



Understanding in-situ ozone production in the summertime through radical observations and modelling studies during the Clean air for London project

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Understanding the chemistry of free-radicals in the urban atmosphere is necessary to understand the lifetime of primary pollutants and the production of secondary pollutants, such as ozone and organic aerosol.

Here we will present measurements of OH, HO₂, HO₂* (HO₂ plus a contribution from larger alkane/alkene/aromatic related RO₂) and total RO₂ radicals taken during the ClearfLo campaign in central London in the summertime. A photostationary steady state (PSS) calculation of OH which considers measured OH reactivity as the sink term and the measured OH sources (of which HO₂+NO reaction and HONO photolysis dominates) compares well with the observed levels of OH. Comparison with calculations from a detailed box model utilising the Master Chemical Mechanism v3.2, however, highlights a substantial discrepancy between radical observations under lower NO_x conditions ([NO] < 2 ppbv) typically experienced during the afternoon hours and indicated that the model was missing a significant peroxy radical sink. Under elevated NO_x conditions ([NO] > 5 ppbv) the model and measurements were in much better agreement. Known radical termination steps, such as HO₂ uptake on aerosols, are not sufficient to reconcile the model measurement discrepancies alone and a PSS calculation of total RO₂ highlights that part of the discrepancy is caused by missing sinks for the higher peroxy radical species. This missing sink is most evident when the air reaching the site had previously passed over central London to the East and when elevated temperatures were experienced. We postulate that uncertainties in the degradation mechanism of complex biogenic and diesel related VOC species which were particularly elevated and dominated OH reactivity under these easterly flows, may account for the model measurement disagreement. This model uncertainty leads to significantly more ozone production predicted using modelled peroxy radical concentrations vs ozone production from peroxy radicals measured at times when NO concentrations are low.