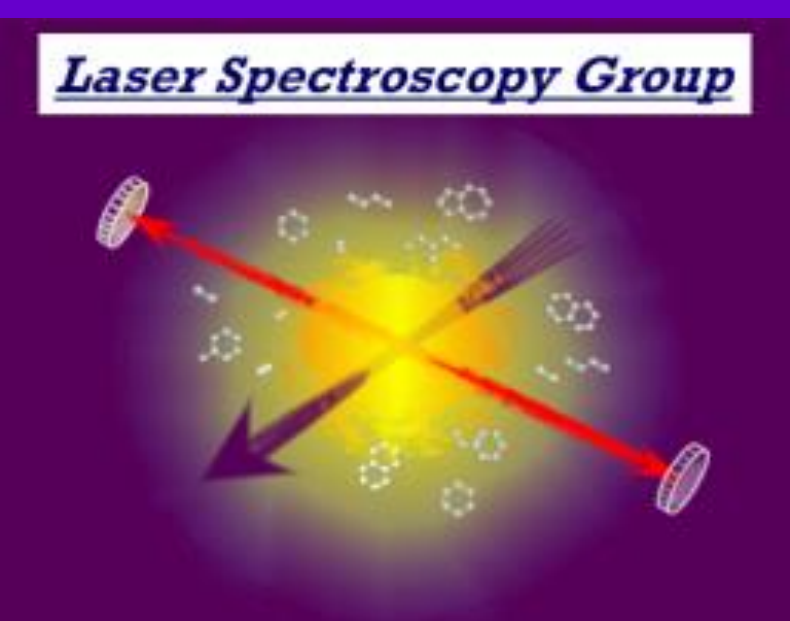




First *in situ* detection of molecular iodine emission bursts from *Laminaria Digitata*



