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BUNIAACIC meeting
Leeds FAGE LIF measurements

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Leeds FAGE LIF measurements – OH & HO_2

The role of OH and HO_2 in the troposphere

- OH reacts with virtually all trace gases, regulating their concentrations, and also their atmospheric lifetimes:

  CO, benzene (toxic), CH_4, HCFCs (greenhouse gases), hydrocarbons (smog), oxygenated VOCs (e.g. carbonyls) (secondary organic aerosols), SO_2, NO_2 (acid deposition) ….

- OH itself has an extremely short lifetime (<1 sec) and as such it's concentration is dependant solely on local chemistry rather than transport

So it is important to measure OH because:

- OH is an ideal target molecule. If a model can predict the concentration of OH successfully – then we have confidence that the chemistry is correct !

OH and HO_2 detection at Leeds

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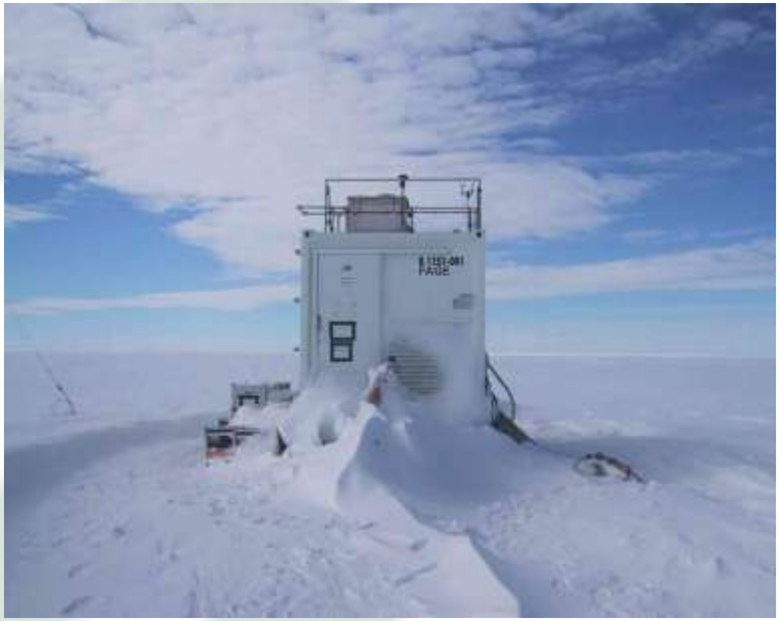
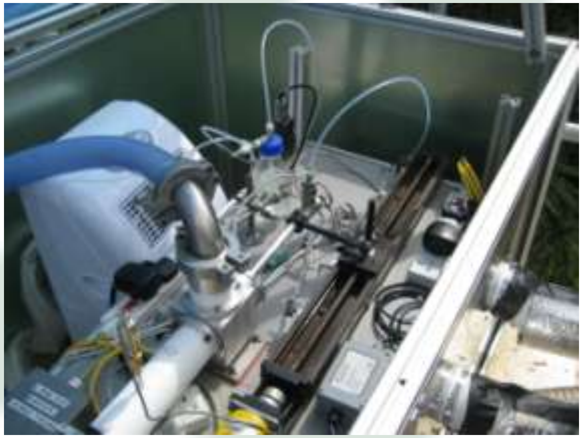


The Leeds FAGE instruments
For OH and HO_2

Leeds FAGE LIF measurements – OH reactivity

- OH reactivity is the rate of OH loss in ambient air - a direct measurement of the total OH sinks.
- Instruments that directly measure OH reactivity, k'_{OH}, have been developed during the last decade to improve constraints.

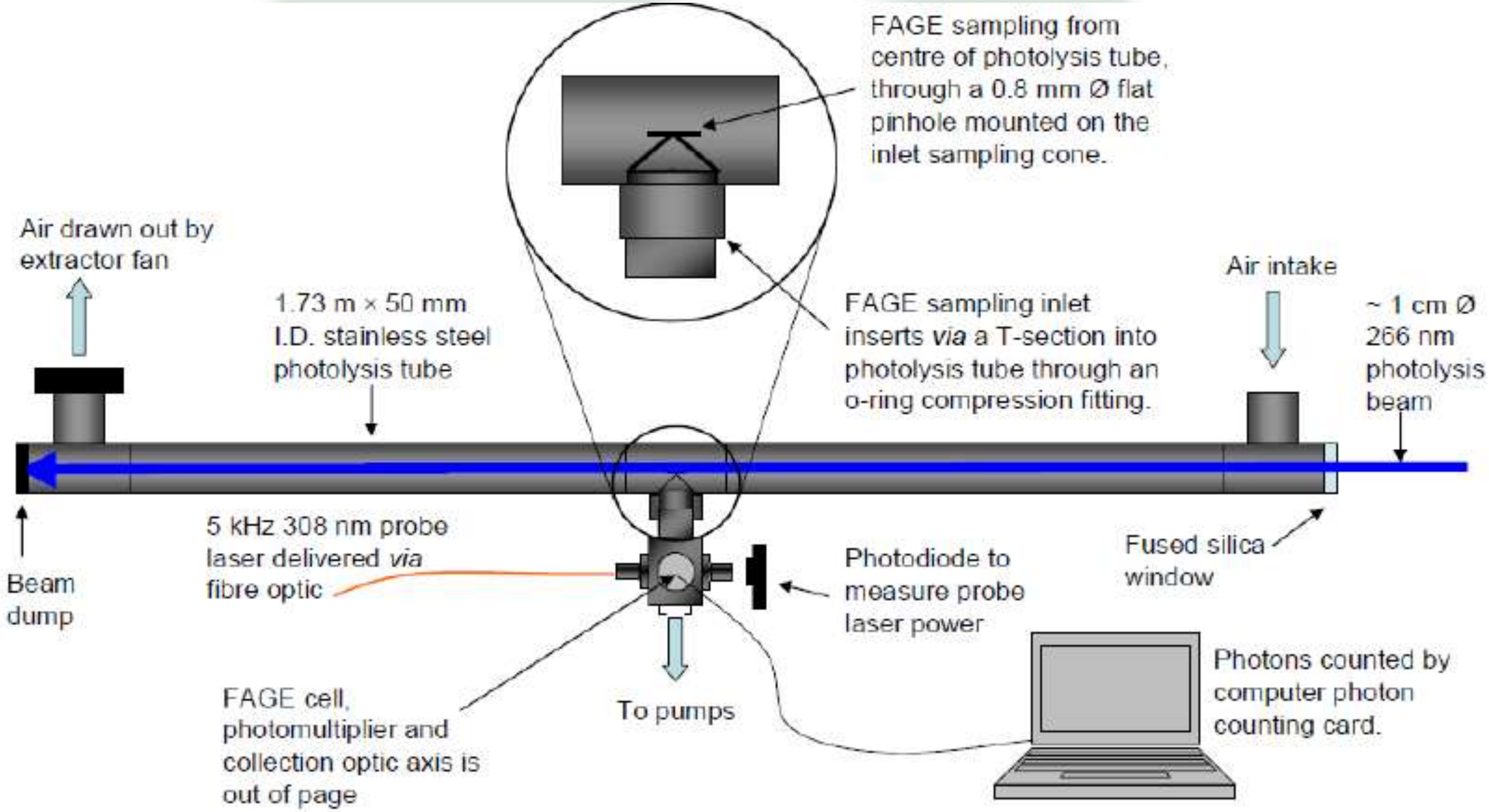
$$OH\ loss\ rate = k'_{\mathrm{OH}}\ [\mathrm{OH}]$$



$$k'_{\mathrm{OH}} = \Sigma\ (k_{\mathrm{CO}}[\mathrm{CO}] + k_{\mathrm{CH4}}[\mathrm{CH_4}] + k_{\mathrm{VOC}}[\mathrm{VOC}] + \ldots)$$

