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Fucus and *Ascophyllum* seaweeds are significant contributors to coastal iodine emissions

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Abstract

Based on the results of a pilot study in 2007, which found high mixing ratios of molecular iodine (I_2) above the intertidal macroalgae (seaweed) beds at Mweenish Bay (Ireland), we extended the study to nine different locations in the vicinity of Mace Head Atmospheric Research Station on the west coast of Ireland during a field campaign in 2009. I_2 mixing ratios from 104 to 393 ppt were found above the macroalgae beds, implying a high source strength of I_2. Such mixing ratios are sufficient to result in photochemically-driven coastal new-particle formation events. Mixing ratios above the *Ascophyllum nodosum* and *Fucus vesiculosus* beds increased with exposure time – after 6 h exposure to ambient air the mixing ratios were one order of magnitude higher than those initially present. This contrasts with the emission characteristics of *Laminaria digitata*, where most I_2 was emitted within the first half hour of exposure. Discrete in situ measurements (off-line) of I_2 emission from ambient air-exposed chamber experiments of *L. digitata*, *A. nodosum* and *F. vesiculosus* substantially supported the field observations. Further online and time-resolved measurements of the I_2 emission from O_3-exposed macroalgal experiments in chamber confirmed the distinct I_2 emission characteristics of *A. nodosum* and *F. vesiculosus* compared to that of *L. digitata*. The emission rates of *A. nodosum* and *F. vesiculosus* were comparable to or even higher than *L. digitata* after the initial exposure period of ~ 20–30 min. We suggest that *A. nodosum* and *F. vesiculosus* may provide an unaccounted and important source of photolabile iodine in the coastal boundary layer and that their impact on photochemistry and coastal new particle formation should be reevaluated in light of their longer exposure at low-tide and their widespread distribution.

1 Introduction

Brown algae include kelps of the genus *Laminaria*, the strongest biological accumulators of iodine currently known. *Laminaria* spp. are a key biogeochemical pump for the

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transfer of iodine from the sea to the atmosphere (Küpper et al., 2011). *Laminaria* accumulates iodide for the provision of an extracellular antioxidant. Its reaction with O_3 on the thallus surface results in the release of I_2 (Küpper et al., 2008). However, the iodine metabolism of other brown algae and their role in marine-atmospheric halogen transfer is much less well understood. The current interest in tropospheric iodine chemistry was initiated by observations of iodine oxide (IO) – a product of iodine atom reaction with O_3 – in the marine boundary layer (MBL) at Mace Head, Ireland (Alicke et al., 1999). Reactive iodine can affect the tropospheric oxidizing capacity through catalytic destruction of O_3, changing the NO_2/NO and HO_2/HO ratios, and by reactivating chlorine and bromine from sea-salt aerosol (Vogt et al., 1999; McFiggans et al., 2000; Bloss et al., 2005; Saiz-Lopez et al., 2008). The photochemically-driven reaction of iodine and O_3 also results in iodine oxide particle (IOP) formation.

Coastal new particle formation via secondary gas-to-particle conversion is an important process determining the concentration of atmospheric aerosols, and ultimately, the concentration of cloud condensation nuclei (CCN) on the regional scale (O'Dowd and Hoffmann, 2005). The nucleation events generally occur around low tide during daylight and have been known to lead to ultrafine particle number concentrations in excess of 10^6 particles cm^{-3} (O'Dowd and Hoffmann, 2005). In recent years, numerous studies have shown that the coastal particle bursts are closely linked to iodine emission from low tidal macroalgae exposure (Huang et al., 2010c; McFiggans et al., 2010). A clear negative correlation between IO (the precursor of IOP) and tidal height, and a positive correlation between IO and solar irradiation, have been observed (Carpenter et al., 2001; Saiz-Lopez et al., 2006b; Huang et al., 2010b). The emission of iodocarbons such as CH_2I_2 from macroalgae was first proposed to be the source of photolabile iodine (Hoffmann et al., 2001; Carpenter, 2003). However, recent field measurements and laboratory experiments show that the emission of molecular iodine (I_2) is the dominant source of iodine and is responsible for the observed iodine chemistry in the coastal

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MBL (McFiggans et al., 2004; Saiz-Lopez and Plane, 2004; Huang et al., 2010b,c).

$$\text{macroalgae} \xrightarrow{\text{emission}} I_2 \xrightarrow{\text{photolysis}} I^{\bullet} \xrightarrow{O_3} IO \xrightarrow{IO/OIO} I_2O_y \quad (y = 2-5)$$

$$\xrightarrow{\text{nucleation}} \text{particles/clusters } (\sim 1\,\text{nm}) \xrightarrow{\text{growth}} \text{CNN}$$

Measurements of I_2 mixing ratios have so far been reported at four different coastal locations: Mace Head and vicinity, Ireland (Huang et al., 2010b,c; Saiz-Lopez and Plane, 2004; Saiz-Lopez et al., 2006), Roscoff, France (Leigh et al., 2010; McFiggans et al., 2010), O Grove, Galicia, Spain (Mahajan et al., 2011), and La Jolla, California (Finley and Saltzman, 2008). The observations of high concentrations I_2 at Roscoff and O Grove are thought to be a consequence of large I_2 emissions from *Laminaria* spp such as *L. digitata* and *L. hyperborea*, which are the dominant species at these measurement sites.