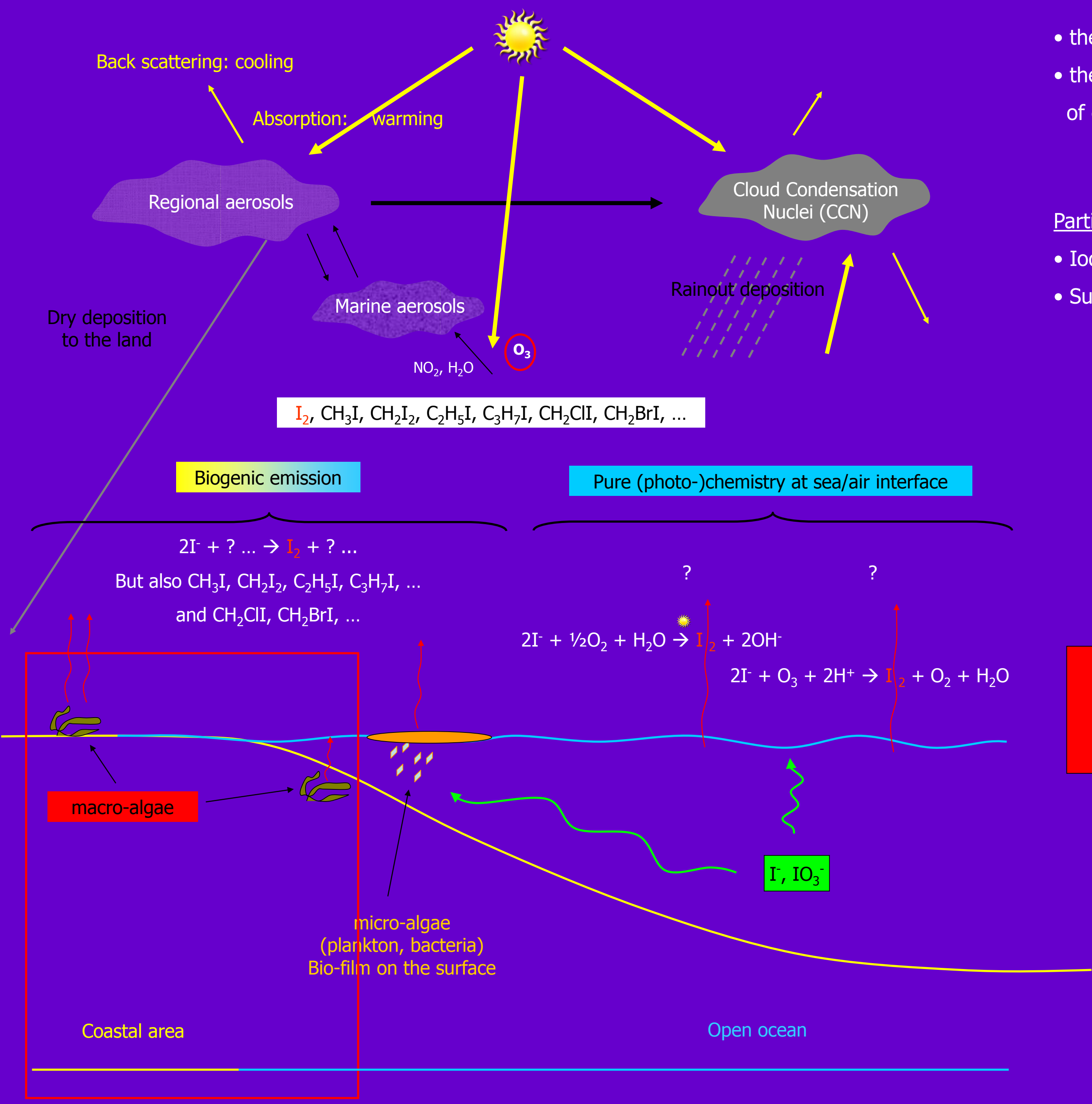
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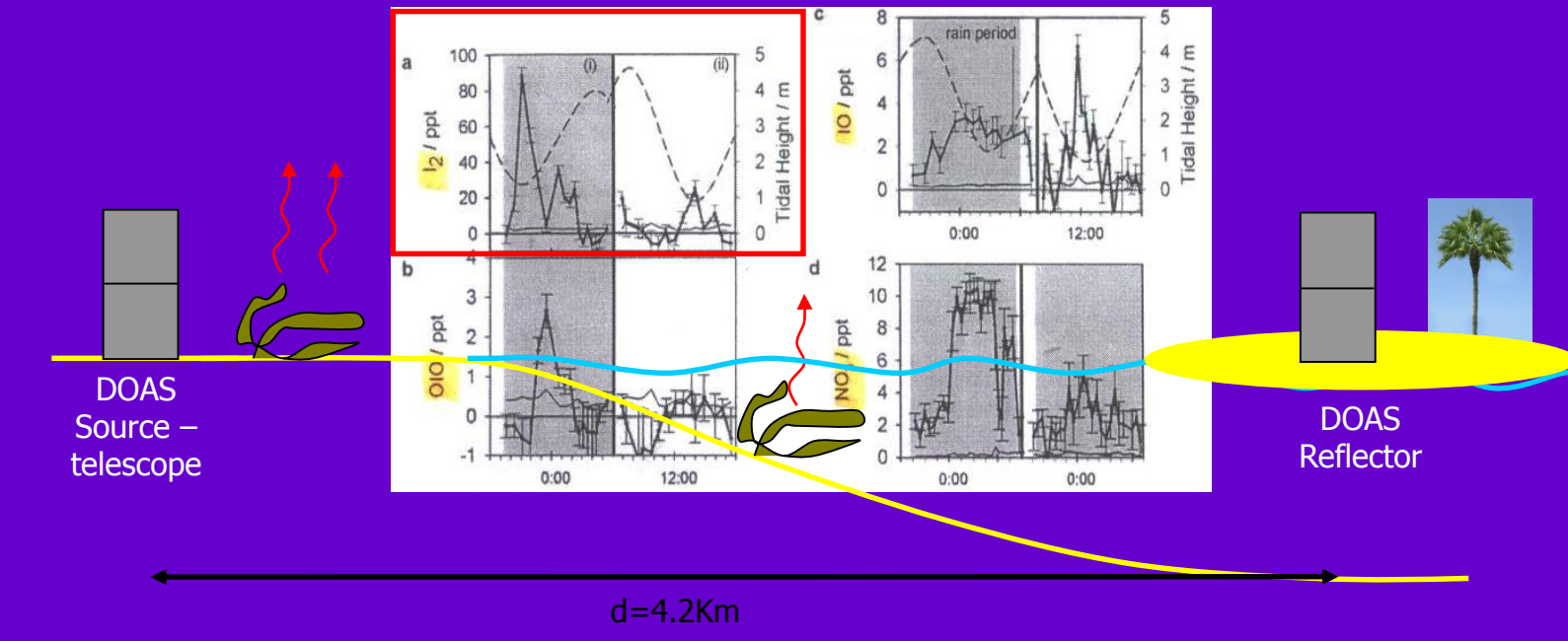
