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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 lifetime
- Lifetime of trace gas X = $1/(k_{OH+X}$ [OH]) and hence depends upon [OH]
- Examples of trace gases removed by OH include:

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

So it is important to measure OH because:

(1) [OH] defines the oxidising capacity or self-cleansing ability of the atmosphere

(2) OH is intimately involved in all aspects of the chemistry related to climate change and air pollution – and hence 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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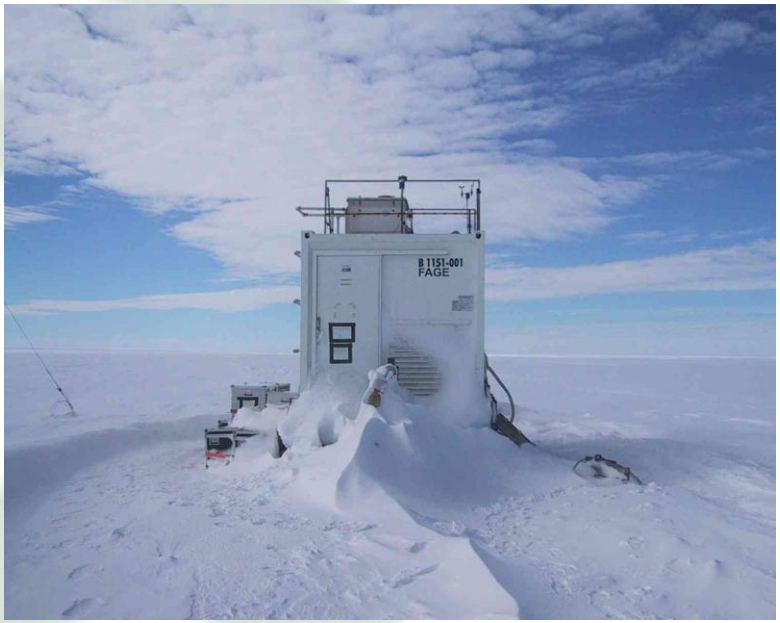

The Leeds FAGE instruments
For OH and HO_2

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.

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

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

Understanding the OH chemistry

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Steady State assumption:

Total OH production rate = Total OH destruction rate

$$P_{(OH)} = [OH] \times k'_{OH}$$

- Photodissociation of O_3 followed by reaction of $O(^1D)$ with H_2O
- Photodissociation of other trace gases: HONO, H_2O_2…
- Ozonolysis of alkenes
- HO_2 + NO

- $k'_{OH} = \Sigma k_{OH+X}[X]$

k_{OH+X} is the bimolecular rate constant
X is the atmospheric reactant

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

Comparison with measured OH (OH reactivity measurement)

Interest in rainforest environments

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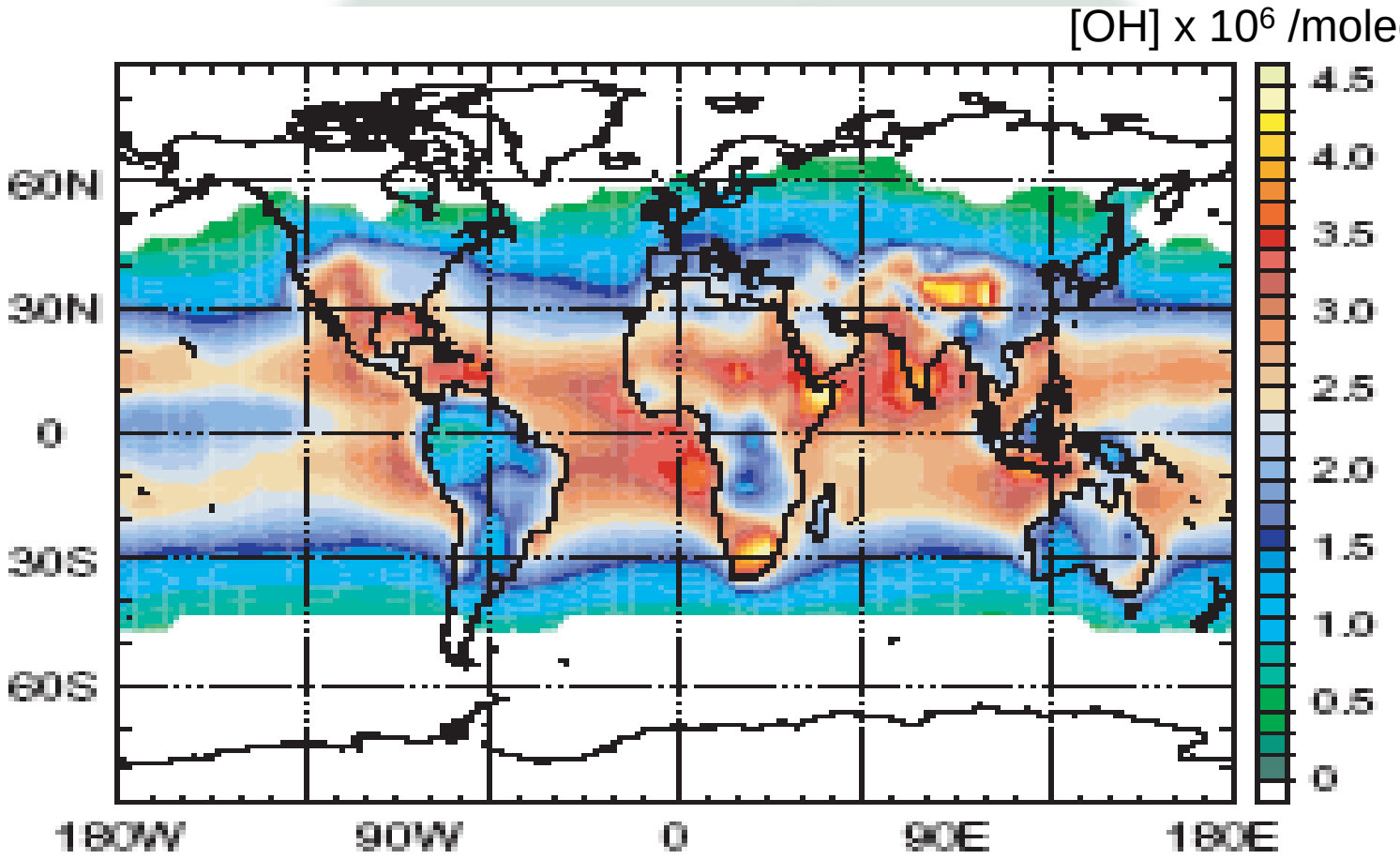
- Until recently measurements of OH and HO_2 in tropical rainforests were sparse
- Global modelling studies highlight a substantial decrease in surface [OH] in rainforest regions



