Geophysical Research Abstracts
Vol. 17, EGU2015-11867, 2015
EGU General Assembly 2015

Understanding HONO concentrations in London, its role as a hydroxyl radical source and the impact on summertime ozone production

Lisa Whalley (1,2), James Lee (3,4), Daniel Stone (1), Jacqueline Hamilton (3), Rachel Holmes (3,4), James Hopkins (3,4), Sebastian Laufs (5), Jörg Kleffmann (5), Dwayne Heard (1,2)

(1) University of Leeds, School of Chemistry, Leeds, United Kingdom (d.e.heard.leeds.ac.uk), (2) National Centre for Atmospheric Science, University of Leeds, Leeds, United Kingdom, (3) University of York, Chemistry Department, York, United Kingdom, (4) National Centre for Atmospheric Science, University of York, York, United Kingdom, (5) Physikalische und Theoretische Chemie / FB C, Bergische Universität Wuppertal (BUW), Gaußstr. 20, 42119 Wuppertal, Germany

Understanding the chemistry of free-radicals in the atmosphere is necessary to understand the lifetime of primary pollutants and the production of secondary pollutants, such as ozone and organic aerosol. In the urban environment, field observations of HONO have revealed elevated concentrations persisting throughout the day and subsequent modelling studies have identified HONO as the major OH precursor. Attempts to reproduce the strong daytime HONO signature in models, however, have revealed that the currently known chemistry is unable to account for the levels observed.

Here we present simultaneous measurements of OH, HO_2, RO_2, OH reactivity and HONO made during the Clean Air for London project in the summer of 2012. HONO concentrations were observed to build up throughout the night, with concentrations exceeding 2 ppbV on several nights. Daytime concentrations were lower, but $\sim$ 300 pptv was observed to persist throughout the afternoon. Box modelling studies, using the Master Chemical Mechanism (MCM) and constrained to the measured HONO, suggest that HONO makes up $\sim$85% of the primary OH budget and just under 50% of the total primary radical budget at noon. The model, however, significantly over-predicts the OH concentrations (and HO_2 and RO_2 concentrations) observed. Unconstrained to HONO, the basic model is unable to reproduce the measured HONO concentrations.

A source of HONO from the reaction of NO_2 with $HO_2.H_2O$, as postulated by Li et al. (Science, 344, 292, 2014), can enhance HONO concentrations considerably and also reduces the discrepancy between modelled and measured radicals by reducing the fraction of HONO acting as a net radical source. With this process included, the model still underestimates the observed HONO by $\sim$ 69% at noon, suggesting that this portion of HONO should still be considered as a primary radical source.

The net in-situ ozone production estimated from the measured peroxy radical concentrations and their reaction with NO is sufficient to account for the daily increases in ozone that were observed. Enhancements in radical concentrations on warm, sunny days, driven by two-fold enhancements in production from HONO and other photolytic sources, have been found to elevate ozone levels beyond the EU air quality recommendations.