Since the daytime reaction cycle of iodine in the coastal MBL is initiated by rapid photolysis of I_2, measurement of iodine close to its source is required for understanding the contribution of macroalgal iodine emissions to local atmospheric processes. However, such field observations are scarce because measurement of I_2 directly above the algal beds is challenging. Efforts have therefore been made to study the I_2 emission profiles of macroalgae through laboratory incubation experiments (Dixneuf et al., 2009; Ball et al., 2010; Nitschke et al., 2011; Kundel et al., 2012; Ashu-Ayem et al., 2012) in order to understand the emission mechanism and to better estimate the flux of I_2 from macroalgae. These studies have mainly focused on *L. digitata* as this species accumulates iodine at up to around 5 % of its dry weight (Küpper et al., 1998; Gall et al., 2004) and emits large amounts of I_2 when exposed to ambient air; the results showed a high variability of I_2 emission rates, with values ranging from 3 to 2500 pmol min^{-1} g FW^{-1} (Bale et al., 2008; Ball et al., 2010; Ashu-Ayem et al., 2012). The I_2 emission profiles of *L. digitata* are characterized by an intense initial burst when first exposed to air followed by an approximately exponential decay over a short period of about 20–30 min (Bale

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et al., 2008; Dixneuf et al., 2009; Ball et al., 2010; Nitschke et al., 2011; Ashu-Ayem et al., 2012).

During a field campaign at Mweenish Bay, Ireland, in August/September 2007, a pilot study of I_2 emissions was carried out directly above macroalgal beds of *Ascophyllum nodosum* and *Fucus vesiculosus* located in the mid-littoral zone. Elevated I_2 mixing ratios of up to 302 ppt were observed after the algae had been exposed to air for several hours (Huang et al., 2010b). This behavior differs from the emission characteristics of *L. digitata* found in laboratory incubation experiments, where I_2 emissions are small or stop completely after prolonged exposure (Dixneuf et al., 2009; Ball et al., 2010; Nitschke et al., 2011). We hypothesized that the temporal behavior of I_2 emission of *A. nodosum* and *F. vesiculosus* would likely be different and of longer duration than that of *L. digitata*. Both *A. nodosum* and *F. vesiculosus* are widely distributed throughout the world and exposed to air even at moderate low tidal levels since they inhabit the mid to upper littoral regions. If the emission indeed increases with time, the impact of these two macroalgae on the local atmospheric iodine chemistry could be more significant than currently believed. This finding would likely apply to numerous other brown algae (Phaeophyceae) species, implying greater macroalgal sea-air transfer of iodine than expected from *Laminaria* emissions only. Moreover, different emission characteristics compared to *Laminaria* spp. may provide an explanation for the frequently observed new particle formation events at the west coast of Ireland considering the large population of *A. nodosum* and *F. vesiculosus* distributed there.

In this paper, we present results of a 2-week field campaign carried out on the west coast of Ireland in August 2009 with a special focus on the investigation of mixing ratios and emission characteristics of I_2 above the macroalgae beds in the field. The results derived from chamber experiments of *L. digitata*, *A. nodosum* and *F. vesiculosus* exposed to ambient air and to ozone are also presented.

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2 Experimental

2.1 Sampling sites

Measurements were carried out at nine different sites in the vicinity of the Mace Head Atmospheric Research Station on the west coast of Ireland (see Fig. 1), from 17 August to 28 August 2009. This area is characterized by a high abundance (but discrete zonation) of brown macroalgae along the coastline. *A. nodosum* and *F. vesiculosus* are dominant algal species in sites #1, #2, #4–7 and can be exposed to the air for up to 6–8 h during low tides (average exposure ~ 4 h at normal low tides). No *Laminaria* spp. were observed in the immediate vicinity of these sites. In contrast, most *L. digitata* algae in sites #3 and #8 are extensively exposed only at around lowest water (spring low tides) and for a much shorter period. Measurements at site #9 (dominated by *A. nodosum* and *F. vesiculosus*) were carried out when *Laminaria* spp. in the nearby site #8 were submerged in sea water. Note that at all sampling sites samples were taken when the wind came from the sea (wind direction 179–287°). The wind speed ranged between 5–11 m s^{-1}.

2.2 Denuder sampling with GC–MS quantification

Molecular iodine was measured using a diffusion denuder system in combination with a gas chromatography–mass spectrometry (GC–MS) method, which provides "point" in situ concentrations of I_2 at the sampling site. Details of this denuder/GC–MS method are given in Huang and Hoffmann (2009) and it will be only briefly described here. Ambient I_2 samples were collected at a flow rate of 500 ml min^{-1} for 5–30 min on brown denuder tubes (6 mm i.d., 50 cm length) which were uniformly coated with ~ 11 mg α-cyclodextrin (α-CD) and trace $^{129}I^-$. The potential interference iodine species such as ICl and HOI were removed by coupling a 1,3,5-trimethoxybenzene-coated denuder upstream of the α-CD/$^{129}I^-$ coated denuder (data not shown here). The inlet of the denuder was set up very close to the algal beds (~ 5–10 cm) during sampling to minimize