Pump-probe reactivity instrument

O_3 + 266 nm (YAG laser) → $O(^1D) + O_2$
$O(^1D) + H_2O$ → 2 OH
OH + sinks → loss   Advantage: no HO_2 generated initially



Interest in rainforest environments

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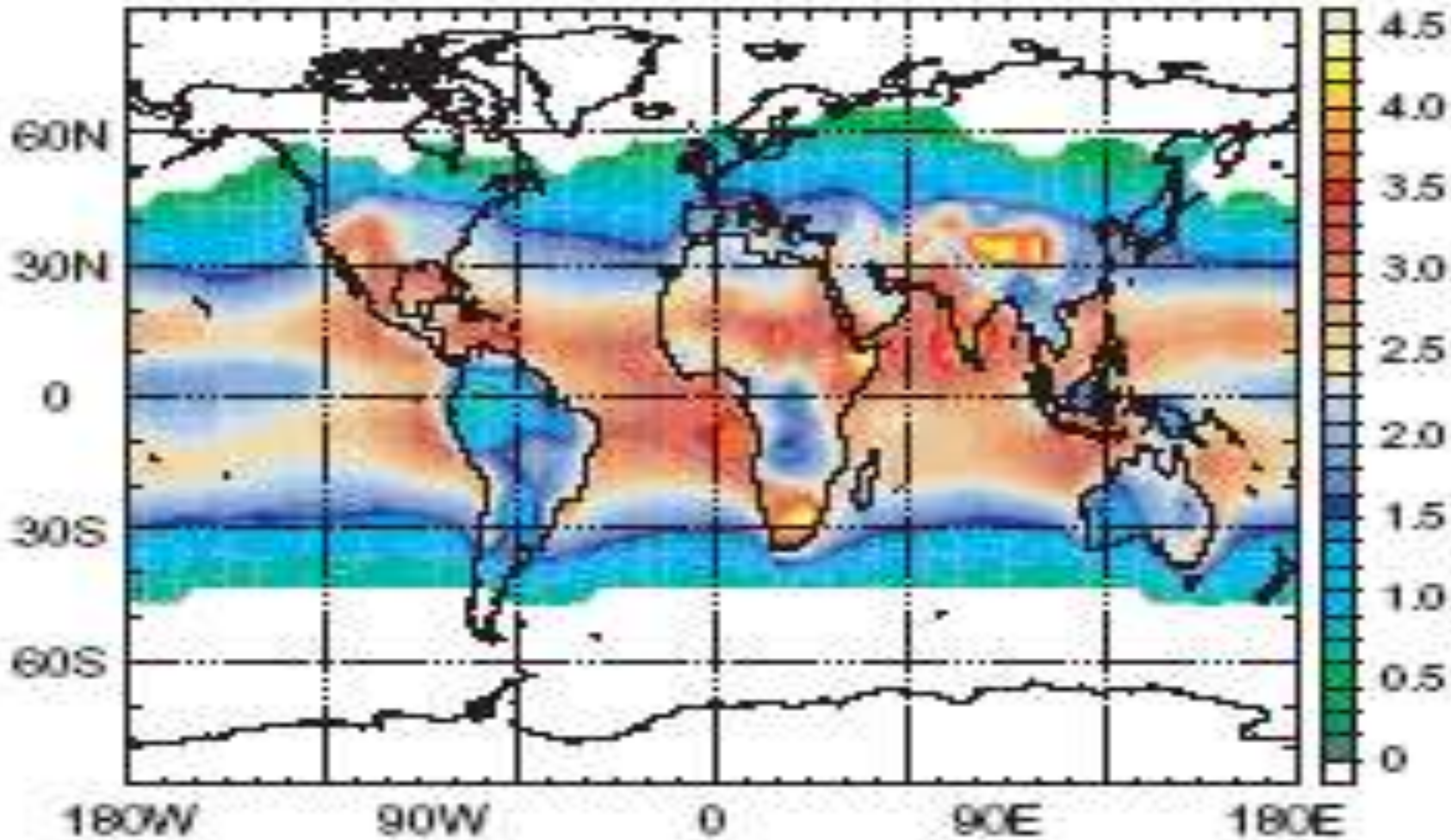
- Until recently measurements of OH and HO_2 in tropical rainforests were sparse
- Global modelling studies highlight a substantial decrease in surface [OH] in rainforest regions

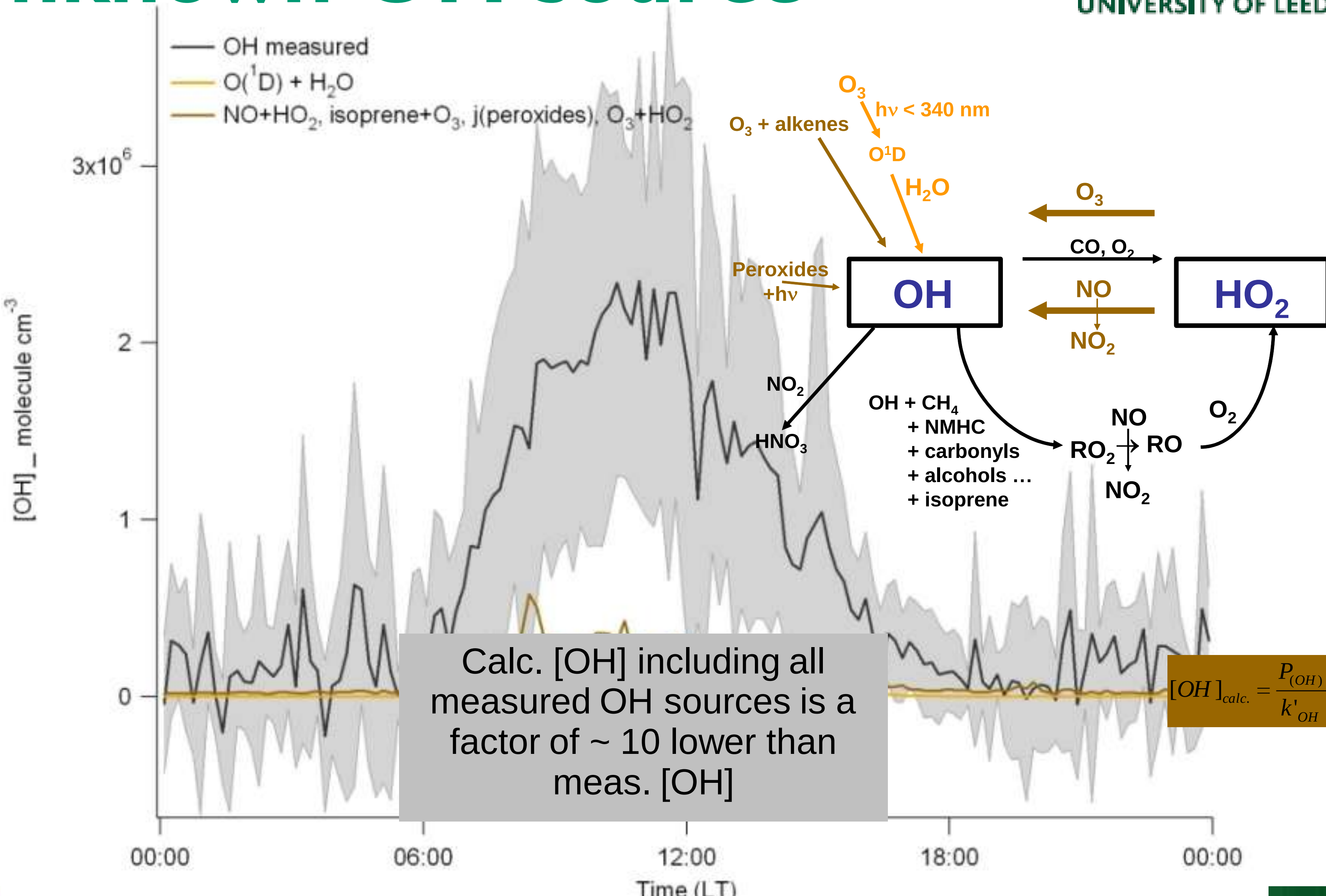
[OH] x 10^6 /molecule cm^{-3}



- Reduced oxidising capacity – could increase the CH_4 lifetime considerably

Lelieveld et al, ACP 2004

Unknown OH source



Calc. [OH] including all measured OH sources is a factor of ~ 10 lower than meas. [OH]

$$[OH]_{calc.} = \frac{P_{(OH)}}{k'_{OH}}$$

Unknown OH source

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Lelieveld *et al*. (Nature, 2008) report high OH observations over Amazon during GABRIEL campaign

