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**Spectroscopic
studies of iodine
emitted by seaweed**

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Spectroscopic studies of molecular iodine emitted into the gas phase by seaweed

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Received: 3 November 2009 – Accepted: 18 November 2009 – Published: 10 December 2009

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Published by Copernicus Publications on behalf of the European Geosciences Union.

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Time profiles of molecular iodine emissions from seven species of seaweed have been measured at high time resolution (7.5 s) by direct spectroscopic quantification of the gas phase I₂ using broadband cavity enhanced absorption spectroscopy. Substantial differences were found between species, both in the amounts of I₂ emitted when the plants were exposed to air and in the shapes of their emission time profiles. Two species of kelp, *Laminaria digitata* and *Laminaria hyperborea*, were found to be the most potent emitters, producing an intense burst of I₂ when first exposed to air. I₂ was also observed from *Saccharina latissima* and *Ascophyllum nodosum* but in lower amounts and with broader time profiles. I₂ mixing ratios from two *Fucus* species and *Dictyopteris membranacea* were at or below the detection limit of the present instrument (25 pptv). A further set of experiments investigated the time dependence of I₂ emissions and aerosol particle formation when fragments of *L. digitata* were exposed to desiccation in air, to ozone and to oligoguluronate stress factors. Particle formation occurred in all *L. digitata* stress experiments where ozone and light were present, subject to the I₂ mixing ratios being above certain threshold amounts. Moreover, the particle number concentrations closely tracked variations in the I₂ mixing ratios, confirming the results of previous studies that the condensable particle-forming gases derive from the photochemical oxidation of the plant's I₂ emissions. This work also supports the theory that particle nucleation in the coastal atmosphere occurs in "hot-spot" regions of locally elevated concentrations of condensable gases: the greatest atmospheric concentrations of I₂ and hence of condensable iodine oxides are likely to be above plants of the most efficiently emitting kelp species and localised in time to shortly after these seaweeds are uncovered by a receding tide.

ACPD

9, 26329–26376, 2009

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1 Introduction

The rapid nucleation of large numbers of ultra-fine aerosol particles has been reported from several field studies conducted at Mace Head on the west coast of Ireland (O'Dowd et al., 2002; O'Dowd and Hoffmann, 2005; Saiz-Lopez et al., 2006). A similar phenomenon was also recently observed during the Reactive Halogens in the Marine Boundary Layer (RHaMBLe) field campaign at Roscoff on the north Brittany coast of France (Whitehead et al., 2009; McFiggans et al., 2009). These nucleation events tend to occur in “bursts” around daytime low tides (but not generally night-time low tides), the most intense events occurring on days with the lowest tides. A fraction of these newly nucleated particles may subsequently grow large enough to act as cloud condensation nuclei (CCN) and hence affect cloud properties and lifetimes, potentially also changing the radiative forcing in coastal regions (see McFiggans et al., 2006, and references therein for a discussion of the properties impacting on aerosol behaviour as CCN).

Parallel studies conducted in laboratory chambers and flow reactors have observed particle formation following the gas phase photo-oxidation of CH_2I_2 (Jimenez et al., 2003) and the head-space gases sampled from above one particular species of kelp seaweed, *Laminaria digitata* (McFiggans et al., 2004). Indeed, the particles formed from *L. digitata* exposure were found to have the same composition (iodine oxides), morphology and hygroscopic behaviour as particles formed from CH_2I_2 . Together, the laboratory and field observations have lead investigators to conclude that particle nucleation in coastal areas follows from the in situ photochemical production of highly condensable iodine oxides derived from iodine-containing precursor gases emitted into the atmosphere by seaweed beds exposed around low tide. Since the McFiggans et al. (2004) publication, further flow reactor studies have confirmed that both halocarbons and molecular iodine are emitted into the gas phase when *L. digitata* is exposed to oxidative stresses e.g. ozone, H_2O_2 or oligoguluronates (Palmer et al., 2005; Küpper et al., 2008), with particle formation observed in the presence of ozone. I_2 emissions have also been seen in studies where the seaweed samples were merely exposed to

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ambient air (i.e. without applying any additional stress): I₂ emission was observed from *L. digitata* by Dixneuf et al. (2009) and Bale et al. (2008), and both I₂ emissions and particle nucleation was observed by Sellegri et al. (2005) from “*Laminaria* and *Fucus*” samples collected from around Mace Head.

Although the nucleation kinetics have yet to be understood in detail and significant uncertainties remain about the photochemistry and reaction rate coefficients for some of the gas phase species, it is generally accepted that particle formation proceeds as follows:

Iodocarbons, I₂ → I atoms → IO → OIO → I₂O_y(y=3 to 5) → stable particle nuclei.

The sequence begins with certain species of seaweed such as *L. digitata* emitting iodocarbons and/or molecular iodine into the atmosphere in response to the stress of being exposed by an ebb tide. *L. digitata* is known to be a prodigious accumulator of iodine from sea water, capable of reaching more than 1% iodine by dry weight (Küpper et al., 1998; Ar Gall et al., 2004). The iodine is stored as the iodide anion, I⁻, partially solvated by water but with its hydration shell disrupted by hydrogen-bonding to organic biomolecules (Küpper et al., 2008). The greatest iodide concentrations are found in the plant's peripheral tissues from where it is released to react with reactive oxygen species (ROS: H₂O₂, O₃, O₂⁻, ¹O₂, HO₂) (Verhaeghe et al., 2008; Küpper et al., 2008). It seems that I₂ is not emitted directly by the seaweed, but rather is the product of chemistry that occurs outside the cell membrane when the plant acts to combat oxidative stresses. Thus I₂ is produced (i) by the reaction between, for example, gas phase ozone and I⁻ when the plant's surface is exposed to the atmosphere at low tide (i.e. iodide acting as an inorganic antioxidant; Küpper et al., 2008), and (ii) by enzymatic reactions between aqueous phase H₂O₂ and I⁻ in the apoplast catalysed by vanadium-dependent haloperoxidases and, in the case of kelp species, the more specialised iodoperoxidase enzymes (Colin et al., 2005; Küpper et al., 2008). Emission of halocarbons is also likely to be a by-product of haloperoxidase activity, and since iodocarbons have a high microbial toxicity, it is thought that they are involved in a chemical defence mechanism in kelp (Küpper et al., 2008).

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Once released into the atmosphere, the iodine-containing source gases undergo photolysis by solar radiation with lifetimes ranging from under 10 s (I_2), to several minutes (e.g. CH_2I_2), to a few days (CH_3I). It was initially thought that CH_2I_2 was the main iodine-containing precursor leading to particle formation under atmospheric conditions (e.g. Jimenez et al., 2003). However, at least in coastal regions, it now seems more likely that molecular iodine provides the dominant iodine atom flux because I_2 concentrations typically exceed those of CH_2I_2 and because I_2 has a substantially shorter photolytic lifetime (McFiggans et al., 2004). The photochemically produced iodine atoms quickly react with ozone to give iodine monoxide radicals (IO). Iodine dioxide radicals (OIO) are then produced as the dominant channel in the reaction between two IO radicals. OIO is thought to undergo its own self reaction to produce I_2O_4 and to react with IO to produce I_2O_3 , both of which, if not already stable nuclei themselves, react with ozone to produce I_2O_5 and/or add further IO and OIO units to yield polymeric iodine oxides and ultimately newly nucleated aerosol particles (Burkholder et al., 2004; McFiggans et al., 2004; Pirjola et al., 2005; Kaltsoyannis and Plane, 2008). It is also probable that OIO co-condenses with other molecules such as H_2SO_4 or low volatility organic compounds (Vuollekoski et al., 2009).

Iodine chemistry also has important impacts on the trace gas composition of the marine boundary layer (von Glasow and Crutzen, 2007). Catalytic cycles driven primarily by the IO radical act to deplete tropospheric ozone and affect the oxidising capacity of the coastal atmosphere by perturbing the partitioning within the NO_2/NO and HO_2/OH radical families (Davis et al., 1996; Bloss et al., 2005; Mahajan et al., 2009). There have now been many observations of IO in the marine atmosphere by long path differential optical absorption spectroscopy (LP-DOAS) – see the tables summarising IO, OIO and I_2 observations in Peters et al. (2005), von Glasow and Crutzen (2007) and Seitz (2009). IO was also detected by LP-DOAS during the RHaMBLe coastal deployment at Roscoff (Mahajan et al., 2009) and additionally by laser induced fluorescence (Whalley et al., 2007) and cavity ringdown spectroscopy (Wada et al., 2007). In contrast there have been far fewer direct spectroscopic observations of atmospheric IO's

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likely precursor, I_2 , and the vast majority of these I_2 observations have been made around the Mace Head area (Saiz-Lopez and Plane, 2004; Bitter et al., 2005; Peters et al., 2005; Saiz-Lopez et al., 2006; Bloss and Ball, 2009; Seitz, 2009). Notably Peters et al. (2005) were unable to find any I_2 above their detection limit of ~ 20 pptv during a campaign at Lilia, Brittany, even in the presence of strong iodocarbon and IO signals. And only recently have direct spectroscopic observations of I_2 been reported at locations other than Mace Head: I_2 has been detected at La Jolla, California, using chemical ionisation mass spectrometry (Finley and Saltzman, 2008) and at Roscoff using LP-DOAS (Mahajan et al., 2009) and broadband cavity ringdown spectroscopy (Leigh et al., 2009).

This work uses broadband cavity enhanced absorption spectroscopy (BBCEAS), a highly sensitive type of optical absorption spectroscopy, to quantify I_2 concentrations in gas flows passed over seaweed samples exposed to desiccation in air and to other stress factors. The aim was to follow the time profiles of I_2 emissions from different seaweed species in order to understand which species contribute to atmospheric I_2 and explain why, for example, I_2 has been known for several years at Mace Head but has only recently been observed at other coastal locations. Two distinct types of experiment were conducted at the Station Biologique de Roscoff (SBR) during the final week of the RHaMBLe coastal deployment in September 2006:

- (i) Incubation experiments were performed on whole plants of 7 different seaweed species – here the aim was to monitor time-dependent I_2 emissions from seaweeds when first exposed to air, and thus to mimic what occurs in their natural environment around low tides.
- (ii) Fragments of *L. digitata* thalli were variously exposed to air, ozone and oligoguluronate in order to monitor their stress response in terms of time-dependent I_2 emissions and how those emissions correlated with any subsequent aerosol particle formation.

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BBCEAS spectra were recorded between 522 and 554 nm in a spectral region where the I_2 molecule possesses characteristic and highly structured absorption bands. The detection limit of the present system for I_2 is around 25 pptv (parts per trillion by volume; 10^{-12} mixing ratio) for an integration time of 7.5 s, thus allowing the emission of even small quantities of I_2 to be monitored at high time resolution. To our knowledge, the direct spectroscopic detection of I_2 from seaweed has only previously been reported for *L. digitata* exposed to ambient air (Bale et al., 2008; Dixneuf et al., 2009). This work extends high time resolution observations of I_2 to other seaweed species and to *L. digitata* exposed to stress factors. Emission rates of I_2 are also provided for both types of experiment.

