Atmos. Chem. Phys. Discuss., 8, S9391–S9397, 2008
www.atmos-chem-phys-discuss.net/8/S9391/2008/

Atmospheric Chemistry and Physics Discussions

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

S. Dixneuf et al.

Received and published: 22 November 2008

We are pleased that our work on the time dependence of molecular iodine emission from *Laminaria digitata* was received rather positively by the two anonymous reviewers whose commendatory remarks on the manuscript are much appreciated. We also welcome the information provided by W. Bloss on progress made by other groups working on closely related topics.

In the following we will outline to what extent the constructive suggestions of the reviewers will be considered in the final submission of this manuscript to ACP.

Referee 1: We agree with all three suggestions by the referee and will (a) amend the definition of the concept "iodovolatisation", (b) state the molar concentration of the H_2O_2 explicitly in the manuscript (p. 16508), and (c) correct reference "(Saiz-Lopez et

al. 2004a)" to "(Saiz-Lopez and Plane, 2004a)".

Referee 2: The questions relating to the quantitative information given in this manuscript will be addressed one by one in our reply to reviewer 2 to overcome the referee's concerns:

1. It seems from Fig 3A and 3B that two different experiments yielded completely different results on the oscillatory behaviour. Where any further experiments performed? i.e. to judge which of these two (if any) were the most representative?

In total 16 long-term experiments on the I_2 emission of *Laminaria digitata* were performed of which 16 showed series of bursts. No time signature was entirely reproducible. All of them had in common that one initial strong burst was observed followed by a number of smaller bursts as shown in Fig. 3(a) and (b). The measurements shown in Fig. 3 were chosen as representative. Exactly uniform conditions for measurements with different plants are impossible to achieve. There are too many (not well-defined) factors that may influence the exact time signature of I_2 emission (also see reply to W. Bloss below).

In the revised manuscript we will add more information on the reproducibility of the data shown in Fig. 3 and the overall number of measurements taken.

2. What are the characteristic oscillatory time frequencies of the I_2 release? Do these correspond with known frequencies of oscillatory behaviour of iodine dynamics?

Each experiment revealed a new unique time signature of emission bursts - examples are shown in Figs. 3. The burst signatures are not reproducible. The measurement in Fig. 3(a) shows a surprising regularity which is dominated by a re-occurring emission period of roughly 25 min. This period is not representative for other measurements (see Figs. 3(b)), where the occurrence of bursts appears regular but with no specific periodicity in the time dependence. Therefore a meaningful connection with characteristic oscillation frequencies in iodine reaction mechanisms cannot be made at this

ACPD

8, S9391–S9397, 2008

Interactive Comment

stage.

3. What are the average enhancements of concentrations during a burst?

It is not quite obvious what information the reviewer is looking for by the "average enhancement of concentrations during a burst". If the question is aiming at the average concentration change of I_2 during a burst, then a satisfactory answer can unfortunately not be given. The IBBCEAS experiment was performed in a static cell and does not deliver information on the spatial emission profile of the plant. Some of the I_2 emitted by the plant may indeed not enter the absorption light path. Furthermore, there may be significant spatial variations in the emission flux (in [molecule per time per area]) so that quantification of the I_2 gas phase concentration in the present experiment is vague. More experiments for quantitative flux measurements are in preparation.

4. Finally, although it is suggested that the bursts may be related to H_2O_2 release, previous research (e.g. Küpper et al., 2002) shows only that H_2O_2 is released quickly and then decays: it does not show the oscillatory behaviour of I_2 shown here. Is this due to a lack of temporal resolution in the latter data, or can the authors suggest another reason?

The experiments outlined in Küpper et al., 2002, lasted only *ca.* 120 min. There was always a delay of at least *ca.* 45 min between the occurrence of an initial strong (primary) burst and the appearance of smaller (secondary) I_2 bursts in our experiments (in the majority of experiments secondary bursts occurred after more than 120 min). There is the possibility that H_2O_2 bursts could have been observed, had Küpper et al. performed longer experiments. Moreover, data points are only shown every few minutes for the first 15 - 20 min, later on in the measurement data points are even sparser at intervals of 10 - 20 min. With this time resolution potential H_2O_2 bursts could have been easily missed as already implied in the reviewer's question. Finally, in the publication by Küpper et al., 2002, *Laminaria digitata* was challenged by different elicitors of H_2O_2 release such as oligoguluronates, which may have had an effect on the

ACPD

8, S9391–S9397, 2008

Interactive Comment

plants physiological reaction modifying the chemical mechanism leading to I_2 emission. The effect of different stress situations of the algae on the production of gaseous I_2 cannot be properly quantified at present. The simultaneous detection of H_2O_2 and I^- (in the liquid phase) together with I_2 in the gas phase would give a better understanding of the underlying chemical defence mechanism of the plant.