Several other field studies also report higher than expected OH at high isoprene

INTEX-A

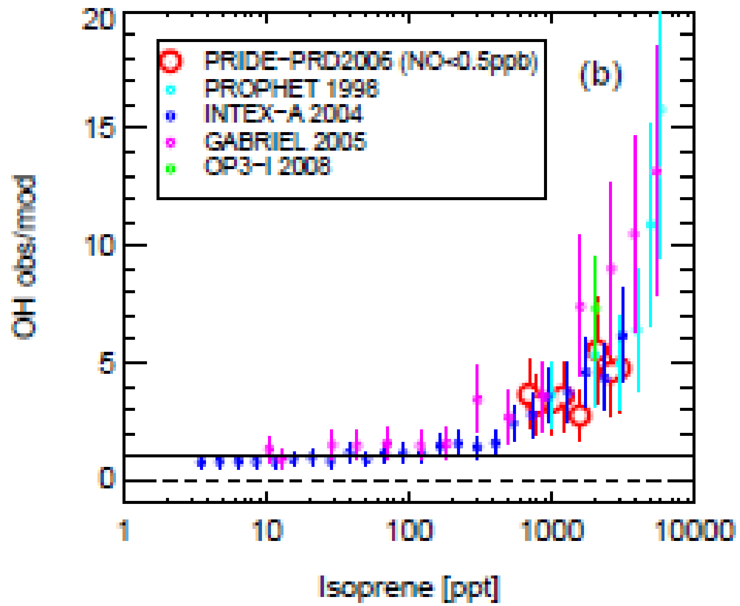
Ren *et al*. (JGR, 2008)

Pearl River Delta, China

Hofzumahaus *et al*. (Science, 2009)

AMMA

Saunois *et al*. (ACP, 2009) predict low OH over the forest using a 2D meteorological model coupled with O_3-NO_x-VOC chemistry



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HO_x chemistry – novel mechanisms

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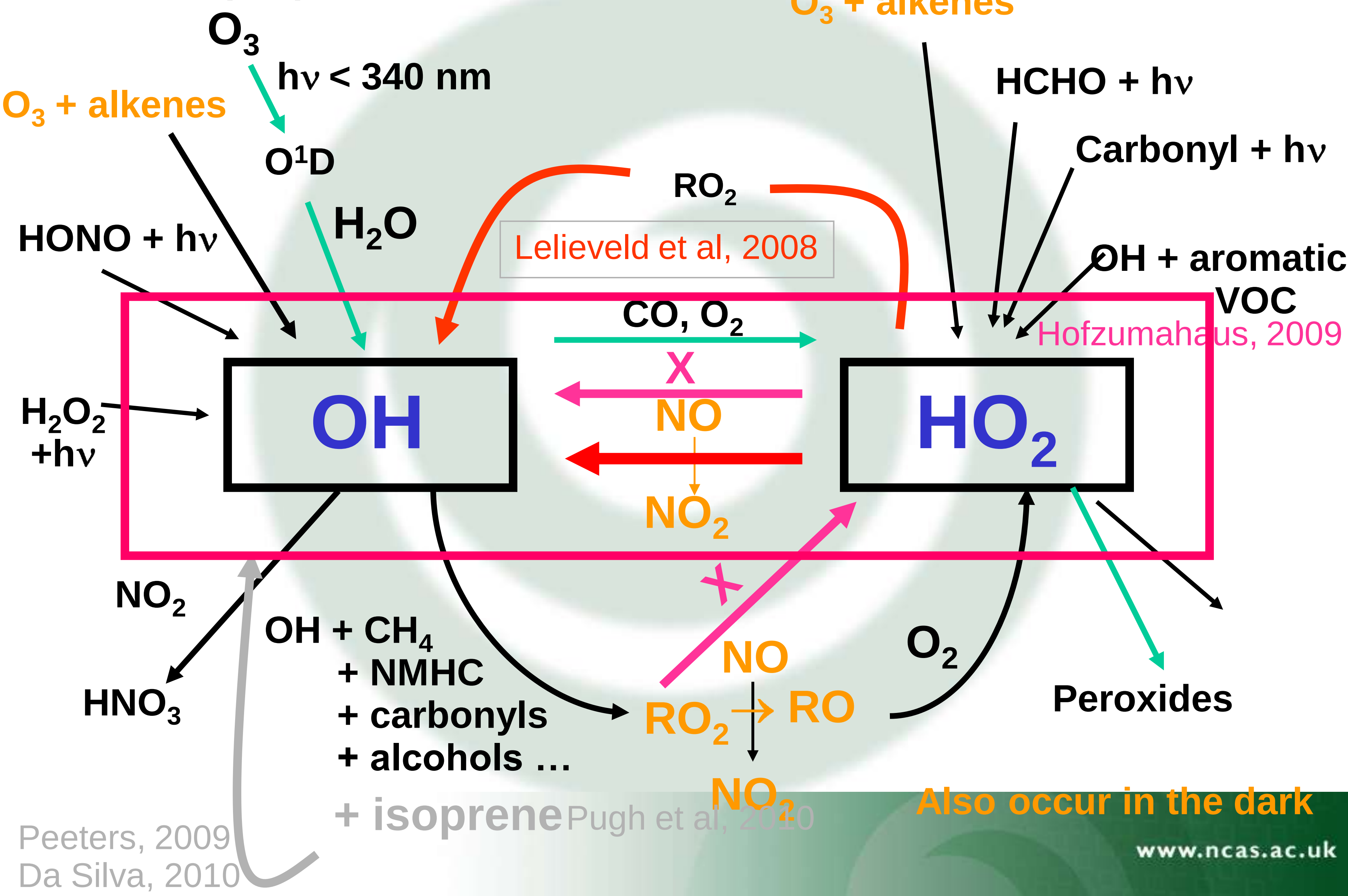
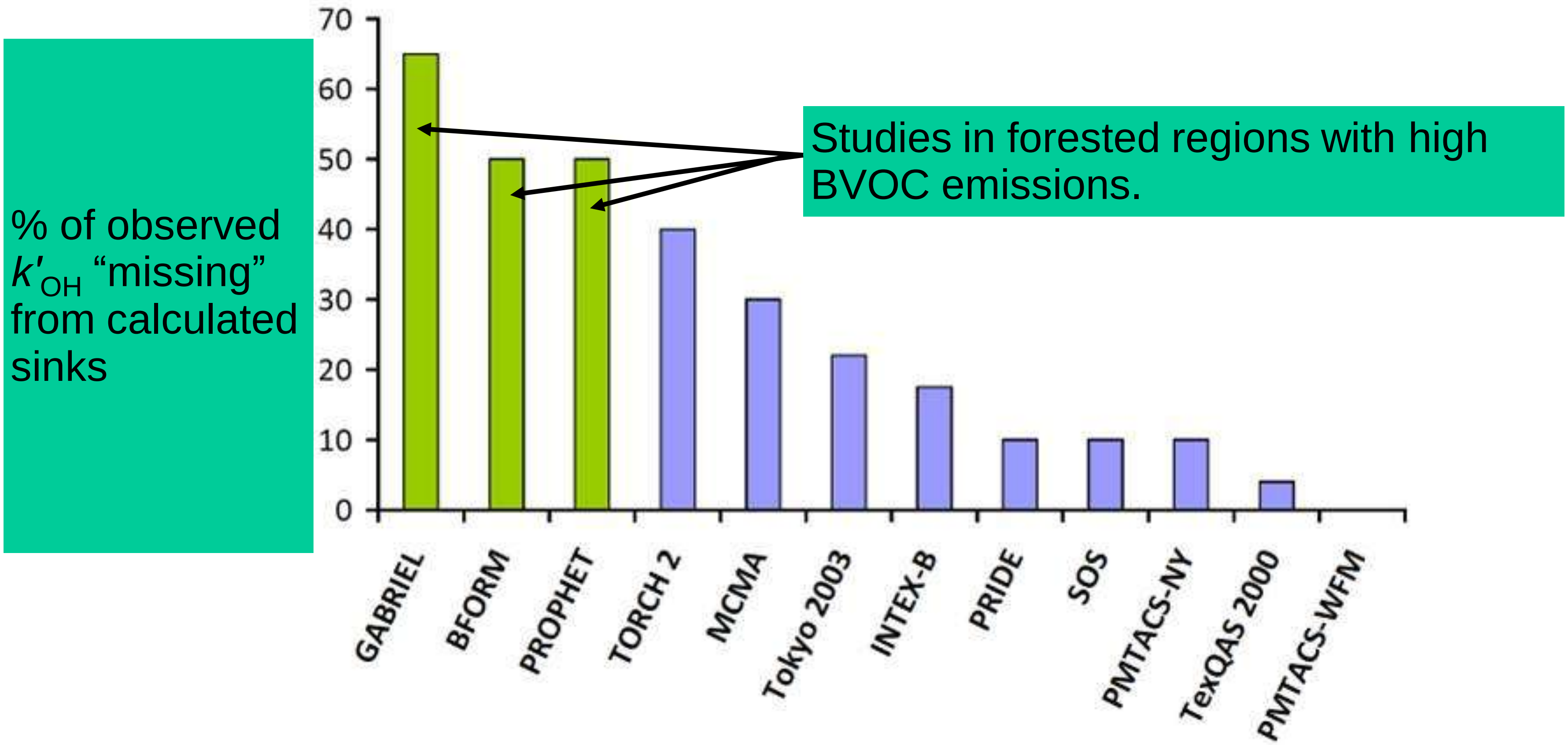
VOC rich troposphere



