



A global inorganic source of reactive iodine to the marine lower atmosphere: field observations and laboratory studies

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Reactive iodine ($IO_x = I + IO$) in the marine boundary layer (MBL) can have a significant impact on the lifetime of oxidising species, by causing ozone destruction and changing the HO_x and NO_x partitioning, and can also contribute to new particle formation. Interest in measuring IO_x species in situ across the Pacific Ocean has been driven in the last few years by satellite observations of enhanced iodine monoxide (IO) column densities over the Pacific 'cold tongue' (Schönhardt et al., 2008), which suggested potential links between biogenic ocean emissions and climatically relevant atmospheric chemistry. Spatially and time-resolved MAX-DOAS and LP-DOAS observations of IO in the Pacific MBL have been reported very recently (Mahajan et al. 2012, Großman et al. 2012, Gómez Martín et al., 2013), indicating a constant and ubiquitous presence of IO_x . The IO mixing ratios in the Pacific are similar in variability and magnitude to those observed in other remote tropical locations, although generally lower. However, satellite observations of IO above the Pacific appear to be inconsistent with its surface spatial distribution and low mixing ratios.

In this paper we present new insights into the global oceanic source of reactive iodine, obtained by analysing correlations between different oceanic variables and IO_x and from new laboratory measurements where such variables are changed in a controlled manner. Similar to previous studies in the Atlantic Ocean (Mahajan et al., 2010, Jones et al., 2010), halocarbons cannot fully account for the IO_x observed in the Pacific. Moreover, enhanced IO mixing ratios are found over the oligotrophic parts of the ocean and during the warm season. Positive correlation of IO_x with sea surface temperature, salinity and iodide, and negative correlation with Chl-*a*, point to a ubiquitous inorganic iodine source. Deposition of O_3 to the sea surface and subsequent reaction with iodide in the interfacial layer, resulting in the release of both I_2 and HOI into the gas phase, is the most plausible explanation. Laboratory experiments have been carried out to quantify and characterise the flux of inorganic iodine precursors produced from this process, as a function of temperature, iodide concentration, ozone concentration, salinity, turbulence and organic species. The I_2 /HOI relative yield has been investigated by selective laser and broad band photolysis, and it has been found that HOI is the major iodine precursor under open ocean conditions. A kinetic model of the interfacial layer of the sea surface has been used to model the laboratory results, from which a parameterised function of the iodine flux has been derived. MBL 1 D modelling using this source function generates IO concentrations in agreement with observations (Carpenter et al., 2013).