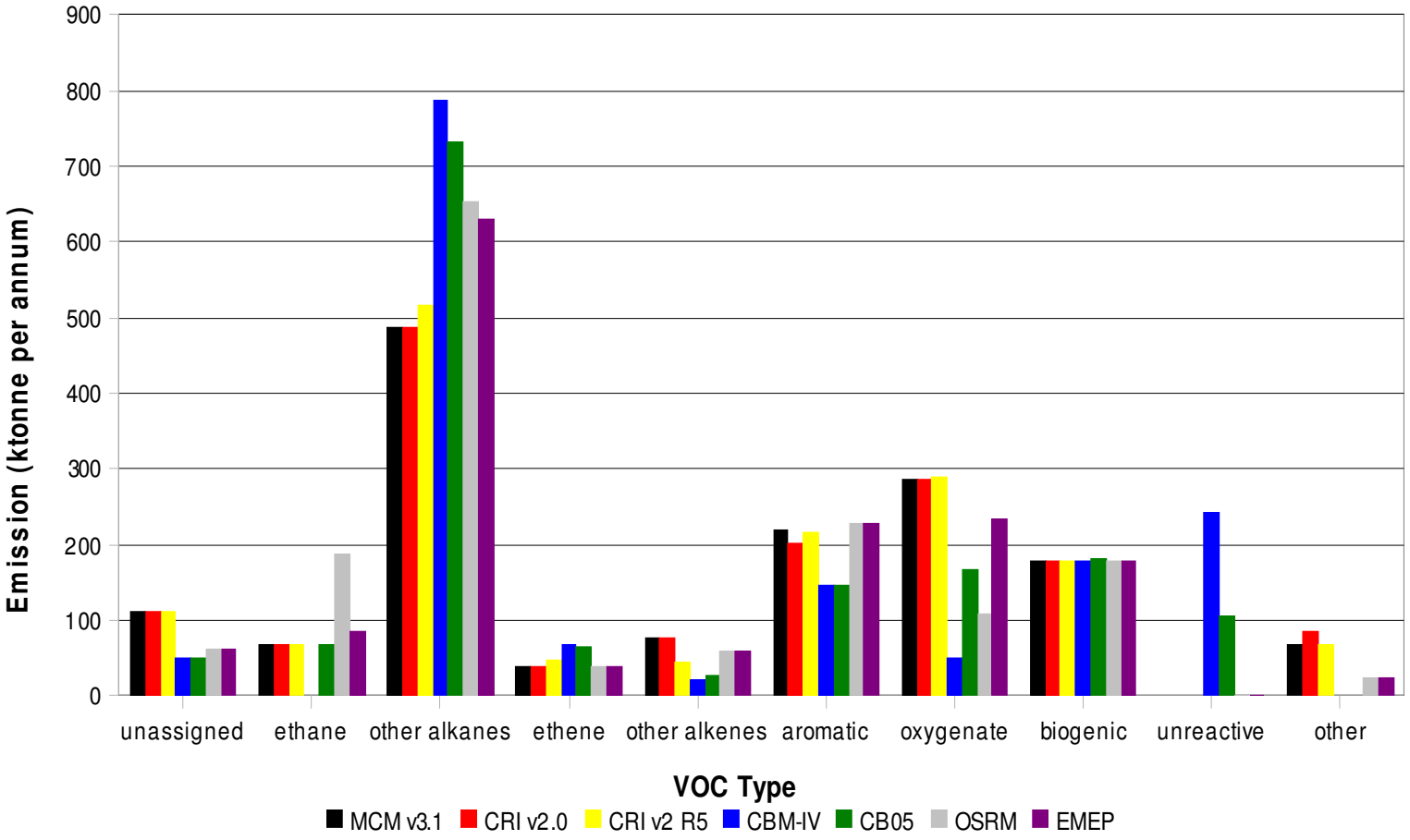



- UK inventory (2002) contained emissions of 664 VOCs from 249 source sectors

# VOC Speciation: Assignment

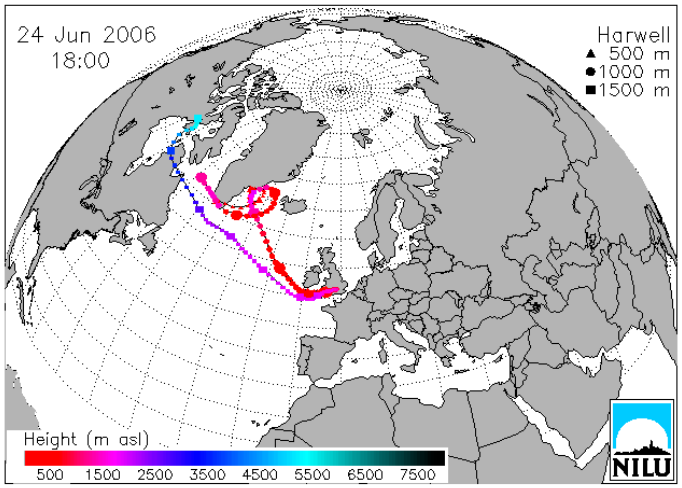
- *CRI/MCM/OSRM/EMEP*
  - *Straightforward for VOCs (and isomers) common to inventory and chemical mechanism (e.g., alkanes)☑*
  - *Other VOCs assigned on basis of structure and reactivity*
  - *Sulphur- and nitrogen-containing VOCs not assigned*
- *CBM and CB05*
  - *CBM-IV assignments from Harvey Jeffries (via Dick Derwent)☑*
  - *CB05 assignments from report by Yarwood et al*
  - *Extended to other VOCs in inventory*
  - *Sulphur- and nitrogen-containing VOCs assigned*

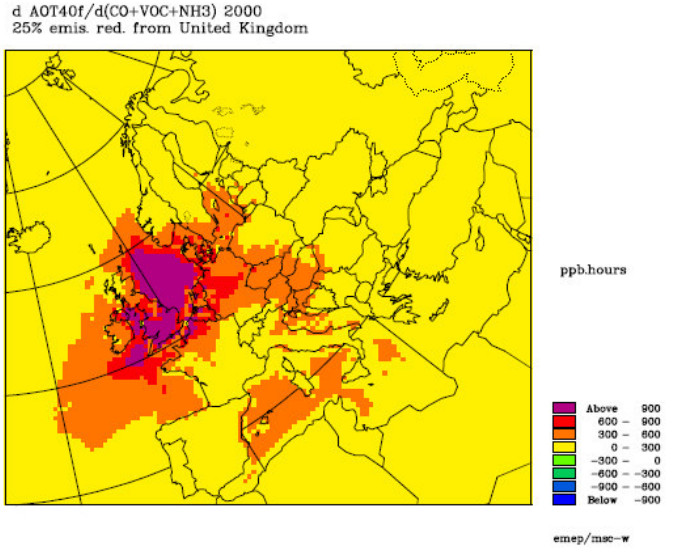
# VOC Speciation: Comparison



# Comparison of Mechanisms

- Boundary-layer trajectory model
  - Based on UK PTM and OSRM
  - Global coverage
  - ‘Multiple’ trajectories
  - Capability to use 8 chemical mechanisms and 3 solvers
  - PM chemistry
- EMEP Unified model
  - Mesoscale Eulerian-gird model
  - Open source code
  - Code modified to use a number of chemical mechanisms: CBM-IV, CB05, OSRM, CRI v2.0 and CRI v2 R5