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potential photolysis of I_2. Although Saiz-Lopez et al. (2004) calculate a lifetime of I_2 of about 6 s under noon, clear sky at Mace Head for this time of year, the relatively low solar flux (as indicated in Fig. 3) for most measurements implies a lifetime that is several times longer. After sampling, the open ends of the denuders were sealed with PP caps and kept under refrigeration until analysis. In the laboratory, the samples were eluted with five 2.0 ml portions of ultrapure water into a 25 ml flask to which 500 µl of phosphate buffer (pH 6.4), 100 µl of 2,4,6-tribromoaniline (2.5 mg l^{-1}, internal standard), 400 µl of sodium 2-iodosobenzoate, and 300 µl of *N*,*N*-dimethylaniline were added. The solution was shaken at room temperature for about 120 min, leading to > 98 % conversion of I_2 into 4-iodo-*N*,*N*-dimethylaniline (Huang et al., 2010a). Finally, the solution was extracted with 100 µl of cyclohexane. 1.0 µl of the extraction solution was injected into a GC–MS system (Agilent 6850 GC interfaced to a 5973N MSD, Agilent Technologies, Santa Clara, CA). A Rtx-5MS fused-silica capillary column (Restek Co., Bad Homburg, Germany) was used for chromatographic separation, and the MS was run in selected ion monitoring (SIM) mode to enhance the sensitivity. The detection limit of the method was below 1.0 ppt for a 15 l sample volume, and the collection efficiency was greater than 98 %. The reported values in this study have been corrected for the mean value of blanks, which were based on the analysis of denuders that had been sealed throughout the campaign.

2.3 Ambient air chamber experiments

L. digitata specimens were collected at Mweenish Bay during spring low tide on 24 August 2009. Since thalli were tightly attached to the rock through their rhizoids, rock and thalli were taken together to avoid injuring the alga. *Laminaria* thalli were kept in sea water during a short transport time of ~ 10 min and then stored in running sea water in a transparent tank placed outside the Martin Ryan Institute-Carna (MRI-Carna) building, where macroalgae were exposed to the natural diurnal light and temperature cycle. The seawater was freshly pumped from the sea and close to the sea temperature in the area. Algal thalli were used within 4 days of collection. When required for the

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incubation experiments, the whole alga together with its anchoring rock was removed from the tank and placed into a 35 l, translucent, polyethylene chamber. Ambient air (O_3 mixing ratio 35–40 ppb) was then drawn through the chamber and the emitted I_2 was collected using the denuder at a flow rate of 500 ml min^{-1}. After the first exposure of 20 min and air sample collection, the alga was removed from the chamber and exposed to outside ambient air for a specified duration of up to several hours (similar to what it would experience during tidal exposure). Afterwards the alga was placed back into the chamber and its emission was measured again.

Whole, submerged *A. nodosum* and *F. vesiculosus* algae were taken directly from the intertidal zone outside the MRI-Carna building and used immediately. Again, algal thalli were usually taken together with small rocks attached to their holdfasts. The transit time from collection in the intertidal zone to beginning an experiment was around 5–10 min, during which algal thalli were kept in seawater. The alga and its anchoring rock were weighed before and after the experiments, and then the alga mass alone was weighed after detaching the rock. About 300–500 g algae were used in individual experiments. When air samples in the chamber were taken, the I_2 mixing ratios in the ambient air outside the chamber were measured simultaneously to correct for background I_2.

2.4 Ozone-exposed chamber experiments

A further set of experiments was carried out at Helgoland, a small island in the North Sea, from 13 May to 20 May 2011. *L. digitata*, *A. nodosum* and *F. vesiculosus* were collected in the intertidal zone (54.18° N, 7.88° E) and stored in a tank of running sea water at the Biological Institute Helgoland of Alfred Wegener Institute. All macroalgae thalli were used within 4 days of collection. In the incubation experiments, a whole macroalgae thallus was removed from the tank and placed in a 4 l, light-tight glass chamber. The chamber was flushed continuously with synthetic air containing 50 ppb O_3 at 4 l min^{-1}. The I_2 emitted was measured by a recently developed time-of-flight aerosol mass spectrometer in combination with a gaseous compound trapping in artificially generated particle (GTRAP-AMS) method (Kundel et al., 2012a), which provided

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a faster, online quantification of I_2. Briefly, α-CD/NH_4Br particles produced by a pneumatic nebulizer were used as selective sampling probe particles to trap gaseous I_2 in the particle phase before AMS measurement. The trapping mechanism is similar to the collection of I_2 with α-CD-coated denuder (Huang et al., 2010a). The trapping step was carried out in a 0.5 l flow tube which was placed between the macroalgae chamber and the ToF-AMS. Due to high resolution of the ToF-MS, the molecular ion of I_2 at *m/z* 253.81 (I_2^+) can be separated from interfering organic fragments and therefore was used for the quantification of I_2. The measurement system was calibrated using a capillary-based diffusion device as an I_2 test gas source (Huang and Hoffmann, 2010). A time resolution of 2.5 min was used for all measurements.

