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The time dependence of molecular iodine emission from *Laminaria digitata*

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Abstract. We present the first in situ detection of molecular iodine emitted from the brown macroalga *Laminaria digitata* under natural stress conditions. We show that the release of I_2 occurs in short, strong bursts with a complex time signature. The new data indicate that algal control of I_2 release in the form of an oscillatory time-dependence may be based on a nonlinear autocatalytic reaction scheme which is closely linked to the production of H_2O_2.

1 Introduction

The release of volatile organic iodine compounds and of molecular iodine (I_2) into the marine boundary layer is recognized to be of fundamental importance for (subsequent) ozone depletion events and marine aerosol formation, which in turn affects global radiative forcing (Carpenter, 2003; von Glasow, 2005). Although biogenic emission of I_2 by macrophytic algae has been suggested to be one of the most important processes responsible for the observed tropospheric iodine concentrations in coastal areas (Saiz-Lopez and Plane, 2004; McFiggans et al., 2004), the dominant sources of molecular iodine, and in particular the mechanisms of I_2 release, are still being debated (Palmer et al., 2005). Significant levels of molecular iodine ($\sim$95 pmol mol^{-1}) were observed during the 2002 NAMBLEX field-campaign at Mace Head (Ireland) by long-path differential optical absorption spectroscopy (LP-DOAS) (Saiz-Lopez and Plane, 2004) and broad-band cavity ring-down spectroscopy (BBCRDS) (Bitter et al., 2005). The I_2 "events" correlated with times of low tide, suggesting that the emissions from macroalgae under stress may be an important direct or indirect source of I_2 in coastal regions (Saiz-Lopez and Plane, 2004). Hence the overall iodine budget in the marine boundary layer may be much more strongly dependent on the emission of molecular iodine from macrophytic algae exposed to ambient air than previously assumed. Moreover, recent studies seem to indicate that the primary source of condensable iodine vapours in coastal areas is indeed molecular iodine (McFiggans et al., 2004; O'Dowd et al., 2002; O'Dowd and Hoffmann, 2005; Saiz-Lopez et al., 2006). In order to explore this hypothesis we applied incoherent broadband cavity-enhanced absorption spectroscopy (IBBCEAS) (Fiedler et al., 2003) (an experimental technique pioneered by our group in the past few years (Fiedler et al., 2003; Ruth et al., 2007; Venables et al., 2006; Gherman et al., 2008)) to detect the I_2 emission of a common brown seaweed species, *Laminaria digitata*, under in situ conditions in the laboratory. The molecule-specific detection limit of IBBCEAS (Venables et al., 2006; Gherman et al., 2008; Vaughan et al., 2008), in which an optically stable cavity is employed, is comparable to that of typical LP-DOAS. However, IBBCEAS features a significantly higher spatial resolution. Combined with good temporal resolution IBBCEAS thus complements LP-DOAS in the search for sources of tropospheric trace gases (cf. Sect. 2).

The choice of *Laminaria digitata*, one of approximately 30 brown algal species (*Phaeophyceae*) of a genus known as kelp, is due to its high average iodine content of about 1.0% of its dry weight (DW) (Verhaeghe et al., 2008; ArGall et al., 2004; Küpper et al., 1998). *Laminaria digitata* is characterized by long, leathery laminae (blades) of relatively large size (up to 2 m). In the British Isles these algae predominantly occur in the upper sublittoral zone of exposed shores (Lewis, 1964), i.e. the majority of *Laminaria digitata* is not exposed to air even at low tides. If put under stress, for example through exposure to ultraviolet (UV) light or elevated levels of ozone, *Laminaria* are known to emit volatile short-lived organo-iodines as well as molecular iodine (Palmer et al., 2005; Laturnus et al., 2004; Leblanc et al., 2006; Carpenter et al., 2000). A recent study shows that iodine is accumulated

