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FIGAERO ToF CIMS measurements of chlorine photochemical activation by nitryl chloride chemistry at a semi-rural site in Beijing

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Severe pollution events across China pose a major threat to air quality and climate through the direct emission of pollutants, but also via the production of photochemically induced secondary pollutants. Nitryl chloride ($ClNO_2$), produced from heterogeneous reactions of dinitrogen pentoxide (N_2O_5) and aerosols containing chloride, is photolysed rapidly in sunlight and activates chlorine. Subsequent daytime oxidation via the chlorine atom can proceed orders of magnitude faster than that of the hydroxyl radical and therefore significantly perturb radical budgets and concentrations of ozone and secondary pollutants. Knowledge of the formation pathways, abundance and fate of these secondary pollutants, which can depend on $ClNO_2$ abundance, is not fully understood but is necessary to support abatement strategies which will efficiently account for both primary and secondary pollutants.

A Time of Flight Chemical Ionisation Mass Spectrometer (ToF CIMS) utilising the Filter Inlet for Gases and AEROsols (FIGAERO) was deployed in Changping, Beijing, during June and July, 2016 as part of an intercollaborative project to assess the photochemical smog in China. Concentrations of $ClNO_2$ regularly exceeded 500 ppt throughout the campaign and reached a maximum concentration of 2.8 ppb, whereas relatively low N_2O_5 concentrations were observed, indicating a rapid heterogeneous production of $ClNO_2$. Correlation of particulate chloride and carbon monoxide during the campaign suggests an anthropogenic chlorine source, also supported by high daytime Cl_2 concentrations. Observations of $ClNO_2$ desorptions using the FIGAERO suggest a possible unaccounted particulate reservoir of active chlorine in highly polluted regions. The persistence of $ClNO_2$ several hours passed sunrise significantly increases the atomic chlorine production rate throughout the day further perturbing standard daytime oxidation processes.

Simultaneous ToF CIMS measurements of Cl_2, $ClNO_2$, HCl, HOCl, OClO and $ClONO_2$ were implemented into steady state calculations using the Master Chemical Mechanism (MCM) to assess how the daytime activation of chlorine competes with OH as a dominant oxidant in this heavily polluted region. The reactions of atomic chlorine with VOCs are traced and assessed via the gas and particle phase measurements of chlorinated VOCs and supporting Proton Transfer Reaction Mass Spectrometer (PTR MS) VOC measurements. This provides the first high frequency measurements of unique tracers for chlorine atom chemistry, several of which are represented in the MCM, in both the gas and particle phase and enable the detailed assessment of their diurnal variation and importance for photochemical smog formation.