OH reactivity

- Previous studies of OH reactivity have generally all found ‘missing’ OH sinks when compared to the OH loss calculated within a constrained box model.



- Tropical regions account for ~80% of global BVOC emission.

OH reactivity during OP3

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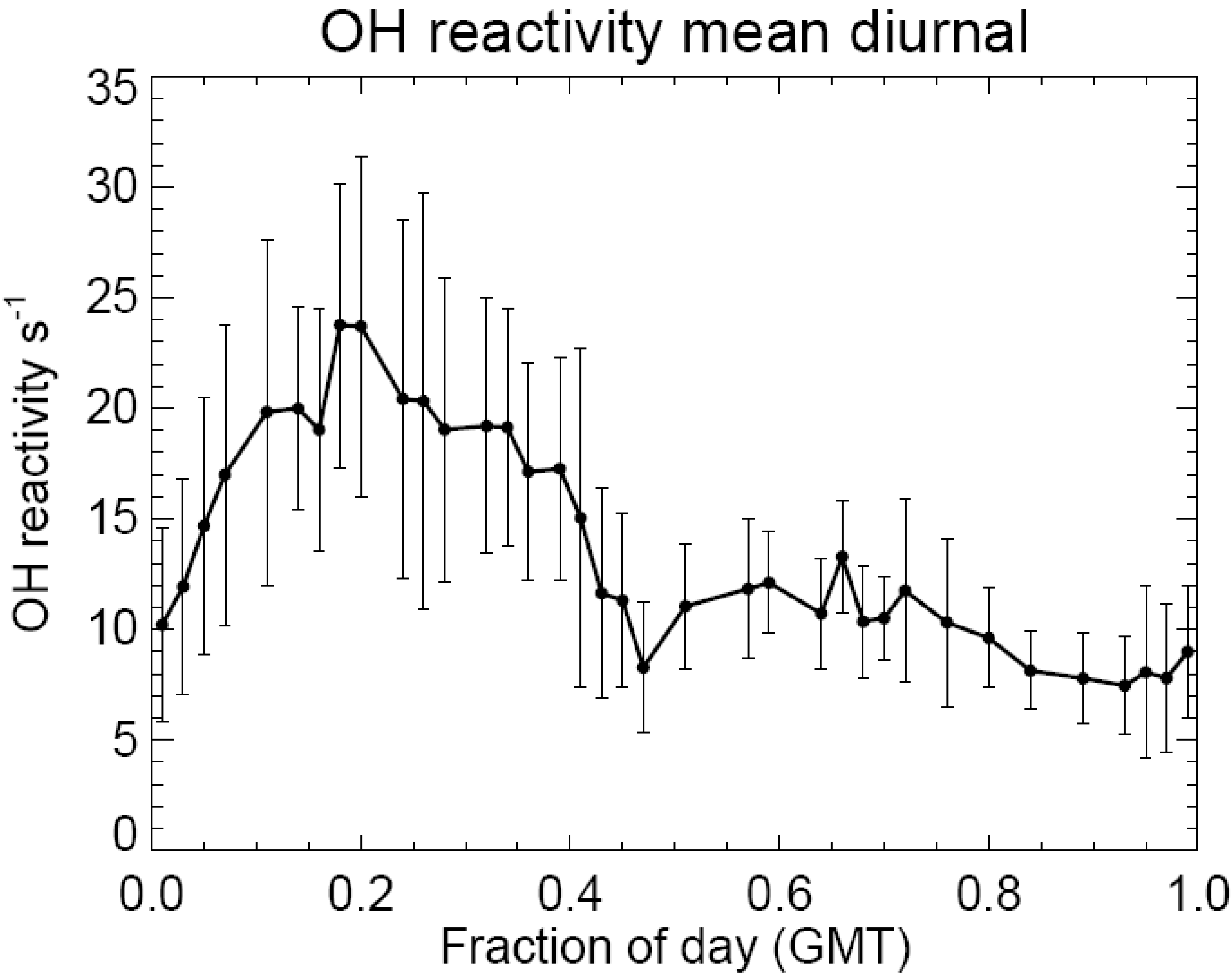