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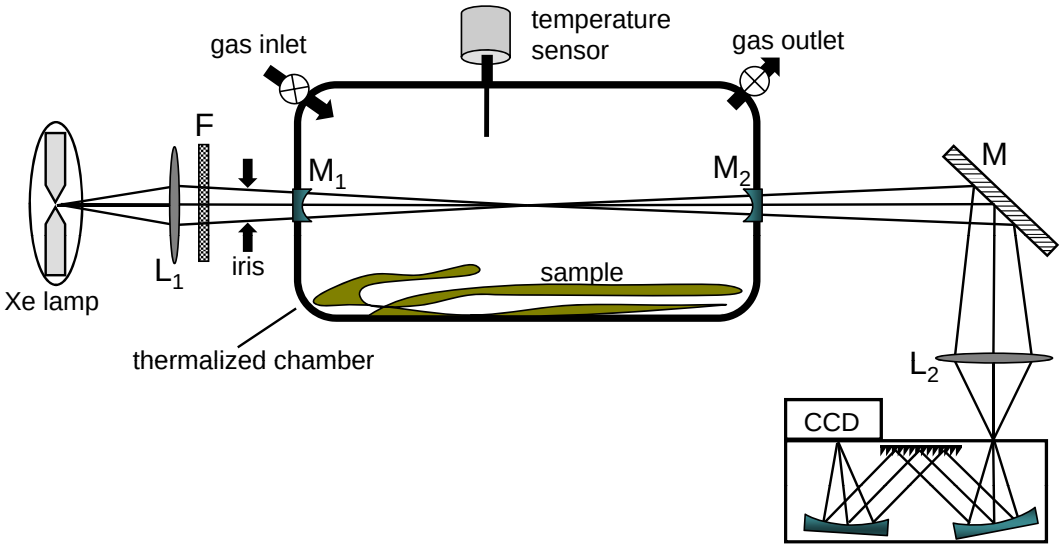

Fig. 1. Schematic representation of the optical set-up. M_1, M_2: high reflectivity mirrors; CCD: charge-coupled device detector; L_1, L_2: achromatic lenses; M: plane mirror. F: optical filters (position not critical). The chamber length of L=75 cm corresponds to the length over which light interacts with the sample gas, the cavity length (separation of M_1 and M_2) was 145 cm. The gas in- and outlets were sealed during the experiments.

in kelp in form of iodide, I^-, providing kelp with an antioxidant that, upon reaction with ozone for instance, can lead to the production of I_2 (Küpper et al., 2008). The emission of I_2 from *Laminaria digitata* was also studied in elicitation experiments (Palmer et al., 2005) where *Laminaria* were anointed with hydrogen peroxide or oligoguluronate solution and halogen production was measured with gas chromatographic mass spectrometry using pre-concentrated samples. Hitherto, no in situ study of I_2 emissions from *Laminaria* under natural stress conditions existed.

2 Experiment

The experimental cavity-enhanced absorption setup is shown schematically in Fig. 1. An optical cavity was formed by two plano-concave dielectric mirrors (Research Electro Optics) with a radius of curvature of 200 cm and a separation of d=145 cm (mirror diameter 2.5 cm). The optical axis in the cavity was directed along the seaweed thallus approximately 10 cm above the sample. The mirror reflectivity as a function of wavelength was established in earlier work (Vaughan et al., 2008) (maximum reflectivity ≈0.9998 at ∼546 nm). The light from a 75 W short arc Xe-lamp was focused into the optical cavity. Intensity variations in the output of the lamp were typically smaller than 1% for the duration of a measurement. The light exiting the cavity was imaged onto the entrance slit (25-μm) of a spectrograph (1200-l/mm grating; Oriel MS127i) equipped with a CCD detector (Andor DV-401BV) cooled to −30°C. The spectral resolution was ∼0.32 nm. The release of molecular iodine from *Laminaria digitata* was monitored in the spectral region between 530 and 553 nm. The lamp emission was filtered in front of the cavity with one band-pass filter (Semrock FF01-543/22-25) which narrowed the spectral range to ≈23 nm (FWHM) centered around 543 nm. The extinction of the gaseous sample inside the optical cavity can be determined using (Fiedler et al., 2003)

$$\varepsilon(\lambda) = \frac{1}{L}\left(\frac{I_0}{I} - 1\right)(1 - R) \quad (1)$$

where ε (λ) [cm^{-1}] is the wavelength-dependent extinction of the sample, $I(\lambda)$ and $I_0(\lambda)$ are, respectively, the intensities of light transmitted by the cavity in the presence and absence of the absorbing species, $R(\lambda)$ is the mirror reflectivity, and L [cm] is the distance over which the gaseous species in the cavity interacts with the light trapped inside the optical cavity (Fiedler et al., 2003). In the present study L corresponds to the length of the chamber (∼75 cm) and spatial variations of I_2 concentrations cannot be detected in the measurements presented. The overall uncertainty of the number density n_{I_2} as derived from ε (λ) using Eq. (1) (and Eq. (2) below) is governed by systematic errors, which mainly arise from the uncertainty in (1–R) and the absorption cross-section σ_{I_2} (Saiz-Lopez et al., 2004b). The uncertainty of the absolute number density is smaller than 20%, the precision of the measurement is however significantly higher.