- Reduced oxidising capacity – could increase the CH_4 lifetime considerably

Lelieveld et al, ACP 2004

Unknown OH source

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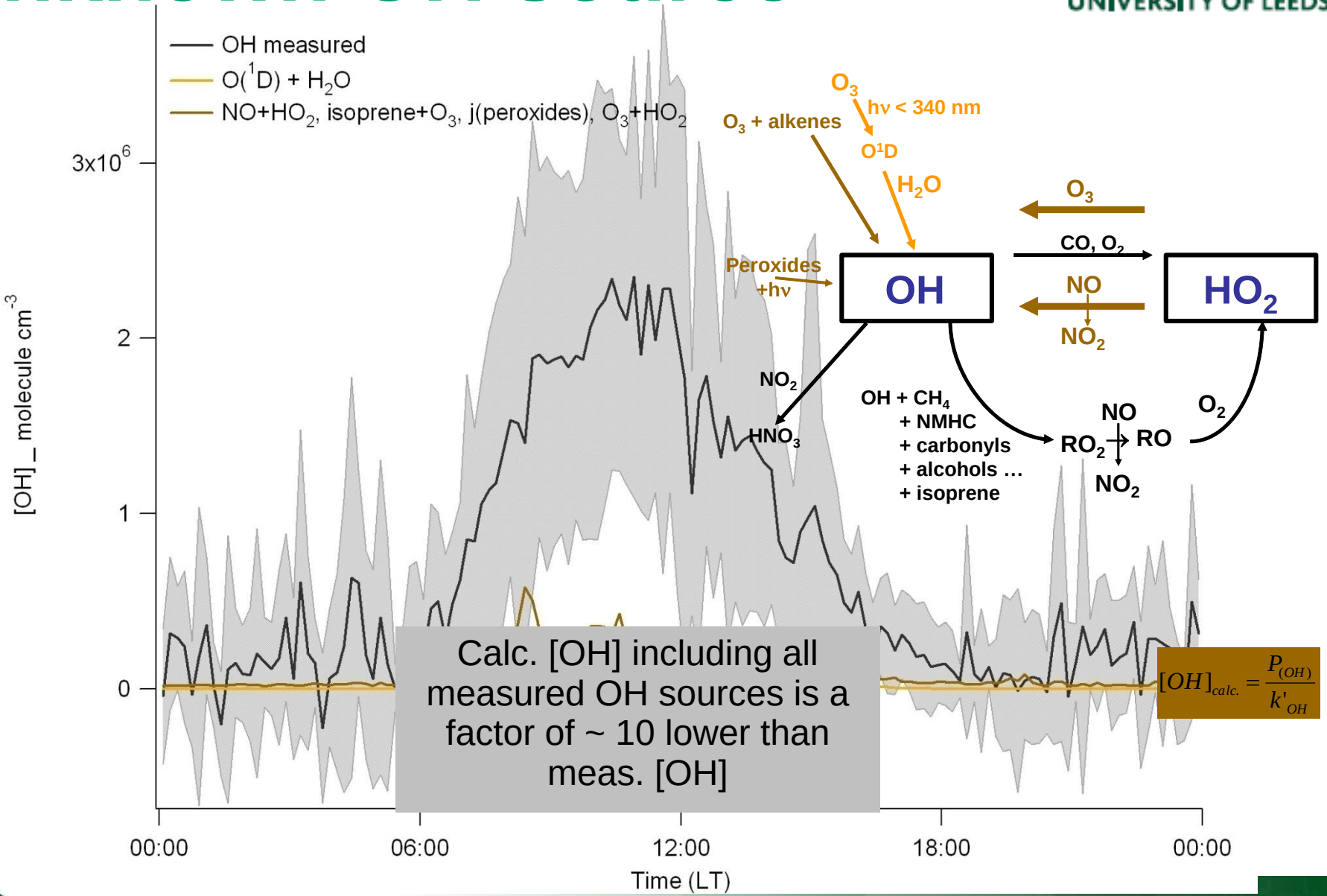

Unknown OH source

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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