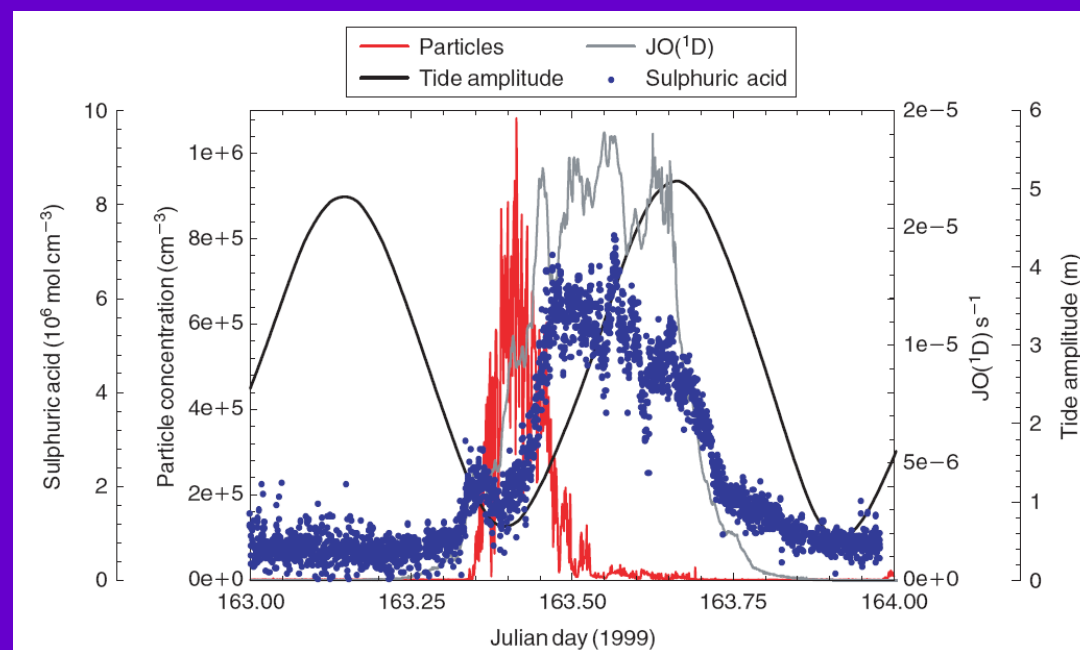
Iodine release in the Marine Boundary Layer (MBL): impact of biogenic emission on air quality and climate



