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IO measurements in the marine boundary layer using laser-induced fluorescence spectroscopy

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The iodine monoxide (IO) radical plays an important role in the chemistry of the marine boundary layer (MBL), being formed by the reaction of ozone with iodine atoms generated by the photolysis of I_2 and photo-labile iodocarbons. IO is implicated in O_3 destruction, autocatalytic release of halogen species from the condensed phase, DMS oxidation and new particle formation. IO has previously been measured using LP-DOAS with absorption paths of several kilometers, which are associated with significant spatial averaging over the halogen source regions.

An *in situ* laser-induced fluorescence (LIF) technique has been developed to detect IO radicals in the MBL. An all solid-state laser operating at 445 nm is used to excite IO in the $A^2\Pi$(v'=2)-$X^2\Pi$(v"=0) electronic transition, with off-resonant fluorescence detected at 520.3 nm. The sensitivity of the instrument is calibrated using the photolysis of N_2O at 185 nm followed by the subsequent reaction of O atoms with CF_3I to generate IO concentrations between 10 – 150 pptv. The detection limit was determined to be 1.0 pptv for a 10 second integration period, with an uncertainty of $\sim$ 30%.

The instrument was successfully deployed in August/September 2006 during the RHaMBLE (Reactive Halogens in the Marine Boundary Layer) campaign in Roscoff, France. Located on a small jetty, the instrument measured significant levels of IO on 11 days, with up to 18 pptv observed. IO displayed a clear diurnal profile with a maximum at low tide, and lower concentrations were observed on some nights.