2 Method

2.1 Sample collection and preparation

Thalli of *Dictyopteris membranacea*, *Saccharina latissima*, *Laminaria digitata* and *Laminaria hyperborea* were collected in the inter-tidal zone close to the Station Biologique de Roscoff (SBR) during the daytime low tide of 22 September 2006. The algae were stored in running sea water in the SBR aquarium, illuminated by natural light passing through the aquarium's many windows. When required for the incubation experiments, whole seaweed plants were removed from the aquarium's tanks, shaken free of excess water and placed in a ten litre, translucent, Nalgene plastic bottle. The bottle plus seaweed was weighed and then sealed with a screw cap. All experiments were conducted within 8 days of harvesting the samples. *Ascophyllum nodosum*, *Fucus serratus* and *Fucus vesiculosus* samples were taken directly from the beach outside the SBR within a few metres of the water's edge and were used immediately. The transit time from the aquarium/beach to beginning an experiment was around 3 min.

Some of the *Laminaria digitata* collected on 22 September was stored separately in one of the SBR's laboratories for use in the stress experiments on 27 and 28 September

(running, aerated seawater at 9–17°C; illuminated by a photon flux of 50–60 $\mu\text{mol photons m}^{-2} \text{s}^{-1}$ with a 12-h-on/12-h-off cycle). Fragments of thalli weighing between 5 and 10 g were cut before the start of each stress experiment, rinsed in seawater, and ≈ 20 g of sample was arranged around the walls of the small glass vessel (volume $\approx 200 \text{ cm}^3$) that served to contain the seaweed in the flow reactor. The samples for stress experiments #1, #3 and #4 were used immediately, whereas the sample for stress experiment #2 comprised the same pieces of thalli used in experiment #1 the previous evening and which had been allowed to recover in aerated seawater overnight. The thalli fragments for stress experiments #3 and #4 were additionally anointed with 10 cm^3 of a solution of oligoguluronates ($150 \mu\text{g cm}^{-3}$) for one minute and then rinsed with seawater before being placed in the flow reactor. Oligoguluronates (GG) are breakdown products of the algal cell wall and are recognised by the algae as an indicator of pathogen attack, provoking an oxidative stress response. The oligoguluronates were prepared by mild acid hydrolysis as previously described by Küpper et al. (2008) and Cosse et al. (2009). The four *L. digitata* stress experiments and all but two of the seaweed incubation experiments were performed in the SBR's cold room (air temperature = 12°C): the two exceptions were the *Dictyopteris membranacea* and the first *Laminaria hyperborea* (healthy specimen) incubation experiments which were performed in a regular laboratory inside the SBR (ambient temperature $\approx 20^\circ\text{C}$).

2.2 Apparatus

The upper panel of Fig. 1 shows a schematic of the apparatus used in the incubation experiments performed on whole seaweed plants. A mechanical pump forced ambient air ($2.8 \text{ litres min}^{-1}$) through an aerosol particle filter and along $\frac{1}{4}$ inch external diameter Teflon tubing that passed through a tube fitting in the screw cap of the Nalgene bottle containing the seaweed sample. A second Teflon tube conveyed gas out of the Nalgene bottle and into 1.5 inch diameter plastic tube enclosing the optical cavity of the BBCEAS instrument. Sample gas vented from the cavity through a small gap between the plastic tube and the cavity's mirror mounts.

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The BBCEAS spectrometer was similar in form and function to an instrument previously used to quantify trace amounts of NO₂ in the atmosphere (Langridge et al., 2006). The spectrometer's light source was a high intensity light emitting diode (Luxeon 3 Watt green LED, peak wavelength = 535 nm) mounted on a fan-cooled heat sink. Light from the LED was coupled into a fibre optic cable abutted up against the emitter's surface and re-collimated at the far end of the fibre by a microscope objective lens. Two turning mirrors then directed the light beam into the optical cavity formed by two highly reflective mirrors (Layertec GmbH). Light transmitted through the cavity's output mirror was collected by an $f=25$ mm lens, focussed into a fibre optic cable, and dispersed and detected as a function of wavelength by a fibre-coupled spectrometer (OceanOptics HR4000) interfaced to a laptop computer.

The lower panel of Fig. 1 shows a schematic of the flow reactor used in the *L. digitata* stress experiments. A mechanical pump forced ambient air (4.8 litres min⁻¹) sequentially through molecular sieve and charcoal traps to scrub the air free from ambient ozone and any volatile organic compounds (VOCs) that might otherwise be oxidised to particle-forming oxygenated-VOCs in the ozoniser. The flow then divided through two metering valves, one line feeding an ozoniser (Penray ozone generator 97-0067-02 with mercury lamp) and water bubbler and the other line feeding a bubbler directly. Any aerosol formed by bubble bursting was removed by particle filters. The flows recombined, passed through the vessel containing the seaweed and flowed into a second larger glass vessel (residence time ≈ 20 s). The purpose of this second vessel was to allow time for newly nucleated particles to grow by the further addition of condensable gases and thus reach a detectable size. The outflow from the aerosol growth vessel was divided three ways between a condensation particle counter (CPC; TSI model 3776, size cut-off $D_p=3$ nm), an ozone monitor (2B Technologies model 202) and a line supplying gas to the BBCEAS cavity. The net flow into the cavity was 3.3 litres min⁻¹.

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2.3 Quantification of I₂ by BBCEAS

The wavelength dependent absorption coefficient of the gas sample – hereafter termed the sample's BBCEAS spectrum – is given by the equation (Langridge et al., 2006; Ball and Jones, 2009):

$$\alpha(\lambda) = \left(\frac{I_0(\lambda)}{I(\lambda)} - 1 \right) \times \frac{1-R(\lambda)}{d} \quad (1)$$

where $I(\lambda)$ is the light intensity transmitted through the cavity when an absorbing gas sample is present within the cavity and $I_0(\lambda)$ is the intensity transmitted when the cavity is flushed with a non-absorbing gas, in this case pure nitrogen (Alphagas N₂, Air Liquide). The remaining parameters in Eq. (1) are cavity's length, $d=116$ cm, and the wavelength dependent reflectivity of the mirrors, $R(\lambda)$. The HR4000 spectrometer recorded spectra of the transmitted light intensity with an integration time of 0.75 s, and ten such acquisitions were averaged together to produce each $I(\lambda)$ or $I_0(\lambda)$ measurement before being saved to the laptop (i.e. a net acquisition time of 7.5 s). In order to minimise noise when calculating the BBCEAS spectra, an averaged $I_0(\lambda)$ spectrum was constructed for each experiment from between thirty and fifty 7.5 s transmission spectra obtained when flushing the cavity with nitrogen, either prior to or after sampling gas from the seaweed container. BBCEAS spectra were then calculated for each $I(\lambda)$ spectrum (i.e. at a time resolution of 7.5 s) using the averaged $I_0(\lambda)$ spectrum in Eq. (1).

The form of Eq. (1) shows that it is vital to know how the cavity mirror reflectivity varies with wavelength if BBCEAS is to be used to make quantitative measurements of trace gas concentrations (Ball and Jones, 2009). A convenient method for deriving $R(\lambda)$ is to record the BBCEAS spectrum of a sample of known composition and thus known $\alpha(\lambda)$. Here we adopt the approach of Langridge et al. (2006): $R(\lambda)$ was determined by flushing the cavity with pure oxygen and recording BBCEAS spectra of the collision-induced ${}^1\Delta_g + {}^1\Delta_g$ ($\nu=2$) \leftarrow ${}^3\Sigma_g^- + {}^3\Sigma_g^-$ absorption band of the O₄ oxygen dimer around 532 nm (Greenblatt et al., 1990; Hermans, 2008). The precise form of the reflectivity versus wavelength curve obtained from fitting the O₄ absorption feature

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was then adjusted to minimise the standard deviation of the residual spectrum when fitting (i) BBCEAS spectra of seaweed emissions containing very high iodine concentrations ($[I_2] > 10\,000$ pptv) on the assumption that their strong I_2 absorption features overwhelmed all other possible absorbers, and (ii) BBCEAS spectra of NO_2 diluted in nitrogen recorded after the Roscoff RHaMBLe campaign. Fitting the detailed differential spectral structure due to I_2 and NO_2 across the entire bandwidth of the present measurements produced subtle refinements in the shape of the $R(\lambda)$ curve, but did not reduce the quality of the fit to the oxygen dimer spectrum which remained the primary factor in determining $R(\lambda)$. The resultant mirror reflectivity curve had a broad, almost flat maximum of $R=99.955\%$ at 525 nm, decreasing smoothly to $R=99.912\%$ at 554 nm. Thus the enhancement factor of the cavity ranged from $1/(1-R)=2230$ at 525 nm to 1140 at 554 nm, corresponding to equivalent absorption paths through the intra-cavity sample of 2.59 and 1.33 km, respectively.

A detailed discussion of how to retrieve absorber concentrations from fitting spectra obtained with broadband cavity-based methods is given by Ball and Jones (2009). Briefly, BBCEAS spectra of gas mixtures usually contain structured absorption features due to molecular absorbers (including in this case the target I_2 molecule) and a broad, featureless absorption due to aerosol extinction and any other absorbers possessing unstructured absorptions over the wavelength range of the measurement:

$$\alpha(\lambda) = \sum_n \alpha_n(\lambda) + \alpha_{\text{cont}}(\lambda) \quad (2)$$

Here $\alpha_n(\lambda)$ are the absorption coefficients of the n structured molecular absorbers and $\alpha_{\text{cont}}(\lambda)$ is the total absorption coefficient of all unstructured contributions to the BBCEAS spectrum. The absorption coefficient of an individual absorber n (e.g. the target species I_2) is given by the product of its absorption cross sections, $\sigma_n(\lambda)$, and its concentration, $[n]$:

$$\alpha_n(\lambda) = \sigma_n(\lambda) \times [n] \quad (3)$$

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(except for the oxygen dimer where its absorption coefficient depends on the square of the molecular oxygen concentration). Differential optical absorption spectroscopy (DOAS) is then applied to separate and individually quantify the structured spectral contributions by fitting reference molecular absorption cross sections to the differential structure in the BBCEAS spectrum (Langridge et al., 2006, 2008; Ball and Jones, 2009). Three structured absorbers were included in the present spectral fitting routine: I_2 from the seaweed emissions, H_2O from ambient humidity and an O_4 contribution due to atmospheric oxygen (although in practice the weak and constant O_4 contribution was subtracted from the BBCEAS spectrum prior to the DOAS fitting). An additional quadratic function represented the remaining continuum absorption, $\alpha_{\text{cont}}(\lambda)$. Once its absorption coefficient had been retrieved by the DOAS analysis routine, the concentration of absorber n was obtained from the gradient of a plot of $\alpha_n(\lambda)$ versus $\sigma_n(\lambda)$, see Eq. (3). Additionally, the 1σ error in this gradient provided a measure of the statistical uncertainty associated with retrieving that absorber's concentration from its differential structure in the BBCEAS spectrum. The statistical fitting error was typically ± 20 pptv for I_2 mixing ratios around the detection limit, rising to $\approx 0.4\%$ of the fitted amount for largest I_2 signals in this study. Figure 2 shows examples of BBCEAS spectra measured during two of the seaweed incubation experiments, overlaid with the $\alpha_{I_2}(\lambda)$ absorption coefficients retrieved by the DOAS fitting routine. The 522–554 nm bandwidth of these spectra spans 18 vibrational bands of the I_2 molecule's B←X electronic transition: this unique spectral signature provides unambiguous identification of I_2 even at high dilution which, allied to the kilometre absorption path lengths achieved inside the cavity, gives the BBCEAS technique its very high sensitivity.