- the ozone concentration in the MBL
- the capacity of the atmosphere to process emissions of greenhouse gases such as methane
- the formation of new particles
- the production of potential cloud condensation nuclei
- human health (iodine deficiency → thyroid disorders, cretinism)

Particles detection [O'Dowd et al 2002]
• Iodine identified in all nucleation mode particles
• Sulphuric acid concentrations insufficient to explain the particles events

Field campaigns on coastal areas:
Gaseous phase (DOAS) [Saiz-Lopez et al 2004]
Tidal cycle of I₂, CH₂I₂, IO, with peak concentration at low tide



Main origin of I₂ and Volatile iodine compounds on coastal areas: STRESSED, AIR-EXPOSED MACRO-ALGAE

Our target: MOLECULAR IODINE I₂

Our model of macro-algae: LAMINARIA DIGITATA

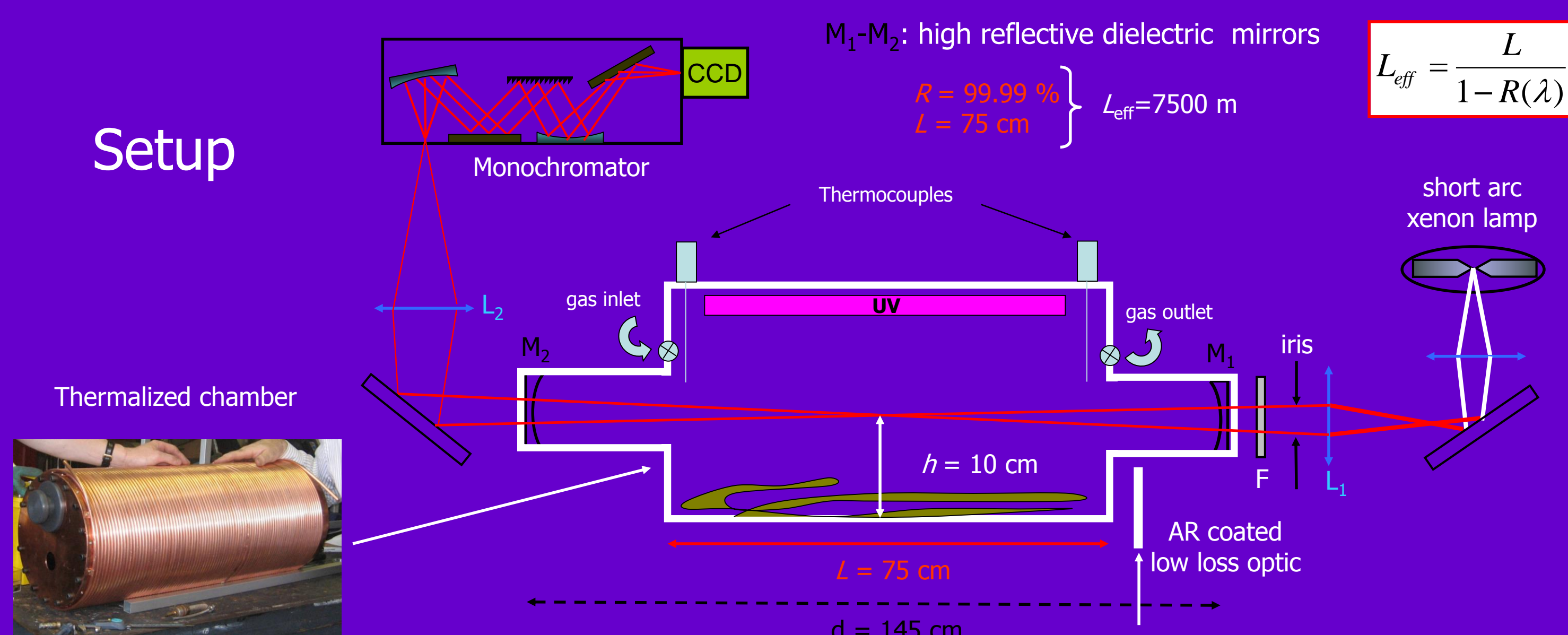
- Sporophyte: macroscopic stage up to 2 meters long
- Strong iodine accumulator (I⁻, IO₃⁻): about 1.0% of its dry weight
- Habitat: Rocky shores, subtidal zone up to 20m

Questions:

- emission process, parameters?
- emission flux?
- gas to particles conversion process? ...

[O'Dowd et al 2002]: O'Dowd et al, J. Geophys. Res. **107**, doi:10.1029/2001JD000555 (2002)
[Saiz-Lopez et al 2004]: A. Saiz-Lopez and J. Plane, Geophys. Res. Lett. **31**, L04112, doi:10.1029/2003GL019215 (2004)

Technique: Incoherent Broad-Band Cavity-Enhanced Absorption Spectroscopy (IBBCEAS) [Fiedler et al 2003]



Extinction measurement and analysis

For small absorption (low concentrations or small cross-sections), the extinction coefficient is given by:

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

where $I_0(\lambda)$: intensity transmitted without the gaseous sample (without the seaweed)
 $I(\lambda)$: intensity transmitted with the gaseous sample (with the seaweed)
 $R(\lambda)$: reflectivity of the cavity mirrors

Analysis for molecular iodine by Singular Value Decomposition (SVD)

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

where $\sigma_{I_2}(\lambda)$: absorption cross-section spectrum of molecular iodine
 a, b, c and n_{I_2} : unknown parameters
 n_{I_2} : iodine number density
 $a + b\lambda + c\lambda^2$: background caused by additional unspecified losses