HO_x chemistry – novel mechanisms

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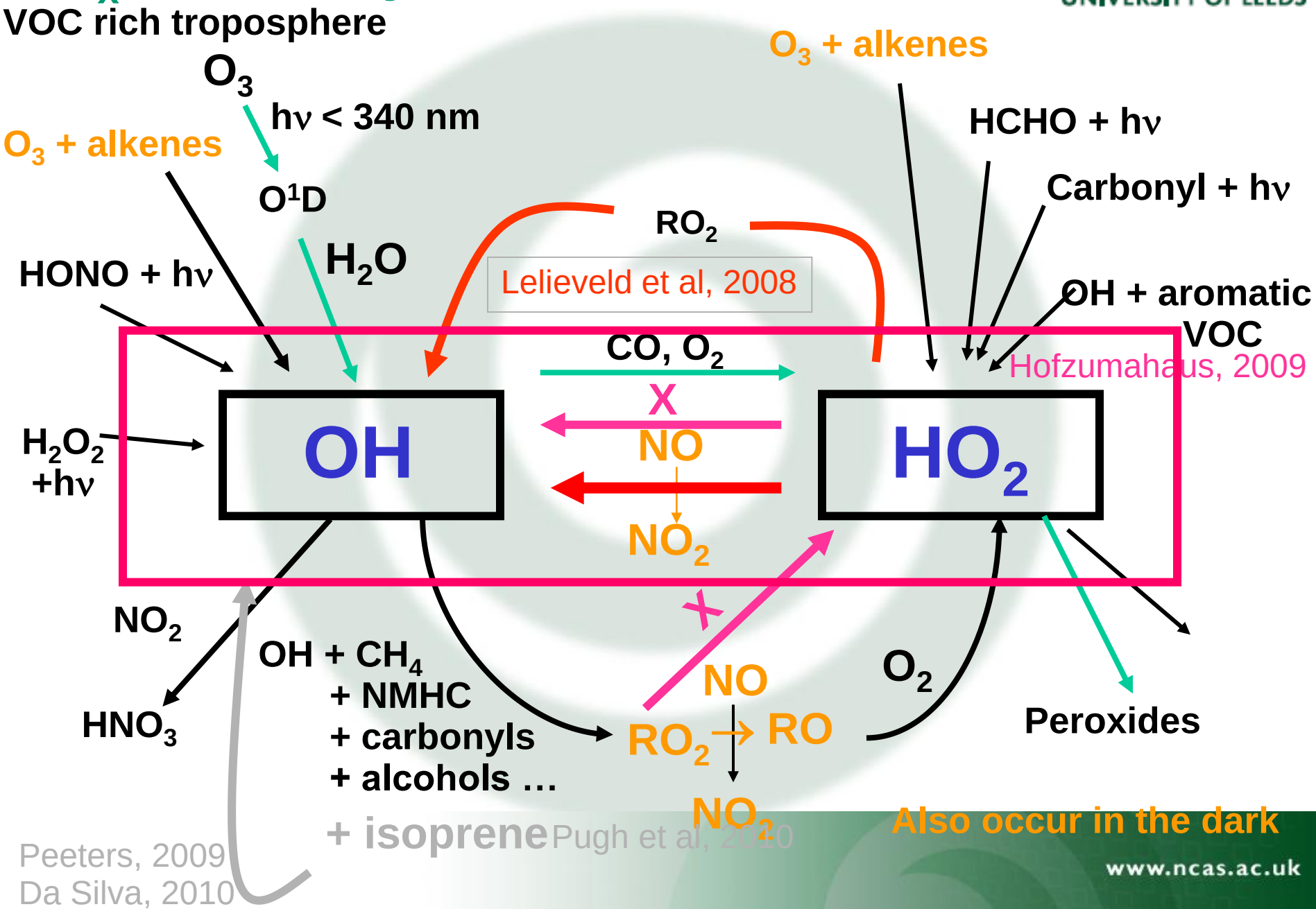
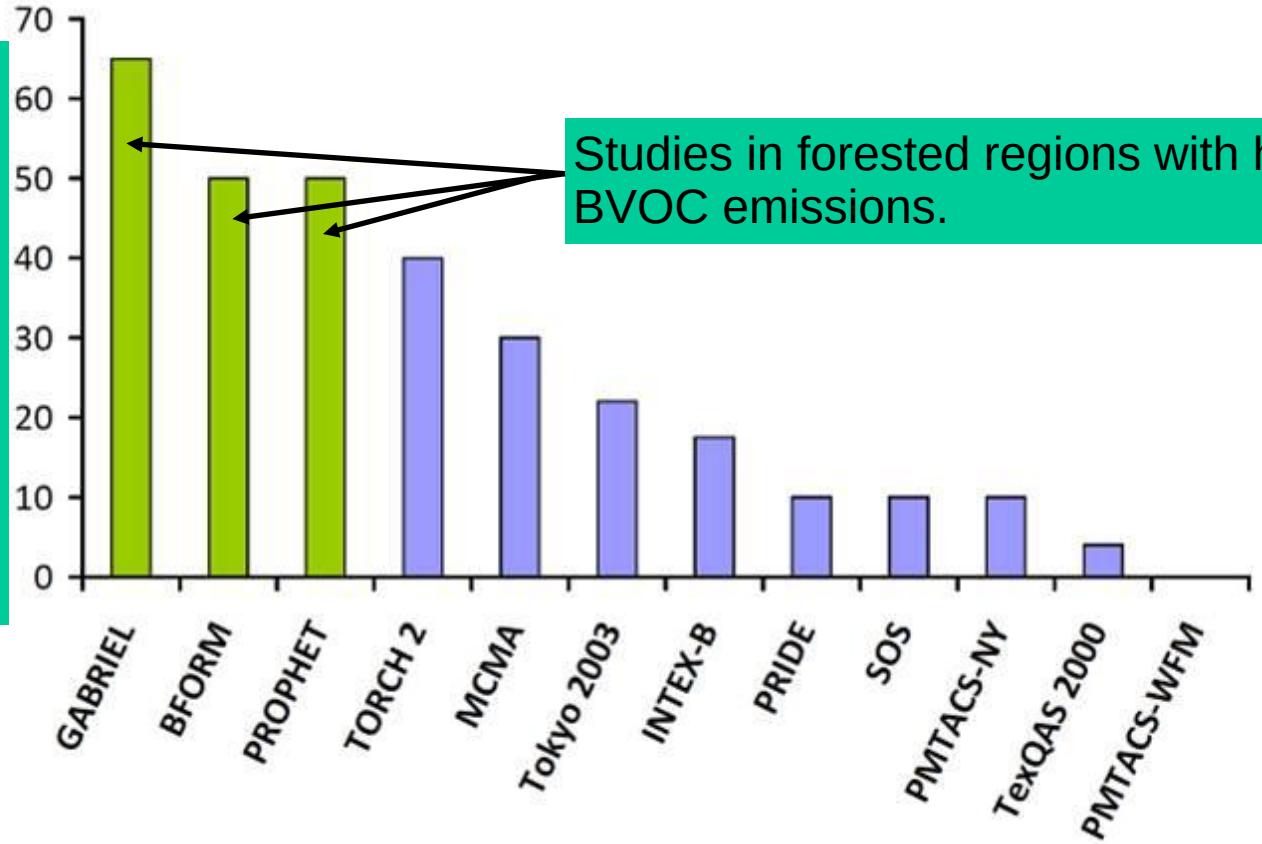


OH reactivity

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

% of observed k'_{OH} “missing” from calculated sinks



Studies in forested regions with high BVOC emissions.