# Chemical Mechanisms 1

- Model can use 8 different chemical mechanisms:

| | *Species* | *Reactions* |
|---|---|---|
| *CBM-IV* | *38* | *95 (13)☑* |
| *CB05* | *70* | *189 (27)☑* |
| *OSRM* | *70* | *197 (25)☑* |
| *EMEP* | *72* | *137 (26)☑* |
| *CRI v1* | *270* | *633 (93)☑* |
| *CRI v2* | *465* | *1202 (185)☑* |
| *CRI v2 R5* | *195* | *569 (96)☑* |
| *MCM v3.1* | *4644* | *13570 (2626)☑* |

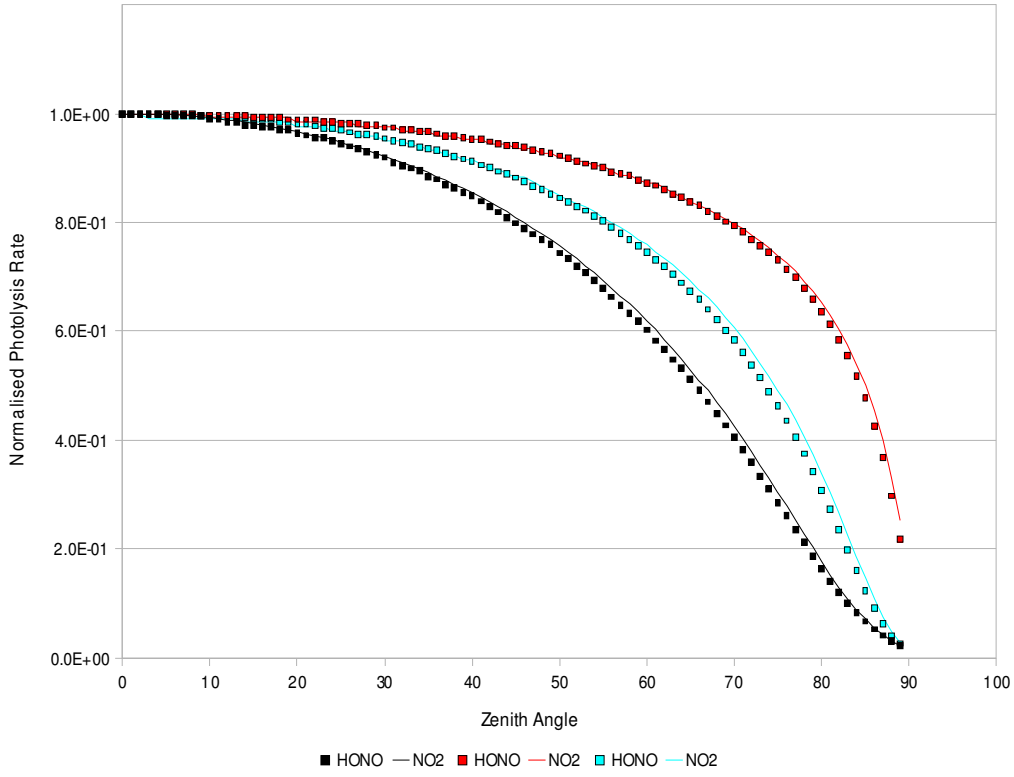
- Common source for VOC speciation

# Chemical Mechanisms 2

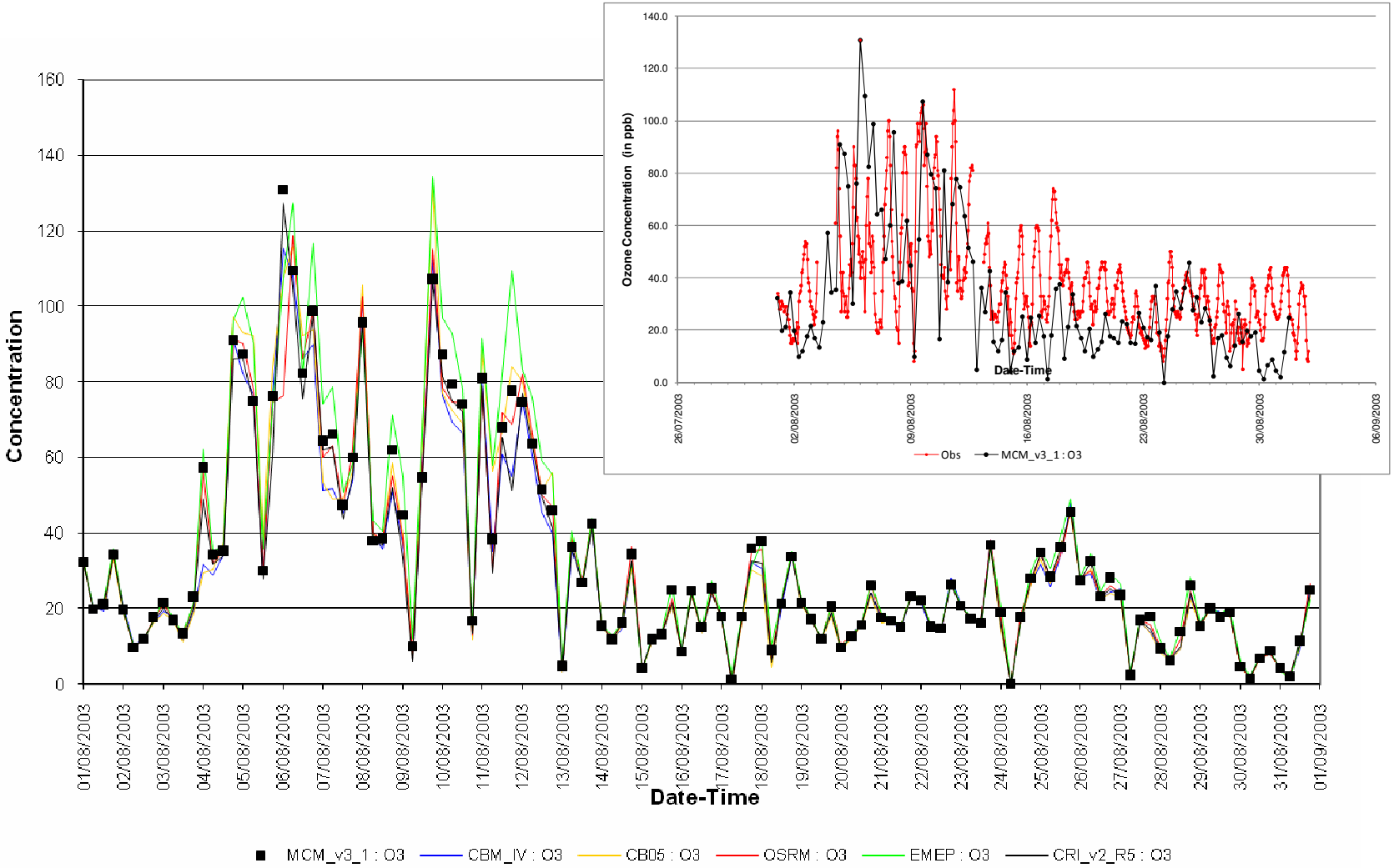
- Mechanisms use common set of parameters
  - *rate coefficients for the inorganic chemistry, 'generic' and 3rd-order reactions, as well as for many of the organic chemistry*
  - *photolysis rates*
  - *deposition velocities*
- Isoprene as common biogenic VOC
- Periods considered
  - *Trajectory model: August 2003, July 2005, June 2006*
  - *EMEP model: July 2005*