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OH reactivity during OP3

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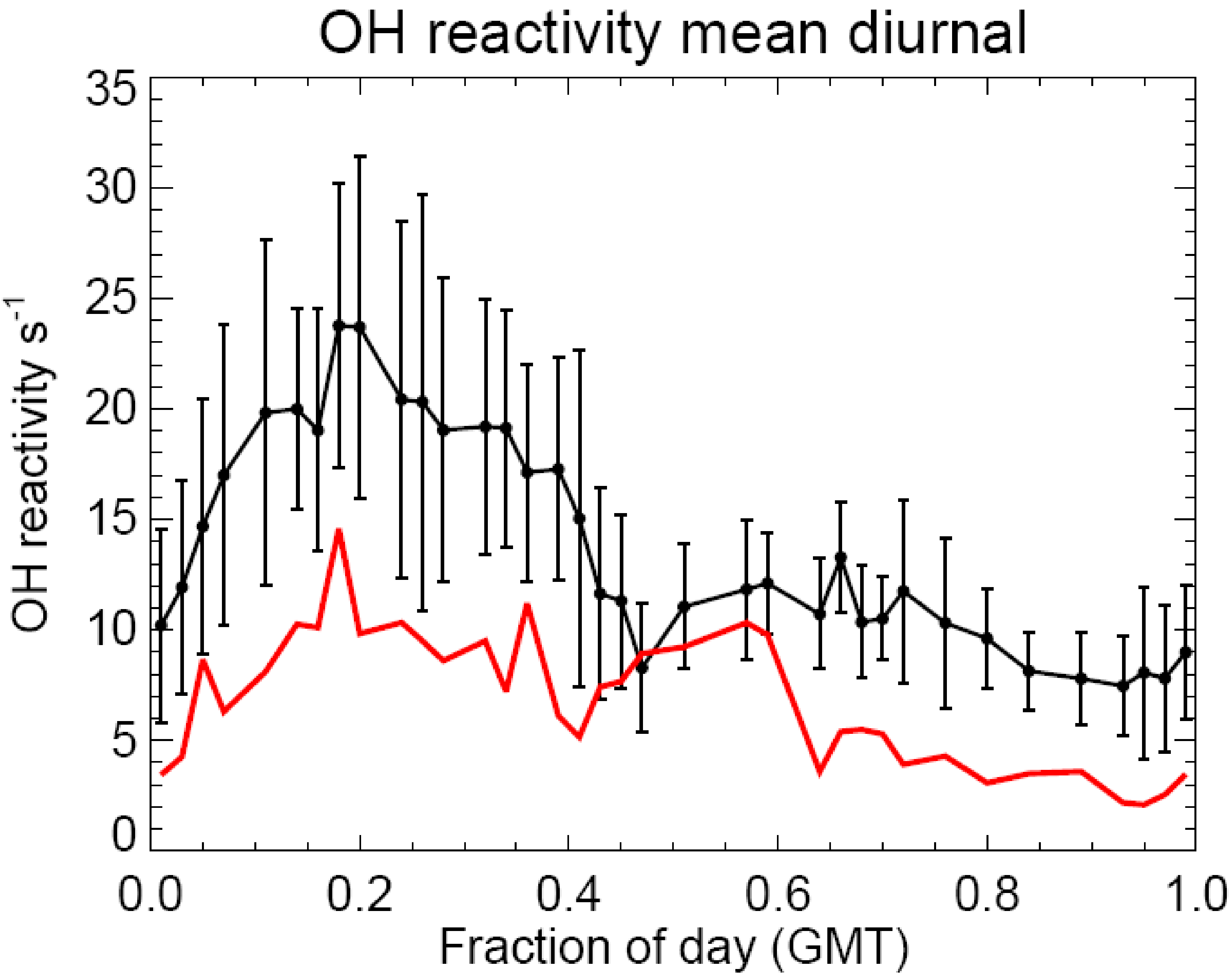

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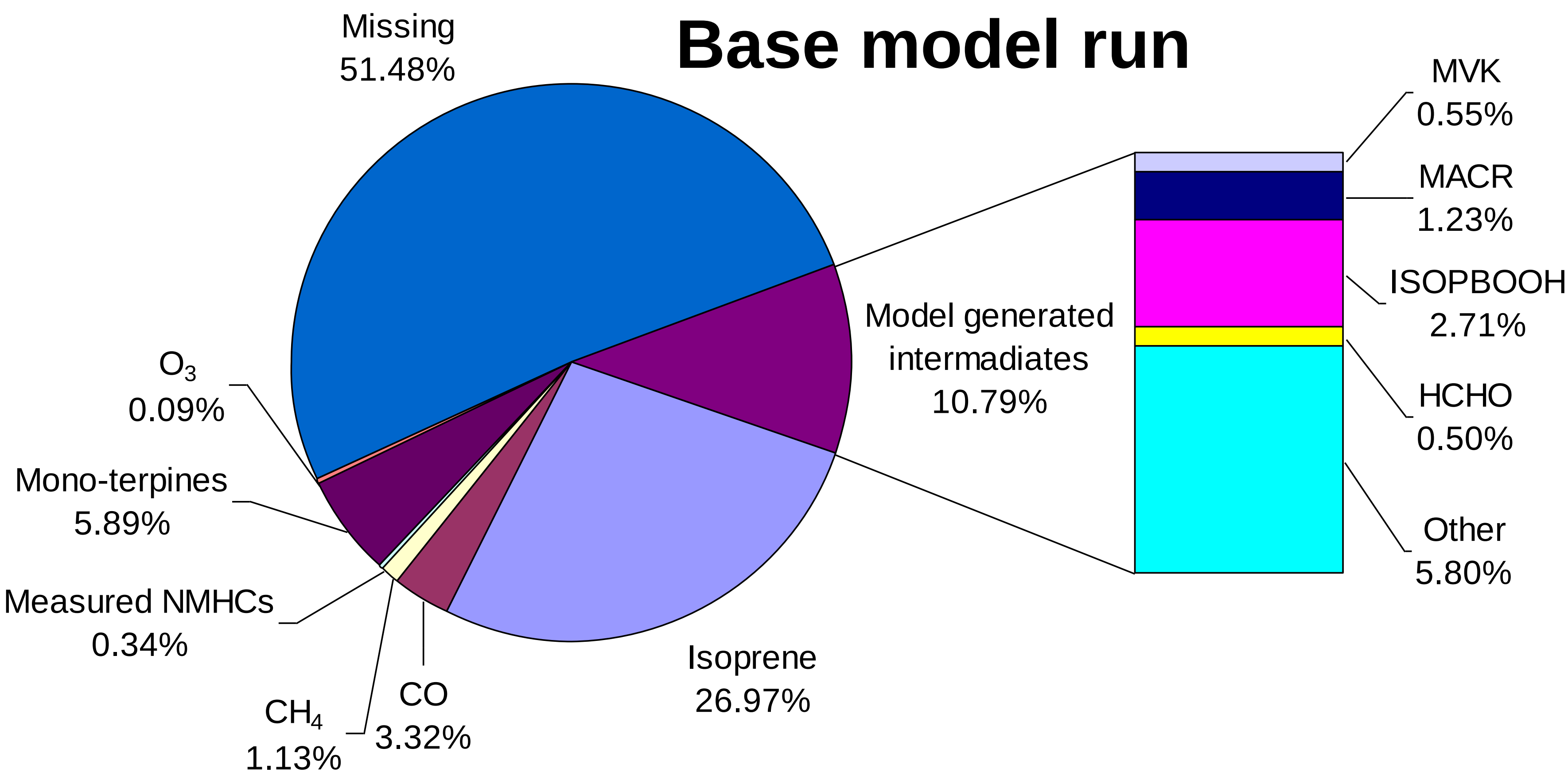
OH reactivity during OP3