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

The Leeds DCMACC box model

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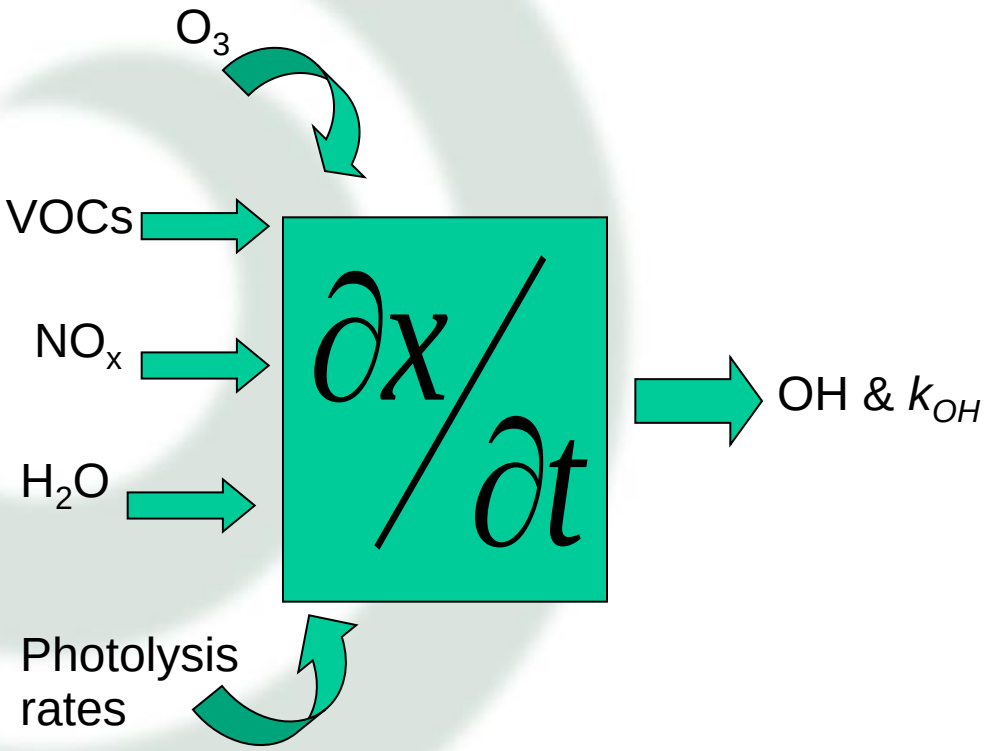
- Dynamically Simple Model of Atmospheric Chemical Complexity
- Observationally constrained box model
- *J*-values calculated by TUV
- Chemistry scheme described by Master Chemical Mechanism (MCM)
- Model run forwards to diurnal steady state



OH reactivity during OP3

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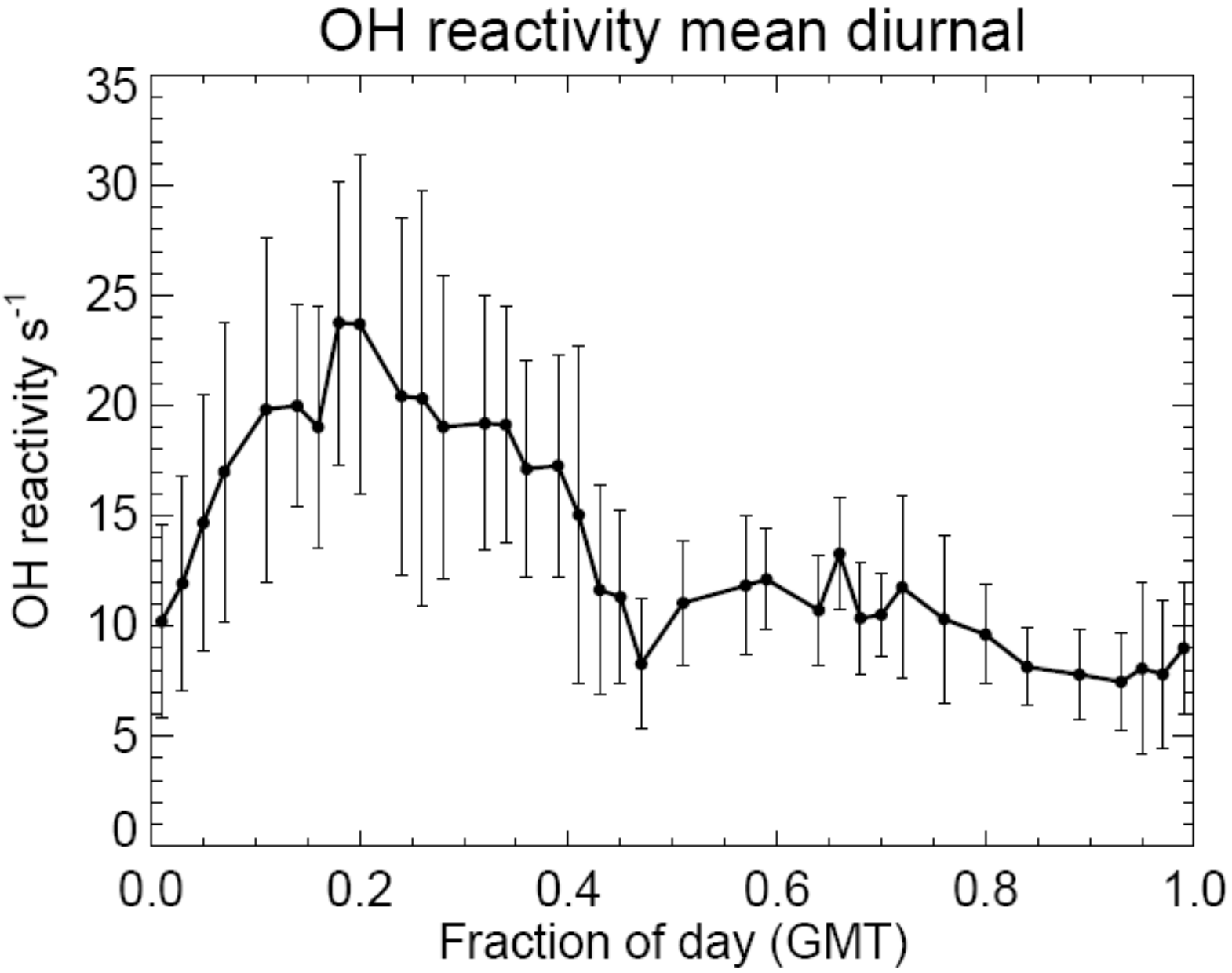