For our study *Laminaria digitata* thalli were cropped at the eastern bank of the entrance to Cork Harbour (51.795 N, 8.252 W near Roches Point) in Southern Ireland – for the results shown in this publication samples were taken on 19 February 2008. Only thalli that were still in seawater were

taken. The seaweed was kept inside a transparent tank filled with mechanically filtered seawater and ambient air bubbling through it. The tank was stored outside the laboratory building, hence the *Laminaria* was exposed to the natural diurnal light and temperature cycle. Seaweed was used within 5 days of collection. To trigger the release of iodine the entire thallus of the seaweed was put under stress by taking it out of the water and placing it into a light-tight cylindrical copper chamber (volume ~51 dm^3, surface area ~83 dm^2), which on the inside was covered with a plastic sheet in order to prevent reactions of the seawater with the copper that might affect the measurements. The chamber was thermally stabilized using refrigerated water (~5°C); the temperature was measured using two K-type thermocouples with an accuracy of approximately 0.5 K. The chamber was filled with ambient air, hence the sample was exposed to very low ozone levels (<15 nmol mol^{-1}). The seaweed was neither cleaned nor dried before absorption measurements commenced. The plants were still covered by a thin layer of seawater and did not dry significantly for the duration of an experiment. It generally took a few minutes between taking a plant out of the water tank and commencement of a measurement.

3 Results and discussion

Figure 2 shows a typical absorption spectrum after placing a *Laminaria* plant into the sample chamber. The extinction, $\varepsilon(\lambda)$, measured with a 10 s integration time, is entirely governed by I_2 absorption. These measurements represent the first direct observation of the release of molecular iodine from *Laminaria digitata* into ambient air. The surprisingly high number density of molecular iodine (n_{I_2}=7.07×10^{10} molecule cm^{-3}, equivalent to 2.75 nmol mol^{-1}) inside the probe volume (i.e. the volume of the optical cavity) was derived by fitting

$$a + b\lambda + c\lambda^2 + n_{I_2}\sigma_{I_2}(\lambda) = \varepsilon(\lambda) \quad (2)$$

to the measured extinction $\varepsilon(\lambda)$ using a singular value decomposition approach (Press et al., 1992). In Eq. (2) a, b, c and n_{I_2} are the fit parameters (for values see caption of Fig. 2). The absorption cross-section of molecular iodine, $\sigma_{I_2}(\lambda)$, was taken from the literature (Saiz-Lopez et al., 2004b) and convoluted to match the spectrometer's resolution. The term $(a+b\lambda+c\lambda^2)$ accounts for an extinction background caused by additional unspecified optical losses (e.g. light scattering).

In total 16 long-term experiments on the I_2 emission of *Laminaria digitata* were performed of which 16 showed series of bursts (none of the time signatures were reproducible). Typical results of the time-dependence of the number density of molecular iodine at ~6.5–8.5°C are shown in Fig. 3. At the beginning of a measurement usually a very strong I_2 absorption burst occurs generally lasting between ca. 1 and 3 h. This initial strong I_2 emission from *Laminaria digitata* was

