



Global Modelling of the total OH reactivity: validation against measurements and atmospheric implications of the ‘missing’ sink

Valerio Ferracci (1), Alexander T. Archibald (1,2), John A. Pyle (1,2)

(1) Department of Chemistry, University of Cambridge, Cambridge, United Kingdom (vf257@cam.ac.uk), (2) National Centre for Atmospheric Science (NCAS), Cambridge, United Kingdom

The removal of most trace gases emitted into the atmosphere is primarily initiated by reaction with the hydroxyl radical, OH. A number of field campaigns over the last two decades have observed the presence of a “missing” sink of the OH radical in a variety of regions across the planet, from urban areas to remote forests: comparison of the direct measurements of the OH loss rate, also known as total OH reactivity, with the sum of individual known OH sinks (obtained *via* the simultaneous detection of species such as volatile organic compounds and nitrogen oxides) indicated that, in some cases, up to 80% of the total OH loss rate was unaccounted for. The implications of this finding are significant, as a potentially major OH sink operating in the atmosphere is not currently accounted for in atmospheric models: the presence of an additional OH sink might, for instance, lead to an increase in the atmospheric lifetime of a number of trace species, including high-impact greenhouse gases such as methane.

The only modelling of the total OH reactivity is currently performed on a regional scale; a thorough assessment of the impact of the missing sink on the chemistry and climate of the planet by global modelling is therefore highly desirable. In this work a chemistry-climate model (the Met Office’s Unified Model with the United Kingdom Chemistry and Aerosols scheme, UM-UKCA) was used to calculate the total OH reactivity at the planetary boundary layer. The model output was validated against available field measurements to verify that the *known* OH sinks observed in the field were reproduced correctly by the model: a good agreement was found between the data from more than 30 field campaigns and the model output. Following this, the effects of introducing novel OH sinks in the chemistry scheme were investigated. The first step was the introduction in the model of the newly characterised reactions of peroxy radicals (RO₂) with OH, the kinetics and products of which have only recently been studied in the laboratory. Results from the UM-UKCA model show that reaction with RO₂ might represent a non-negligible OH sink in remote environments, but cannot reconcile field measurements of the total OH reactivity with the sum of the individual sinks. To address this, an unspecified additional sink was added to the model in a series of simulations reproducing different scenarios (*e.g.*, different OH recycling probabilities through the oxidation of the additional sink) with a view to establishing the impact of the additional OH sink on the oxidative capacity of the lower atmosphere.