



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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With greater than 50 % of the global population residing in urban conurbations, poor urban air quality has a demonstrable effect on human health. OH and HO₂ radicals, (collectively termed HO_x) together with RO₂ radicals, mediate virtually all of the oxidative chemistry in the atmosphere, being responsible for the transformation of primary emissions into secondary pollutants such as NO₂, O₃ and particulates.

Here we present measurements of OH, HO₂, partially speciated RO₂ (distinguishing smaller alkane related RO₂ from larger alkane/alkene/aromatic related RO₂), ClNO₂ and OH reactivity measurements taken during the ClearfLo campaign in central London in the summer of 2012. Comparison with calculations from a detailed box model utilising the Master Chemical Mechanism v3.2 tested our ability to reproduce radical levels, and enabled detailed radical budgets to be determined, highlighting for example the important role of the photolysis of nitrous acid (HONO) and carbonyl species as radical sources. Speciation of RO₂ enabled the break-down of ozone production from different classes of VOCs to be calculated directly and compared with model calculations. Summertime observations of radicals have helped to identify that increases in photolytic sources of radicals on warm, sunny days can significantly increase local ozone concentrations leading to exceedances of EU air quality recommendations of 60 ppbV.

The photolytic breakdown of ClNO₂ to Cl atoms can more than double radical concentrations in the early morning; although the integrated increase in radical concentrations over a 24 hr period in model runs when ClNO₂ photolysis is included is more modest. On average we calculate just under a 1 ppb increase in ozone due to the presence of ClNO₂ in London air.

OH reactivity was found to be greatest during morning and evening rush hours. Good agreement between the modelled OH reactivity and observations could be achieved when reactivity associated with model generated photo-oxidation products was considered in addition to the measured primary OH reactants. Carbonyl species such as formaldehyde, acetaldehyde and acetone have been identified as the VOC class dominating organic OH reactivity. As such, together with the direct radical source contribution by photolysis, these species dominate local ozone production in London. Modelling studies comparing the observed carbonyl concentrations with model predictions suggest that over 50% of the total concentration may be directly emitted and, hence, London's in-situ chemistry may be considered to contribute significantly to the ozone levels observed.