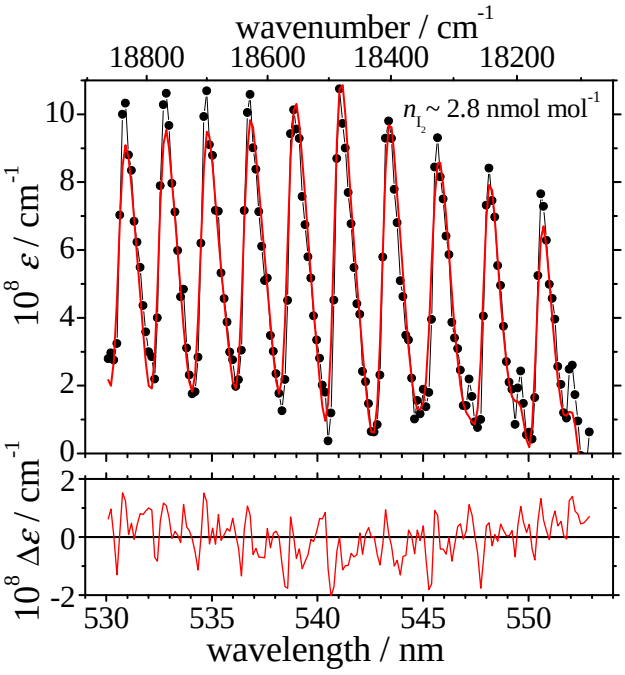

Fig. 2. Typical absorption spectrum of the gas mixture above a *Laminaria* thallus out of water in the dark. Dots and thin line: measured extinction, $\varepsilon(\lambda)$. Solid line: fit using Eq. (2) with a=−2.84×10^{-5} cm^{-1}, b=1.03×10^{-8} cm^{-1} nm^{-1} and c=−9.462×10^{-11} cm^{-1} nm^{-2}, n_{I_2}=7.07×10^{10} molecule cm^{-3}. The structure in the spectrum is due to I_2 released from the plant. The optical loss causing the broad featureless background in this spectrum cannot be specified in this experiment. The lower panel shows the unweighted absolute fit residuals.

also recently corroborated by I_2 photolysis measurements in a flow and subsequent detection of the iodine atoms released, as well as by observing the weak I_2 fluorescence directly (Bale et al., 2008). Subsequently smaller quasi-oscillatory iodine bursts are typically observed for the duration of many hours. Each experiment revealed a new unique time signature of emission bursts. Figure 3 shows two examples which were chosen since they illustrate the range of time dependences that were observed. The I_2 number density in Fig. 3a shows a surprising regularity which is dominated by a re-occurring emission period of roughly 25 min. In several cases the amplitude in the fast Fourier transform spectra of the time-dependent number density exhibited several significant maxima in frequency space. The corresponding periods however are not representative for other measurements (compare Fig. 3a and b). Some measurements show very limited periodicity.

It is important to note that the release of molecular iodine constitutes a non-equilibrium process. Molecular iodine released from the aqueous solution layer on the plant is transported by diffusion and/or convection into the detection light beam (ca. 10 cm above the plant) used for the absorption

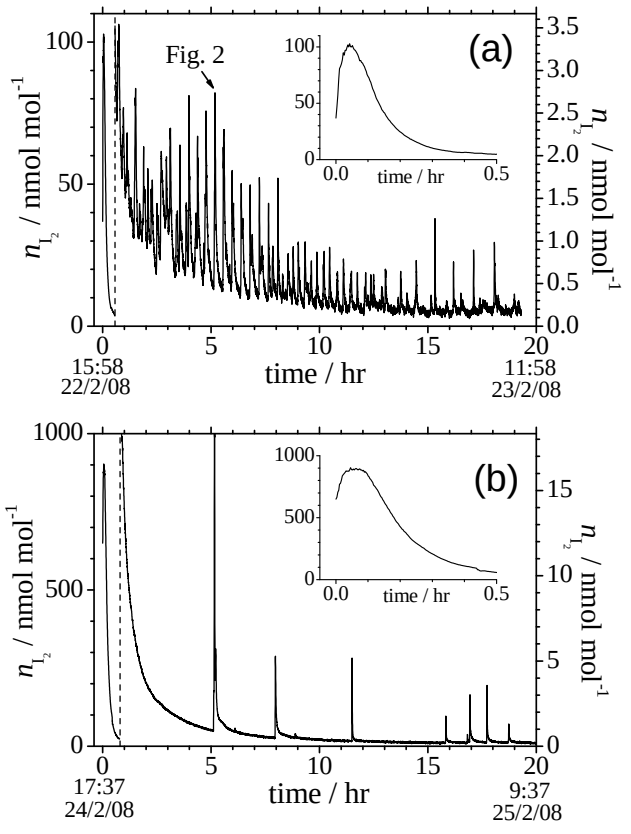

Fig. 3. Time-dependences of the I_2 mixing ratio [nmol mol^{-1}] in the probe volume inside the sample chamber containing a fresh thallus of *Laminaria digitata*. The inserts show the first 30 min of the measurements. The traces left and right of the vertical dashed lines refer to the scales on the left and right axes respectively. The traces are connected at the dashed line. **(a)** Blade length 87 cm, stipe length 30 cm (no holdfast), 25 g DW. **(b)** Blade length 90 cm, stipe length 40 cm (including holdfast), 33 g DW. The temperature inside the chamber during the experiment was ∼6.5–8.5°C and the plant was in complete darkness. The arrow in (a) indicates the time when the spectrum shown in Fig. 2 was recorded.

measurement. During this process gaseous I_2(g) is not in equilibrium with solid I_2(s) gradually building up on the chamber walls. I_2 adsorption on the walls is in fact not important for the results shown in Fig. 3, because the emission of I_2 in short individual bursts was also observed in experiments using uncovered plants outside the chamber. Hence, in the first approximation, the detected iodine number density is a measure for the overall release of I_2, i.e. the measured time-dependence is unambiguously caused by the *Laminaria* sample in response to external, natural stress. For this assertion to be valid it is assumed that the efficiency of I_2 transport away from the plant is uniform in time and space and does not depend on the I_2 concentration itself. Even though the situation in the present experiment may thus be represented in a simplified way, the most important implication of the results presented in Fig. 3 can be adequately discussed on the basis of this hypothesis.

