



The Spatial Distribution of IO_x and impacts upon HO_x and NO_x at a Coastal Site

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The release of iodine compounds into the marine atmosphere can affect a number of aspects of atmospheric composition: Iodine species can participate in catalytic ozone destruction cycles, which may be augmented by bromine species; reactions of iodine compounds can perturb the OH:HO₂ and NO:NO₂ ratios, heterogeneous loss of reservoir compounds such as HOI and IONO₂ can lead to removal of HO_x and NO_x, and higher iodine oxides can contribute to the formation and/or growth of aerosol particles. Several recent field campaigns have investigated the impact of iodine chemistry upon atmospheric composition, at both coastal sites (e.g. Mace Head, Roscoff) and open ocean locations (e.g. Cape Verde). In this work, we focus upon understanding the effect of the spatial distribution of iodine emissions upon HO_x and NO_x levels at coastal sites, using new observations to re-evaluate previous field campaign data.

We present an analysis of results from two new instruments which measure point inorganic iodine species concentrations: A laser induced fluorescence (LIF) instrument for the detection of IO radicals, and a resonance fluorescence (RF) system for the detection of iodine atoms, and the total photolabile iodine content. Both instruments were deployed at Mace Head, Ireland during July-August 2007, during which period point measurements of IO (up to 34 ppt), I (up to 20 ppt) and total photolabile iodine content (up to 180 ppt I₂ equivalent; nighttime) were made at the shoreline site.

A detailed photochemical box model is employed in a lagrangian sense to simulate the evolving chemical composition resulting from the emission of significant amounts of molecular iodine from the intertidal zone exposed at low tide. The modelled inorganic iodine species (I₂, I, IO) are consistent with the levels measured by the LIF and RF systems. The model is used to explore the transient response of the NO_x and HO_x families at the Mace Head site to heterogeneous iodine emissions: The transit time between the intertidal iodine emission zone and the shoreline site where previous measurements of HO_x, NO_x etc. have been made (for example, during the NAMBLEX and ACSOE campaigns) is insufficient for steady-state to become established, although this assumption has been made in earlier model studies of such data. In this work, the model is used to explore the short-term perturbation of the HO_x and NO_x radical chemistry by the iodine emissions, considering the envelope of typical chemical and meteorological conditions encountered at Mace Head. The limitations arising from uncertainties in the iodine kinetics and photochemistry are quantified, and implications of the results for the interpretation of observations of HO_x and NO_x in similar coastal locations considered.