Results: time-dependence of iodine elution from a *Laminaria digitata* thallus

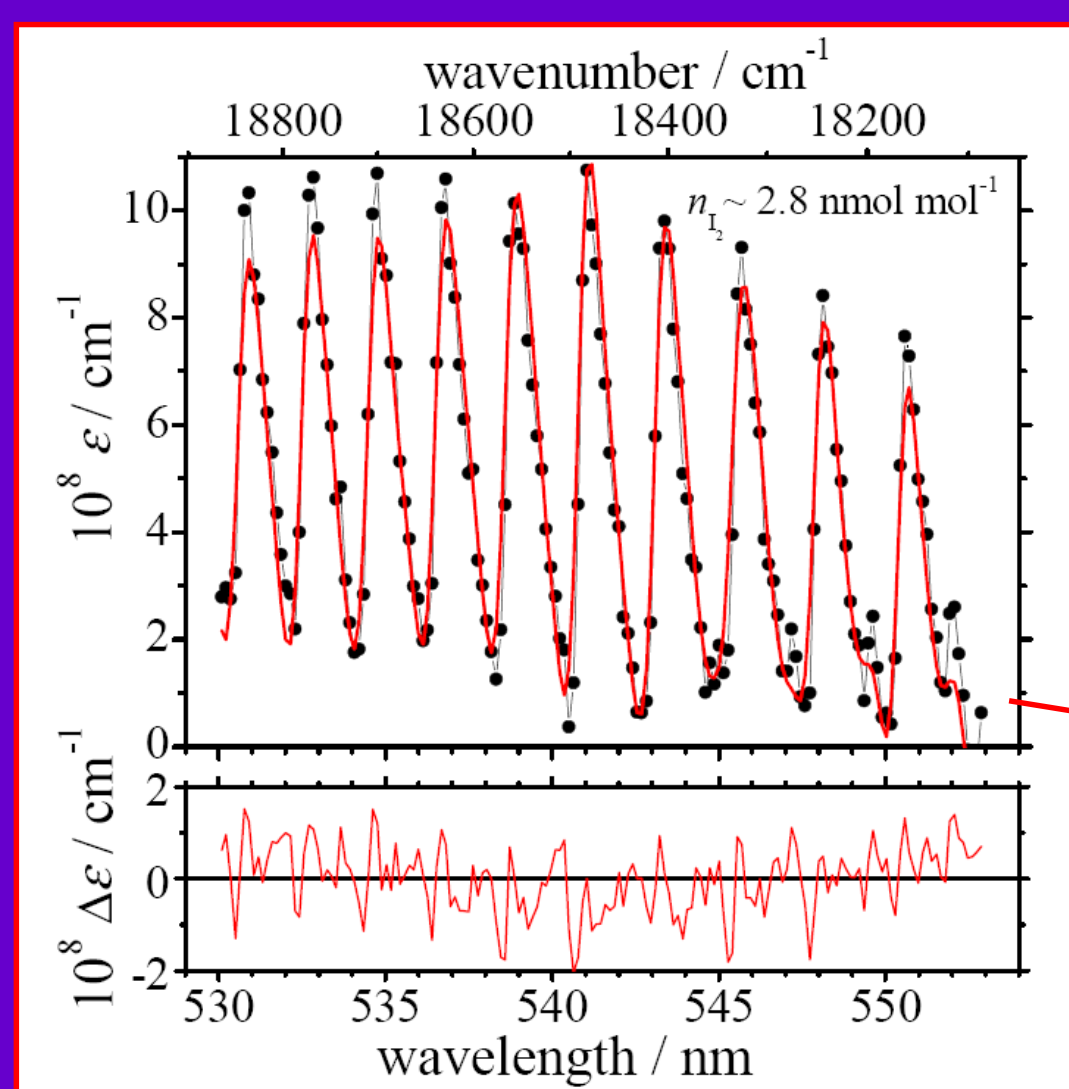
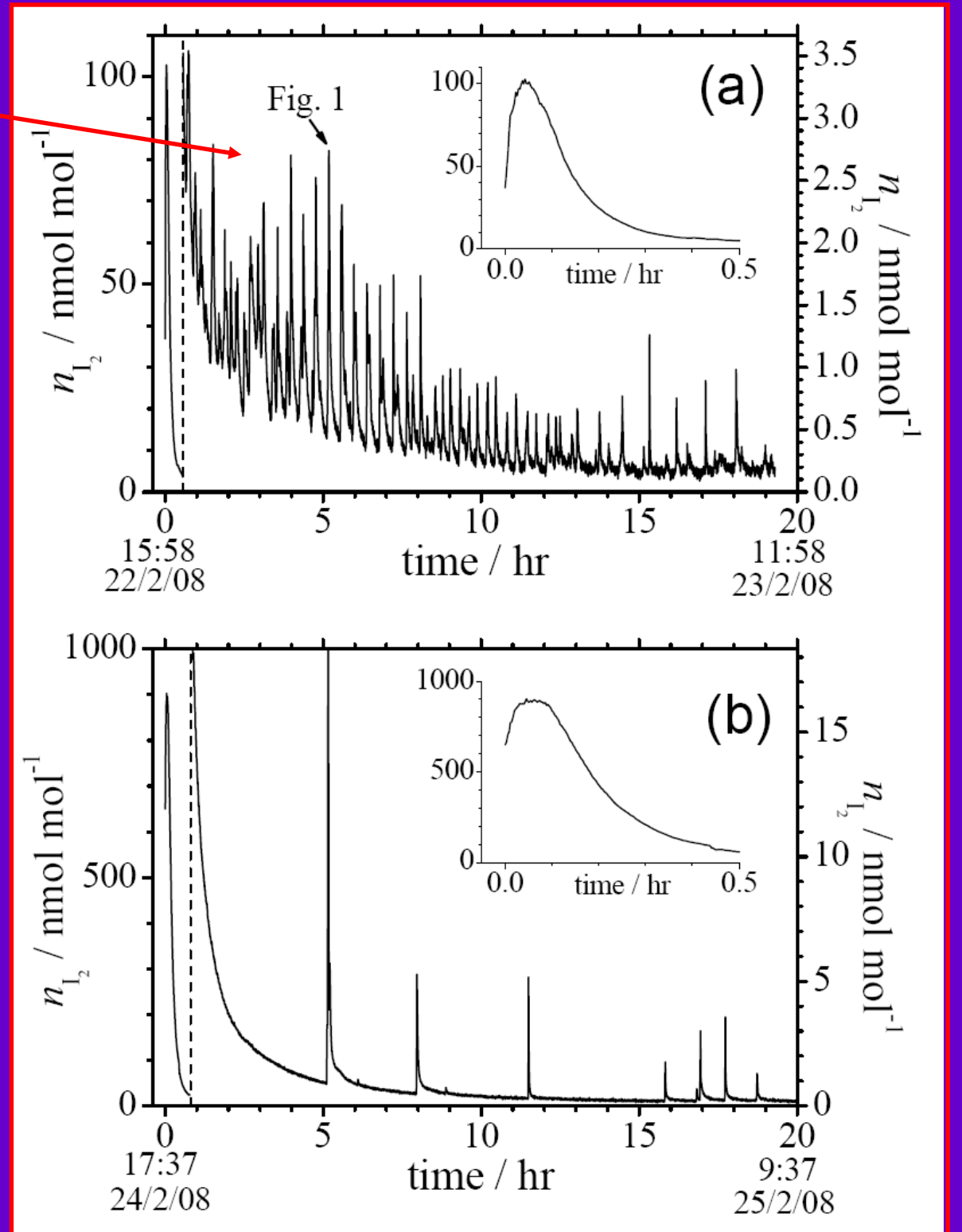