OH reactivity during OP3

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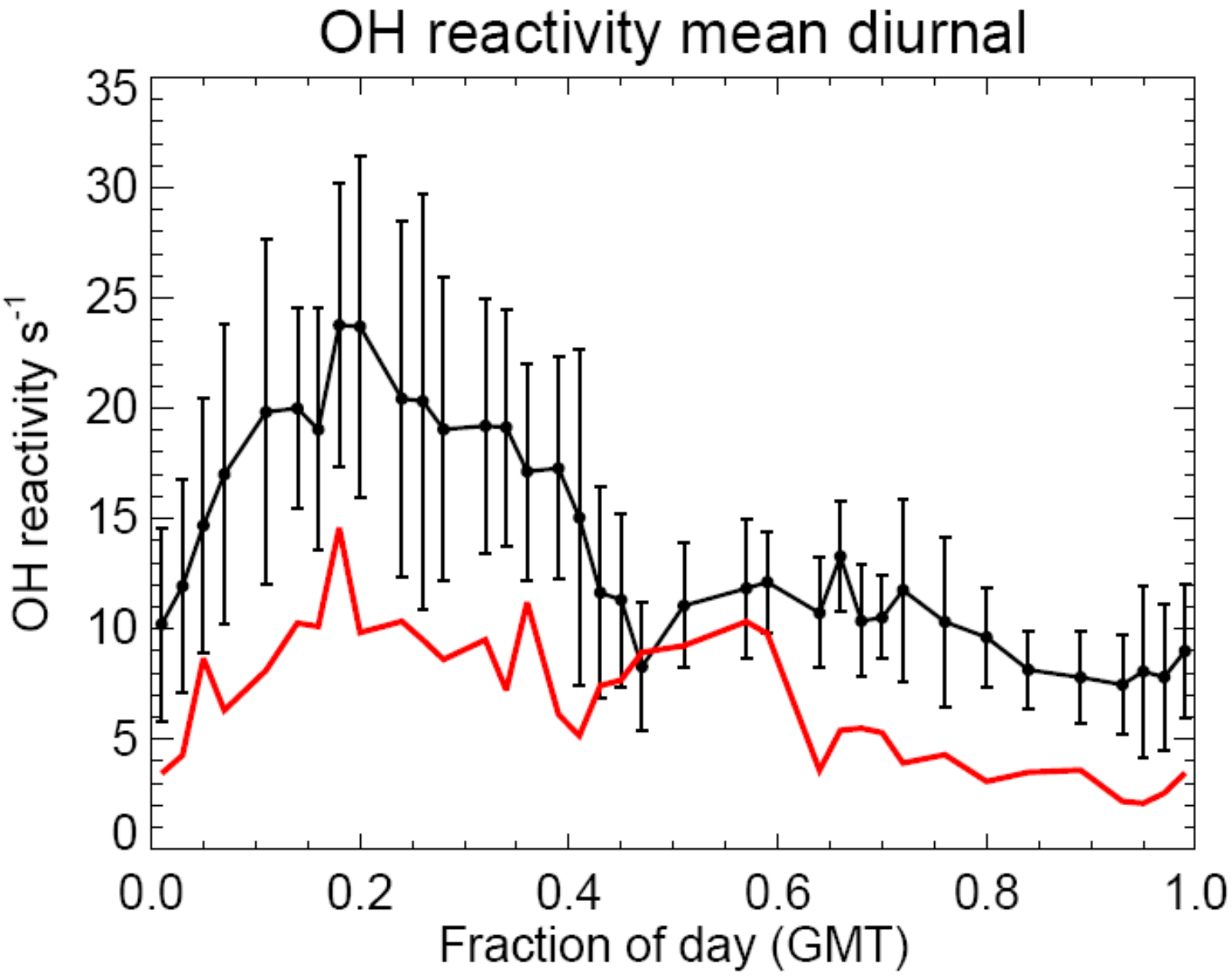

