

Field measurements and modelling of OH, HO₂ and OH reactivity in low NO_x environments

Lisa Whalley,^{1,2} Trevor Ingham,^{1,2} Daniel Stone,¹ Stewart Vaughan,¹ Hannah Bunyan,¹ Ingrid George,³ Peter Edwards,⁴ Mat Evans^{5,6} and Dwayne Heard^{1,2,*}

¹School of Chemistry, University of Leeds, Woodhouse Lane, Leeds, LS2 9JT, UK

²National Centre for Atmospheric Chemistry, University of Leeds, Woodhouse Lane, Leeds, LS2 9JT, UK

³US Environmental Protection Agency, 109 TW Alexander Drive, Durham, NC 27709, USA

⁴ESRL, National Oceanic and Atmospheric Administration, 325 Broadway, Boulder, CO 80305-3328, USA

⁵Department of Chemistry, University of York, York, YO10 5DD, UK

⁶National Centre for Atmospheric Chemistry, University of York, York, YO10 5DD, UK

* Corresponding author: d.e.heard@leeds.ac.uk

The abundance of OH controls the photochemical turnover rate and the lifetimes of trace gases in the atmosphere. Field measured concentrations of OH and HO₂ radicals, and comparison with the results of box model simulations, for example using the detailed *Master Chemical Mechanism*, 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 not captured in models. This paper will present results and model calculations from recent field experiments in a range of low NO_x environments, namely:

(a) Seasonal OH and HO₂ measurements over a whole year at Cape Verde in the remote Atlantic Ocean (1, 2), where a strong correlation with the rate of ozone photolysis and perturbations from halogen chemistry were observed, (b) Ground and aircraft OH, HO₂ and OH reactivity measurements in and above the Borneo rainforest (3,4), where there are significant missing sources and sinks of OH (Figure 1) and where recycling of OH is needed to give agreement with models (Figure 2), (c) Night-time aircraft measurements over the UK, where significant HO₂ levels were observed, strongly correlating with NO₃ radicals, indicating closely coupled chemistry, and (d) OH and HO₂ measurements in clouds during a hill cap cloud study in Germany, where in cloud HO₂ concentrations could only be modelled successfully if there is heterogeneous processing on the surface of aerosols.

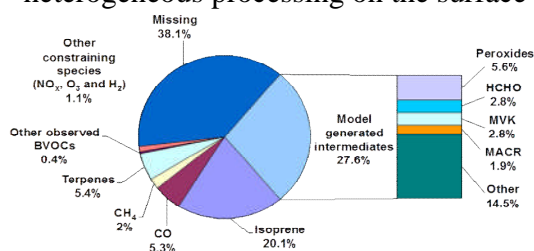


Figure 1. Percentage loss of OH in the Borneo rainforest via reaction with measured sinks and with intermediates calculated by the Master Chemical Mechanism. Note the large fraction of missing reactivity.

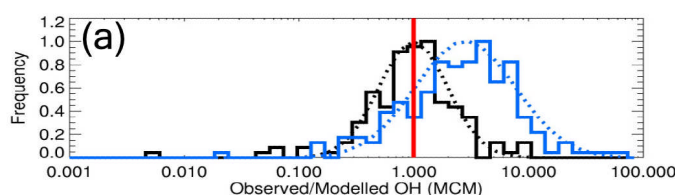


Figure 2. Ratio of measured (BAE146 aircraft) to modeled (MCM) OH concentrations above the Borneo rainforest for isoprene < 15 ppt (black) and for isoprene > 15 ppt (blue). ~ 3 OH molecules need to be recycled in order to bring the modeled OH into line with the measurements (4).

References

- (1) Vaughan, S. *et al. Atm. Chem. Phys.* **2012**, 12, 2149-2172.
- (2) Whalley, L.K. *et al. Atm. Chem. Phys.* **2010**, 10, 1555-1576.
- (3) Whalley, L.K. *et al. Atm. Chem. Phys.* **2011**, 11, 7223-7233.
- (4) Stone, D. *et al. Atm. Chem. Phys.* **2011**, 11, 6749-6771.