3 Results and discussion

3.1 I_2 mixing ratios on the west coast of Ireland

At the Mace Head station intense bursts of new particles have been frequently observed, with concentrations often reaching in excess of 10^6 cm^{-3} (O'Dowd and Hoffmann, 2005). Airborne measurements further reveal that such particle bursts are almost ubiquitous along the coastline in the vicinity of Mace Head (O'Dowd et al., 2007). Close to the plume head the growth rate of nucleated particles can be as high as several hundred nanometers per hour, indicating the presence of a high concentration of precursor gases. Table 1 shows the results from nine different sampling sites in the vicinity of Mace Head station. It is evident that elevated levels of I_2 were indeed present over the local source regions (macroalgae beds). Based on model study predictions that 80–100 ppt I_2 is required for iodine-oxide particle bursts (Saiz-Lopez et al., 2006a), the mixing ratios of I_2, ranging from 104 ppt to 393 ppt, observed in all sampling sites would be sufficient to result in photochemically-driven new-particle formation events. It should be noted that the highest I_2 mixing ratios were consistently observed above *Laminaria* beds.

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The I_2 mixing ratio of 547 ppt measured over a short time period of 5 min immediately after exposure of the *L. digitata* beds is one of the highest observations reported to date. Similar "point" in situ techniques at other coastal locations have also found high mixing ratios at sites close to *Laminaria* spp. belts: a daytime maximum of 350 ± 100 ppt was reported at O Grove (Mahajan et al., 2011) and 50 ppt was observed at Roscoff (McFiggans et al., 2010). These measurements are consistent with the current consensus that *Laminaria* spp. are very strong emitters of I_2. What the observations reported in Table 1 also indicate, however, is that the I_2 mixing ratios observed above the *A. nodosum* and *F. vesiculosus* mixed beds are a significant proportion of those above the *L. digitata* beds (with an average of 134 ppt versus 301 ppt, respectively). This observation is inconsistent with the macroalgae incubation experiments of Ball et al. (2010) which showed that I_2 emissions from *A. nodosum* and *F. vesiculosus* were several orders of magnitude lower than those from *Laminaria* spp. Their measurements were carried out over a short initial exposure period (~ 10–17 min), and we attribute this apparent contradiction to the distinct time-dependent emission characteristics of these species discussed below. We note that, in the vicinity of Mace Head, *A. nodosum* and *F. vesiculosus* are extensively exposed to the air during most low tides, whereas the exposure of *Laminaria* beds is limited to extremely low water (spring low tide) events. The different exposure profiles, together with the elevated mixing ratios observed, leads us to suggest that *A. nodosum* and *F. vesiculosus* could be the main sources of I_2 in the vicinity of Mace Head during most low tides, whereas *Laminaria* spp. would be the major contributor to I_2 emissions at spring low tides. This suggestion is supported by the observation that new particle formation events occur on more than half of the days at Mace Head and are therefore not limited to spring low tides. Moreover, the new particle formation events observed at Mace Head station are often characterized by number size distributions with "apple", "bump" or "mixed" shapes (Vana et al., 2008). Ehn et al. (2010) explained these particle formation characteristics on the basis of an inhomogeneous distribution of precursor gases. Our findings of high I_2 mixing ratios above the *A. nodosum* and *F. vesiculosus* beds, when taken together

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with the inhomogeneous distribution of these two macroalgae species (whose habitat is restricted to a number of small areas around Mace Head), are consistent with the suggestion of Ehn et al. (2010).

3.2 I_2 emission characteristics

3.2.1 Field observations

The emission characteristic is one of the most important factors determining iodine flux from macroalgae to the atmosphere. However, relevant studies are scarce and have mainly concentrated on *L. digitata* (Dixneuf et al., 2009; Ball et al., 2010; Nitschke et al., 2011; Ashu-Ayem et al., 2012). Laboratory incubation experiments have revealed that I_2 emissions from this species are intense within the first few minutes when subjected to air exposure but decrease strikingly afterwards (Dixneuf et al., 2009; Ball et al., 2010; Nitschke et al., 2011; Ashu-Ayem et al., 2012). This time dependence was also observed in our field observations. As shown in Fig. 2, the average I_2 mixing ratio measured above the *L. digitata* beds at Mweenish Bay was 547 ppt over the first 5 min of exposure, but decreased to 239 ppt over the interval of 15–20 min.

Figure 3 shows the temporal profile of I_2 emission (averaged over a 30 min sampling time) at a fixed sampling site, dominated by *A. nodosum* and *F. vesiculosus* at Mweenish Bay. A lower mixing ratio was observed at the beginning of ebbing tide when the macroalgae were just exposed to the ambient air. However, the mixing ratio increased gradually with exposure time, reaching a value of one order of magnitude higher than the initial value after about 6 h (1/2 tidal cycle). This emission profile is markedly different from that of *L. digitata*. It may at first appear that the increased emissions of I_2 from *A. nodosum* and *F. vesiculosus* at Mweenish Bay are a consequence of elevated O_3 concentration in the ambient air, which we observed in our previous field studies (Huang et al., 2010b). However, this effect is unlikely to be the case as the O_3 concentrations were relatively stable (35–39 ppb, measured by an ozone analyzer, Model 1008-RS, Dasibi Environmental Corp., Glendale, USA) over two consecutive

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days (20–21 August 2009). The data measured at a similar O_3 level (36–39 ppb) but from a previous study in 2007 also fit well into the emission profile. The intensity of solar irradiation had no noticeable impact on the emission of I_2 (see Fig. 3) as Ashu-Ayem et al. (2012) have also observed in incubation studies.