Figure 1 Typical absorption spectrum of the gas mixture above a *Laminaria* thallus out of water in the dark – range 530-553 nm. Dots and thin line: measured extinction, $\epsilon(\lambda)$. Solid line: fit using eq. (2) with $a = -2.84 \times 10^{-5} \text{ cm}^{-1}$, $b = 1.03 \times 10^{-8} \text{ cm}^{-1} \text{ nm}^{-1}$ and $c = -9.462 \times 10^{-11} \text{ cm}^{-1} \text{ nm}^{-2}$, $n_{I_2} = 7.07 \times 10^{10} \text{ molecules cm}^{-3}$. The period peak structure in the spectrum is the I₂ absorption spectrum due to molecular iodine released from the plant. The lower panel shows the unweighted absolute fit residuals.

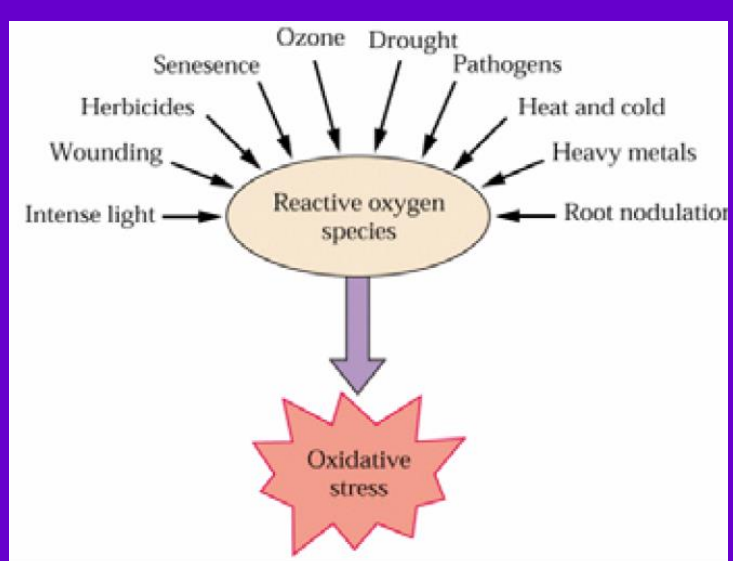
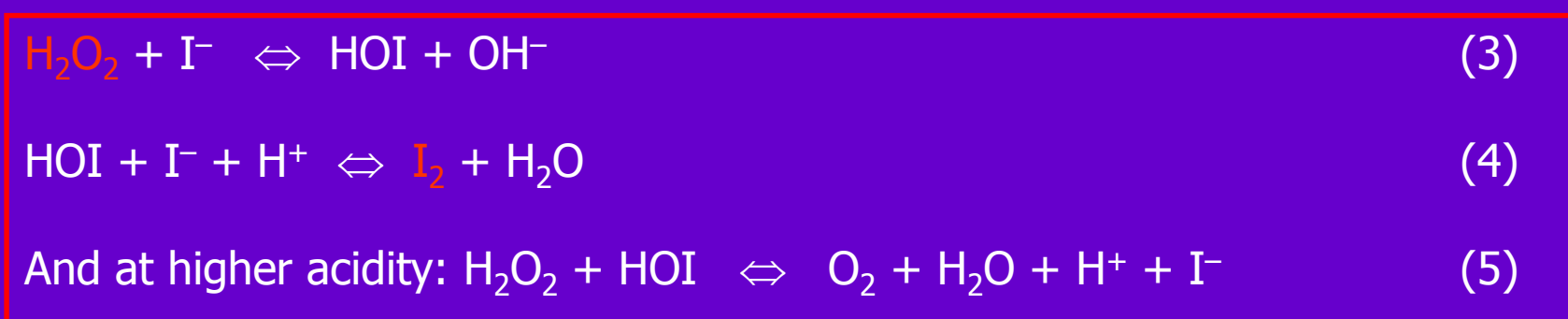
Figure 2 Time-dependences of the I₂ mixing ratio [nmol mol⁻¹] in the probe volume inside the sample chamber containing a fresh thallus of *Laminaria digitata*. The traces left and right of the vertical dashed lines refer to the scales on the left and right axes respectively. The traces are connected at the dashed line. (a) Blade length 87cm, stipe length 30 cm (no holdfast), 25g dry weight (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 Figure 1 was recorded.



[Fiedler et al 2003]: S. E. Fiedler, A. Hese, A. A. Ruth, Chem. Phys. Lett. **371**, 284–294 (2003)

Potential processes leading to the oscillatory elution of molecular iodine from *Laminaria digitata*

It is known that oxidative stress can activate a massive efflux of iodine from *Laminaria* species resulting in the elution of molecular iodine and volatile halogenated compounds (so-called "iodovolatilisation"). However, the exact time-dependence of this process has never been observed previously. The fact that molecular iodine is released in distinct bursts (irrespective of their exact time signature) is an indication for a particular biochemical activity in the *Laminaria* organism and environment. Whether the inhomogeneous distribution of I₂ in *Laminaria* species could lead to spatial disparities in the I₂ release and hence possibly to the occurrence of bursts cannot be determined from these first measurements. Since our approach integrates over the entire specimen, even strong spatial differences in the physiological and chemical effectiveness of I₂ release cannot be detected. It is likely that the observed bursts are a consequence of the known stress-induced production of H₂O₂ in *Laminaria digitata*, whether spatially-dependent effects do play a role or not [Küpper et al 2003]. The key (aqueous phase) reactions in this system are suggested to be:



and several other reactions including production of I₃⁻ and IO₃⁻ ions. Hence the production of H₂O₂ and the release of I₂ may be strongly correlated. In order to test whether H₂O₂ production may trigger the (quasi-periodic) release of molecular iodine, an experiment was performed in which "old" water from the seaweed tank was placed in the sample chamber. The result is shown in Fig. 3. It is important to note the similarity of the qualitative behaviour of the I₂ emissions in our experiments to the H₂O₂ release in *Laminaria digitata* as shown in Ref. [Küpper et al 2001] and [Küpper et al 2001]. This experiment demonstrates the importance of the presence of H₂O₂ for the elution of I₂. No additional bursts were observed in this experiment after the initial emission maximum, showing the role of the living seaweed in the emission behaviour observed on Fig. 2.

Outlook

Study of external parameters: UV light, temperature, moisture, oxygenation, ozone level, emission flux...