2.4 Choice of molecular absorption cross sections

The I_2 absorption cross sections used to fit the BBCEAS spectra were adapted from the values of Saiz-Lopez et al. (2004). Available on a wavelength grid of $\delta\lambda=0.1$ nm, the literature cross sections were still too coarse to fit the fine detail of the I_2 differential structure in the present BBCEAS spectra. Instead I_2 absorption spectra were

calculated on a wavelength grid of $\delta\lambda=0.02$ nm at the HR4000 spectrometer's resolution (Gaussian function 0.22 nm FWHM) using the I_2 molecule's spectroscopic constants and the PGOPHER spectral simulation package (Martin et al., 1986; Western, 2009). Absorption cross sections were then obtained by applying a scaling constant to the simulated I_2 spectrum such its differential spectral structure best matched the differential structure in the Saiz-Lopez et al. (2004) cross sections over the 522–554 nm wavelength range. We estimate that the uncertainty in the simulated I_2 cross sections is 15%, compared to the 12% uncertainty quoted for the literature cross sections. Water vapour cross sections were calculated from the HITRAN 2004 spectral database (Rothman et al., 2005) and degraded to the spectrometer's resolution. It was not found necessary to include the possibility of water absorption lines becoming partially saturated over the very long effective path lengths encountered inside a BBCEAS cavity (Langridge et al., 2008) because the water lines at the current green wavelengths are more than an order of magnitude weaker than those at the red wavelengths of the Langridge et al. (2008) study. The higher resolution O_4 cross sections of Hermans (2008) were preferred over those of Greenblatt et al. (1990). However no information is provided about the uncertainty of the Hermans cross sections, and we estimate an uncertainty of $\sim 5\%$ in the differential cross sections of the 532 nm O_4 band by comparison with the cross sections of Greenblatt et al. (1990) and the cavity ringdown study of Sneep and Ubachs (2005). Since the reflectivity of the cavity mirrors was determined from BBCEAS spectra of this O_4 dimer band, the uncertainty in the O_4 cross sections translates directly into a systematic 5% uncertainty in the cavity enhancement factor and thus an additional 5% uncertainty in the mixing ratios of all absorbers retrieved from fitting the BBCEAS spectra.

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3 Results

3.1 Incubation studies on whole seaweed plants

A total of ten incubation experiments were performed on seven different seaweed species during the period 27–30 September 2006. The results of these incubation experiments are summarised in Table 1, and I_2 emission time profiles from five experiments are shown in Figs. 3 and 4. Repeat experiments using different samples of the same species were generally not possible owing to the time constraints of the RHaMBLe field campaign. However repeat experiments were performed for *Saccharina latissima*($\times 3$) and *Laminaria hyperborea*($\times 2$), in part because some of the samples showed signs of mechanical damage or decay (this is noted in Table 1). The initial air-exposure phase of the *L. digitata* stress experiment #1 in Sect. 3.2 provides a second repeat for that species.

Figure 3 shows time series of I_2 mixing ratios observed from three seaweed species: *Dictyopteris membranacea* (Fig. 3a), *Ascophyllum nodosum* (Fig. 3b) and a young healthy plant of *Saccharina latissima* (Fig. 3c). Each data point represents the I_2 mixing ratio retrieved from fitting a single BBCEAS spectrum, and thus the emission profiles in Fig. 3 et seq. have a time resolution of 7.5 s (Note: the HR4000 spectrometer's software was configured to record $I(\lambda)$ spectra in batches of 10×7.5 s acquisitions when initiated by the operator, rather than by continuous acquisition; hence the data points in time profile plots are clustered in batches of ten, with occasional short breaks). The red data points are the I_2 mixing ratios in gas that had previously flowed over the seaweed samples and the lighter coloured yellow data points are I_2 mixing ratios retrieved from fitting BBCEAS spectra recorded when the cavity was flushed with dry nitrogen. The latter spectra have the same 7.5 s acquisition time and were calculated using individual $I_0(\lambda)$ spectra instead of individual $I(\lambda)$ spectra in the denominator of Eq. (1). The error bars accompanying each data point combine both the statistical uncertainty (i.e. gradient error) associated with retrieving the I_2 mixing ratio and the systematic uncertainties in the I_2 cross sections (15%) and the cavity enhancement

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factor (5%). The statistical fitting error dominates for I₂ mixing ratios around/below the detection limit (e.g. Fig. 3a and all flushed cavity data points), whereas the systematic errors begin to dominate for I₂ mixing ratios above a few hundred pptv (e.g. sample data points in Fig. 3b and c).

5 The time series in Figures 3b and 3c shows that the *A. nodosom* and *S. latissima* samples produced gas phase I₂ at mixing ratios of several hundred parts per trillion by volume. Characteristic absorption bands of I₂ were clearly visible in the BBCEAS spectra confirming the presence of I₂: for example, the BBCEAS spectrum in the upper panel of Fig. 2 corresponds to one of the red data points in the profile for *S. latissima* (Fig. 3c). Conversely no I₂ emissions were detectable from the *D. membranacea* sample (Fig. 3a). In addition to the tick marks denoting I₂ mixing ratios on the main vertical axis, each time series plot gives the corresponding I₂ emission rates on the right hand axis in units of picomoles of I₂ emitted per minute per gramme fresh weight of the sample (pmol min⁻¹ gFW⁻¹). Since emission rates take account of the sample's weight and the volumetric flow rate through the apparatus, they provide a more directly comparable quantity than mixing ratios when considering the results of different experiments and when comparing the results of this work with previous studies. Consequently, the single *S. latissima* plant (60 g) of Fig. 3c is an approximately ×10 more potent emitter of I₂ than the 460 g *Ascophyllum* sample of Fig. 3b even though their measured peak I₂ mixing ratios only differ by around a factor of two. The summary Table 1 provides emission rates along side the measured I₂ mixing ratios for all ten incubation experiments performed on the whole seaweed plants, listing the different species in approximate order of increasing emission rates. Table 1 also includes the peak I₂ mixing ratios and peak emission rates for samples whose emission profiles possessed an obvious maximum. Note that the uncertainties quoted for the emission rates in Table 1 are proportionately larger than the corresponding uncertainties quoted for the mixing ratios because they incorporate an additional uncertainty associated with measuring the gas flow rate through the apparatus.

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Figure 4 shows I_2 time series for samples of *L. digitata* and *L. hyperborea*, both of which were found to produce substantial amounts of I_2 . The profiles in Fig. 4 are characterised an immediate, very strong burst of I_2 with mixing ratios peaking in excess of 10 000 pptv, i.e. $[I_2] > 10$ ppbv (parts per billion by volume, 10^{-9} mixing ratio). The strong I_2 burst is followed by an approximately exponential decay with fitted half-lives of 8 and 5 min for *L. digitata* and *L. hyperborea* respectively (see insets in Fig. 4). The peak emission rates for these samples are approximately an order of magnitude larger again than the peak emission rate of the *S. latissima* sample in Fig. 3c, although *S. latissima* has a broader emission profile. A second experiment was performed on a partially decayed *L. hyperborea* specimen towards the end of the campaign (last entry in Table 1): this sample produced a peak I_2 mixing ratio of 87 000 pptv, the largest of all of the seaweed incubation experiments, and sustained a double peaked emission profile over the 18 min duration of the experiment.

The flushed cavity data shown in the I_2 time series plots of Figs. 3 and 4 perform two important quality assurance roles. First, the scatter in these data about their mean provides the most direct measure of the I_2 detection limit in each experiment. For example, for Fig. 3a, the standard deviation in the whole set of flush data points before and after the seaweed sample is 24 pptv. This value is reported in Table 1 as the uncertainty in the mean mixing ratio for the flushed cavity data, and is typical of the I_2 detection limits in this work. (For comparison, the average error bar on the flush data points in Fig. 3a is ± 19 pptv, indicating that the 1σ gradient error of the $\alpha_n(\lambda)$ versus $\sigma_n(\lambda)$ plots probably slightly underestimates the statistical uncertainty of the DOAS retrieval.) The average I_2 concentration for the sample data points in Fig. 3a is only 2 pptv (standard deviation = 26 pptv), and thus it is easy to conclude that this sample of *D. membranacea* did not emit detectable amounts of I_2 . Secondly, the long-term stability of the BBCEAS system can be gauged by comparing the flush data points before and after sampling from the seaweed vessel, and usually any systematic drifts were negligible within the scatter of the flush data points. However, sometimes after an experiment on a large I_2 emitter the flushed cavity data points would lie significantly above zero and would be

accompanied by I₂ structure remaining in the BBCEAS spectra (e.g. the positive offset in the final flushed cavity data points in Fig. 4a). This was attributed to small amounts of residual I₂ coating the internal surfaces of the apparatus: in these instances, the Nalgene sample bottle and the tube surrounding the cavity were rinsed with distilled water and dried before the next experiment and the $\frac{1}{4}$ inch diameter Teflon delivery tube was replaced.

The remaining entries in Table 1 summarise two experiments performed on *Fucus* samples and two experiments on partially decayed *S. latissima* plants. No statistically significant I₂ emission was detected from *F. serratus*, and only small amounts of I₂ (max ~50 pptv) close to the detection limit were observed from *F. vesiculosus*. Both of the decayed *S. latissima* samples showed clear evidence of I₂ emission, though at substantially lower rates than the healthy young specimen whose emission profile appears in Fig. 3c. Whilst the decayed samples may be under-representative of *S. latissima*'s usual I₂ emission rates, their entries are retained in Table 1 to illustrate the following point. The I₂ emission rates for the three *S. latissima* samples span more than a factor of ten (i.e. comparable to the differences between species). It seems likely therefore that I₂ emission rates depend on the age and/or health of the plant. In partial support of this idea, the dry weight iodine content of *L. digitata* is known to be higher in small, young plants (Ar Gall et al., 2004). However it is not necessarily the case that damaged plants are smaller emitters because, as noted above, the partially decayed *L. hyperborea* sample produced considerably more I₂ than its healthy counterpart.

3.2 *Laminaria digitata* exposed to stress factors

A second distinct set of experiments were performed on fragments of *L. digitata* thalli exposed to various stress factors inside the flow reactor. Time profiles of the I₂ emissions measured by BBCEAS (also at 7.5 s time resolution) are shown for three of these experiments in Figs. 5 to 7. Additionally, Table 2 summarises the peak and averaged I₂ mixing ratios for all four stress experiments, together with pertinent information about the ozone mixing ratio and aerosol particle number concentrations co-measured in the

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gas flow. Table 2 also provides corresponding I_2 emission rates calculated from the measured mixing ratios, the sample's fresh weight and the volumetric gas flow through the apparatus.

