



Measurements of OH and HO₂ Radicals and OH Reactivity at Tropical Locations Using Laser-Induced Fluorescence Spectroscopy

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The OH radical is the dominant daytime oxidant in the atmosphere. Together with the closely coupled HO₂ radical, these two species (termed HO_x) play an important role in determining the composition of the atmosphere. Tropical latitudes are active regions of atmospheric chemistry due to high solar radiation, humidity and temperature. For these reasons, field measurements of HO_x in the tropics are crucial to improve understanding of atmospheric chemistry through model – measurement comparisons. Due to the low number of HO_x measurements in the tropics, these comparisons are sparse. An aircraft campaign over the pristine Amazon rainforest found HO_x concentrations to be high^{1,2}. It has been proposed that this is due to a previously overlooked OH recycling mechanism via the oxidation of isoprene^{1,2}. The need to determine if this is ubiquitous across tropical rainforest regions is necessary.

The Leeds FAGE instrument was deployed at the Bukit Atur Global Atmospheric Watch Station, Borneo (5.0°N, 117.8°E) from April – July 2008 as part of the OP3 project (Oxidant and Particle Photochemical Processes above a South-East Asian tropical rainforest) to measure OH and HO₂ concentrations and the OH chemical lifetime by Fluorescence Assay by Gas Expansion (FAGE). These measurements represent the first ground based [HO_x] measurements in a tropical rainforest. Chemical activity differed significantly throughout the measurement period. HO_x concentrations were elevated in July (average peak [OH] = 5.3×10^6 molecule cm⁻³) compared to April (average peak [OH] = 2.5×10^6 molecule cm⁻³), attributed to higher OH sinks in April. Measurements of the OH chemical lifetime can be used to quantify unknown OH sinks. The OH chemical lifetime displayed a diurnal cycle that correlated with isoprene concentrations. At this site isoprene represents the major OH loss route but there are significant unknown fractions. Model calculations result in an under prediction of HO_x when measured sinks are included, indicating a missing HO_x source. Both OH and HO₂ were observed at night.

Measurements of HO_x at the Cape Verde Atmospheric Observatory (16.9°N, 24.9°W) were made from May – June 2007 as part of the RHaMBLe (Reactive Halogens in the Marine Boundary Layer) programme. The site is located adjacent to the ocean with an absence of macro algae, providing conditions analogous to open ocean, clean marine air. However, background tropical conditions were not dictated by simple chemistry. Peak OH and HO₂ concentrations were 9×10^6 molecule cm⁻³ and 6×10^8 molecule cm⁻³, respectively. HO₂ was observed at night between $5 - 20 \times 10^6$ molecule cm⁻³. Modelling studies determined oxygenated-VOCs and halogen chemistry to play an important role in HO_x chemistry.

A comparison of HO_x measurements at tropical open ocean and tropical rainforest locations shows that HO_x chemistry varies greatly throughout the tropics. Higher HO_x sinks in tropical rainforest environments result in a decrease of HO_x compared to the tropical open ocean.

1. Lelieveld, J., T. M. Butler, et al. (2008). Atmospheric oxidation capacity sustained by a tropical forest, *Nature*, 452(7188): 737-740.
2. Martinez, M., Harder, H., et al. (2008). Hydroxyl radicals in the tropical troposphere over the Suriname rainforest: airborne measurements, *ACPD*, 8, 15491-15536.