



Measurements of free radicals in a megacity during the Clean Air for London Project

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Free radicals control the photo-oxidative chemistry of the atmosphere, being responsible for the transformation of primary emissions into secondary pollutants such as NO_2 , O_3 , multifunctional species and particulates. Here we present measurements of OH, HO_2 and RO_2 radicals and OH reactivity recorded at North Kensington, Central London, during two Intensive Operational Periods (IOPs) of the Clear Air for London (Clearflo) project in the summer and winter of 2012. OH and HO_2 were measured using laser-induced fluorescence (LIF) spectroscopy at low pressure (the FAGE technique), and RO_2 was measured using the recently developed ROXLIF technique, which utilises an external flow-reactor interfaced to FAGE, and which is able to discriminate between HO_2 and organic peroxy radicals. Through control of reagent gases we are further able to provide a separate measurement of those RO_2 species which are known to give an interference for HO_2 measurements (namely alkene, aromatic and large-chain alkane derived RO_2). OH reactivity was measured using laser-flash photolysis combined with FAGE. Low concentrations of radicals were observed during the winter IOP, with mixing ratios of $[\text{OH}] \sim 0.04$ pptv, $[\text{HO}_2] \sim 0.4$ pptv, and $[\text{RO}_2] \sim 1.6$ pptv at noon, all displaying a negative correlation with NO. The photolysis of O_3 and subsequent reaction of $\text{O}(\text{1D})$ with H_2O vapour was only a minor contribution to radical production in winter, with photolysis of HONO a major radical source. The summer IOP coincided with the London Olympic Games, with a number of pollution events, with ozone peaking at 100 ppbv (exceeding EU air quality directives) and elevated radical concentrations (peak $[\text{OH}] \sim 0.14$ pptv, $[\text{HO}_2] \sim 4$ pptv, $[\text{RO}_2] \sim 6.4$ pptv) being observed. The net rate of ozone production was calculated from radical observations and agreed well with measured ozone production, suggesting that advection/dilution by continental air-masses was not playing a significant role in determining ozone concentrations in London at that time. The ability to partially speciate RO_2 enabled the contribution towards ozone production from different types of parent VOCs to be assessed. Steady-state analyses, using OH reactivity measurements to constrain the rate of loss of OH, gave reasonable agreement for $[\text{OH}]$ but an additional HO_2 sink was required to match $[\text{HO}_2]$. The photolysis of HONO and carbonyl species and the decomposition of PAN were the dominant sources of radicals in London in summer.