Taking the seaweed out of the water tank and placing it into the setup must momentarily increase the stress level of the seaweed and hence probably triggers the initial strong I_2 burst (insets Fig. 3). An important aspect thereby is the change of temperature. The *Laminaria* organism is quite sensitive to temperature change (Bolton and Lüning, 1982) and already perishes in water upon prolonged exposure to temperatures higher than 22°C. Our intention was to study the kelp organism under conditions similar to those on the shoreline. Therefore the air temperature was chosen according to the temperature measured when harvesting the seaweed, i.e. ∼8°C. It is not known at present whether keeping seaweed in captivity for hours up to several days changes the physiological reaction of the plant. In this context the most important aspect concerns the role of bacteria and microorganisms putting stress on the seaweed. Keeping algae in a closed tank (with the water temperature varying between 8 and 16°C, depending on weather conditions) probably enables bacteria to proliferate, thus changing stress levels for the plant. However, this scenario may not be very different for algae in rock pools by the sea. It is important to note that some experiments performed within ca. 3.5 h of harvesting algae also showed secondary bursts in the I_2 emission.

It is also known that oxidative stress can activate a massive efflux of iodine from *Laminaria* species resulting in the elution of molecular iodine (so-called "iodovolatilisation") (Küpper et al., 1998; Palmer et al., 2005). However, the time-dependence of this process had not been observed previously. However, from the present experiments the influence of ozone on the I_2 emission efficiency cannot be quantified. The ambient ozone mixing ratio in the laboratory was always below 15 ppbv (as measured by an ozone monitor). It was noted that by deliberately increasing the ozone mixing ratio significantly the overall I_2 emission efficiency increased substantially. To quantify this effect more experiments under ozone-free conditions are necessary. Ambient air ozone levels were chosen to study the plant under realistic, quasi in situ conditions.

The fact that molecular iodine is released in distinct bursts is an indication for some specific biochemical activity in the *Laminaria* organism and its immediate aqueous environment. The possibility that the inhomogeneous distribution of I_2 in *Laminaria* species (Verhaeghe et al., 2008; ArGall et al., 2004; Amat and Srivastava, 1985) could lead to spatial disparities in the I_2 release and hence the occurrence of bursts cannot be determined from these first measurements. Our approach integrates over the entire specimen, therefore even strong spatial differences in the physiological and chemical effectiveness of I_2 release cannot be detected. Independent of the I_2 distribution, it is likely that the observed bursts are a consequence of the known stress-induced production of H_2O_2 in *Laminaria digitata* (Küpper et al., 1998; Leblanc et al., 2006; Colin et al., 2003). The key (aqueous phase)

reactions in this system are suggested to be (Küpper et al., 1998):

$$H_2O_2 + I^- \leftrightarrow HOI + OH^- \quad \text{(R1)}$$

$$HOI + I^- + H^+ \leftrightarrow I_2 + H_2O \quad \text{(R2)}$$

In addition there can be production of O_2 by the reaction of H_2O_2 with HOI at higher acidity (Valent et al., 1998; Schmitz, 2001):

$$H_2O_2 + HOI \rightarrow O_2 + H_2O + H^+ + I^- \quad \text{(R3)}$$

and several other reactions including production of I_3^- and IO_3^- ions (Leblanc et al., 2006; Küpper et al., 2001). Hence the production of H_2O_2 and the release of I_2 may be strongly correlated. In order to test whether H_2O_2 production may trigger the quasi-periodic release of molecular iodine, an experiment was performed in which 200 ml of "old" water from the seaweed tank was placed in the sample chamber. The water contained some residual organic material of jelly-like consistency (bacteria and parts of rotten seaweed), its composition was not well-defined. 15 ml of an aqueous H_2O_2 solution of 9.11 mol dm^{-3} was added to ∼200 ml of the water without a living *Laminaria* plant present. The result of this experiment is shown in Fig. 4. A strong I_2 emission burst was observed resembling the initial bursts shown in the inserts of Fig. 3. It is important to note the similarity of the qualitative behaviour of the I_2 emissions in our experiments to the H_2O_2 release in *Laminaria digitata* as shown in Figs. 2b, 2c and 3 in Küpper et al. (2001) and in Fig. 3 in Küpper et al. (2002) (conclusions regarding the potential occurrence of secondary short H_2O_2 bursts in the experiments by Küpper et al. (2002) cannot be drawn since the measurements by Küpper et al. (2002) were taken at a significantly lower time resolution and much shorter overall duration in comparison to our long-term experiments). Fig. 4 demonstrates the importance of the presence of H_2O_2 for the elusion of I_2. No additional bursts were observed in this experiment after the initial emission maximum.