3.2.2 Chamber studies

During the campaign, I_2 emissions from *L. digitata*, *A. nodosum* and *F. vesiculosus* were also investigated in a flow chamber at Mweenish Bay. The algal samples were exposed to the ambient air that flowed into the chamber to simulate the natural process of exposure. The results, after correction for background concentration in the ambient air, show that the emission rates from *A. nodosum* and *F. vesiculosus* rose significantly upon prolonged exposure (see Fig. 4a, b) whereas *L. digitata* emission rates decreased strikingly over time (see Fig. 4c). This temporal behavior was observed in both daytime and nighttime experiments, providing substantial support for the field observations reported above. Figure 4 also shows that the initial emission rates of *A. nodosum* and of *F. vesiculosus* were relatively constant although different specimens were used. The relative standard deviations (RSDs) is 12 % (n = 3) for *A. nodosum* and 18.8 % (n = 3) for *F. vesiculosus*, respectively. In contrast, the initial I_2 emissions by *L. digitata* differed significantly between specimens (RSD 74 %). Variable emissions between plants has been found in a relatively large sample size (Ashu-Ayem et al., 2012) and may arise from the inhomogeneous accumulation of iodine in individual algae. Additionally, iodine emission differs across parts of the thallus, and Nitschke et al. (2011) have shown that the stipe of *L. digitata* emits up to 19 times more I_2 compared to the distal blade. The *L. digitata* #1 studied here had a bigger and longer stipe than *L. digitata* #2 (16 cm length, ~ 1.5 cm i.d. versus 10 cm length, ~ 1.2 cm i.d.) and would be expected to emit more I_2.

The time profile of I_2 emissions from *L. digitata*, *A. nodosum* and *F. vesiculosus* were further investigated in a simulation chamber using the online GTRAP-AMS method (Kundel et al., 2012a). Algae in chamber experiments were directly exposed to 50 ppb

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O_3. Moreover, the online GTRAP-AMS provided a much higher time resolution compared to the off-line denuder method and therefore enables us to look at a more detailed profile of I_2 emissions from macroalgae. The results (see Fig. 5) provide strong evidence that the I_2 emission rate from *A. nodosum* and *F. vesiculosus* rises with increasing exposure time over a period of hours, while *L. digitata* displays the opposite behavior, emitting a strong, short pulse immediately on exposure. These measurements further support our findings from field measurements and ambient air-exposed chamber studies.

3.3 Potential contribution of *Fucus* and *Ascophyllum* seaweeds to coastal iodine level

It is beyond the scope of the present work to investigate the biochemical mechanism governing the distinct I_2 emission feature between different macroalgal species, but it is tempting to hypothesize that it is linked to different physiological adaptations of *Ascophyllum*, *Fucus* and *Laminaria* to their differing positions in the littoral zone. The location of their habitat in the littoral zone governs the frequency and duration of exposure to air at low tide and therefore the extent of exposure to ozone and desiccation stress. It is clear that *L. digitata* is able to emit much larger amounts of I_2 within the first exposure of ~20–30 min than *A. nodosum* and *F. vesiculosus*. However, a major finding of this study is that the emission rates of *A. nodosum* and *F. vesiculosus* are comparable to or even higher than *L. digitata* after the initial exposure period (see Figs. 4 and 5) and are sustained over a period of several hours. Due to measurement limitations, we have not yet been able to reconstruct detailed emission profiles of these three macroalgae under natural conditions, nor do we compare their overall emission rates over an integrated low-tide period. Leigh et al. (2010) concluded that, in comparison to *Laminaria* spp., the contributions from *A. nodosum* and *F. vesiculosus* to the total I_2 emissions were negligible in the coastal region around Roscoff by assuming a lower and constant emission rate throughout the low tide period (derived from the first exposure period of ~10 min in incubation studies, taken from Ball et al., 2010) for

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A. nodosum and *F. vesiculosus*. Nevertheless, these authors also showed that the I_2 mixing ratios calculated from the emissions of *Laminaria* spp. were lower than observed values, and suggested the presence of an additional source to account for the discrepancy. Our results show that upon exposure to 50 ppb O_3 in a synthetic air stream the first 10 min integrated I_2 emission rates of *A. nodosum* (0.014 pmol min^{-1} g FW^{-1}) and *F. vesiculosus* (0.049 pmol min^{-1} g FW^{-1}) are indeed much lower than that of *L. digitata* (4.23 pmol min^{-1} g FW^{-1}). However, the first 1 h integrated I_2 emission rates are 159, 69, 19 pmol h^{-1} g FW^{-1} for *L. digitata*, *A. nodosum* and *F. vesiculosus*, respectively. It is expected that the sum of I_2 emitted by *A. nodosum* and *F. vesiculosus* could be comparable to or even larger than that from *L. digitata* under natural conditions considering their distinct time-dependent emission trends and the longer exposure time of *A. nodosum* and *F. vesiculosus* in comparison to *L. digitata* (the former two inhabit upper littoral zone while the later in the sublittoral zone). It should be noted that *A. nodosum* and *F. vesiculosus* (both Fucales) are commonly found on the coasts of North Atlantic Ocean and that *Fucus* species are widely distributed along rocky coasts throughout the world. Therefore, Fucales and other large, morphologically complex brown algae may provide an unaccounted and important source for the observed tropospheric iodine level and their impact on the photochemistry and coastal new particle formation should be reevaluated.

