

OH reactivity in a south east Asian tropical rainforest

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1. Introduction

- OH is the dominant daytime oxidant in the troposphere.
- The largest contribution to the global oxidation capacity is from the tropics, with around 80% of the global CH₄ removal occurring in the tropical troposphere.¹
- In order to understand variations in OH radical concentrations both source and sink terms must be understood.
- The overall sink of OH is currently poorly constrained. Observations of total OH reactivity enable actual OH losses to be quantified.
- Tropical forests are responsible for almost half of all biogenic VOC emissions into the atmosphere.²
- OH reactivity observations were made in a tropical forest as part of the Oxidant and Particle Photochemical Processes (OP3) field study in Borneo during 2008.



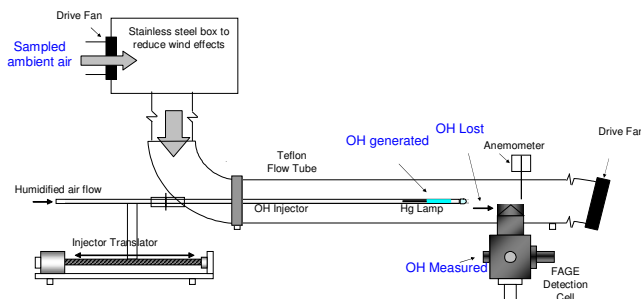
Field site within the tropical rainforest during the OP3 campaign, Sabah, Borneo.

2. The Leeds OH reactivity instrument

- OH reactivity (k_{OH}) is the pseudo 1st order rate coefficient for loss of OH in ambient air - a direct measurement of the total OH sinks.

$$k_{OH} = \sum k_{OH+VOC}[VOC] + k_{OH+CO}[CO] + \dots$$

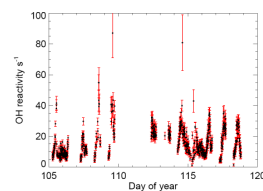
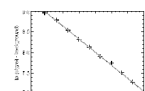
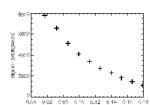
- The University of Leeds OH reactivity instrument³
 - OH is made in the centre of a turbulent flow of ambient air
 - The movable OH injector allows the residence time to be changed
 - OH is detected via Fluorescence Assay by Gas Expansion (FAGE)
 - A plot of $\ln(\text{OH signal})$ against residence time yields k_{OH}



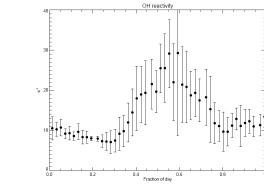
$$-\frac{d[OH]}{dt} = (k'_{OH} + k'_{physical})[OH]$$

$$\ln[OH]_t = -(k'_{OH} + k'_{physical})t + \ln[OH]_0$$

An exponential OH decay is observed with the rate of change of OH being equal to the OH concentration multiplied by the measured OH loss rate, which is a combination of the chemical loss rate and the rate of loss of OH to the walls of the flow tube. A plot of $\ln(\text{OH signal})$ against time yields a gradient equal to the total rate coefficient for OH loss.



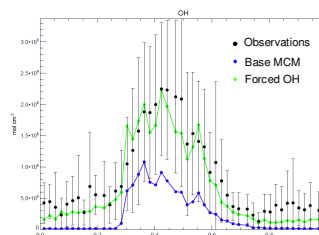
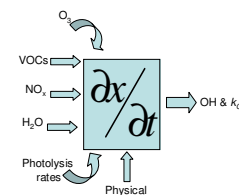
Time series of the OH reactivity observations made during OP3. Error bars in red indicate $\pm 1\sigma$ measurement uncertainty.



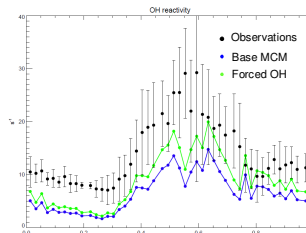
Campaign average diurnal profile of observed OH reactivity. The variability bars indicate $\pm 1\sigma$ standard deviation of the observations within each 30 minute time bin.

3. Can we explain the observed reactivity?

- An observationally constrained box model, using the full MCM chemistry scheme, has been used to interpret the observations of OH reactivity made during OP3.

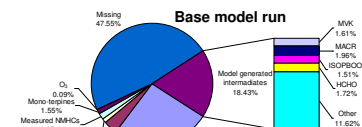


Observed [OH] (black), with variability bars indicating $\pm 1\sigma$ standard deviation. Base model calculated [OH] (blue) shows a clear underestimation of observations.¹³ Model calculated [OH] in which a fictional OH source has been introduced (green).

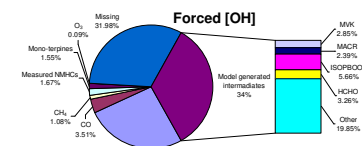


Observed OH reactivity (black) compared with model calculations. Base MCM chemistry scheme (blue) and MCM chemistry with OH forced to be of a similar level to observations (green).

- The observationally constrained MCM chemistry scheme can not explain the OH concentrations observed during OP3. The effect of this on OH losses has been investigated by forcing the modelled [OH] to approximately match observed levels.



Pie charts show missing OH reactivity and contributions from observed and unconstrained species within the model.



- Base model underpredicts OH reactivity at midday by ~48%, and peak [OH] by ~50%, a common feature in low NO_x and high isoprene locations.^{8,13}
- Introducing a fictional OH source to force modelled [OH] to approximately match observed [OH], reduces model underprediction of OH reactivity to ~32%.
- Model generated oxidation products of primary VOCs, in particular isoprene, are found to be important sinks for OH.

4. Conclusions

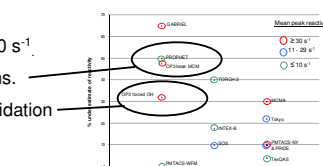
- OH reactivity observations were made in a tropical rainforest as part of the OP3 campaign, with an average daily maximum of ~30 s⁻¹.
- MCM chemistry scheme constrained with supporting observations cannot explain the observed OH reactivity or OH concentrations.
- Increasing [OH] to approximately match observed levels improves calculated reactivity, highlighting importance of isoprene oxidation but still underpredicting by 32%.
- Unmeasured oxidation products, such as peroxides, are important OH sinks and currently poorly constrained.
- Laboratory work is needed to address uncertainties in isoprene oxidation scheme, and confirm or disprove theoretical studies.

5. Acknowledgements

> University of Manchester for water vapour observations
 > J. Hopkins & C. Jones (University of York) for GC-FID NMHC observations
 > J. Lee & S. Moller (University of York) for O₃, NO_x & CO observations
 > Malaysian collaborators for their help during the project
 > NERC for funding

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Summary of model underprediction of OH reactivity for past field campaigns⁴⁻¹² as a function of anthropogenic influence on sampled air masses.