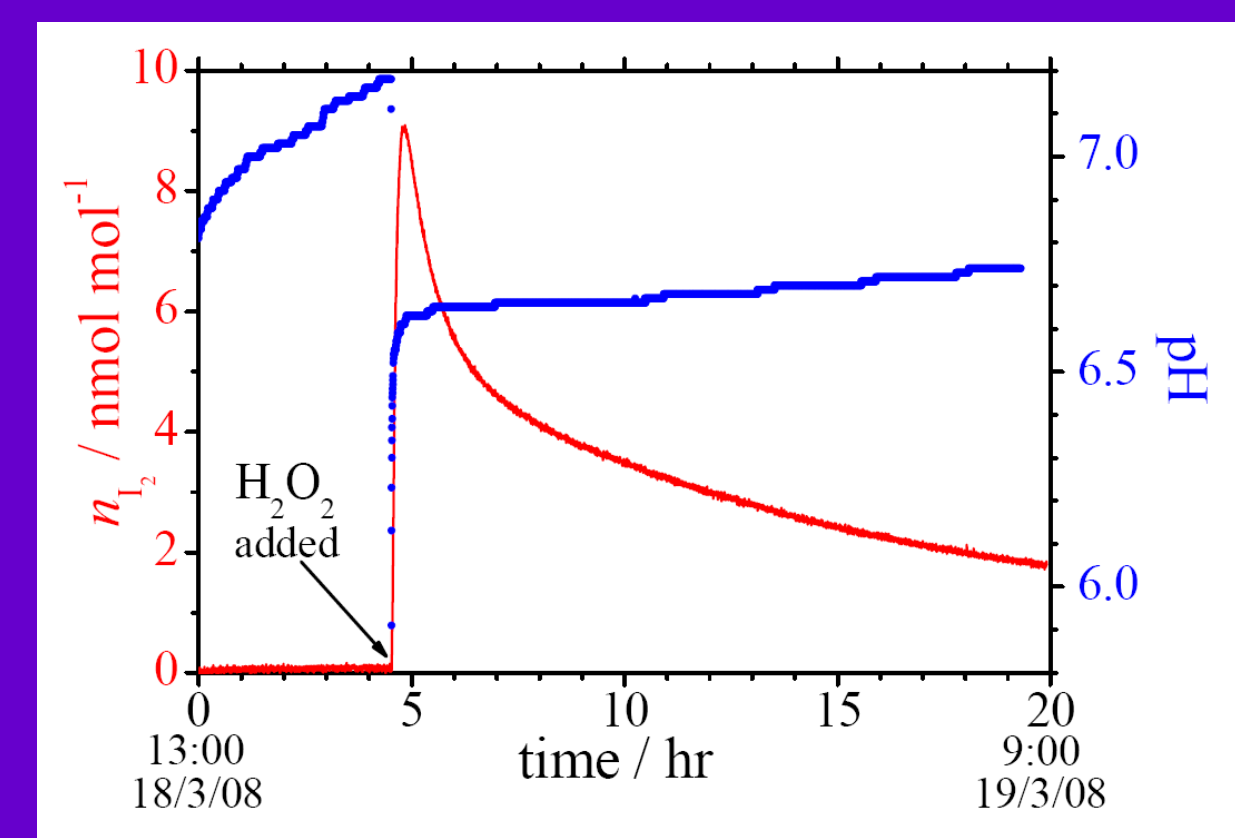


Figure 3 Time-dependence of the I₂ mixing ratio [nmol mol⁻¹] in the probe volume inside the chamber containing 200 ml of "old" seawater from the storage tank. *Laminaria digitata* had been kept in this water for 19 days. At 4hr45min, 15 ml of H₂O₂ solution (30%) were added to the seawater, triggering the immediate emission burst of I₂ (solid line: I₂ number density) resembling the initial bursts shown in the inserts of Fig. 2. The pH (solid circles) was monitored simultaneously. The experiment was performed in the dark at ~6.5-8.5°C.

As already known from previous studies, 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 H₂O₂ and I₂ in aqueous solutions show oscillatory behaviour leading to quasi-periodic emissions of gaseous I₂. In particular, strong oscillatory behaviour is found in the "iodine-clock" Briggs-Rauscher and Bray-Liebafsky reactions. Although the general theory of these "clock" reactions is well established, the detailed understanding of the individual reactions is still far from complete. It is plausible that the I₂ bursts observed in the present study are initiated by the stress-induced H₂O₂ production of *Laminaria digitata*. These 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 such oscillation-like emissions of I₂ 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. Probably, when washed up on the shore the plant activates defense 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.

[Küpper et al 2003]: F. C. Küpper, N. Schwiweigt, E. Ar Gall, J.-M. Legendre, H. Vilter and B. Kloareg, *Planta* **207**, 163–171 (1998).
[Küpper et al 2001]: F. C. Küpper, B. Kloareg, J. Guern and P. Potin, *Plant Physiol.* **125**, 278–291 (2001).
[Küpper et al 2002]: F. C. Küpper, D. G. Müller, A. F. Peters, B. Kloareg and P. Potin, *J. Chem. Ecol.* **28**, 2057–2081 (2002).