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Observations of inorganic and organic chlorine and their contribution to Cl radical concentrations in winter time Manchester, UK

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Oxidation in the troposphere governs the fate of trace gases and has an important influence on air quality and climate with many studies showing that Cl atoms from photolysis of nitryl chloride ($ClNO_2$) may contribute significantly to the total oxidising capacity (e.g. Osthoff et al., 2008; Bannan et al., 2015). $ClNO_2$ is considered the major precursor of chlorine radicals yet limited measurements of other inorganic and organic chlorine species reduce the certainty of their contribution to Cl radical concentrations.
We observe a range of signals indicating the detection of organic and inorganic chlorine compounds during winter in Manchester, UK including Cl2, HOCl, $ClNO_2$, $ClONO_2$, CnH2n-1OCl and CnH2n-1O_2Cl ($2 \leq n \leq 5$) compounds using a high resolution time of flight chemical ionisation mass spectrometer (ToF-CIMS) using iodide reagent ions. We do not detect low mass poly-chlorinated species such as dichloromethane (CH2Cl2) or chloroform (CHCl3) although the ToF-CIMS is sensitive to these species. Whilst most organic compounds exhibit behaviour suggestive of both primary and secondary sources, several correlate strongly with NO at times where the sampled air mass is dominated by local vehicular emission. The incidence of direct shortwave radiation is strongly coupled to the variation of daytime Cl2 concentrations on short time scales, as well as other photochemical organic species and ozone production.