# Photolysis

- EMEP model has 17 photolysis processes
- Other chemical mechanisms have additional photolysis processes
- Identified process and provided scaling factors
- Example shown for HONO (using $NO_2$)

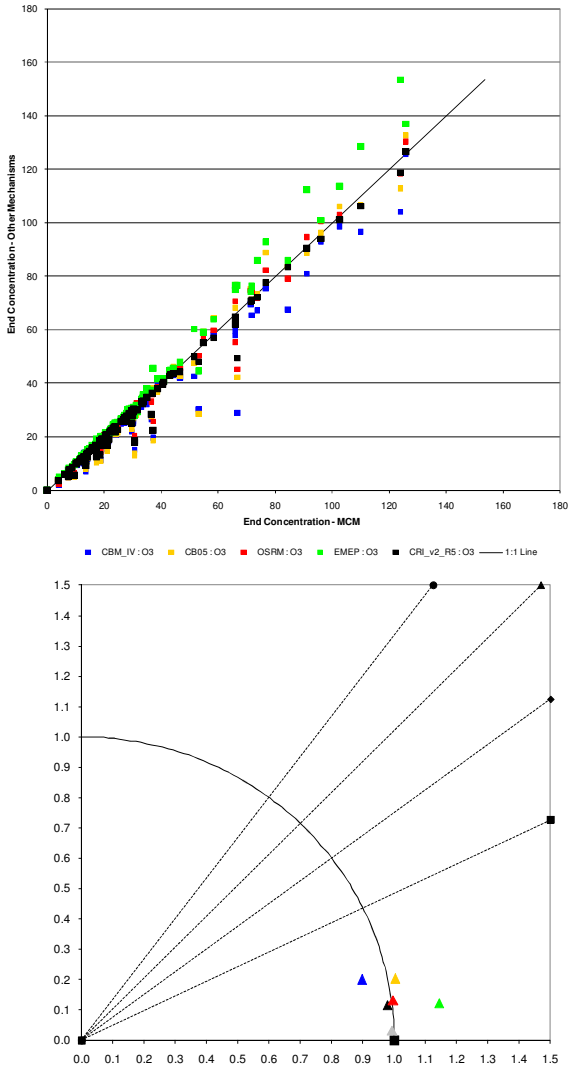


# Harwell, August 2003: Ozone

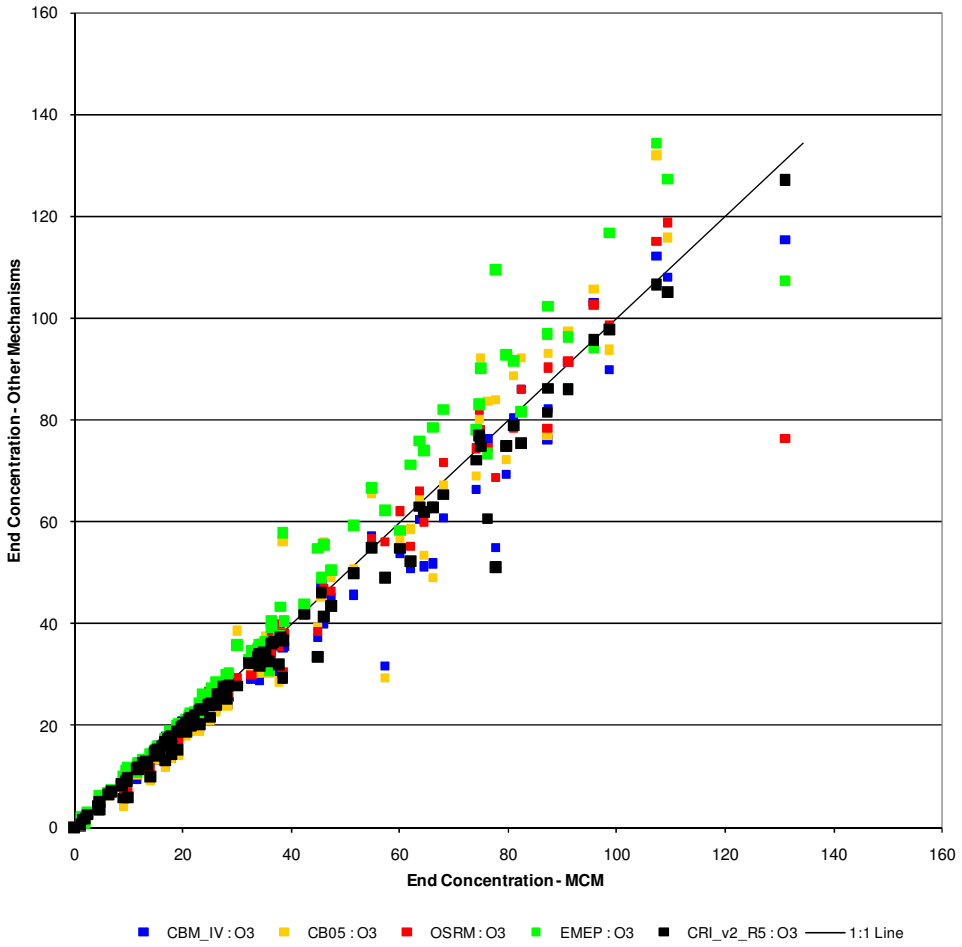


# Analysis

- MCM v3.1 taken as reference mechanism
- Various statistical parameters derived
  - *mean and fractional biases*
  - *linear regression*
  - *Taylor plots*
- Analysis automated and results derived for many of the species