Base model run



OH reactivity during OP3

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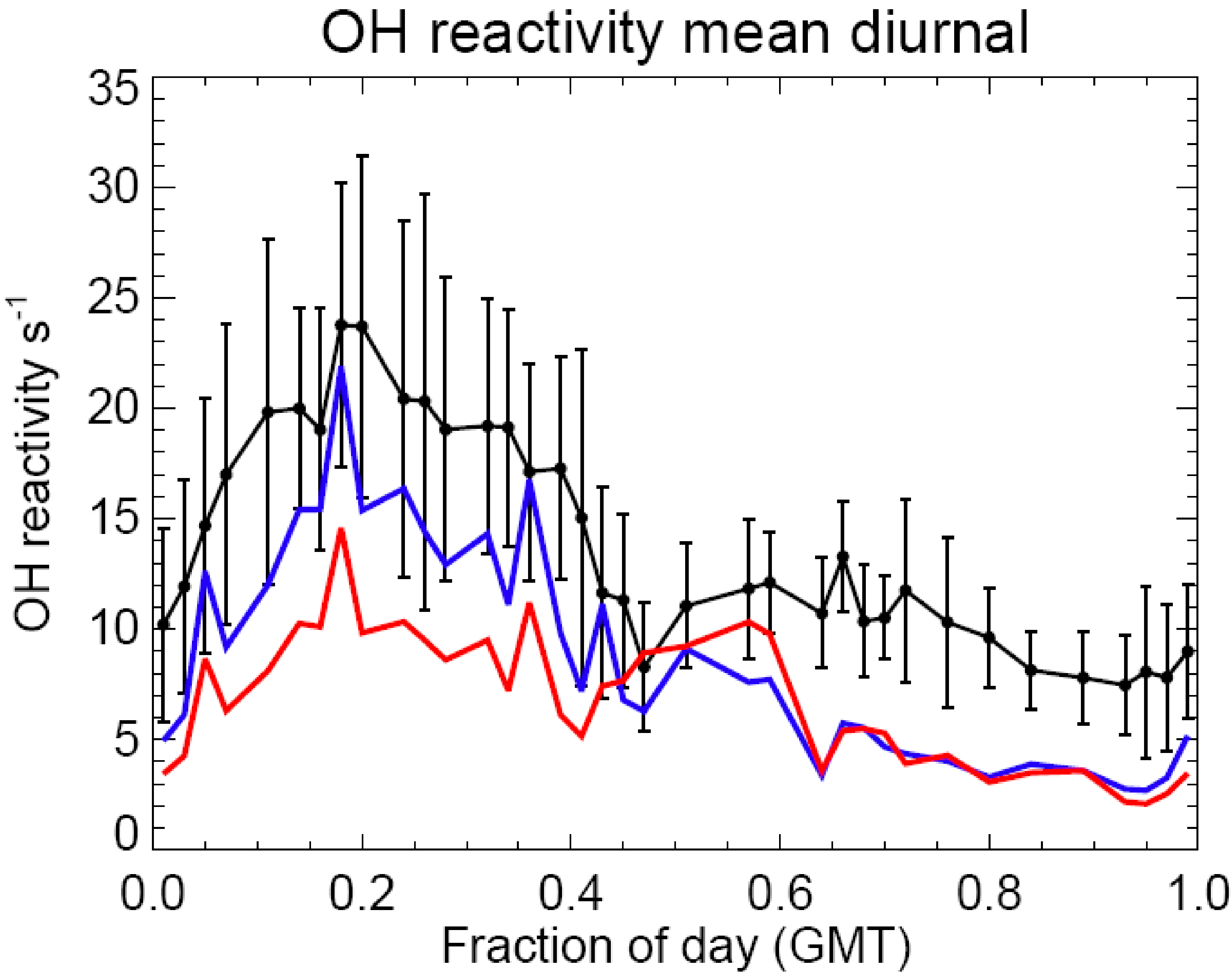

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OH reactivity during OP3

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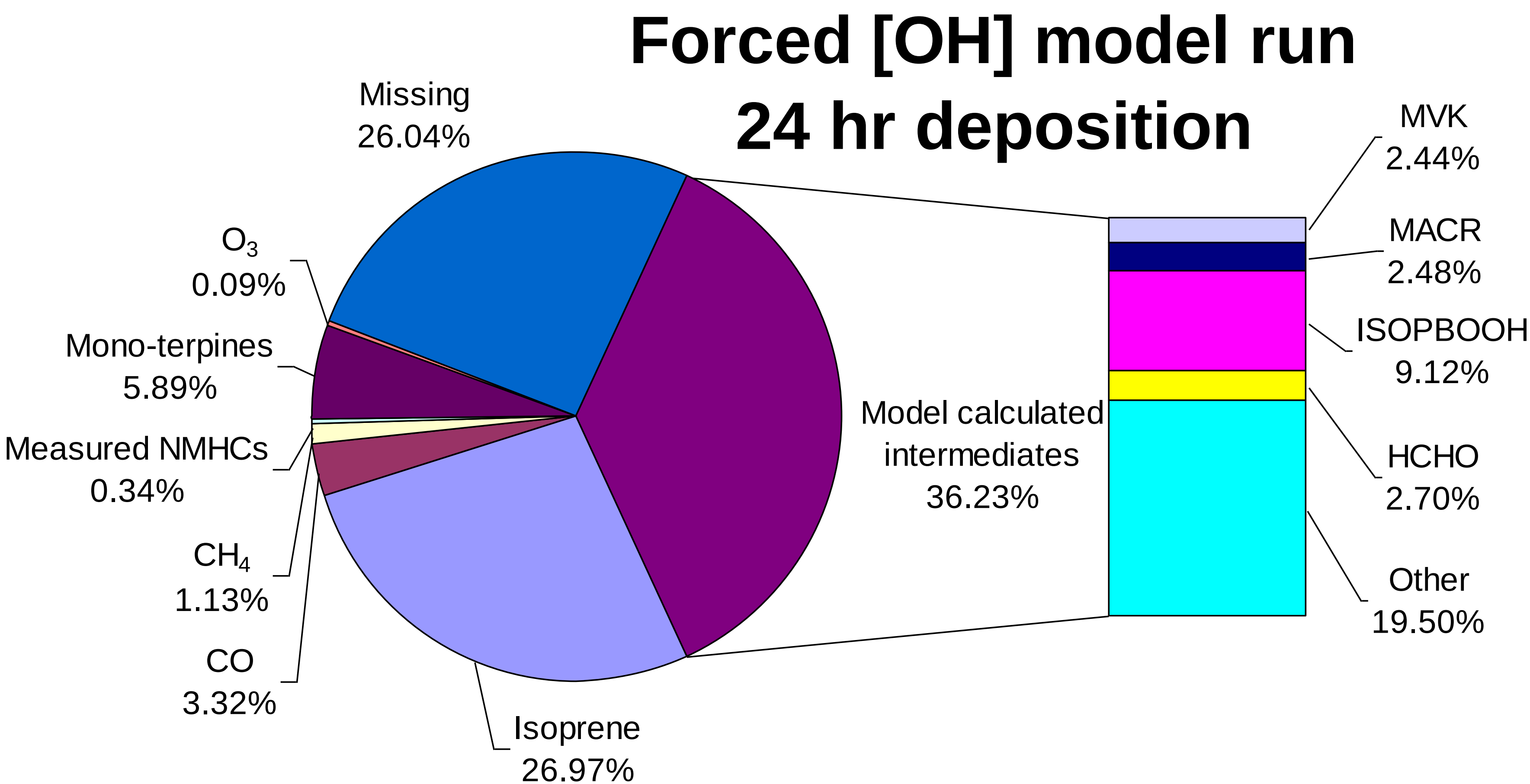

OH reactivity during OP3

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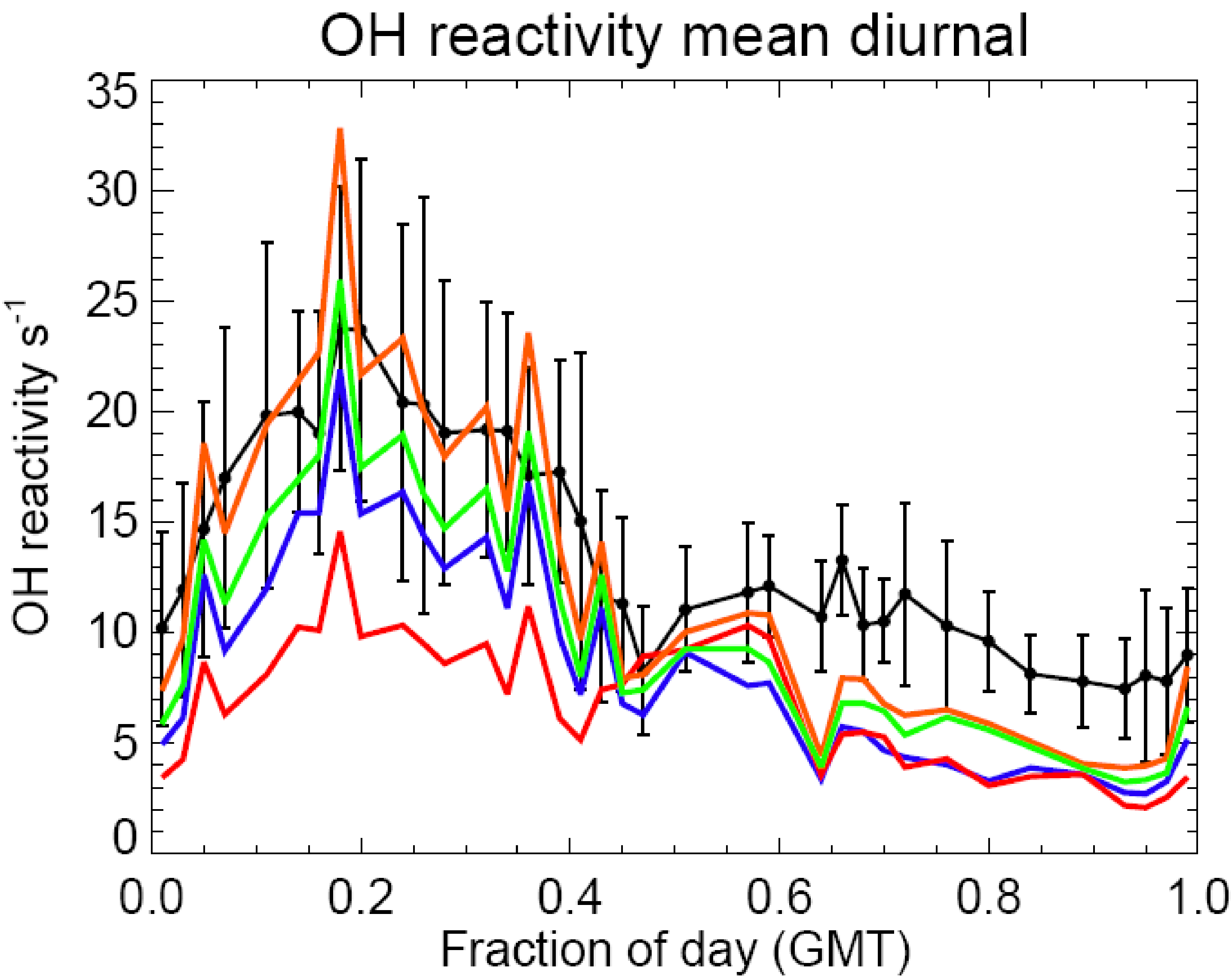