4 Summary

The mixing ratio of I_2 above the macroalgae beds at nine different locations on the west coast of Ireland has been measured using diffusion denuders in combination with a gas chromatography-mass spectrometry (GC-MS) method. The results show the occurrence of elevated I_2 levels above macroalgae beds, ranging from 104 ppt to 393 ppt, which is in line with a previous pilot study (Huang et al., 2010b). Most importantly, it is found that the mixing ratio above the *A. nodosum* and *F. vesiculosus* beds correlates positively with their exposure time, reaching a value of one order of magnitude higher

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than the initial emission after exposing to ambient air for ~6 h. In contrast, the mixing ratio above the *L. digitata* beds decreases with increasing exposure time. This feature can be attributed to the distinct time-dependent I_2 emission characteristic of macroalgae confirmed in two sets of chamber experiments. A particularly interesting aspect is the different emission profiles over time – of *Fucus* and *Ascophyllum* on the one hand, and *Laminaria* on the other. The results derived from these chamber experiments indicate that the emission rates of *A. nodosum* and *F. vesiculosus* are comparable to or even higher than that of *L. digitata* after the initial exposure period of ~20–30 min. Given the longer low-tide exposure time of *A. nodosum* and *F. vesiculosus* (as they usually inhabit the upper littoral zone and therefore easily exposed to air) as well as their large distribution on the coasts of Atlantic and Pacific Oceans, we suggest that *A. nodosum*, *F. vesiculosus* and possibly other Fucales may provide an important and unaccounted source for the observed tropospheric iodine level and that their impact on the photochemistry and coastal new particle formation should be reevaluated. Furthermore, more studies are needed to determine whether other macroalgae that are often exposed to ambient air during low tide are also significant contributors to coastal emissions of I_2.

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Table 1. The mixing ratio of I_2 at different sites on the west coast of Ireland.

Site #	I_2 (ppt)	Number of sample	Dominant macroalgae	Location
1	173.4 ± 88.9	13	*A. nodosum* and *F. vesiculosus*	53° 18′ 33″ N, 9° 49′ 41″ W, ~ 150 m away from MRI-Carna
2	141.4 ± 16.7	2	*A. nodosum* and *F. vesiculosus*	53° 18′ 39″ N, 9° 50′ 34″ W, close to Mweenish bridge
3	393.2 ± 177.8	2	*L. digitata*	53° 17′ 36″ N, 9° 50′ 12″ W, ~ 3.5 km southwest of MRI-Carna
4	112.1 ± 21.5	3	*A. nodosum* and *F. vesiculosus*	53° 22′ 51″ N, 9° 48′ 57″ W, ~ 9 km north of MRI-Carna, close to Glinsk house hotel
5	133.4 ± 20.1	2	*A. nodosum* and *F. vesiculosus*	53° 25′ 04″ N, 9° 49′ 14″ W
6	159.1 ± 31.4	2	*A. nodosum* and *F. vesiculosus*	53° 24′ 26″ N, 9° 54′ 56″ W
7	105.9 ± 27.8	2	*A. nodosum* and *F. vesiculosus*	53° 22′ 59″ N, 9° 55′ 22″ W
8	208.9	1	*L. digitata*	53° 19′ 28″ N, 9° 54′ 19″ W, ~ 250 m away from Mace Head station
9	104.0 ± 18.7	2	*A. nodosum* and *F. vesiculosus*	53° 19′ 29″ N, 9° 54′ 17″ W, ~ 100 m away from Mace Head station

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Fig. 1. The denuder sampling sites on the west coast of Ireland.

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Significant contributors to coastal iodine emissions

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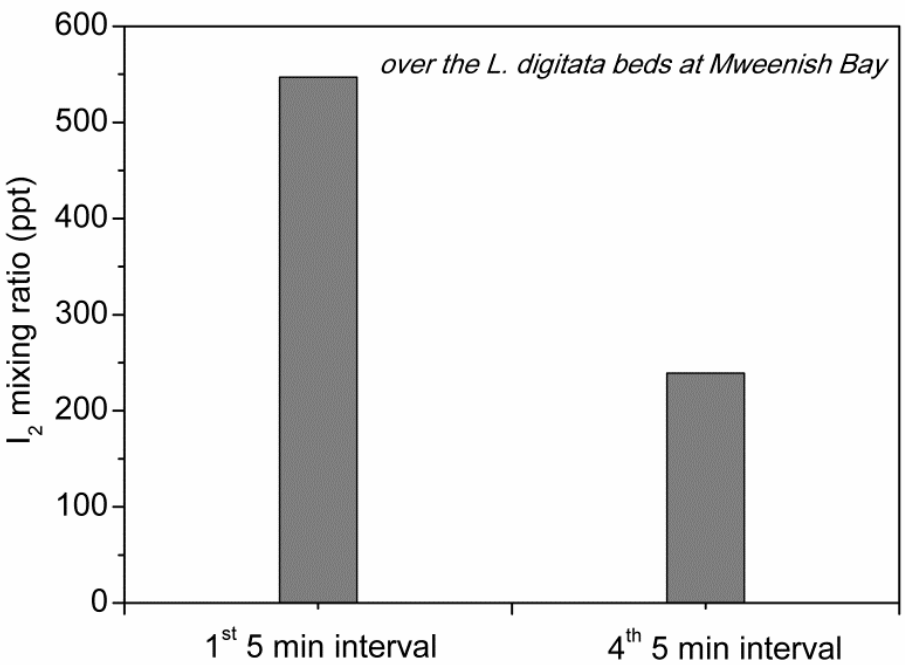

