

Assessing the Oxidative Capacity of the Atmosphere: MCMA-2003 as a Case Study

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The current understanding of oxidative capacity is assessed in the polluted atmosphere, using the Mexico City Metropolitan Area (MCMA) as a case study. Measurements from the MCMA-2003 field campaign are used to constrain a photochemical box model in order to study the impact of primary HO_x radical production and RO_x radical cycling on photochemical ozone and the oxidation of VOCs that is relevant for secondary organic aerosol (SOA) formation. A preliminary assessment of the differences in average concentration profiles of OH and HO₂ from MCMA-2003 and MCMA-2006 is presented.

Time-resolved HO_x (OH and HO₂) radical fluxes were experimentally quantified from the photolysis of nitrous acid (HONO), formaldehyde (HCHO), ozone (O₃), acetaldehyde (CCHO), glyoxal (CHOCHO) and the reaction of alkenes with O₃. The Master Chemical Mechanism (MCMv3.1), constrained for these primary HO_x radical fluxes and radical sinks (103 VOC, NO, NO₂, CO, and SO₂), is used to calculate primary HO_x radical fluxes from other closed shell molecules, i.e. that form as VOC oxidation products. HCHO is found to be the most important source, dominating the overall HO_x radical flux shortly after sunrise. HO_x radical production from HCHO is matched only by O₃ photolysis during high O₃ days (and HONO in the early morning); photolysis of secondary products is estimated to contribute some 30% to primary HO_x radical fluxes at noontime. MCMv3.1 is used to identify the VOC precursors of photochemical HCHO. Noontime concentrations of HONO reached 120 ppt on some days, indicating a substantial source of daytime HONO is operative in Mexico City. HONO formation is separated into dark-, daytime- and photo-stationary steady state (PSS) sources.

MCMv3.1 is also used to predict OH, HO₂, RO₂ and RO concentrations (in sum termed RO_x). Measured and modeled concentrations are compared for the following case studies: HO_x-unconstrained, OH-constrained, HO₂-constrained, HO_x-constrained. For

the HO_x-unconstrained case, a significant under-prediction of OH and HO₂ radicals is observed in the early morning. This “missing reactivity” is highest during peak photochemical activity and leads to significant under-prediction of both VOC oxidation and ozone production throughout the day. The chain length, defined as the number of times a newly created OH radical will be regenerated via the RO_x cycle, is up to 15 times higher in the HO_x-constrained versus the unconstrained case in the early morning. A lack of oxidative capacity at high NO_x levels in the model results in under-prediction of ozone production and the formation of semi-volatile organic gases (SOG); the latter relevant for SOA formation. Among the gas-phase processes considered, the source for “missing reactivity” is most likely linked to uncertainties in our understanding of VOC chemistry.