It is clearly outside the scope of the present work to provide an exhaustive description of the chemical reactions governing the systems studied here. However, as already known from previous studies (Leblanc et al., 2006), the iodine species distribution in aqueous solutions is strongly influenced by several parameters such as pH, total iodine concentration, temperature, and the redox state of the solution. Generally, many chemical reactions involving H_2O_2 and I_2 in aqueous solutions show oscillatory behaviour leading to quasi-periodic emissions of gaseous I_2. In particular, strong oscillatory behaviour is found in the "iodine-clock" Briggs-Rauscher (Briggs and Rauscher, 1973) and Bray-Liebhafsky (Bray and Liebhafsky, 1931) reactions. Although the general theory of these "clock" reactions is well established (Furrow and Noyes, 1982a; Noyes and Furrow, 1982b), the detailed understanding of the individual reactions is still far

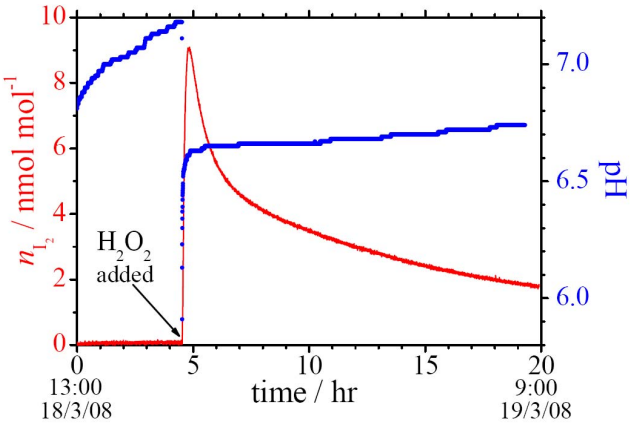

Fig. 4. Time-dependence of the I_2 mixing ratio [nmol mol^{-1}] in the probe volume inside the sample chamber containing ∼200 ml of "old seawater" from the storage tank. *Laminaria digitata* had been kept in the water for 19 days, causing it to be in a not well-defined, jelly-like state. At 4hr 45min, 15 ml of an aqueous H_2O_2 solution of 9.11 mol dm^{-3} was added to the seawater, triggering the immediate release of I_2 (solid red line: I_2 number density). The pH (solid blue circles) was monitored simultaneously (PASCO Scientific pH electrode 699-085; resolution 0.001). The experiment was performed in the dark.

from complete. It is plausible that the I_2 bursts observed in the present study are initiated by the stress-induced H_2O_2 production of *Laminaria digitata*, which might be a defence reaction to protect the plant against the penetration of bacteria and microorganisms. The bursts are part of the previously proposed iodovolatilisation processes and probably occur also in other seaweeds and macroalgae. It is therefore reasonable to suppose that short emission bursts of I_2 can be observed in coastal areas, corresponding to chemical "iodine clocks" initiated by biological systems. The physiological significance of the bursts is unclear at present. When washed up on the shore the plant activates defence mechanisms that protect it against the attack of "microorganisms" and drying out. In this context an autocatalytic reaction scheme could be an appropriate way to control the iodine emission of the plant.

Even though in these first experiments we have not yet been able to estimate an I_2 flux [mol s^{-1} kg^{-1} DW] for *Laminaria digitata*, our results strongly support the hypothesis by (Saiz-Lopez and Plane, 2004a) that biogenic emission of I_2, especially direct emission from algae, is a very important natural process in the marine boundary layer, that impacts on the tropospheric photochemistry both on regional and global scales. Studies of the influence of other parameters (exposure to light or elevated ozone levels and other relevant conditions) are currently in progress with the specific goal to establish a reasonable accurate estimate of the flux of I_2 emissions per unit weight of algae under realistic conditions.

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