In the first experiment, two pieces of thalli (total 21 g fresh weight) were exposed to desiccation in air for 20 min, after which 90 ppbv of ozone was added to the gas flow. The I_2 emission profile is shown in Fig. 5. The seaweed initially produced an intense emission burst (peak $[I_2] \approx 2300$ pptv) that relaxed rapidly with a half-life of ~ 1.6 min. Note that ozone was scrubbed from the air supply for all of the stress experiments, and this first phase of stress experiment #1 was conducted under ozone-free conditions. After normalising for weight, the averaged I_2 emission rate of these *L. digitata* fragments in response to air-exposure (2.98 ± 0.83 pmol min⁻¹ gFW⁻¹) was same as the emission rate observed in the incubation experiment performed on a whole plant (3.17 ± 0.81 pmol min⁻¹ gFW⁻¹). This is an important result because it shows that mechanical stress (cutting the thallus into fragments) does not seem to influence the I_2 emission rate in *L. digitata*. It is likely that the shorter half-life for this emission's decay compared to the incubation experiment is attributable to the gas flow's shorter residence time in the flow reactor apparatus compared to the 10 litre Nalgene bottle, rather than indicating a change in the emission dynamics.

A second phase of I_2 emission was observed to follow directly after ozone was added to the gas flow some 20 min into the experiment. Previous studies have shown that ozone elicits I_2 emission from *L. digitata* (Palmer et al., 2005; Küpper et al., 2008), and in this case the addition of ozone caused a sample that had largely relaxed from its initial air-exposure stress to re-start emitting I_2 . The profile of the second ozone-induced emission is noticeably lower (peak $[I_2] = 600$ pptv) and broader than the air-exposure burst, but the integrated amounts of I_2 emitted during the two events were similar: ≈ 50 pmol gFW⁻¹ (calculated from the product of the average emission rates and the experiments' durations given in Table 2). This amount still only represents a very small fraction of the *L. digitata* sample's likely $\sim 1\%$ iodine by dry weight (Küpper et al., 1998). The insert in the lower panel of Fig. 5 shows that no aerosol particles were detected

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by the condensation particle counter prior to the addition of ozone. Particle formation was however observed coincident with the second ozone-induced I_2 emission, even though the I_2 mixing ratios were considerably lower than for the initial air-induced I_2 burst. These two regimes are clearly represented in the correlation plot of I_2 mixing ratio versus particle number concentration in the main plot in the lower panel of Fig. 5: (i) a flat “arm” of the plot showing no particle formation in the absence of ozone even at high $[I_2]$ and (ii) a second steeply-sloping arm showing a rapid, approximately linear increase in particles with I_2 mixing ratio (slope = $620 \text{ particles cm}^{-3} \text{ pptv}^{-1}$) once a threshold concentration of $I_2 \approx 400 \text{ pptv}$ had been reached. Thus we conclude that while ozone isn’t necessarily required to elicit I_2 emissions from *L. digitata*, ozone is required by the subsequent chemistry that oxidises iodine into condensable iodine oxides. This is entirely consistent with the known chemistry of the iodine oxides. The stress experiments were conducted in a largely glass apparatus under the SBR cold room’s fluorescent strip lighting. Room light photolyses I_2 to I atoms which then react with ozone to produce IO and thence higher oxides, the direct gas phase reaction between $I_2 + O_3$ being very slow. (Indeed, ozone stress experiment #4 (below and Fig. 7) will show that particle nucleation ceased immediately the seaweed reactor vessel and the aerosol growth vessel were covered with a black cloth, though the I_2 emissions continued.)

At the end of the first stress experiment, the *L. digitata* fragments were removed from the flow reactor and stored in aerated seawater overnight. The same fragments were then used the next day in the second experiment to test how seaweed that had previously been stressed by ozone would react to a second stress event. On initial exposure to air, the sample produced multiple bursts of several hundred pptv I_2 . A technical issue prevented the BBCEAS instrument from recording this initial phase, and so the emission profile in Fig. 6 begins about 30 min after the sample had first been exposed to air, by which time the I_2 emission had relaxed to $\sim 70 \text{ pptv}$ (relative to an offset in the initial flush cavity data points). Ozone at 90 ppbv was then added to the gas flow at $t=4 \text{ min}$ in Fig. 6. The I_2 concentration increased abruptly to 300 pptv,

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but rather than following the usual exponential-type decay, a broad I_2 emission was sustained for the next 50 min reaching a maximum of 450 pptv shortly before the end of the experiment. Very little particle production was observed until the I_2 mixing ratio rose through a threshold of $[I_2] > 205$ pptv towards the end of the experiment (lower panel of Fig. 6). Again there was an approximately linear relationship between particle number concentration and I_2 mixing ratio above the threshold ($330 \text{ particles cm}^{-3} \text{ pptv}^{-1}$). The I_2 emission rate averaged throughout this experiment was (within uncertainty) the same as the average emission rate for the second ozone-induced I_2 emission phase from this sample in stress experiment #1 (see Table 2). Thus the primary effect of previously having undergone a stress event seemed to be to change the shape of the emission profile rather than to limit the sample's ability to emit I_2 .

A third stress experiment was performed on two fragments of freshly cut *L. digitata* thalli that had been anointed with GG solution to stimulate a response to pathogen attack. A single intense burst of I_2 emission up to 2500 pptv was observed when the samples were first placed into the flow reactor, followed by a smooth decay in the emissions with a half-life of 3.2 min (see Table 2). Thus, although the emission profile was slightly more prolonged, it was not significantly stronger than for the initial air-induced I_2 emission in stress experiment #1. No particle formation was observed, as expected, because ozone had been scrubbed from this experiment's air supply.

The final experiment exposed fragments of *L. digitata* to simultaneous air + ozone + GG stresses. This combination yielded by far the largest emission rates of any experiment in this work ($\approx \times 10$ larger peak emission rate than even the incubation experiment on the partially decayed *L. hyperborea* sample). The top panel of Fig. 7 shows a very intense initial burst of 25 000 pptv of I_2 , followed by a sustained period of smaller but nevertheless still quite strong emissions ($I_2 \approx 1500$ pptv). Then 35 min into experiment #4, and without any apparent increase in the stress factors, the I_2 emissions increase again: I_2 mixing ratios were sustained at 7000–20 000 pptv for more than 40 min, before decaying away towards the end of the experiment. Curiously, there was a third smaller burst of I_2 when the ozone was turned off around $t = 120$ min suggesting that

the *L. digitata* sample reacted to the removal of a stress factor by increasing its I₂ emissions. Particle formation was observed throughout stress experiment #4 until a black cloth was placed over the apparatus $t=110$ min to exclude the room light (middle panel of Fig. 7); but there was no noticeable change in the I₂ emissions when the apparatus was covered. The particle number concentrations observed in this experiment were substantially larger than in previous experiments #1 and #2, no doubt due to the higher I₂ mixing ratios. The bottom panel of Fig. 7 shows an approximately logarithmic relationship between particle numbers and I₂ indicative of a roll-off in particle formation rates at high I₂ mixing ratio.

4 Discussion

4.1 Incubation studies on whole seaweed plants: species-dependent I₂ emission rates

The incubation studies show that the various seaweed species investigated in this work yielded substantially different I₂ emissions. I₂ mixing ratios ranged from below the BBCEAS instrument's detection limit of 25 pptv up to 87 000 pptv for the partially decayed *L. hyperborea* sample. Thus the I₂ mixing ratios (and their corresponding emission rates) span at least three and a half orders of magnitude. The entries in Table 1 have been grouped by species and are listed in approximate order of increasing emission rates: *D. membranacea* \approx *F. serratus* \leq *F. vesiculosus* $<$ *A. nodosum* $<$ *S. latissima* $<$ *L. digitata* \approx *L. hyperborea*. This ranking is broadly consistent with the order in which iodine content increases within seaweed plants themselves (e.g. Küpper et al., 1998; Teas et al., 2004; Martinelango et al., 2006). But the variation in I₂ emission rates is proportionately far greater than the species-dependent differences in iodine content. For example, iodine concentrations in *L. digitata* are some 7–30 times greater than in *F. vesiculosus*, yet the I₂ emission rates from *L. digitata* were found here to exceed those from *F. vesiculosus* by around 3 orders of magnitude, suggesting that

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the physiological functions of iodine is different in these two species. The above ranking also mirrors how the seaweed speciation changes moving seawards through the inter-tidal zone at Roscoff, with the largest emitters *L. digitata* and *L. hyperborea* living in deeper waters further from the shoreline: a map of seaweed habitats in the Roscoff area is shown in Leigh et al. (2009). As well as the inter-species differences, substantial variability was observed in I₂ emission rates for the few repeat incubation experiments on the same species (*S. latissima*×3 and *L. hyperborea* ×2) suggesting that I₂ emissions also depend on the age and/or health of plants. Natural populations contain a distribution of ages and will inevitably include some unhealthy/damaged individuals. Each of these make their own particular contributions to the net emissions into the atmosphere, and thus more systematic future investigations of I₂ emission rates ought to consider plants of different ages and condition.

During RHaMBLe, strong tidal dependences were seen in atmospheric I₂ and IO measurements made by long path DOAS over the channel between the SBR and the Ile de Batz (Mahajan et al., 2009), and in the point measurements of I₂ (Leigh et al., 2009), IO (Whalley et al., 2007; Wada et al., 2007) and aerosol particles (Whitehead et al., 2009) located at the RHaMBLe measurement site on the jetty in front of the SBR. The various data sets are also summarised in the Roscoff overview paper introducing this RHaMBLe special issue (McFiggans et al., 2009). The modelling study of Leigh et al. (2009) sought to understand the temporal and spatial variability of I₂ emission into the atmosphere by linking emission rates parameterised from this study to the distribution of seaweed habitats around Roscoff. The model provided a good qualitative and a reasonable quantitative explanation of the tidal signatures in the I₂ measurements in terms of the most efficient, most distant I₂ emitting seaweeds only becoming exposed around the lowest low tides. It has also been observed at Cape Grim in Australia that large biomasses of the fucoid alga *Durvillaea potatorum* appear to play a very limited role in contributing to particle formation because, despite its common name of the *southern bull kelp*, this species does not emit I₂ (Cainey et al., 2007). Thus the linked RHaMBLe observations/modelling and the Cainey et al. (2007) study reveal the

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importance algal speciation plays in understanding the iodine chemistry and resultant particle formation at a given site. Kelps are far better emitters of I_2 whereas fucoids are poorer emitters and accumulators. These differences strongly suggest a link between the evolution of kelps from the order of Laminariales, which evolved more recently than the order of Fucales and Dictyopterales (Rousseau et al., 2001), and their capacity to emit iodine. During this evolution, it seems that kelps developed new biochemical adaptations in their use of halides related to their capacity to specifically oxidise iodide using vanadium-dependent haloperoxidases. Most algae feature bromoperoxidases that can react with either bromide or iodide. However Laminariales species are the only brown algae where iodoperoxidase activities (i.e. specific for iodide) have been detected (Almeida et al., 2001; Colin et al., 2005). In these algae, the occurrence of such an enzyme (likely to be present in the apoplast) should explain (i) the very high amounts of iodide accumulated in their cell walls and (ii) their higher efficiency for enzymatic iodide oxidation with the concomitant removal of H_2O_2 produced during oxidative stresses such as exposure to air, desiccation or GG elicitation. The latter process could also explain how I_2 emission can occur even in the absence of strong external oxidants such as ozone. The exception among fucoids is the genus *Ascophyllum*, which possess two distinct isoforms of bromoperoxidases, one of them being located very superficially at the thallus surface (Krenn et al., 1989). The existence of the external isoform may explain *Ascophyllum*'s I_2 emission rates which are not directly correlated with particularly high iodide content in this species, but instead depend on enzymatic capacities to efficiently oxidise iodide. This hypothesis agrees with the Leigh et al. (2009) modelling study which showed that the occurrence of rockweed in the mid-littoral zone of sheltered habitats complements the I_2 emissions from the large (but more distant) beds of Laminariales, the former providing a substantial fraction of the I_2 detected at the RHaMBLe measurement site. Rockweed beds may also emit more constantly than kelps because they are naturally exposed more frequently (even for small tides) and for longer durations.