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OH reactivity during OP3

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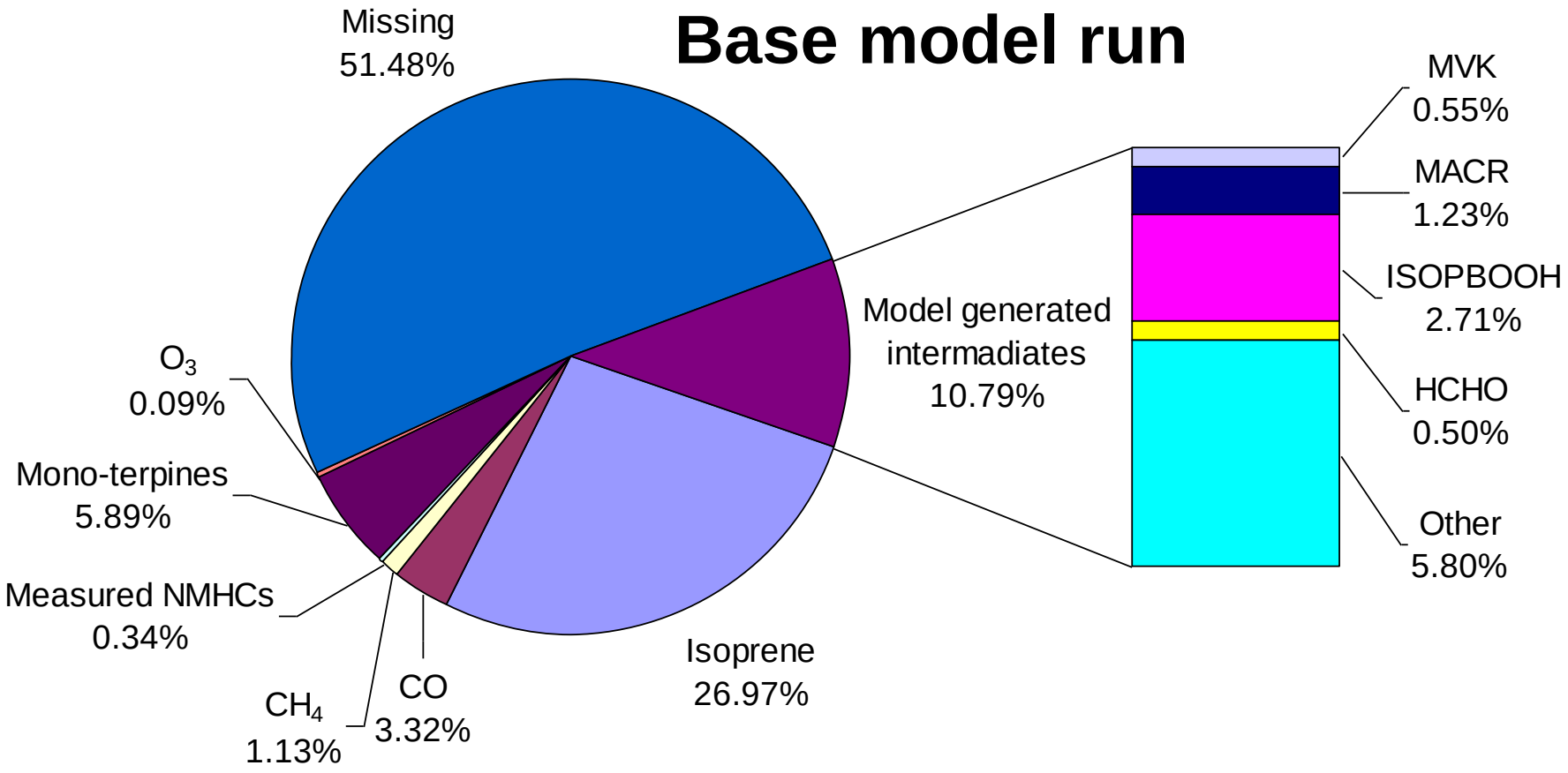

OH reactivity during OP3

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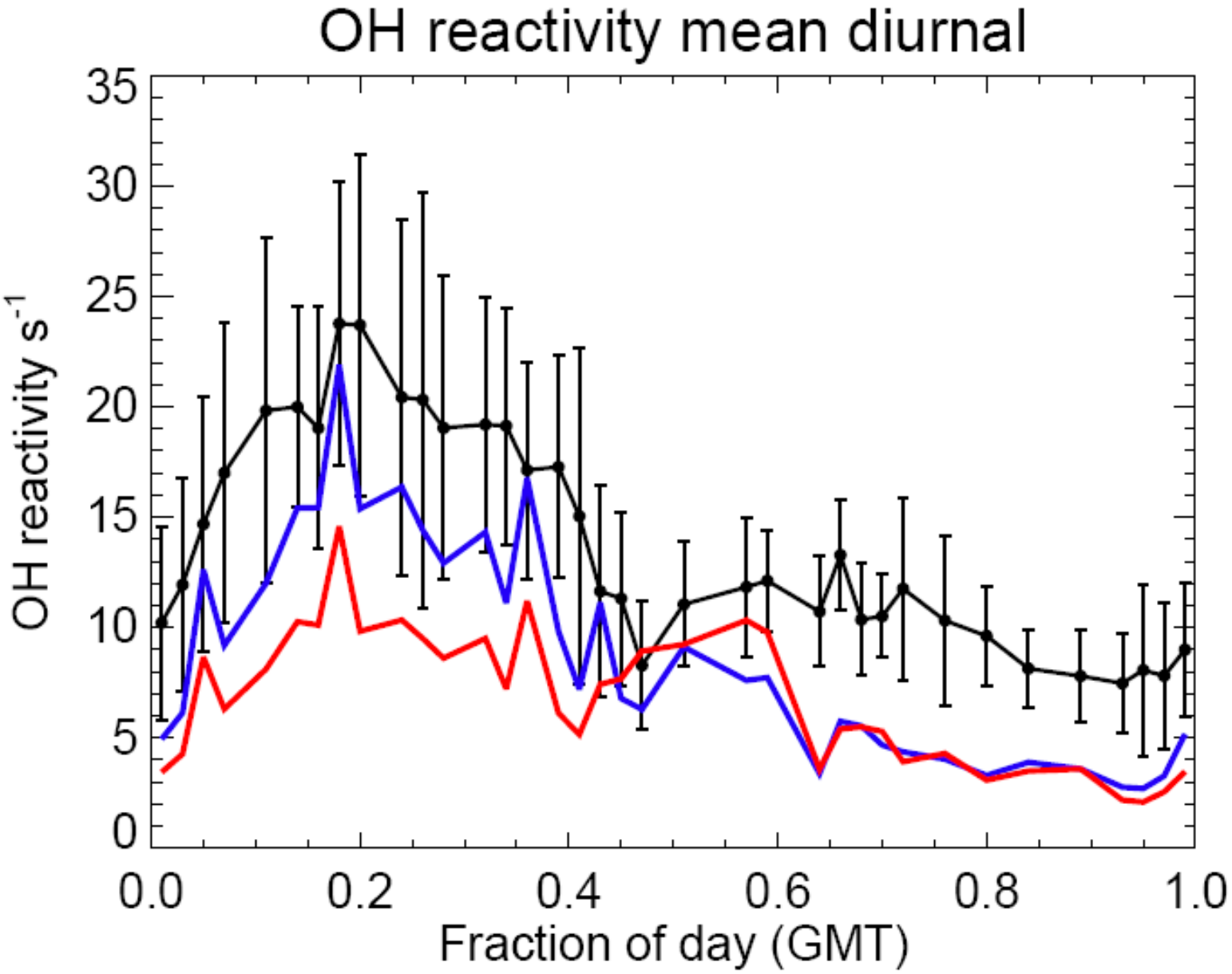