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OH reactivity during OP3

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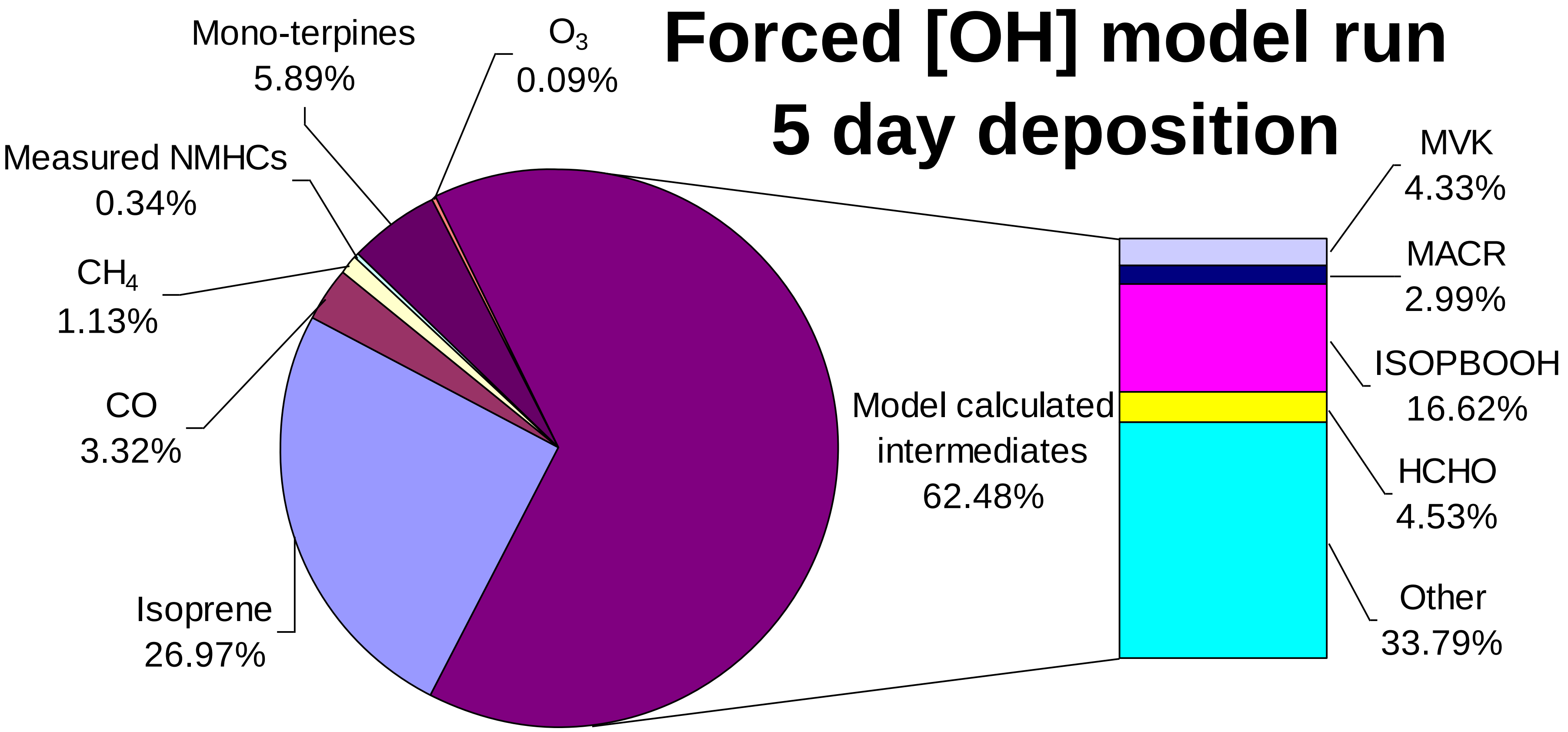
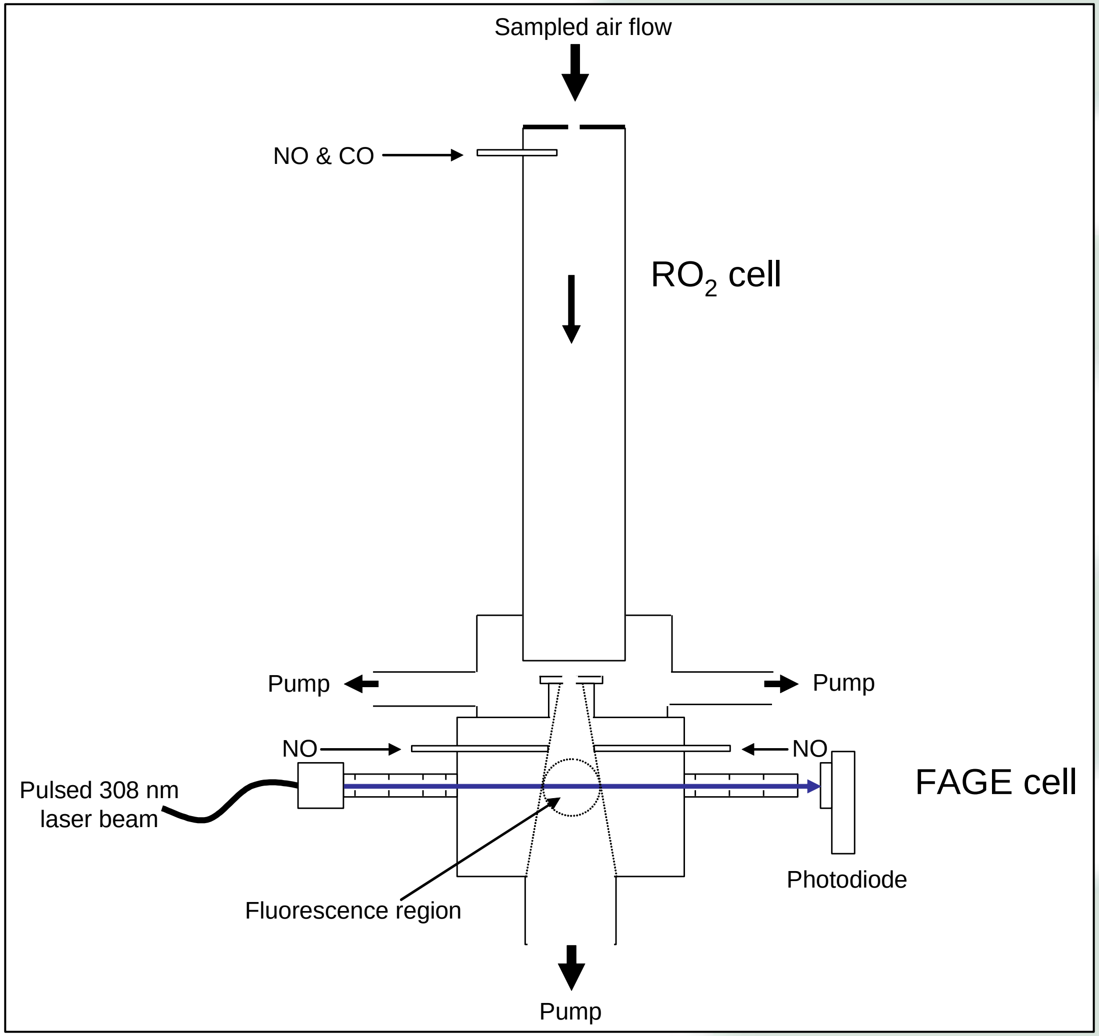
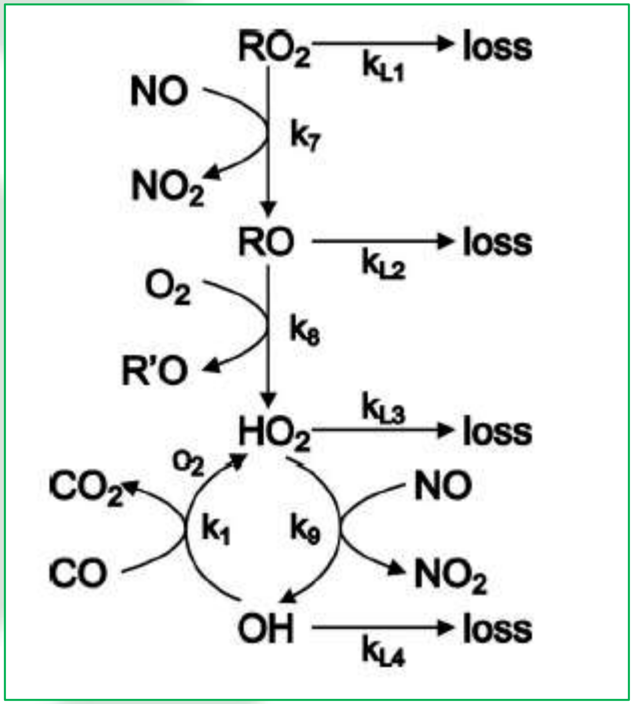