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It is worth recalling that the present incubation experiments tried, as far as possible, to avoid applying any other stress to the plant samples beyond desiccation in ambient air to mimic the effect of the seaweeds becoming exposed at low tide. Although ozone was not scrubbed from the air supply for the incubation experiments, it was likely that the ozone concentrations were low (even compared to ambient amounts) for experiments performed in the SBR cold room. An average ozone concentration of 3 ppbv was measured during the final incubation experiment on 30 September. The *D. membranacea* and the first *L. hyperborea* (healthy specimen) incubation experiments were performed in a regular laboratory on the afternoon of 27 September when the ozone concentration outside at the RHaMBLE measurement site was between 27 and 32 ppbv, and this reasonably represents an upper limit for the ozone concentration inside the SBR building. Thus the I₂ emissions observed during the incubation experiments arise from certain seaweed species responding strongly to very dilute (or at most ambient ≈30 ppbv) concentrations of ozone. An alternative explanation is that air-exposure itself (i.e. without ozone) is sufficient to trigger the seaweeds' stress response. This theory carries some weight because I₂ emissions were still observed when fragments of *L. digitata* were exposed to ozone-free scrubbed air during the first stress experiment, their weight-normalised emission rate being comparable to the rate seen in the incubation experiment on the whole *L. digitata* plant.

Two other groups have also reported time-resolved gas-phase I₂ emissions from *L. digitata* exposed to air. Dixneuf et al. (2009) performed a set of 16 chamber measurements using incoherent broadband cavity enhanced absorption spectroscopy (IBBCEAS) to quantify I₂ mixing ratios above whole *L. digitata* thalli. Their chamber operated as static system filled with ambient air from the laboratory (measured [O₃] < 15 ppbv), and the IBBCEAS method had a 10 s acquisition time enabling rapid variations in I₂ concentrations to be tracked. (IBBCEAS is related to the BBCEAS detection method used in this work, the major difference being the use of an arc lamp instead of an LED as the light source). The highest I₂ mixing ratios (up to several 100 ppbv) were observed in the first 1–3 h after the samples were placed into the

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chamber. This initial part of the time profiles is similar to the immediate strong emission burst followed by a relatively smooth decay observed here for *L. digitata* exposed to air in the incubation experiment and the first desiccation-only phase of stress experiment #1. Beyond the initial burst, the I_2 time profiles were additionally characterised by a series of emission pulses with highly variable regularity and periodicity extending throughout the 20 h duration of the Dixneuf et al. (2009) experiments. The only occasions when secondary I_2 emission bursts were observed in the present work were for the *L. digitata* ozone re-stressing experiment (#2) and the multiple stress experiment (#4), although perhaps the present profiles are too brief to observe such a phenomenon from experiments performed under more natural conditions. Further quantitative comparisons with the Dixneuf et al. (2009) study are difficult because no I_2 emission rates were reported.

Bale et al. (2008) used I_2 photolysis followed by resonance fluorescence of I atoms to quantify I_2 emitted by a 50 g sample of *L. digitata* placed in the Pyrex glass flask of a flow reactor. The seaweed sample was harvested at Mace Head and used within 30 min, and the flow reactor operated under synthetic air from a cylinder (i.e. no ozone). The I_2 mixing ratio peaked at around 300 ppbv within ten minutes of the sample being placed into the flow reactor, corresponding to a very large peak emission rate of $2500 \text{ pmol min}^{-1} \text{ gFW}^{-1}$. The emissions subsequently decayed away until a second I_2 burst was provoked by agitating the flask. Thus the Dixneuf et al. (2009), Bale et al. (2008) and the present studies all show that *L. digitata* produces substantial amounts of I_2 on exposure to air containing sub-ambient or no ozone, with the former two studies recording even higher I_2 mixing ratios than observed here.

Earlier studies have also monitored the I_2 emissions from seaweeds indirectly using wet chemical detection methods with comparatively slow time responses: 15–30 min acquisition times for sampling I_2 onto starch-coated denuder tubes (Sellegrì et al., 2005) or an ≈ 1 h acquisition time for extraction of I_2 into alkaline ethanol solution and measuring the iodide anion's absorption at 255 nm (Palmer et al., 2005; and discussed further by Küpper et al., 2008). The first study focussed on particle formation rates

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on exposure of seaweed samples to ambient air, whilst the latter focussed on I_2 and halocarbon emission rates and particle production when *L. digitata* samples were exposed to stress factors (these aspects are discussed in following sections). However both studies also report I_2 emission rates for seaweed samples exposed to air alone which, given the time responses of their detection methods, are best compared with I_2 emission rates averaged over the present BBCEAS time series. A good level of agreement exists: the average emission rates of around $3 \text{ pmol min}^{-1} \text{ gFW}^{-1}$ observed for the *L. digitata* incubation experiment and the desiccation-only phase of stress experiment #1 lie within the emissions range quoted by Palmer et al. (2005) for *L. digitata* exposed to air from below their detection limit up to $9 \text{ pmol min}^{-1} \text{ gFW}^{-1}$. Additionally, Sellegri et al. (2005) observed 24 pptv I_2 per kg of seaweed in chamber experiments conducted on “*Laminaria sp.* and *Fucus sp.* seaweeds widely found in the Mace Head tidal area.” This equates to an I_2 emission rate of about $0.8 \text{ pmol min}^{-1} \text{ gFW}^{-1}$ for the 800 litres min^{-1} flow rate through their seaweed chamber, which is in reasonable agreement with the present results for *L. digitata* but substantially larger than for either of the fucoid species investigated here.

4.2 *Laminaria digitata* exposed to stress factors: I_2 emission rates

Comparisons can also be made with the work of Palmer et al. (2005) for experiments where *L. digitata* samples were exposed to stress factors. For exposure to 90 ppbv of ozone, we observed average emission rates of $2.05 \pm 0.57 \text{ pmol min}^{-1} \text{ gFW}^{-1}$ for the second ozone-induced I_2 emission phase in stress experiment #1 and $2.15 \pm 0.58 \text{ pmol min}^{-1} \text{ gFW}^{-1}$ for the ozone re-stressing experiment #2, both of which were similar to the average emission rates observed for *L. digitata* exposed to air alone (3.17 ± 0.81 and $2.98 \pm 0.83 \text{ pmol min}^{-1} \text{ gFW}^{-1}$). Palmer et al. (2005) observed a comparable $2.9 \text{ pmol min}^{-1} \text{ gFW}^{-1}$ for 80 ppbv of ozone, a value which, like the present ozone data, lies within the range of emission rates Palmer et al. (2005) measured for their samples exposed to air alone. All of the present ozone exposure experiments

were conducted at $[O_3] \approx 90$ ppbv, so this study provides no further information on how I_2 emissions scale with ozone concentration. Palmer et al. (2005) did observe I_2 emission rates up to $130 \text{ pmol min}^{-1} \text{ gFW}^{-1}$ at $[O_3] = 160$ ppbv, and the only occasion such large emission rates were encountered in the present study was for the air + ozone + GG multiple stress experiment #4 (average and peak emission rates of 78 and $390 \text{ pmol min}^{-1} \text{ gFW}^{-1}$ respectively).

Whereas Palmer et al. (2005) observed enhanced I_2 emission rates up to $38 \text{ pmol min}^{-1} \text{ gFW}^{-1}$ in response to GG stress, the average I_2 emission rate measured in this work for GG stress ($3.29 \pm 0.89 \text{ pmol min}^{-1} \text{ gFW}^{-1}$) was essentially the same as for air-exposure alone. *L. digitata* has been shown to release large amounts of iodide into the aqueous phase in response to GG, e.g. $2.7 \times 10^{-7} \text{ mol}(I_{(aq)}^-) \text{ gFW}^{-1}$ over a 30 min period (Küpper et al., 2008), and so presumably the present sample did likewise. Apart from innate biological variability, the only explanation we offer for the apparently low I_2 emission rates seen in our GG stress experiment is that it is possible that the availability of a suitable oxidant was sufficiently limited under the ozone-scrubbed conditions of our GG experiment #3 that only a small fraction of the emitted $I_{(aq)}^-$ was oxidised into gas phase molecular iodine. The difference in the apparent I_2 emission rates between the Palmer et al. (2005) and the present GG experiments could be explained if the iodide released by the *L. digitata* samples formed another iodine-containing gas, such as HOI, that would have also been collected by the alkaline extraction method employed by Palmer et al. (2005) but that would not be detected by the present BBCEAS instrument which specifically targets gas phase I_2 . (Indeed it is not yet known which oxidised iodine species – I_2 or HOI or $I_3^-(aq)$ or a mixture of these – is produced by the haloperoxidase enzymes). It is interesting to note that ten-fold larger I_2 emissions were subsequently observed when the same GG stress was accompanied by 90 ppbv of ozone in stress experiment #4.

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4.3 *Laminaria digitata* exposed to stress factors: particle formation rates

Particle formation was seen in all *L. digitata* stress experiments where ozone was added, subject to the I_2 mixing ratios being above certain threshold values. Particle production tracked the I_2 emissions closely, with both the large scale variations in I_2 and the more rapid periodic behaviour (especially in experiment #4) being reflected in the particle numbers. Approximately linear relationships were observed between I_2 and particle number concentrations once the I_2 mixing ratios exceeded 400 and 200 pptv in ozone stress experiments #1 and #2, respectively. However, the greatest aerosol production corresponded with the very high I_2 mixing ratios observed during the multiple air + ozone + GG stress experiment #4. Here particle number concentrations were maintained between 200 000 and 800 000 cm^{-3} until the apparatus was covered after 110 min to exclude the room light. That no change was apparent in the I_2 emissions when light was excluded (middle panel of Fig. 7) indicates that light is required to initiate the particle-forming iodine oxidation chemistry but is seemingly not necessary for the I_2 emission itself. In contrast to the linear relationships in experiments #1 and #2, the bottom panel of Fig. 7 shows a roll-off in particle numbers suggesting that coagulation and/or condensational growth was capping the number concentration at high $[I_2]$. Sellegri et al. (2005) used a nano-scanning mobility particle sizer (SMPS) to monitor the diameter of particles formed in their chamber study and did indeed observe larger particles at high seaweed loadings (i.e. at higher I_2 concentrations). The same authors also report a linear relationship of 2800 particles cm^{-3} pptv $^{-1}$ between particle production and I_2 concentration between 0–400 pptv I_2 but with no apparent threshold behaviour (cf. 620 particles cm^{-3} pptv $^{-1}$ above threshold for experiment #1 in the bottom panel of Fig. 5). An approximately linear relationship was also reported by Palmer et al. (2005) and Küpper et al. (2008) between total integrated particle numbers and varying amounts of I_2 emission from *L. digitata* exposed to differing ozone concentrations. Interestingly, no correlation was found between particle numbers and total iodocarbon concentrations showing that the particles' source gas is I_2 rather than

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iodocarbons, a result that is confirmed by the close relationship between I_2 mixing ratios and particle numbers found in this study. Palmer et al. (2005) also noted significant inter-sample variability in particle production rates for equivalent amounts of ozone, and attributed this to biological variability in the *L. digitata* samples. Non-linear processes in the iodine oxidation chemistry (e.g. the bimolecular self-reaction of IO) and in the nucleation kinetics (e.g. the roll-off behaviour in Fig. 7) would be expected to further amplify the effects of biological variability in I_2 emission rates.