OH reactivity during OP3

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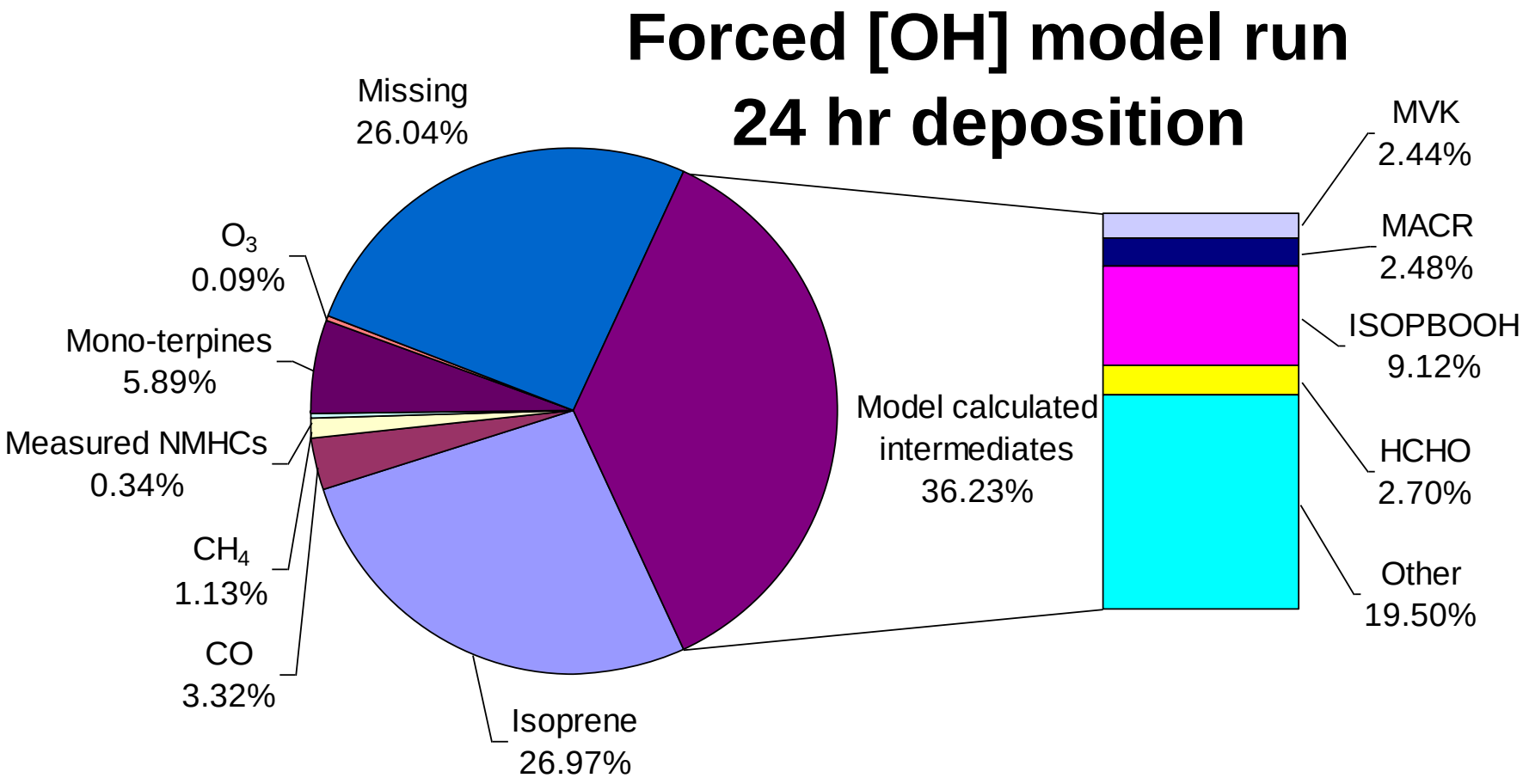

OH reactivity during OP3

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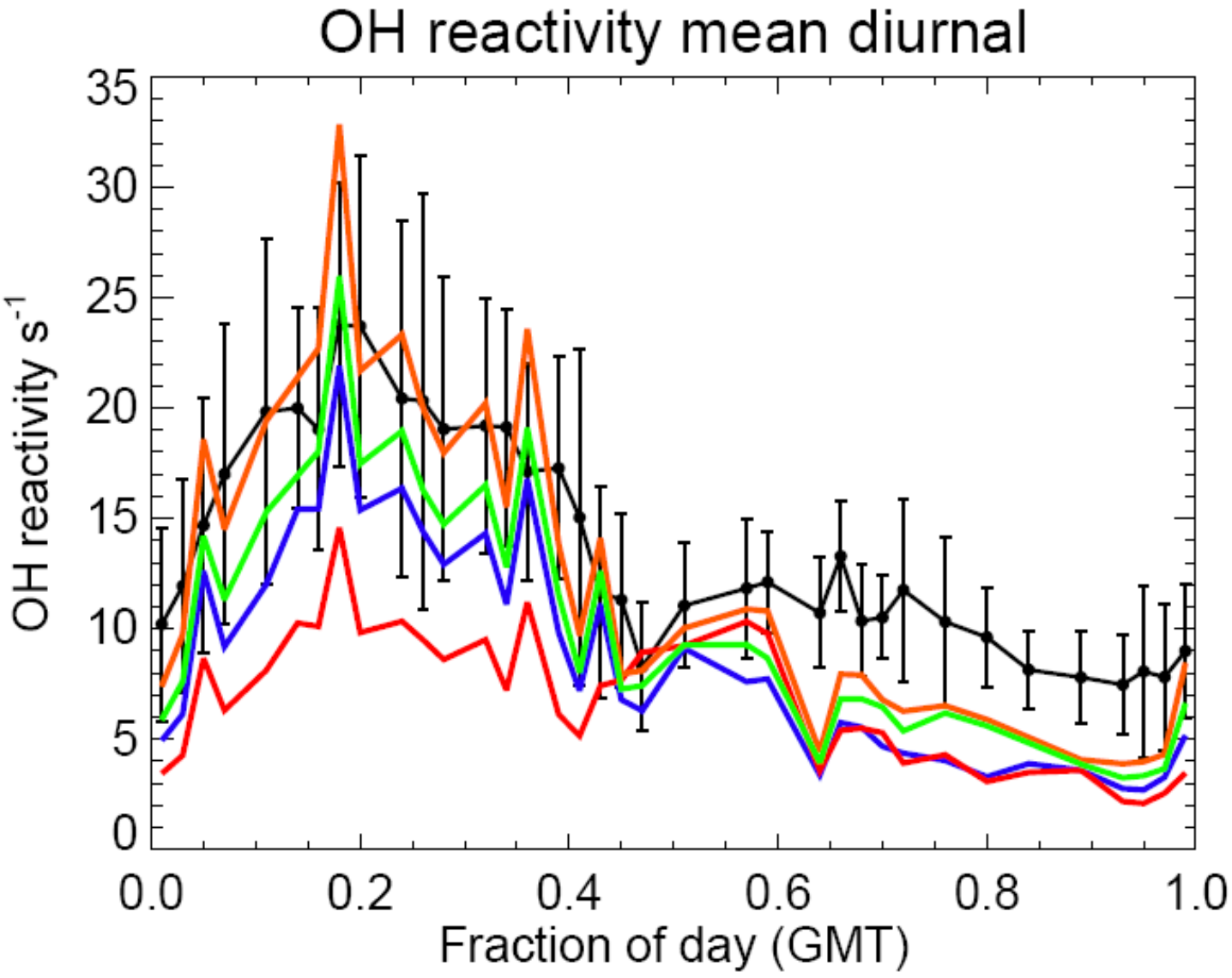

