

Field measurements of free radicals to improve understanding of fundamental chemical processes in the troposphere

Dwayne E Heard

University of Leeds, United Kingdom

Author list (excluding presenting author)

Abstract

Chemical oxidation in Earth's atmosphere proceeds via chain reactions mediated by free radicals, removing natural and anthropogenic emissions. The OH radical removes methane and initiates the formation of secondary pollutants, for example ozone, nitrogen dioxide and secondary organic aerosols. The short lifetime of radicals means that comparison of field measurements of their concentrations with calculations from numerical models constitutes one of the best ways to evaluate how well we understand the fundamentals of chemical mechanisms in the atmosphere. At Leeds, we use a box model which utilizes the detailed *Master Chemical Mechanism*, containing ~ 7,000 chemical species and ~17,000 reactions to describe the complete oxidative degradation of 135 emitted volatile organic compounds. The presentation will show free radical measurements using the FAGE technique and model comparisons for environments which span an extremely wide range of NO_x, from the marine boundary layer (MBL) of the tropical Atlantic Ocean, to Beijing, a megacity of more than 20 million inhabitants, and from the roof-of-the-world at almost 5000 m on the Tibetan plateau. Comparison between measurements of OH, HO₂, RO₂ and OH reactivity and model calculations highlight gaps in our understanding of fundamental chemical processes both in the gas-phase and at aerosol surfaces. In the clean tropical MBL, around 20% the OH reactivity is unaccounted for, halogen chemistry influences both the lifetime of methane and ozone destruction, and an important loss of HO₂ is via heterogeneous uptake. In winter in Beijing, significant OH concentrations are observed in haze events, with photolysis of HONO generated on aerosol surfaces completely dominating OH production. In summer in Beijing, there are significant missing OH sinks and sources, and model comparisons with HO₂ and RO₂ measurements as a function of NO_x reveal inadequacies in the model description of the chemistry and kinetics of highly complex RO₂ species.

Early Career Scientist

NO, I am not an early career scientist.

IGAC Activities

TOAR: Tropospheric Ozone Assessment Report

IGAC Regional Working Groups