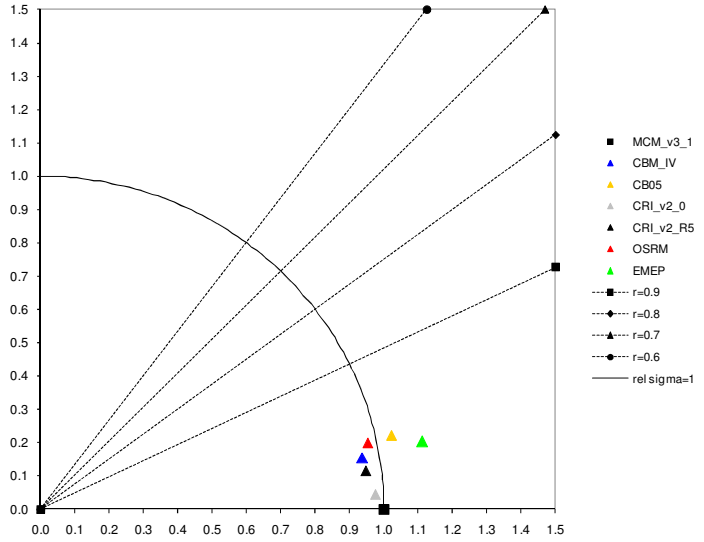


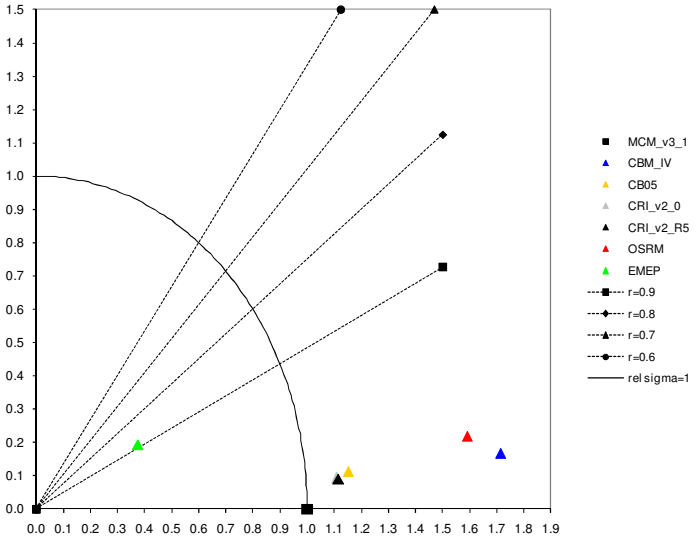
# Comparison with MCM v3.1

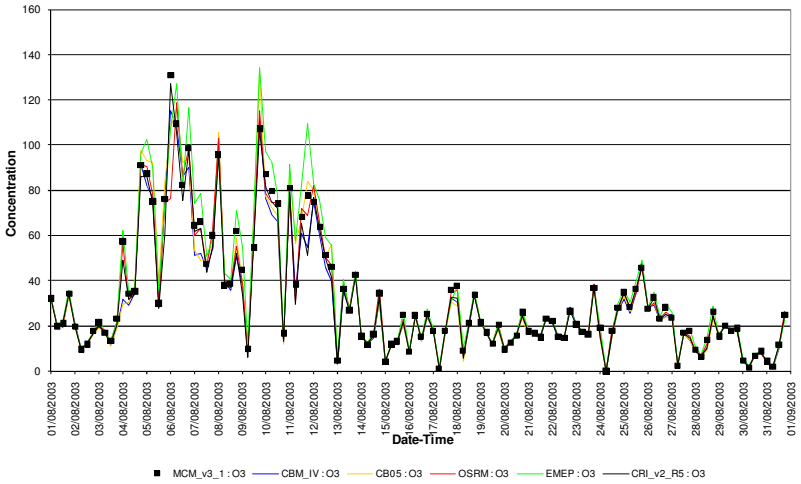


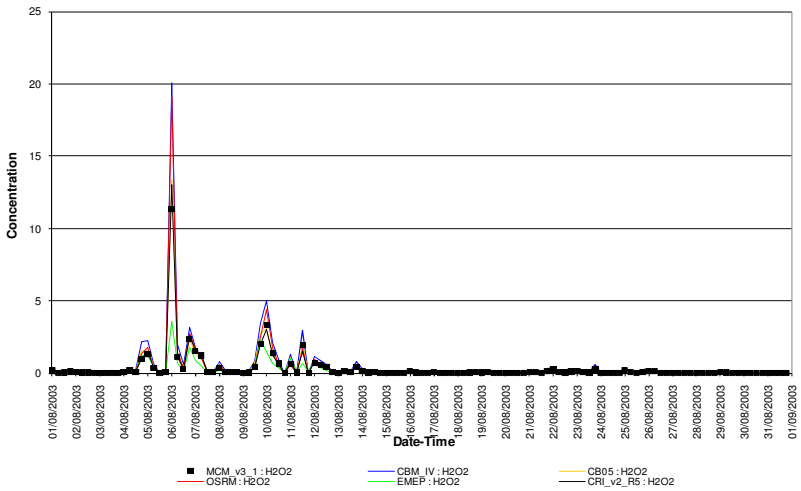

- All mechanisms give similar [$O_3$]
- CRI v2.0 developed by Mike Jenkin to replicate MCM
- CBM-IV slightly underpredicts compared to MCM
- CB05 now good agreement at low [$O_3$]
- EMEP overpredicts at higher [$O_3$]

