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Interpretation of In-Situ Measurements of Iodine Monoxide in Coastal Regions Using Laser-Induced Fluorescence Spectroscopy

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Iodine species are present in coastal and open ocean regions due to the release of I_2 and iodocarbons from macro and micro algae. The photolysis of these molecules yields iodine atoms, which react with ozone to produce iodine monoxide (IO). IO is involved in ozone depletion cycles, the partitioning of HO_x and NO_x, and the formation and growth of new particles.

A novel point source Laser Induced Fluorescence (LIF) instrument was deployed to measure IO in September 2006 at Roscoff, France as part of the Reactive Halogens in the Marine Boundary Layer (RHaMBLe) programme (1σ instrument uncertainty = 23%)^1. The maximum IO mixing ratio was 30 ± 7.1 pptV (10 s integration period, limit of detection = 1.4 pptV) at this semi-polluted coastal site (NO_x levels = 1 – 5 ppbV). The closest macroalgae beds known to strongly emit I_2 (laminaria) were $\sim$ 300 m from the LIF instrument. IO displayed a strong anti-correlation with tidal height which is consistent with previous studies. IO was also dependent on solar irradiation and meteorological conditions. The dominant source of IO at this site was the photolysis of I_2.

The measurements provided by this instrument aim to address the main uncertainties associated with iodine chemistry. Co-ordinated measurement of IO by point source (LIF) and spatially averaged (Long Path Differential Optical Absorption Spectroscopy) instruments confirm the presence of IO hotspots due to non-uniform macroalgae distribution at this location (resulting in a spatially variable I_2 source). The ratio of point source/spatially averaged IO is determined by meteorological conditions and distance of the instrument from macroalgae beds. Co-located point source I_2 (Broadband Cavity Ringdown Spectroscopy) and IO (LIF) measurements correlated on some days but cannot be explained by our current knowledge of iodine chemistry.

The influence of NO_x on IO has been investigated. The detection of IO by LIF at the Roscoff site shows that IO can survive in a high NO_x environment, at a distance from the iodine source region. The LIF measurements display an anti-correlation with NO_x. A modelling study shows that this is due to an iodine recycling scheme via $IONO_2$. The effect of NO_2 is to initially lead to IO suppression (displayed by an anti-correlation of IO with NO_x) and then to prolong the atmospheric lifetime of IO through decomposition of $IONO_2$.

Night-time IO was detected on two out of four nights at levels of 1 – 2 pptV, providing further evidence for the presence of night-time IO. The night-time source of I atoms is proposed to be via $I_2 + NO_3 \rightarrow I + INO_3$, ^{2,3}.

Co-located point source measurements of IO and particle number provide clear evidence for the link between IO and new particle formation. Over 18 days of simultaneous measurements, IO and particle number displayed a linear relationship. On all occasions, IO levels increased before an increase in particle number was observed.

The influence of IO on the important daytime oxidants OH and HO_2 has been investigated by modelling studies. IO was found to decrease the HO_2/OH ratio due conversion of HO_2 to OH via ($HO_2 + IO \rightarrow HOI$, $HOI + h\nu \rightarrow OH + I$). The high levels of IO detected at Roscoff can result in an enhancement of OH at up to 50%. However, the impact of IO on HO_x decreases as NO_x levels increase, until IO actually results in a decrease in OH ($NO_x > 1.55$ ppbV).

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