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OH reactivity during OP3

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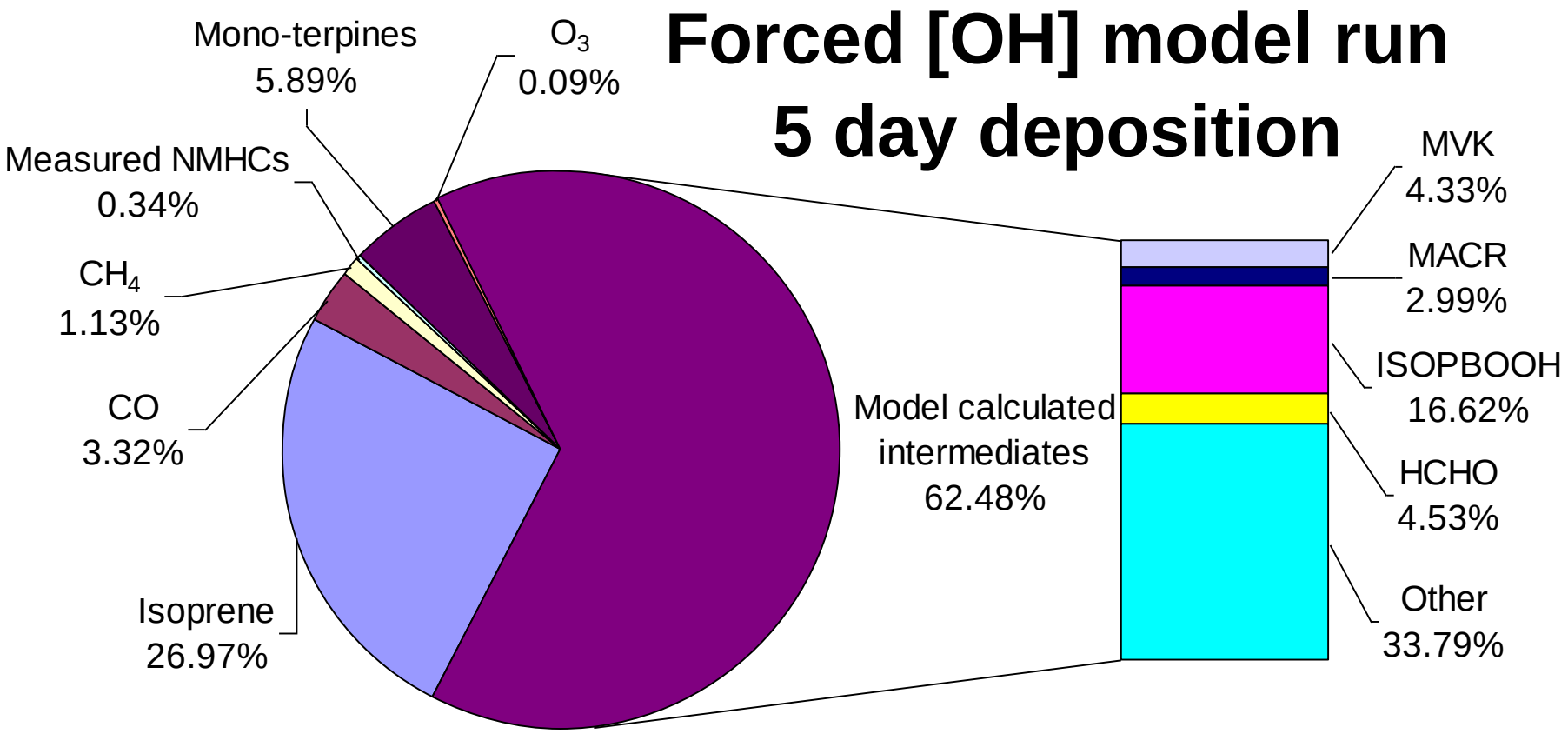

OH reactivity during OP3 - Summary

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- OH reactivity was measured over 2 weeks during OP3, with average daily reactivity peaking at ~23.7 ± 7.7 s^{-1}.
- Base model underpredicts day time reactivity by ~51%, consistent with other studies in low NO_x, high reactivity environments.
- Increasing [OH] to observed levels improves calculated reactivity, highlighting importance of isoprene oxidation products, but still underpredicting by 26%.
- Reducing the lifetime with respect to physical loss of intermediates from 24 hrs to 5 days results in the observed OH reactivity being reproduced.
- Poorly constrained oxidation products of isoprene chemistry (such as hydroperoxides, epoxides and carbonyls) may provide a significant sink for OH.