# Taylor Plots: $O_3$ and $H_2O_2$

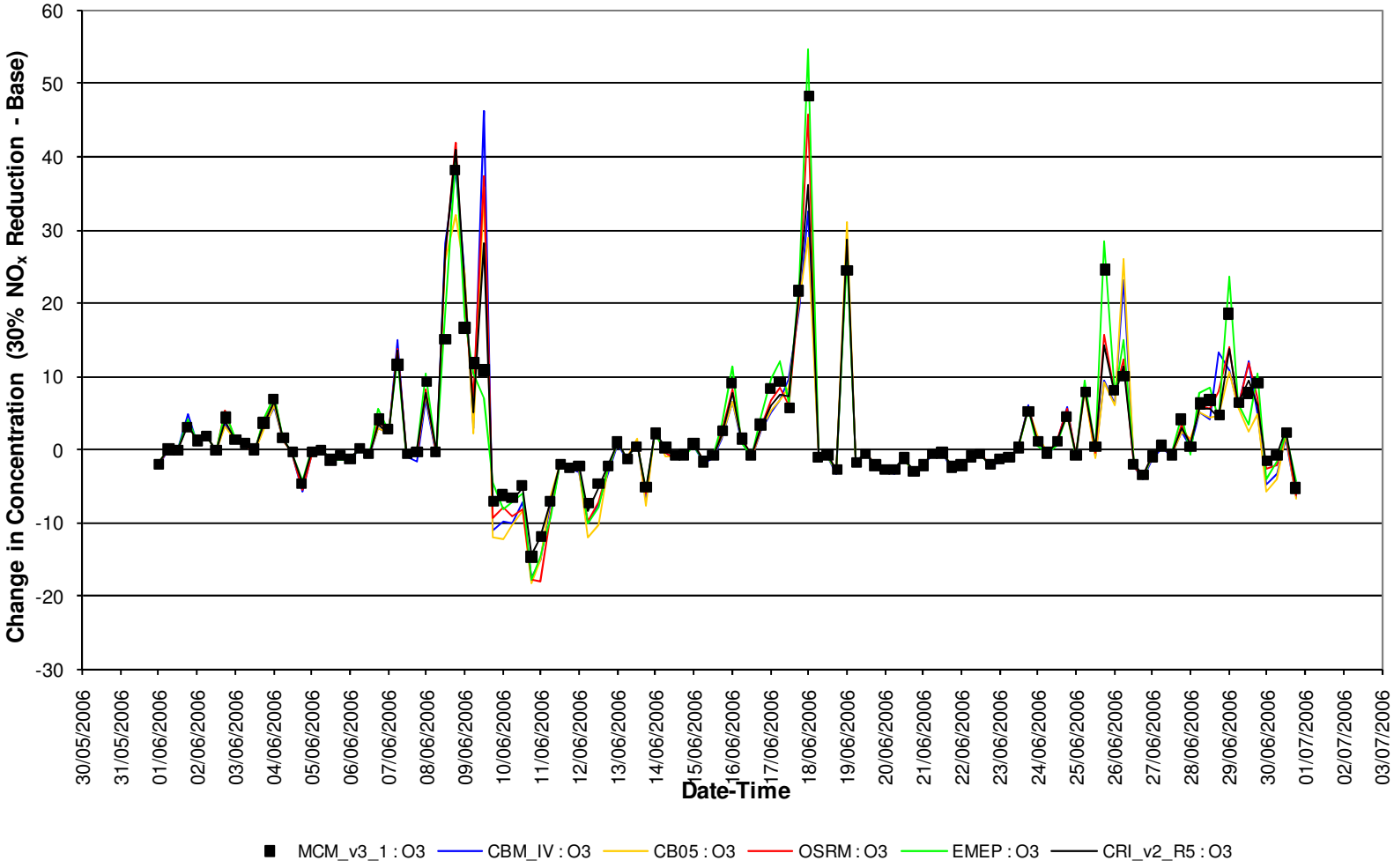


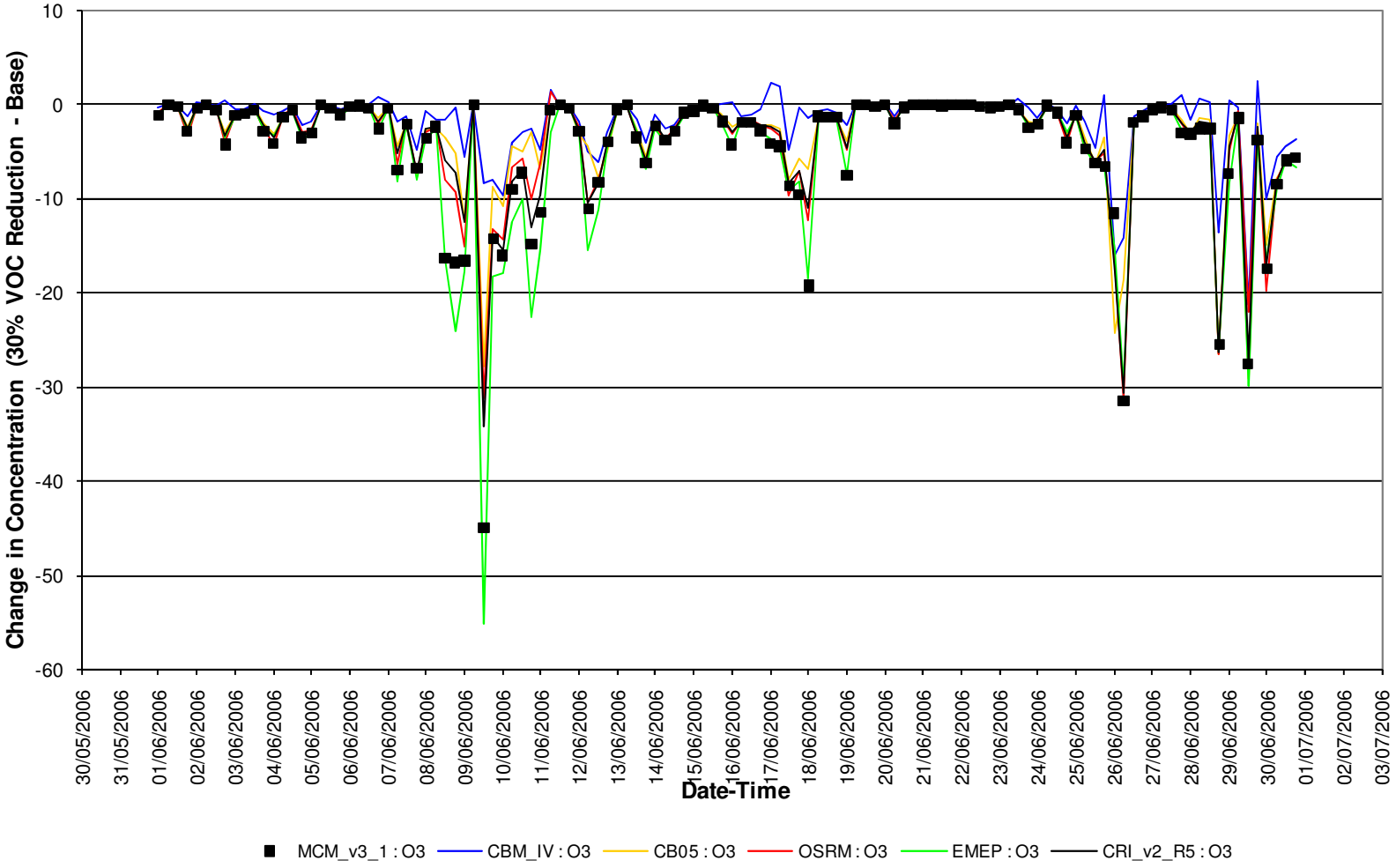



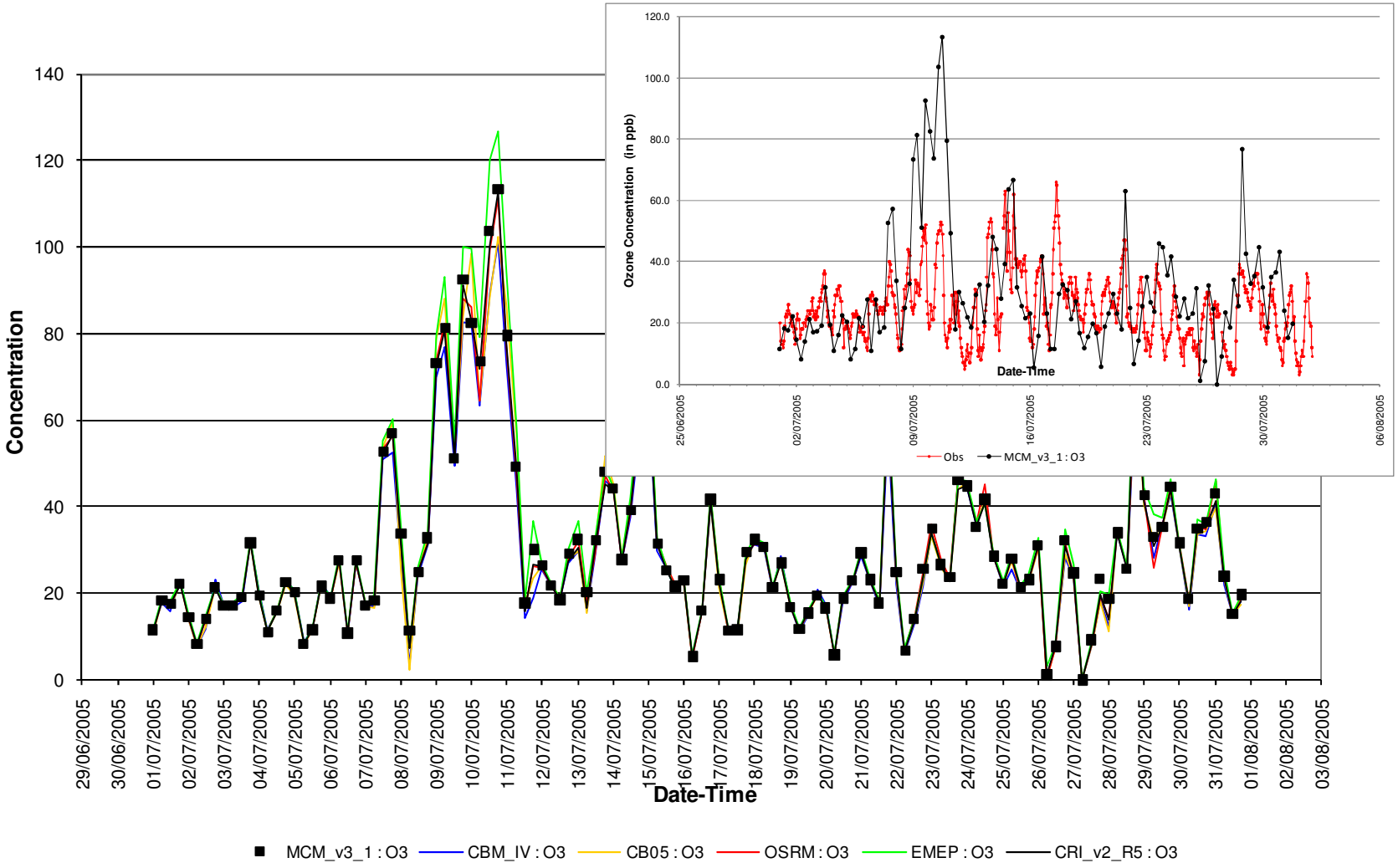
# 30% $NO_x$ Emission Reduction



# 30% VOC Emission Reduction

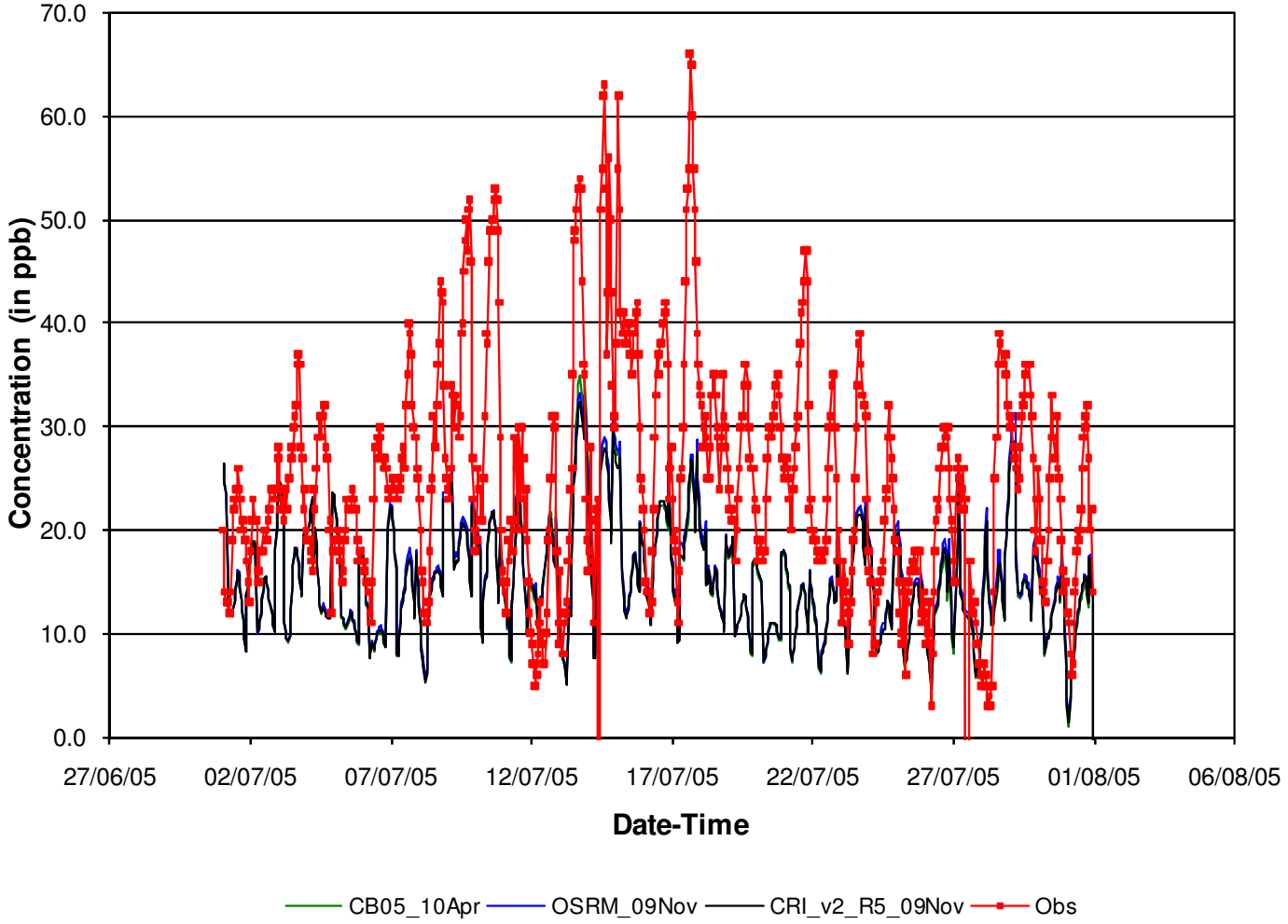


# Harwell, July 2005: Ozone



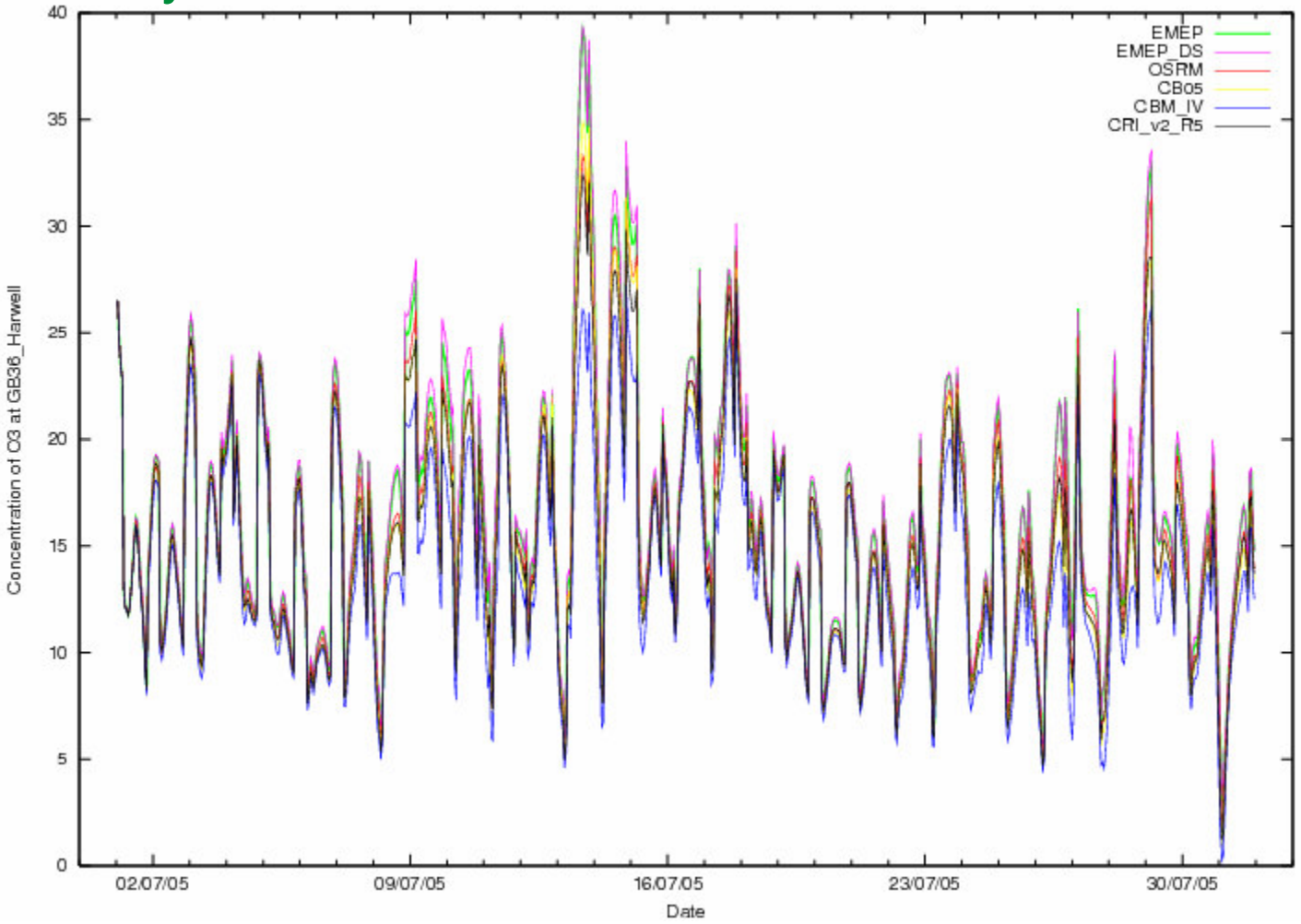