Fig. 2. I_2 mixing ratio against the exposure time of *L. digitata* beds. Here, the first sample (from 0–5 min) was taken when *L. digitata* was just exposed to air. Following an interval of 10 min for setting up the second sampler, the second sample (from 15–20 min) was taken. The data set is limited to two measurements because the *L. digitata* beds were accessible only at a single spring low tide at Mweenish Bay.

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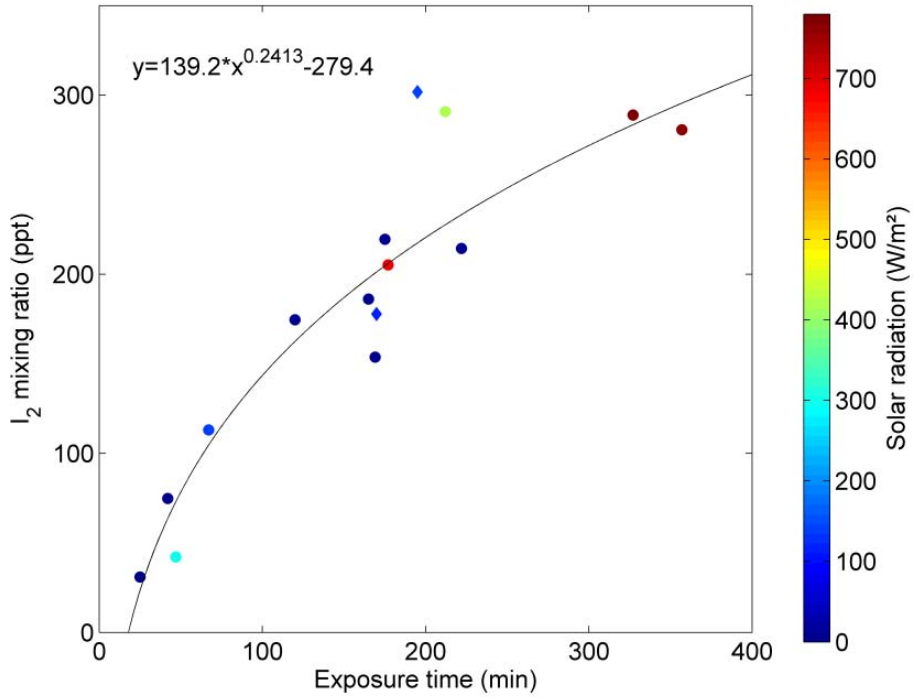

Fig. 3. I_2 mixing ratio above the *A. nodosum* and *F. vesiculosus* mixed beds at Mweenish Bay, Ireland as a function of algal exposure time and solar irradiation. Each data point represents the mean value over a sampling period of 30 min. Note the symbol, solid circle represents data from this work and solid diamond represents data from the 2007 campaign (Huang et al., 2010b). The O_3 concentrations in the surrounding air were 35–39 ppb over the course of measurements.