The available studies show a consistent pattern that increased I_2 emissions lead to greater particle production. Key results from the present study are that (i) I_2 emissions from the largest emitters, *L. digitata*, *L. hyperborea* and to a lesser extent *S. latissima*, are strongly varying functions of time and (ii) variations in I_2 mixing ratios have been shown to translate directly onto highly time dependent particle formation rates (at least for *L. digitata* in the ozone stress experiments). The idea that particle formation occurs in localised emission hot-spots was proposed by Burkholder et al. (2004) to reconcile the high IO concentrations required to model particle nucleation from OIO in their laboratory experiments with the much lower IO amounts detected in the atmosphere over extended DOAS light paths. Additionally, Saiz-Lopez et al. (2006) modelled iodine oxide clustering to form particles and concluded that the majority of I_2 emission and particle nucleation was located in only 8% of their 4.2 km DOAS light path used at the NAMBLEX campaign (i.e. above the inter-tidal zone where the seaweeds have their main habitats). The present results corroborate the hot-spot hypothesis: atmospheric I_2 emissions are likely to be localised over plants of the most efficiently emitting kelp species and localised in time being strongest when the seaweeds are first uncovered by the ebbing tide, and it is this combination of spatially and temporally localised concentrations of condensable iodine precursors that facilitates particle nucleation.

Unfortunately, no clear relationship between ozone deposition and I_2 emission emerges from this work. There is a modest anti-correlation between O_3 and I_2 in Fig. 7, e.g. the shallow dip in O_3 concentration around the prolonged second I_2 emission event, and this could be explained by greater O_3 deposition onto the seaweed's

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surface increasing the rate of inorganic reactions like $I_{(aq)}^- + O_3$ that liberate I_2 into the gas phase. Support for that causal link is, however, obscured by periodic structure in the O_3 time series and a corresponding in-phase periodicity to the I_2 emissions. As noted above, this periodic structure also appears (in phase) in the particle counts because particle formation depends on both I_2 and O_3 . Periodic structure is also seen in the ozone time series in the stress experiment #2 and in the particle counts once nucleation starts towards the end of the experiment (lower panel of Fig. 6). Oscillatory behaviour in particle production rates has been observed in previous chamber studies exposing *L. digitata* to ozone (Küpper et al., unpublished work; as discussed in Palmer et al., 2005). The origin of this behaviour remains unclear, however it may be related to periodic changes in the O_3 deposition rate onto the seaweed's surface (and hence have a biological component) because no such undulations are observed in aerosol nucleation experiments that use iodine crystals as their I_2 emission source (G. McFiggans, personal communication, 2009).

5 Conclusions

I_2 emissions from seven different seaweed species were investigated during ten incubation experiments aimed at mimicking exposure of seaweed plants to air at low tide. Seaweed samples were taken directly from the beach immediately prior to the experiment or were harvested from the inter-tidal zone and stored in the seawater aquarium at the Station Biologique de Roscoff. All experiments were performed on whole seaweed plants in order to minimise the stress experienced by the samples. An additional four experiments investigated I_2 emission and particle formation from *L. digitata* exposed to desiccation in air, ozone and oligoguluronate stress factors. The various experiments were performed during the final week of the RHaMBLe Roscoff deployment, and generally it was impractical within that time constraint to repeat individual experiments. Nevertheless some general conclusions may be drawn:

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(i) Substantial differences were observed in the I_2 emission rates for the various seaweed species on exposure to air. I_2 emissions spanned $3\frac{1}{2}$ orders of magnitude and increased in the order: *Dictyopteris membranacea* \approx *Fucus serratus* \leq *Fucus vesiculosus* $<$ *Ascophyllum nodosum* $<$ *Saccharina latissima* $<$ *Laminaria digitata* \approx *Laminaria hyperborea*. The most potent emitters (*L. digitata* and *L. hyperborea*) produced I_2 mixing ratios peaking between 15 000 and 87 000 pptv. Direct spectroscopic detection of I_2 at levels of a few hundred pptv was also confirmed from *S. latissima* and *A. nodosum*. No emissions of I_2 were detectable from *D. membranacea* or *F. serratus*, and at most only modest emissions were observed from *F. vesiculosus* (max \approx 50 pptv compared to the BBCEAS detection limit of 25 pptv). There is also evidence that I_2 emissions depend on the age/physiological state of the plant. These incubation experiments were performed under conditions of low ozone ($[O_3] \approx 3$ ppbv in the cold room) or at most ambient ≈ 30 ppbv concentrations. Exposure to ozone has previously been shown to be a strong external oxidative stress for *L. digitata* (McFiggans et al., 2004; Palmer et al., 2005; Küpper et al., 2008) which produces I_2 via inorganic reaction of ozone with iodide released from the plant's accumulated stock. However the present low-ozone incubation experiments additionally suggests that I_2 is a product of detoxification processes involving haloperoxidase enzymes that certain seaweed species use to counter internal oxidative stresses due to exposure to air alone. A combination of inorganic and enzymatic production of I_2 seems likely in the seaweed's natural environment when plants are exposed to ambient air at low tides.

(ii) The fast time resolution of the BBCEAS detection method (7.5 s) allowed the time dependence of the I_2 emission to be investigated. The large emitters tended to produce a burst of I_2 when first exposed to air. This phenomenon had been observed previously for *L. digitata* (Bale et al., 2008; Dixneuf et al., 2009) and this work shows that *L. hyperborea* behaves similarly. *S. latissima* exhibited a more broadly peaked I_2 time profile and *A. nodosum* produced I_2 emissions tending

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towards a steady plateau. The shape of the time profile has important consequences for particle formation rates in the natural environment. Particle nucleation is usually a non-linear process requiring high concentrations of condensable gases to be localised in “hot-spots” (e.g. Burkholder et al., 2004), and this work suggests that the strongest hot-spots are likely to be found over areas of kelp species in the first few minutes after having been exposed by a receding tide.

(iii) I_2 emissions were observed when fragments of *L. digitata* thalli were exposed to 90 ppbv of ozone and oligoguluronate (GG) stress. For example, the addition of ozone restarted I_2 emissions from a *L. digitata* sample that had largely relaxed following its initial I_2 burst on exposure to air. The application of such external stresses produced modest changes in the shape of I_2 time profile (typically prolonging the emissions) but did not noticeably increase the average I_2 emission rate compared to air-exposure alone. In contrast, Palmer et al. (2005) and Küpper et al. (2008) observed larger I_2 emissions for GG stress and at ozone concentrations in excess of those used here. Very large, sustained emissions were however observed from *L. digitata* exposed to the combined stress factors of air + GG +90 ppbv of O_3 .

(iv) Particle formation accompanied the I_2 emissions in all *L. digitata* stress experiments where ozone was present (90 ppbv) together with light, provided that the I_2 mixing ratio was above certain threshold levels. The particle number concentrations closely tracked variations in the I_2 mixing ratios: a linear relationship was observed at modest I_2 mixing ratios, with evidence of a roll-off in particle numbers at high I_2 presumably due to coagulation and/or condensational growth of the particles. No significant particle formation was observed without ozone, or in the dark when ozone was present. These observations tally with current understanding of the nucleation mechanism: light is required to photolyse I_2 molecules into I atoms which then react with ozone to produce condensable iodine oxides.

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We hesitate to recommend emission factors based on this work because so few replicate observations were performed. Further studies are needed with multiple replicates to generate statistically robust emission rates across sample populations, including investigating how the I_2 emission rates of individual species depend on the age and health of the samples, and potentially also on the season of the year (e.g. Ar Gall et al., 2004). However, parameterised versions of the emission rates observed in this work have been “tested” by being used as inputs into the Leigh et al. (2009) model of the emissions, transport and photo-destruction of molecular iodine during the RHaMBLe Roscoff campaign. The model produced good qualitative agreement (especially for the tidal signatures) with the I_2 amounts detected by BBCRDS at the RHaMBLe measurement site and the path-averaged DOAS measurements of I_2 in the channel between Roscoff and the Ile de Batz. The model showed that whilst the largest emitting kelp species made the dominant contributions to the total burden of atmospheric iodine species, they made relatively modest contributions to the I_2 signals detected by BBCRDS and DOAS owing to dilution and photolysis of their emissions whilst being transported from deep-water habitats furthest away from the measurement locations. Indeed in order to generate quantitative agreement with the measured I_2 amounts, the model had to assume 100% efficient recycling of I atoms back to I_2 after photolysis (i.e. the photolysis sink was turned off in the model which, of course, is physically unreasonable during daylight). This suggests that the model had underestimated the net I_2 source, and the most likely candidate for a missing source is small patches of nearby seaweeds containing modest emitters like *Ascophyllum* that are too fine-scale to be represented on the map of seaweed habitats used in the model. A main conclusion of this modelling exercise is that the I_2 amounts observed at a given location (and thus also the IO and particle concentrations etc arising from atmospheric processing of I_2) depend crucially on the spatial distribution of seaweed species around the measurement site. This is probably also why spectroscopic measurements of I_2 and the phenomenon of coastal ultra-fine particle nucleation were first identified at Mace Head. *L. digitata* is abundant around the Mace Head area and the nearest *L. digitata* beds

lie within 120 m of the shoreline laboratories at the Mace Head Atmospheric Research Station, compared to the kilometre distances at Roscoff.

Acknowledgements. The authors wish to thank the staff at the Station Biologique de Roscoff for their logistical support and hospitality during the RHaMBLe project. The Natural Environment Research Council funded the RHaMBLe consortium through several grant awards including NE/D00652X/1 (Leicester University) and NE/D006570/1 (Manchester University).

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Table 1. Iodine mixing ratios, emission profiles and emission rates observed during air exposure experiments performed on whole seaweed plants.