# EMEP Model: Harwell, July 2005, $O_3$

## Preliminary Results



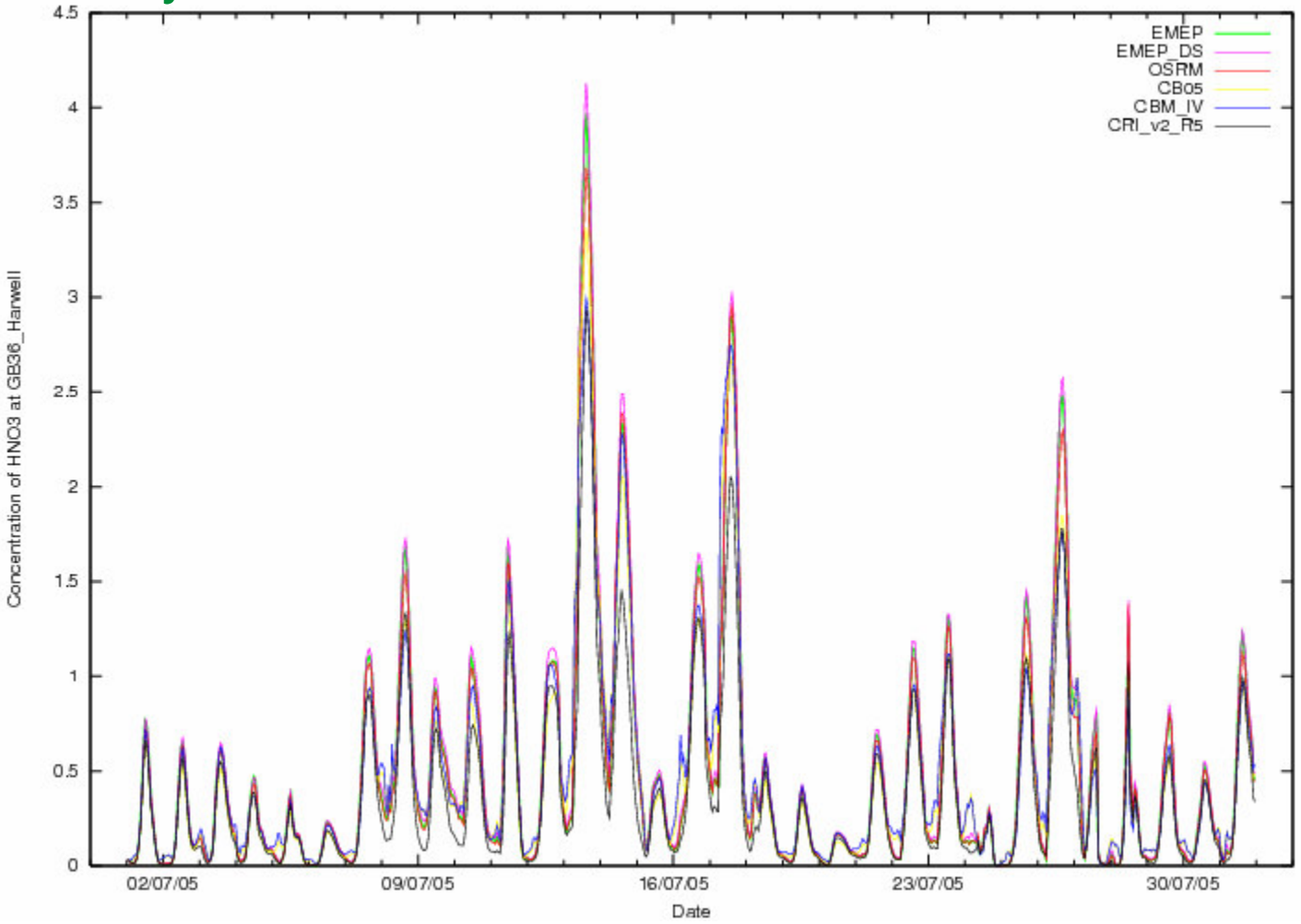
# EMEP Model: Harwell, July 2005, Ozone

## Preliminary Results



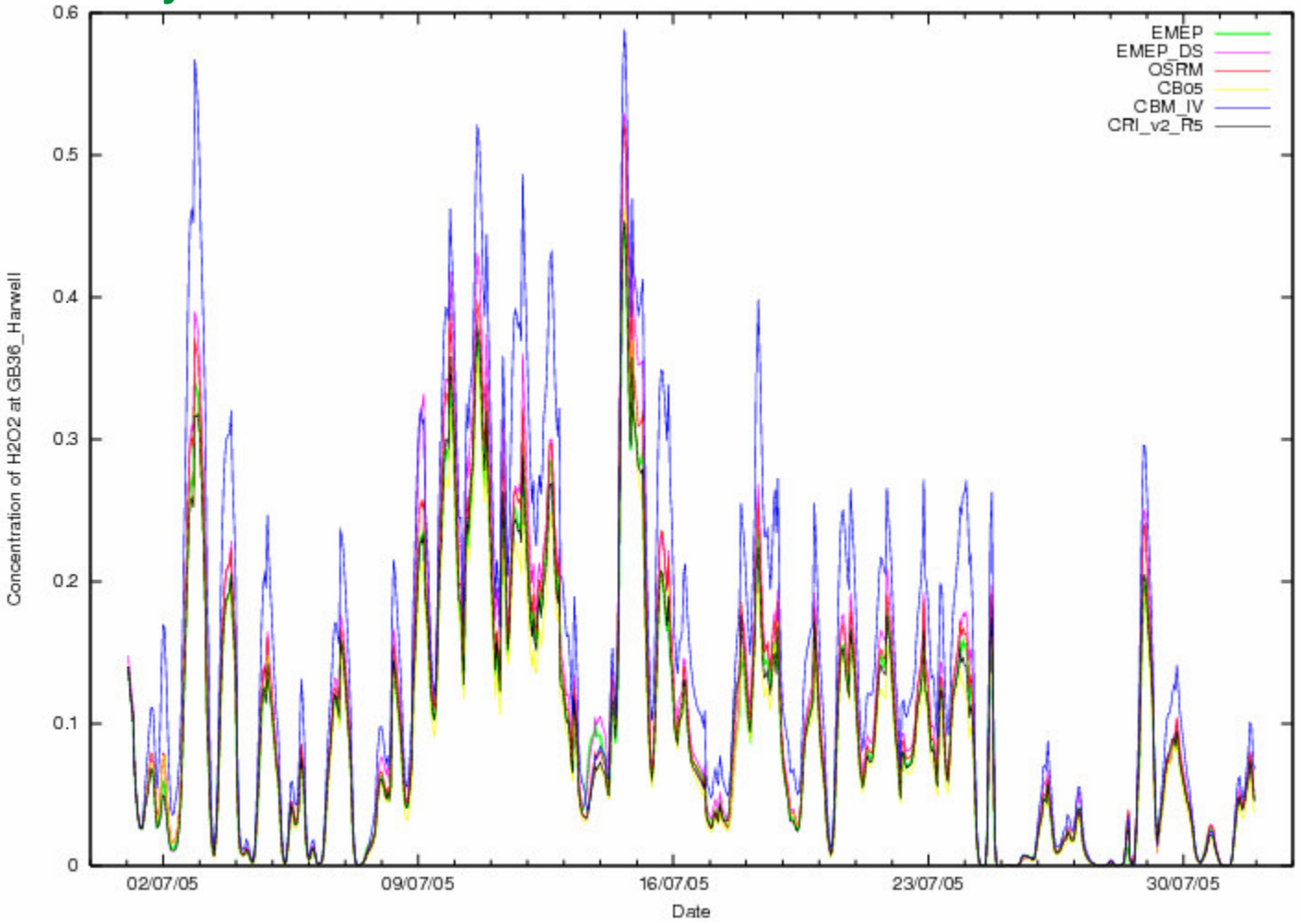
# EMEP Model: Harwell, July 2005, $HNO_3$

## Preliminary Results



# EMEP Model: Harwell, July 2005, $H_2O_2$

## Preliminary Results



# Related Activities

- CB06 under development - reactivity between CBM-IV and CB05
- CRI v2 (-R5) introduced into WRF/CMAQ (?)
- Mechanism intercomparison planned by Dick Derwent

# Summary

- Comparison of 7 Photochemical Mechanisms undertaken
- Generally give similar $O_3$ concentrations. Greater differences for other species, which has implications for PM
- Similar trends in reactivity in the two modelling systems
- CB05 and OSRM closest to MCM/CRI
- Further comparison in progress using EMEP unified model
- Paper in preparation