Field measurements and modelling of OH, HO_2 and OH reactivity in low NO_x environments

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Introduction

The abundance of OH controls the photochemical turnover rate and the lifetimes of trace gases in the atmosphere. Field measured concentrations of OH and HO_2 radicals, and comparison with the results of box model simulations, for example using the detailed *Master Chemical Mechanism* (MCM), provide a sensitive test of our understanding of the rates of atmospheric processes. Field measurement of OH reactivity enables quantification of sinks for OH which are missing in models. Here we present results and model calculations from recent field experiments in a range of low NO_x environments

Technique

Field observations of the radicals were made using Laser Induced Fluorescence (LIF) spectroscopy at low pressures (FAGE technique):

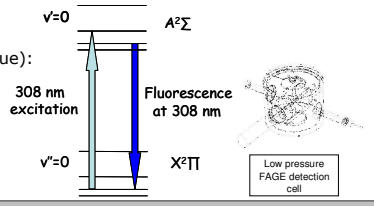
⇒ Ambient air drawn into a low pressure cell (< 4 Torr)

⇒ Laser beam passed perpendicular to air stream

⇒ On resonance 308 nm OH fluorescence detected by PMT

⇒ HO_2 titrated to OH by reaction with NO

⇒ OH reactivity measured in a turbulent flow reactor, with a movable OH injector coupled to a LIF detector

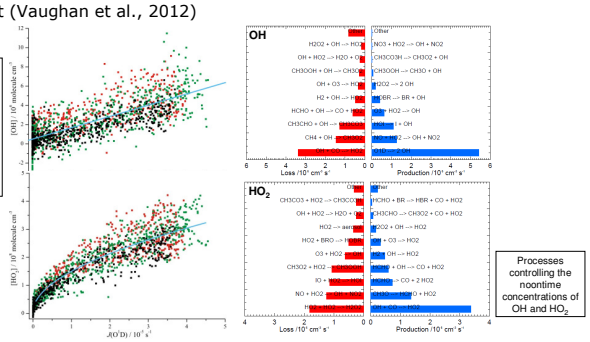


1. Seasonal Oxidants Study

• Tropical regions have high HO_x production rates due to high solar irradiance, warmth and humidity

⇒ Estimated that ~ 80 % of global CH_4 oxidation occurs in the tropics (Bloss et al. 2005)

• SOS took place at the Cape Verde Atmospheric Observatory in 2009 and provided the first seasonal measurements of both OH and HO_2 in a tropical marine environment (Vaughan et al., 2012)



• The summer months typically exhibited highest concentrations of OH and HO_2

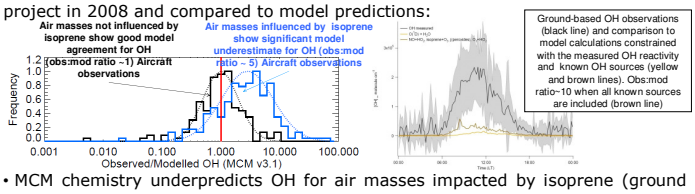
• OH and HO_2 exhibited a strong correlation with the rate of ozone photolysis

• Radical concentrations were sensitive to small concentrations of halogen oxides ([IO] = 1.4 ppt, [BrO] = 2.5 ppt observed at the site using DOAS)

2. Oxidant and Particle Photochemical Processes

• In tropical forested environments where biogenic VOC emissions are high and NO_x concentrations are low, low OH concentrations and extended CH_4 lifetimes are predicted due to rapid reactions of OH with sink species such as isoprene (Lelieveld et al., 2002)

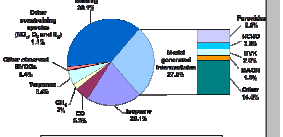
• To assess the oxidative capacity of tropical forests, observations of OH, HO_2 and OH reactivity in and above the Borneo rainforest were made as part of the OP3 project in 2008 and compared to model predictions:



• MCM chemistry underpredicts OH for air masses impacted by isoprene (ground level and aircraft) suggesting missing OH sources in the model (Stone et al., 2011, Whalley et al., 2011)

• HO_2 concentrations are well replicated suggesting that the missing chemistry does not generate HO_2

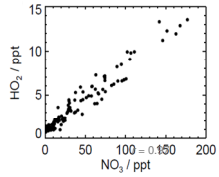
• The model underestimates the measured OH reactivity; this discrepancy is reduced if the lifetimes of modelled intermediates is extended demonstrating the importance of the VOC oxidation products



3. ROle of Nighttime chemistry in controlling the Oxidising Capacity of the AtmOsphere

• Night time chemistry, driven primarily by the nitrate radical NO_3, plays a significant role in governing the composition of the troposphere

• RONOCO represents the first aircraft-based night-time measurements of OH, HO_2 and NO_3. Flights were made during summer and winter around the UK and aimed to assess the importance of OH and HO_2 at night and the processes controlling radical concentrations



HO_2 vs NO_3 during a nighttime flight

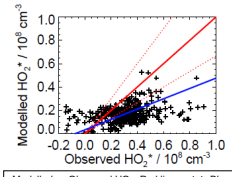
• $[HO_2]$ was strongly correlated to $[NO_3]$

• OH was not measured above the limit of detection of the instrument (6.4 – 18 x 10^5 molecule cm^{-3})

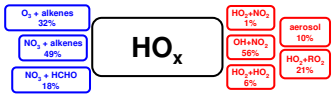
• Tendency for model to under-predict $[HO_2]$

• NO_3 important for radical initiation and radical propagation

• Models need to include appropriate NO_3 + alkene and NO_3 + RO_2 chemistry to model nighttime oxidation chemistry with success



Modelled vs Observed HO_2. Red line = 1:1; Blue line = line of best fit



Schematic highlighting main reactions controlling $[HO_x]$ at night

4. Hill Cap Cloud Thuringer-2010

Photo of FAGE instrument at the Schmucke site during a cloud event. Radicals were sampled from the top of the 22 m tower alongside ancillary measurements

• Clouds occupy ~ 15% of the troposphere and can potentially reduce gas-phase oxidation by efficient uptake of radicals into droplets (Lelieveld & Crutzen, 1990, 1991; Tilgner et al., 2005).

• Gas-phase measurements of OH and HO_2 were made at Mt. Schmucke, Thuringer Wald both in-cloud and out of cloud and observations have been compared with simple model predictions:

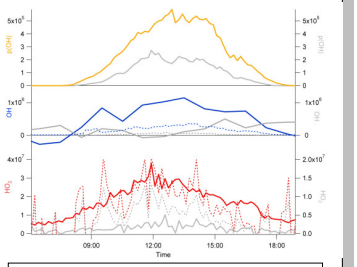
•~ 65% reduction in $J(O^1D)$ on average during cloud events

• low concentrations of OH were observed out of cloud, but concentrations were below the limit of detection in-cloud

•~ 90% reduction in $[HO_2]$ during cloud events observed on average

•Model is able to replicate $[HO_2]$ out of cloud but over-estimates $[HO_2]$ in-cloud

• To replicate $[HO_2]$ in-cloud observations, a first order loss rate of HO_2 to clouds = 0.2 s^{-1} is needed suggesting that heterogeneous processes in clouds do perturb gas-phase radical chemistry



Average diurnal of j(OH), [OH] and $[HO_2]$ during cloud events (grey) and out of cloud (colour). Model estimates, in cloud (grey dash) and out of cloud (colour dash) for OH and HO_2 are also shown

6. References

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7. Acknowledgements

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