Other measurement capabilities

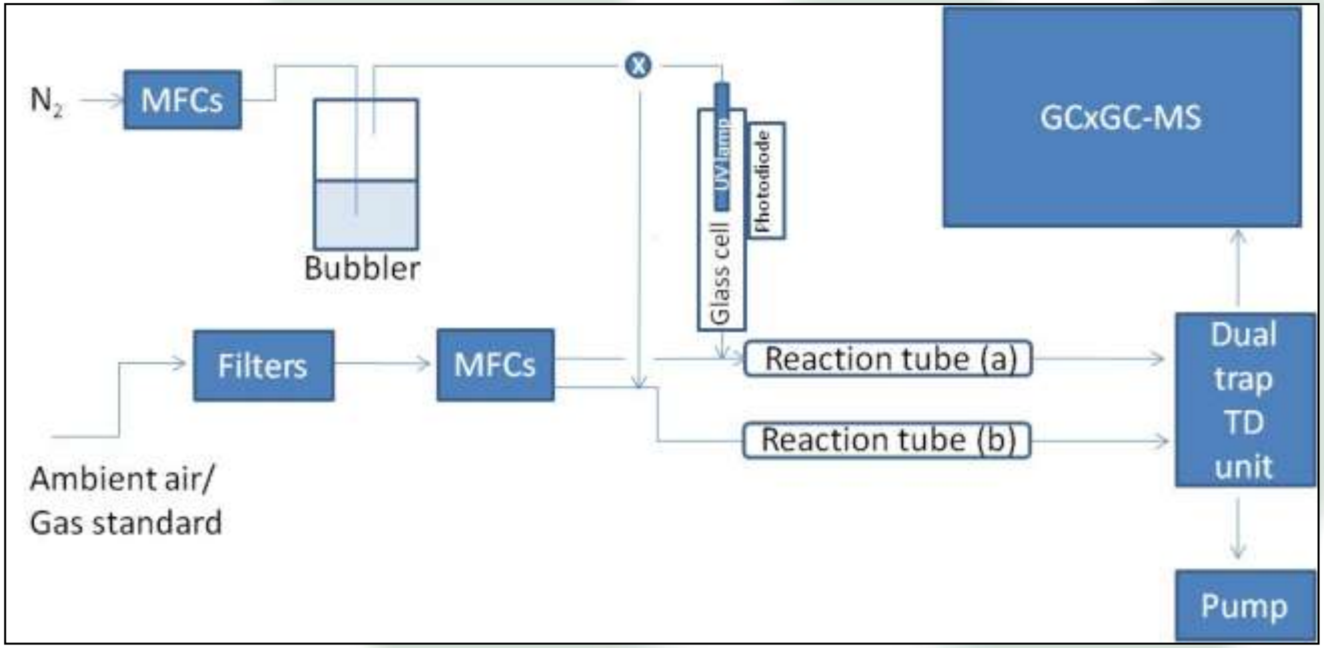
- RO_2 (speciate between HO_2, alkane-derived RO_2 and alkene-derived RO_2





Other measurement capabilities

- $j(O^1D)$, spec. rad.
- HCHO (Hottle et al. Environ. Sci. Tech. 2009)
- Glyoxal (Huisman et al. Anal. Chem. 2008)
- method to determine missing OH reactivity:



Summary

• Previous measurements during OP3 have revealed significant uncertainties in our understanding of radical sources and sinks

• Novel OH sources can help to reduce the model – measurement discrepancy but not solve the problem entirely

• In terms of the OH reactivity, there is certainly enough carbon in the model, but the model is particularly sensitive to the deposition lifetime of key species – need to constrain this better

•The model reactivity is dominated by poorly constrained intermediate VOCs

• Opportunities to measure key oxidation products – HCHO, glyoxal using LIF

• Now possible to identify key VOC oxidation products/functional groups that may be dominating OH reactivity

Human modified Tropical Forest Call

• For unpolluted forested regions occupying a significant fraction of the planet's surface, and characterised by large emissions of biogenic VOCs, for example isoprene, constrained box models using the detailed *Master Chemical Mechanism* (MCM) and Earth System Models using more simplistic schemes, calculate low concentrations of OH owing to the rapid removal by reaction with plant emissions.

• Recent measurements in tropical regions by several groups show these calculations to be too low by up to an order of magnitude, and hence overestimate the lifetime of methane, a greenhouse gas, and underestimate the rate of oxidation leading to secondary products including organic aerosols.

•There is currently no consensus on the source of this missing OH, with one suggested mechanism by Peeters et al., based on theoretical, computer calculations, being inconsistent with evidence obtained in the laboratory and field measurements of other key species.

•This is a very serious shortcoming when considering biosphere-atmosphere-climate feedbacks for these regions, and calculating the regional impact on climate of deforestation or changes in land-use.

Human modified Tropical Forest Call

- How well to models and measurements agree in Human modified tropical forests?
- If NOx levels are higher do we do a better job at modelling OH?
- Can we better constrain or test models with new measurement capabilities (e.g HCHO, partically speciated RO2)?
- Impact on methane lifetime