

OH reactivity in a south east Asian tropical rainforest

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1. Introduction

- OH is the dominant daytime oxidant in the troposphere.
- OH dependence on sunlight and water vapour results in the largest contribution to the global oxidation capacity being from the tropics, with around 80% of the global CH₄ removal occurring in the tropical troposphere¹.
- 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.
- Tropical forests are responsible for almost half of all biogenic VOC emissions into the atmosphere².
- OH reactivity observations were made in a tropical forest as part of the Oxidant and Particle Photochemical Processes (OP3) field study to Borneo during 2008.



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

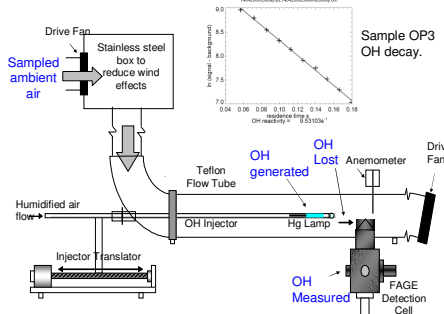
2. OH reactivity measurements during OP3

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

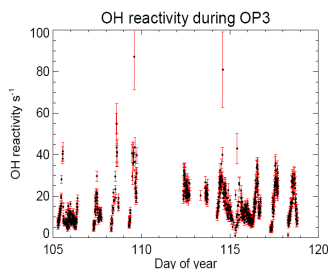
$$k_{OH} = \sum k_{OH+VOC}[VOC] + k_{OH+CO}[CO] + \dots$$

- The University of Leeds OH reactivity instrument³

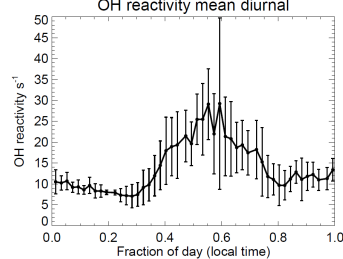
- OH is made in the centre of a turbulent flow of ambient air
- The movable OH injector allows the residence time to be changed
- OH is detected via Fluorescence Assay by Gas Expansion (FAGE)
- A plot of $\ln(\text{OH signal})$ against residence time yields k_{OH}



Schematic of the Leeds OH reactivity instrument



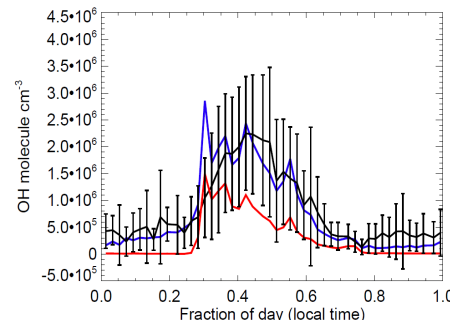
Time series of the OH reactivity observations made during OP3. Error bars in red indicate 1-sigma measurement uncertainty.



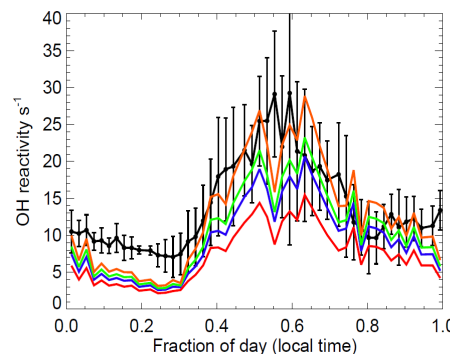
Campaign average diurnal profile of observed OH reactivity. The variability bars indicate ± 1 standard deviation of the observations within each 30 minute time bin.

3. Can we explain the observed reactivity?

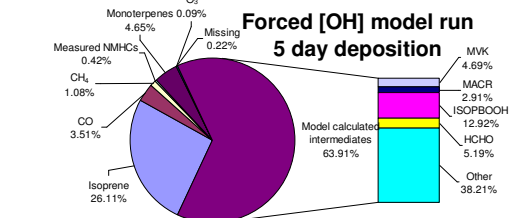
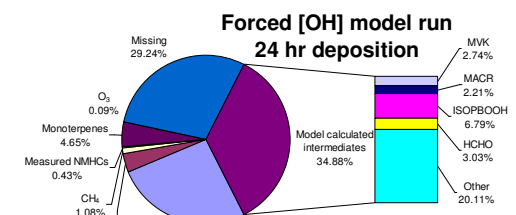
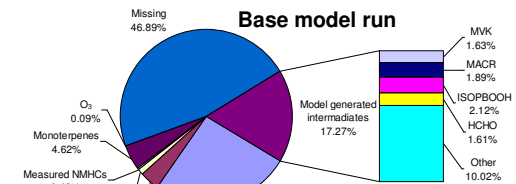
- An observationally constrained box model, using the full MCM chemistry scheme, has been used to interpret the observations of OH reactivity made during OP3.



Observed [OH] (black), with variability bars indicating ± 1 standard deviation of the observations. Base model calculated [OH] (red) shows a clear underestimation of observations¹³. Model calculation where a fictional OH source has been introduced to increase [OH]



Observed OH reactivity (black) compared with model calculations. Base model with 24 hour physical loss (red). Model calculations where [OH] was forced to observed levels with physical loss rates of: 24 hours (blue), 2 days (green) and 5 days (orange).

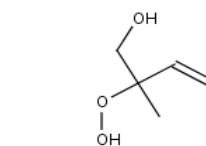
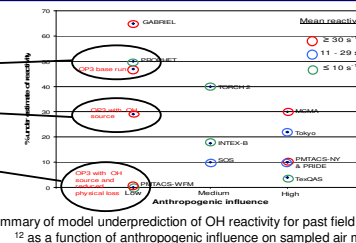


Pie charts show missing OH reactivity and contributions from observed and unconstrained species within the model.

- Base model underpredicts noon OH reactivity by $\sim 47\%$, and peak [OH] by $\sim 85\%$, a common feature in isoprene rich locations^{8,13}.
- Introducing a fictional OH photolysis source to match observed [OH], reduces model underprediction of OH reactivity to $\sim 29\%$.
- Reactivity found to be sensitive to physical loss rate of un-constrained oxidation products. A 5 day lifetime with respect to physical loss results in the forced OH model reproducing the observed OH reactivity during the day.

4. Conclusions

- OH reactivity was measured over 2 weeks during OP3, with average daily reactivity peaking at $\sim 26.7 \pm 7.7 \text{ s}^{-1}$.
- Base model underpredicts day time reactivity by $\sim 47\%$, 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 29%.
- Reducing the lifetime with respect to physical loss of intermediates from 24 hrs to 5 days results in the observed OH reactivity being reproduced.
- Missing OH sink may be from poorly constrained isoprene oxidation products or unmeasured primary emitted species.
- Unmeasured / poorly understood oxidation products of isoprene chemistry (such as hydroperoxides, epoxides and carbonyls) may provide a significant sink for OH.



Concentrations of unmeasured hydroperoxides, such as ISOPBOOH (above), are a major uncertainty in the OH₂ budget.

7. Acknowledgements

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

University of Manchester for water vapour observations
Malaysian collaborators for their help during the project
NERC for funding

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