



Molecular iodine emissions in coastal marine environments: link to new particle formation

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The atmospheric chemistry of iodine in the marine boundary layer is important for a number of reasons. These include the role of the iodine oxides IO and OIO in depleting ozone and affecting the HOx and NOx cycles, the activation of chlorine and bromine from sea-salt aerosols, the ability of higher iodine oxides to form new particles in the remote atmosphere, and the enrichment of iodine in marine aerosols and the subsequent transport of this essential dietary element to the continents. We have recently reported observations by long path differential optical absorption spectroscopy (DOAS) of I₂ during low tide at Mace Head, Ireland. Simple scaling suggests that this coastal emission could approach 2 Tg per year, making it a major contribution to the global iodine budget. DOAS measurements of IO and OIO radicals were also performed during the campaign. A photochemical box model shows that the ratio of IO to I₂ in the DOAS beam (~ 1 : 2) can only be explained if the I₂ (and most of the IO) is actually contained in a small fraction of the DOAS path. This would be caused by I₂ release from exposed macro-algae at each end of the DOAS path. This result implies that the local I₂ mixing ratio approaches 100 ppt, which has now been confirmed using *in situ* measurements by broadband cavity ring-down spectroscopy and by inductively coupled plasma-mass spectrometry. The photochemical model also contains

a full treatment of particle nucleation by condensation of I_2O_3 , formed by the recombination of IO and OIO, and growth by further condensation and coagulation. This model shows that the phenomenon of ultra-fine particle bursts in coastal locations such as Mace Head, where the concentration of particles ($D = 3 - 10$ nm) can reach $\sim 10^6 \text{ cm}^{-3}$, appears to be explained by I_2 photochemistry. We will also consider the subsequent evolution of these particles to form condensation nuclei.