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Interactive comment on “The time dependence of molecular iodine emission from *Laminaria digitata*” by S. Dixneuf et al.

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The authors may be interested to note our recent work concerning coastal marine boundary layer iodine chemistry. Following on from the observations of Saiz-Lopez et al. (2006) and Bitter et al. (2005), which indicated that the major contributor to inorganic iodine activity at Mace Head was a shoreline molecular iodine source, measurements of a number of inorganic iodine species were performed at Mace Head in summer 2007. Measurements made included I atoms / total photolabile iodine content measured by Resonance Fluorescence (RF; Bale et al., 2007, 2008), IO radicals measured by laser-induced fluorescence (Commane et al., 2008) and molecular iodine measured using an LED-driven broadband cavity-enhanced absorption spectrometer (S. Ball, private communication). In the case of the RF instrument, the total atmo-

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spheric photolabile iodine content is obtained by measuring the iodine atoms evolved when ambient air is subject to broadband UV-visible photolysis. A strong correlation was observed between levels of all these species and low tide, with the levels (both absolute and relative) of the iodine species observed in good agreement with those predicted by Saiz-Lopez et al. (2006) under the hypothesis of a local, littoral iodine source - nicely consistent with the observation of direct molecular iodine production from *laminaria digitata* reported here by Dixneuf et al.

Of particular relevance to the discussion in the current paper of Dixneuf et al., we performed measurements of the total photolabile iodine released by freshly harvested seaweed samples from Mace Head. Our procedure and results are more fully described in Bale et al. (2008) but briefly, we harvested seaweed samples from the intertidal zone at Mace Head, and placed 50 g (wet weight) samples in a 2-litre pyrex vessel, through which synthetic air was flowed at a rate of 10 litres / min. The outflowing air was sampled into the RF instrument, and the iodine content measured, as both the total photolabile iodine content, and by monitoring the fluorescence due to molecular iodine; the I₂ levels inferred from the two measurements were in agreement, indicating that molecular iodine dominates the (photolabile) iodine content emitted, at least in the case of *laminaria digitata* which was the only species for which a measurable response was detected. For *laminaria*, we observed an increasing iodine flux, peaking at approximately 300 ppb after about 10 mins, before decaying to ca. 20 ppb after 1 hour. Agitating the flask caused a further burst of iodine to be released. Data was obtained on a 10 second timescale, but no oscillatory behaviour, other than the general signal rise and fall with a periodicity of several tens of minutes, was observed. From our data, the I₂ flux in the un-agitated flask peaked at about 300 ppb, corresponding to a maximum I₂ production flux of 2.5×10^{16} molecules kg⁻¹ s⁻¹ for *wet* *laminaria digitata*.

Our seaweed measurements were motivated by observations of molecular iodine release from harvested seaweed samples performed using a broadband cavity-enhanced

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absorption spectrometer during the recent RhAMBLE (Reactive Halogens in the Marine Boundary Layer) campaign at Roscoff, France in September 2006 (McFiggans et al., in preparation). It is intriguing to note the different temporal behaviour between these measurements - oscillatory iodine release in the experiments of Dixneuf et al., sporadic bursts of I₂ in the experiments of Ball and co-workers, and a smooth rise / fall of iodine emission without evident oscillations in our measurements. One reason may be the different stress factors present - our (Mace Head) experiments on seaweed samples used synthetic air, which was dry and ozone free. The samples will therefore have been subject to some desiccation (although the seaweed was "wet" throughout the procedure). In contrast the experiments of Dixneuf et al. were presumably performed at constant saturation vapour pressure, although with ambient air so ozone at mixing ratios of 20-30 ppb is likely to have been (initially) present. A second difference may be the age of the samples - in our experiments all samples were used within 30 minutes of harvesting, while the measurements reported in this paper were performed on samples a few days old, and it is possible that keeping seaweed in captivity may change its stress levels and hence iodine release. In the future it would be interesting to compare these effects in a controlled situation, to complement the laboratory measurements of Palmer et al. (2005).

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