Species	Fresh weight (g)	Duration (min)	I ₂ emission profile	I ₂ mixing ratio (pptv)			I ₂ emission rates (pmol min ⁻¹ gFW ⁻¹)	
				Flush (mean)	Sample (mean)	Sample (peak)	Sample (mean)	Sample (peak)
<i>Dictyopteris membranacea</i>	180	12	Below detection limit (see Fig. 3a).	0±24	2±26	–	0.0012±0.016	–
<i>Fucus serratus</i>	580	14	Below detection limit	1±24	20±33	–	0.0039±0.0065	–
<i>Fucus vesiculosus</i>	500	10	Small signal (~50 pptv) appears after 5 min, remains close to detection limit.	4±21	34±31	–	0.0079±0.0072	–
<i>Ascophyllum nodosum</i>	460	17	Gentle rise up to constant ~300 pptv over 10 min. (see Fig. 3b).	2±21	254±42	416±89	0.063±0.017	0.104±0.030
<i>Saccharina latissima</i> (3 plants, partly decayed)	260	21	Gentle rise up to ~170 pptv over duration of the experiment	–14±23	125±28	225±40	0.055±0.017	0.099±0.026
<i>Saccharina latissima</i> (1 large plant, decayed)	300	12	Small signal ~60 pptv in first 5 min, then decays to below detection limit	–4±24	38±26	–	0.015±0.010	–
<i>Saccharina latissima</i> (1 small healthy plant)	60	36	Immediate emission of ~300 pptv, rises to ~500 pptv after 15 min, then decays to ~150 pptv (see Fig. 3c)	5±23	290±51	528±86	0.55±0.15	1.01±0.26
<i>Laminaria digitata</i>	300	38	Immediate strong emission, decreases with half-life of 8 min (see Fig. 4a)	2±18	8300±1300	23 600±3700	3.17±0.81	9.03±2.30
<i>Laminaria hyperborea</i>	300	57	Immediate strong emission, decreases with half-life of 5 min (see Fig. 4b)	–4±41	1760±290	14300±2300	0.67±0.17	5.45±1.39
<i>Laminaria hyperborea</i> (partly decayed)	280	18	Very strong emission (~80 000 pptv) peaking after 5 min; second emission peak (~65 000 pptv) at 9 min.	5±30	47 200±7500	86 900±13 700	19.3±4.9	35.6±9.1

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Table 2. Iodine mixing ratios, emission profiles and emission rates observed during the *Laminaria digitata* stress factor experiments.

Experiment	Fresh weight (g)	Stress factor	Duration (min)	I_2 emission profile	I_2 mixing ratio (pptv)		I_2 emission rates ($\text{pmol min}^{-1} \text{gFW}^{-1}$)	
					Sample (mean)	Sample (peak)	Sample (mean)	Sample (peak)
#1 (27 Sep 2006)	21	air exposure	20	Immediate strong emission, decreases exponentially with half-life of 1.6 min. No detectable aerosol particle production (see Fig. 5).	314±59	2330±370	2.98±0.83	22.1±5.7
		ozone (90 ppbv)	23	I_2 emissions resume with a broader profile than air-exposure stress, slower decay with half-life of 5.2 min. Peak in aerosol particles ($140\,000 \text{ cm}^{-3}$) corresponds with peak in I_2 (see Fig. 5).	216±41	615±99	2.05±0.57	5.84±1.50
#2 (28 Sep 2006)	21	air exposure then ozone (90 ppbv)	52	Sample from experiment #1 was left in sea water to recover overnight and then re-used in #2 Exposure to air initially produced I_2 mixing ratios up to ~900 pptv in multiple bursts, decays to ~70 pptv (relative to offset in early cavity flush data). Exposure to ozone produced a sustained emission peaking at ~450 pptv approx 40 min after ozone added. Few particles ($<100 \text{ cm}^{-3}$) until 40 min, then $80\,000 \text{ cm}^{-3}$ peaking together with I_2 (see Fig. 6).	227±41	450±73	2.15±0.58	4.27±1.10
#3 (28 Sep 2006)	20	air + GG	32	Immediate strong emission of ~2500 pptv, followed by exponential decrease with half-life ~3.2 min.	330±60	2510±400	3.29±0.89	25.0±6.4
#4 (28 Sep 2006)	14	air + GG + ozone at 90 ppbv	145	Immediate very strong emission of ~25 000 pptv I_2 , decaying to shallow minimum of ~1500 pptv after 20 min. Second broad, intense I_2 peak (~20 000 pptv) appears without any apparent increase in stress factors, and is sustained emissions over next 40 min. Particle production (2×10^5 to $1 \times 10^6 \text{ cm}^{-3}$) continues until seaweed reactor & aerosol growth vessel covered with black cloth at 110 min (see Fig. 7).	5430±860	26 900±4300 (first max)	77.8±19.8	386±98 (first max)
						19 400±3100 (second max)		279±71 (second max)

GG stress: sample anointed with 10 cm^3 of GG solution ($150 \mu\text{g cm}^{-3}$) for 1 min, rinsed in sea water and then loaded into the flow reactor vessel.

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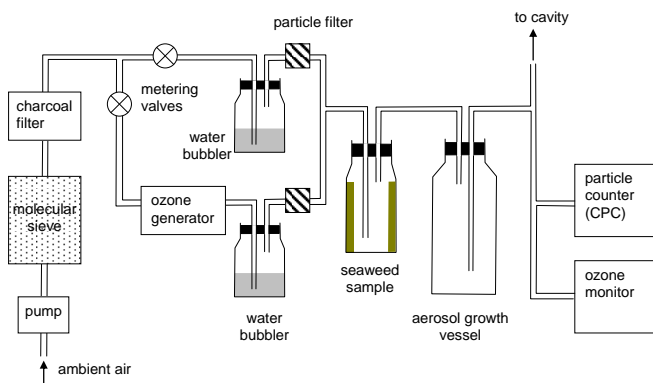
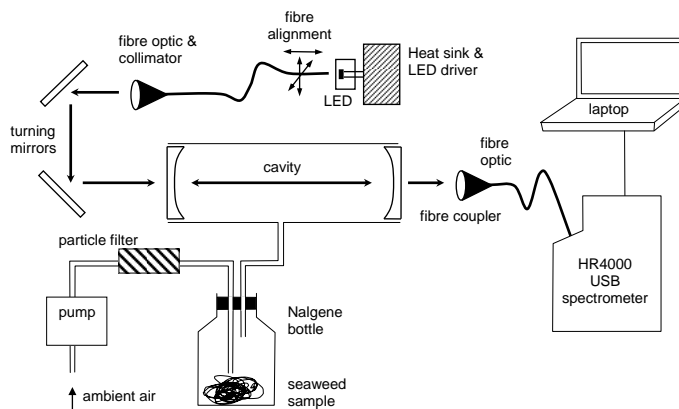


Fig. 1. Schematic diagrams of the apparatus and the BBCEAS spectrometer used in the seaweed incubation experiments (upper panel) and the flow reactor used in the *Laminaria digitata* stress experiments (lower panel).

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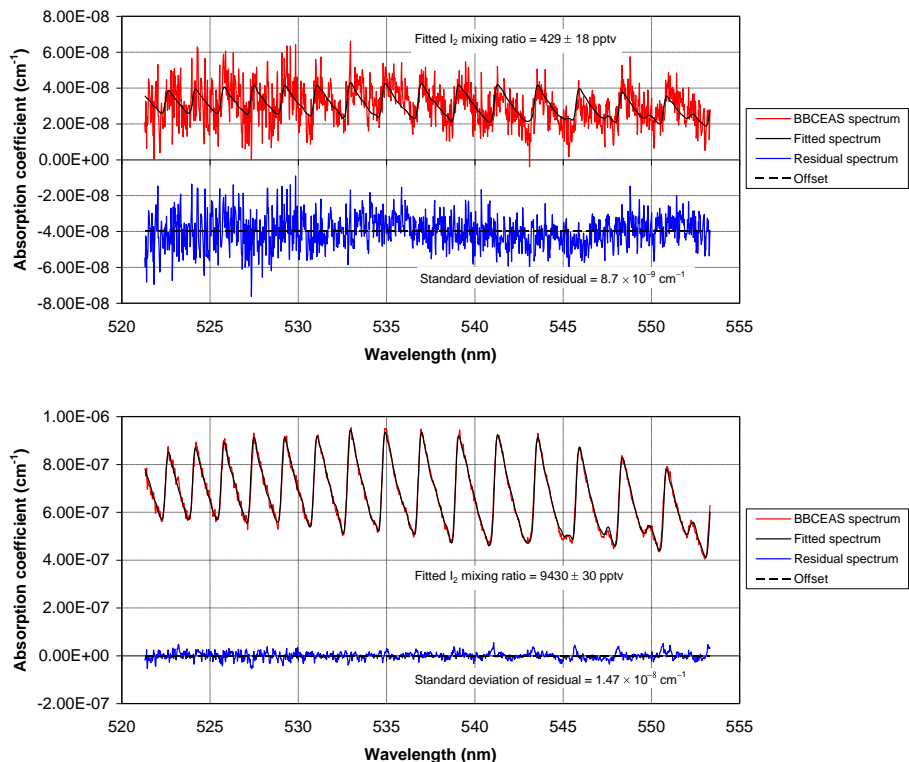


Fig. 2. Example BBCEAS spectra of I₂ emitted from *Saccharina latissima* (upper panel) and *Laminaria digitata* (lower panel). The measured BBCEAS spectrum is shown in red overlaid by the I₂ absorption cross sections scaled to produce the optimum fit to the BBCEAS spectrum (black). The residual spectrum is shown in blue (measurement minus fitted spectrum), offset below zero by $4 \times 10^{-8} \text{ cm}^{-1}$ for clarity in the upper panel. The BBCEAS spectra were obtained with an integration time of 7.5 s. The uncertainties quoted for the retrieved I₂ mixing ratios on this figure are the statistical errors in the I₂ amounts arising from fitting the molecule's differential structure in the BBCEAS spectrum.

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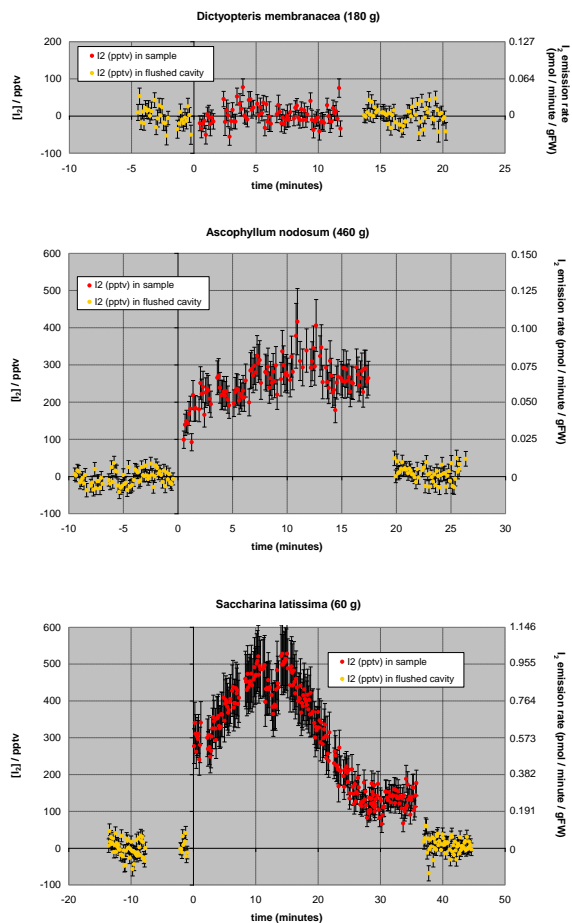


Fig. 3. Time series of the I_2 mixing ratios (left axis) and corresponding I_2 emission rates (right axis) observed in the incubation experiments on *Dictyopterus membranacea* (top), *Ascophyllum nodosum* (middle) and a young, healthy *Saccharina latissima* plant (bottom).