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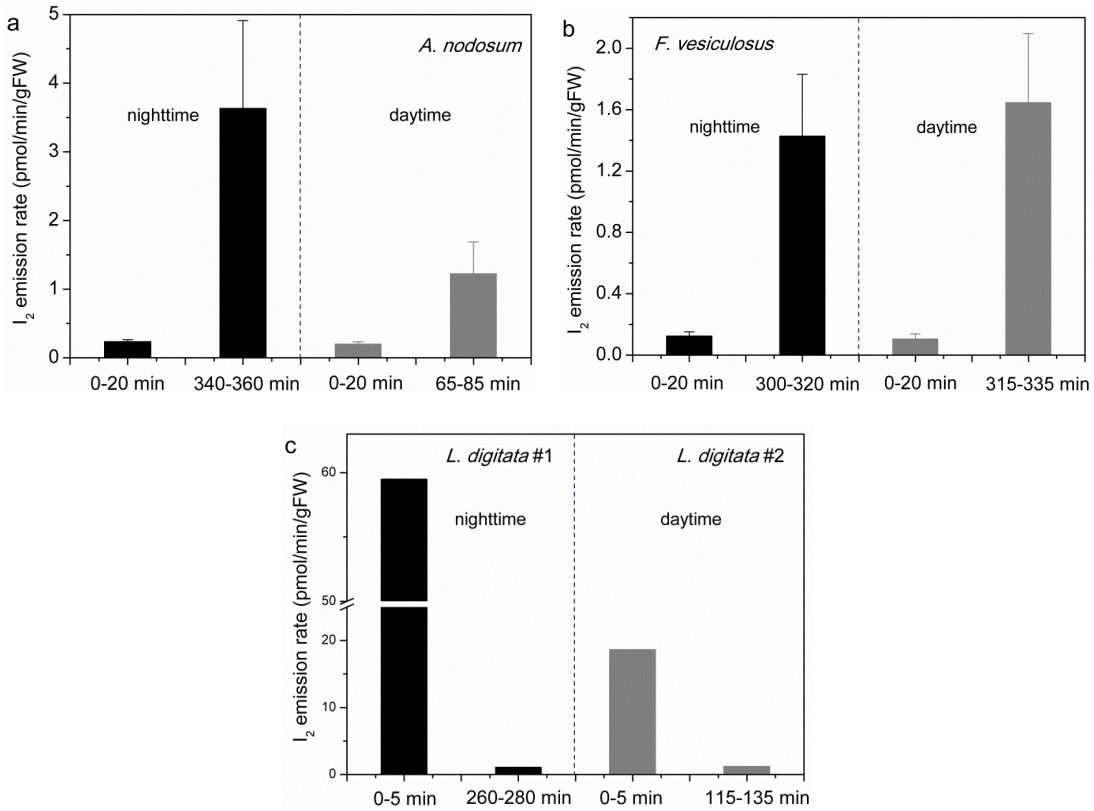

Fig. 4. The time-dependent I_2 emission rates of *A. nodosum* **(a)**, *F. vesiculosus* **(b)** and *L. digitata* **(c)** at daytime and nighttime when subjected to ambient air exposure in a flow chamber at Mweenish Bay. Note the difference in scale of *L. digitata* emissions.

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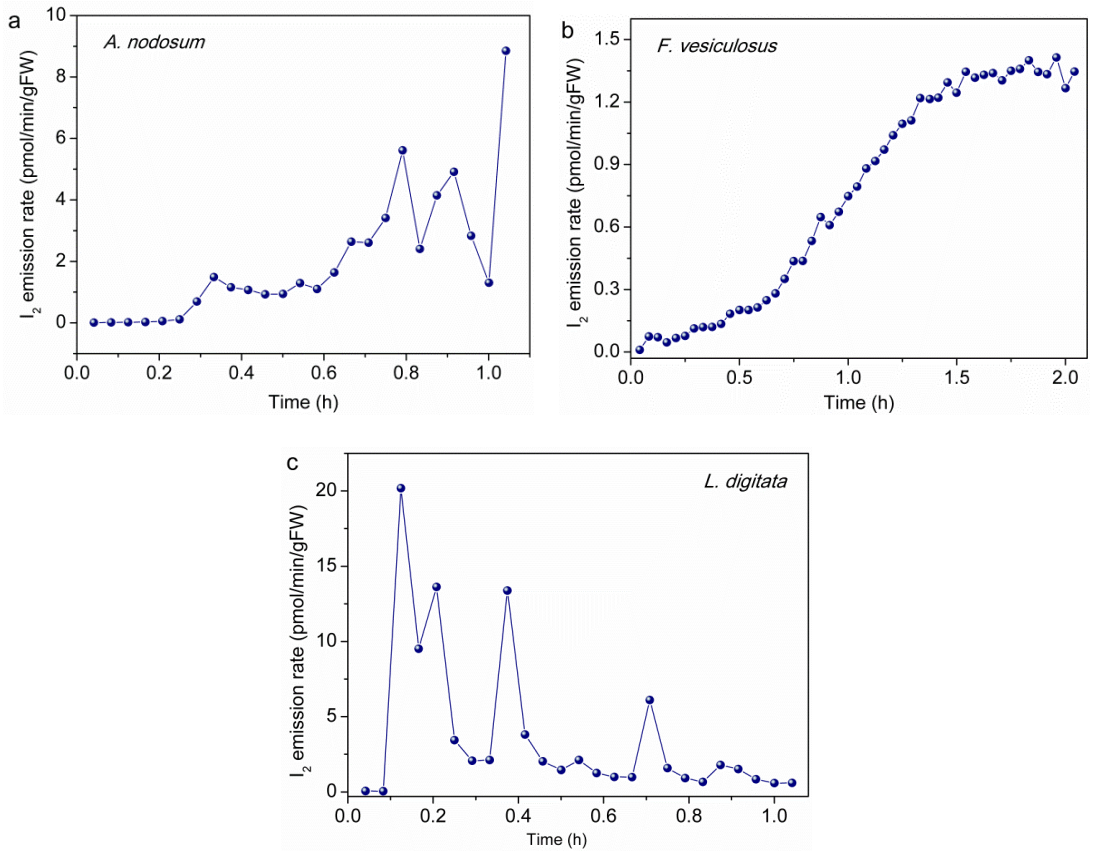

Fig. 5. A typical time-dependent I_2 emission rate of *A. nodosum* **(a)**, *F. vesiculosus* **(b)** and *L. digitata* **(c)** when exposed to 50 ppb O_3 in synthetic air in a simulation chamber (modified from Kundel et al., 2012).

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