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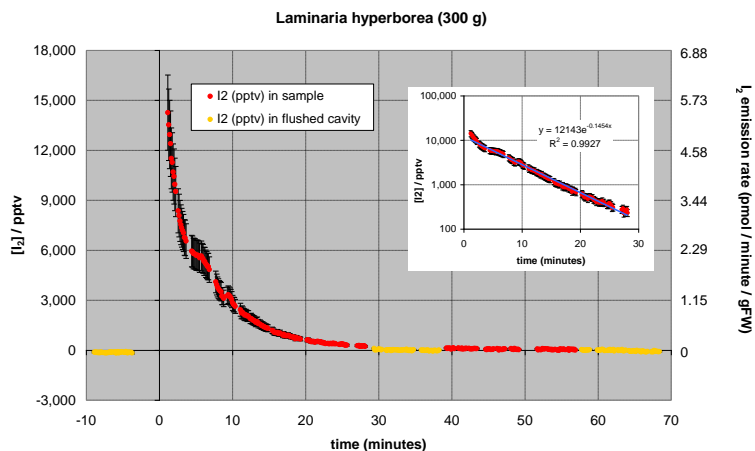
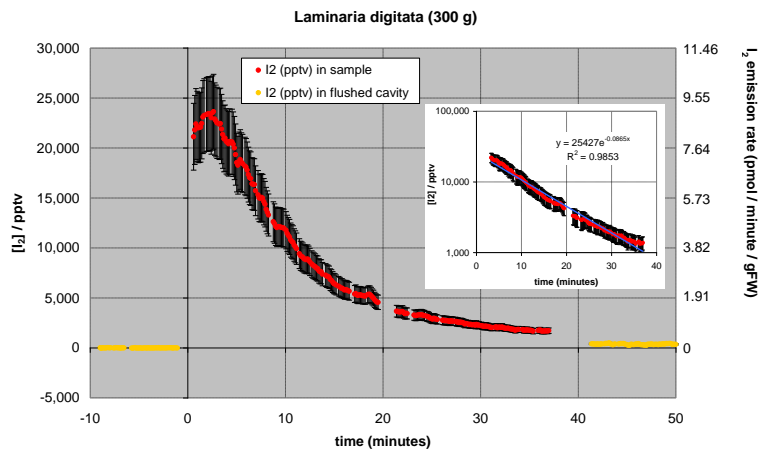


Fig. 4. Time series of the I_2 mixing ratios (left axis) and corresponding I_2 emission rates (right axis) observed from *Laminaria digitata* (top) and *Laminaria hyperborea* (bottom: healthy sample). The insets show the I_2 mixing ratios re-plotted on a logarithmic scale: the straight line overlaying these data points are fits to exponential decays from which the emission half-lives were estimated.

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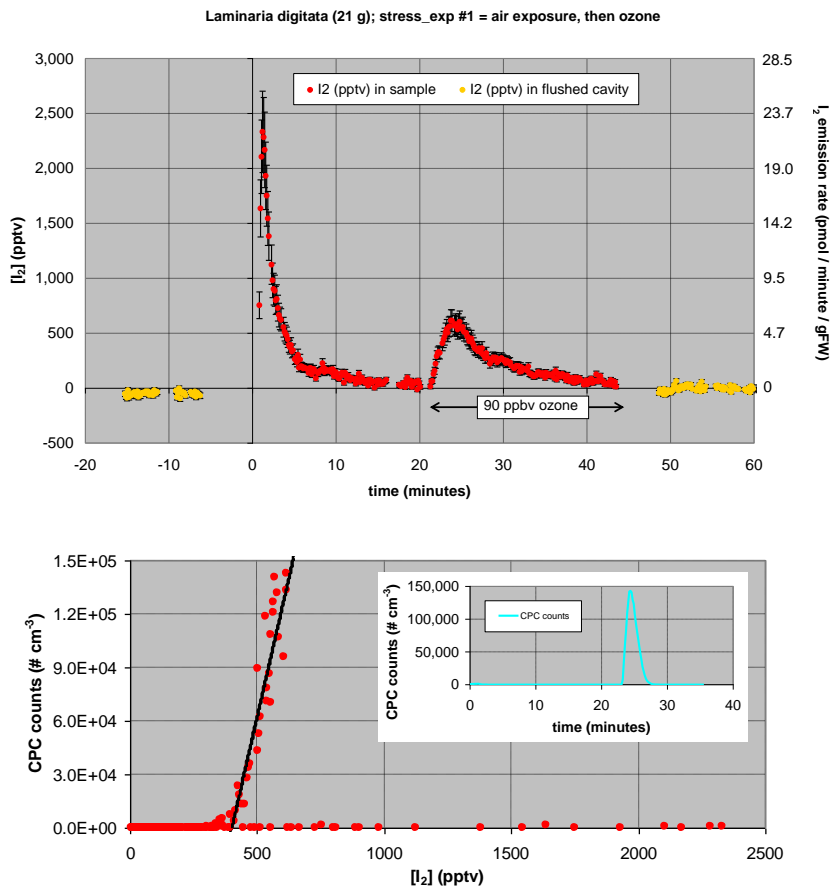


Fig. 5. Time series of I_2 mixing ratios and emission rates for *L. digitata* stress experiment #1. Ozone was scrubbed from the air flow for the first 20 minutes of the experiment, after which ~ 90 ppbv of ozone was added. The inset to the lower panel shows the particle formation event observed co-incident with the second ozone-induced I_2 emission burst. The lower panel also shows a correlation plot of particle counts versus I_2 mixing ratio, with the heavy black line being a linear fit to the particle data during the ozone-induced emission burst.

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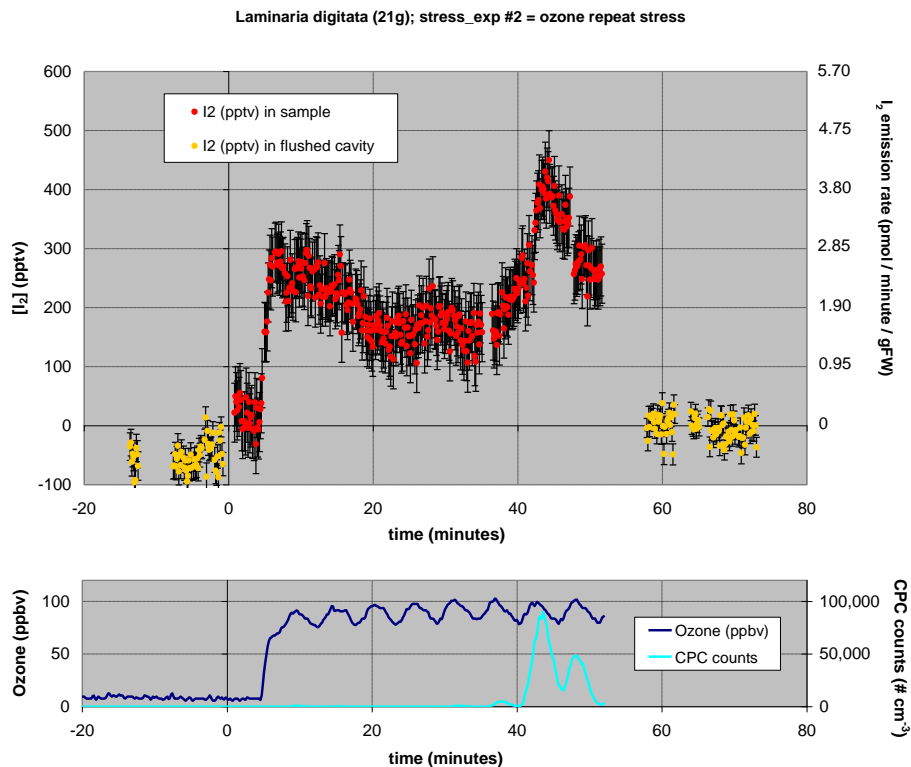


Fig. 6. Time series of I₂ mixing ratios and emission rates for the *L. digitata* ozone re-stressing experiment #2 (upper panel). The lower panel shows time series of the ozone concentration (dark blue) and the particle number concentration (light blue).

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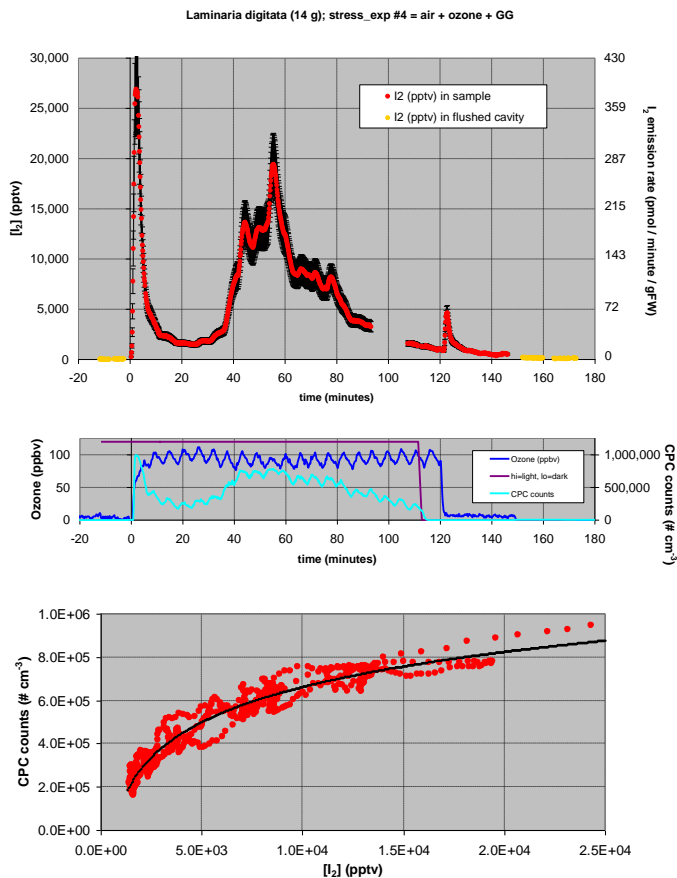


Fig. 7. Time series of I_2 mixing ratios and emission rates for the *L. digitata* air + ozone + GG multiple stress experiment #4 (upper panel). The middle panel shows time series of the ozone concentration (dark blue), the particle number concentration (light blue) and whether the seaweed vessel was exposed to the room lights (purple). The bottom panel shows a correlation plot of particle counts versus I_2 mixing ratio for data between $t=3$ and 110 min (i.e. excluding the upward part of the first strong emission event and all data after the seaweed vessel was covered). The heavy black line is a fit of the type: $CPC\ counts = A \times \log[I_2] + B$.

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