W. Bloss: The comment by Bloss is of relevance for the discussion in our manuscript - the information provided on the interesting work by Bale et al., 2008, was not available at the time of publication of Dixneuf et al., 2008.

In the seaweed experiment reported by Bale et al., 2008, a flow cell was used to indirectly measure I_2 emissions from *Laminaria digitata* via photolysis and subsequent detection of the iodine atoms released, and directly by observing the I_2 fluorescence. The authors express their confidence in the calibration methods used.

The comment's main issue concerns the "different temporal behaviour" observed by Bale et al. (a smooth rise and fall of iodine emission) in comparison to our work, where additionally short I_2 emission bursts were found. Bloss hypothesizes the differences to be due to (a) the different stress factors present in the experiments, and (b) the age of the seaweed sample.

The data shown in Fig. 8 in Bale et al. do not represent enough evidence to conclude that there is a difference in the temporal behaviour of I_2 emission in the two experiments. Bale et al. only show one measurement of *ca.* 50 min in comparison to our long-term measurements of up to 20 hours. All of our measurements have a strong initial rise and fall of I_2 emission in common lasting between *ca.* 0.5 hr to a few hours without the appearance of secondary bursts (see insets in Fig. 3). Weak secondary bursts were always observed after this initial phase in the experiments, when the plant had settled into its new environment.

The effect of different stress factors on the I_2 emission of the plant is difficult to quantify. Therefore we will only comment on the most striking aspects that distinguish the two

ACPD

8, S9391–S9397, 2008

Interactive Comment

experiments:

Bale et al. do not describe the state of the *Laminaria* organism, they only state its wet weight (50 g). The temperature in the flow cell is not given. It is also not clear whether the plant was in the dark during the experiment or exposed to light. It is not stated where the seaweed was kept between harvesting it and placing it into the experiment. The flask agitation during the experiment is not described in detail. Bloss claims that the plant was not put under stress by ozone exposure owing to a flow ($10\ dm^3\ min^{-1}$) of dry ozone-free synthetic air over the plant.

From our 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. Bale et al. must have also exposed the seaweed to (ozone containing) ambient air immediately before the measurement when placing it into the flow cell. In fact, we think that the most important stress factor triggering the initial burst is due to taking the seaweed out of the water and placing it into the setup. An important factor thereby is the change of temperature. The *Laminaria* organism is very sensitive to temperature change (Bolton and Lüning, 1982) and already perishes in water upon prolonged exposure to temperatures higher than 23°C. Working at room temperature and gradually desiccating the seaweed - conditions chosen by Bale et al. - is likely to have an effect on the iodine chemistry in the aqueous surface layer on the plant or the plant itself. Our intention, however, was to study the kelp organism under conditions similar to those on the shoreline. Therefore air and water temperature was chosen according to the conditions we found upon harvesting the seaweed, i.e. water temperature *ca.* 10°C, air temperature *ca.* 8°C. Whether keeping seaweed in captivity for some days changes its stress level is speculative at present. In this context the most

ACPD

8, S9391–S9397, 2008

meaningful aspect concerns the role of bacteria and microorganism putting stress on the seaweed (neither Bloss mentions this aspect in his comment, nor is it considered by Bale et al.). Keeping the algae in a closed tank (without circulating the water) probably enables bacteria to proliferate, thus changing stress levels for the plant. However, this may not be very different for rock pools. In this context it is important to note that some experiment that were performed within *ca.* 3.5 hr of harvesting also showed secondary bursts in the I_2 emission.

We agree with Bloss that in the future more work is needed to study the seaweed reaction under well defined stress-conditions. Some parts of the discussion outlined here will be added to the revised submission to ACP, making clear that quantitative (absolute) statements concerning the I_2 emission from *Laminaria digitata* are hard to establish. Bale et al., 2008, will be added to the reference list.

Since the results from the RhAMBle campaign (McFiggans et al.) and the finding of "sporadic bursts of I_2 in the experiments by Ball and co-workers" are still unpublished we are unable to comment on this aspect.

References

Bale, C. S. E., Ingham, T., Commane, R., Heard, D. E., and Bloss, W. J.: Novel measurements of atmospheric iodine species by resonance fluorescence, J. Atmos. Chem., 60, 51-70, (2008).

Bolton, J. J., and Lüning, K.: Optimal growth and maximal survival temperatures of atlantic *Laminaria* species (Phaeophyta) in culture, Marine Biol., 66, 89-94, (1982).

Küpper, F. D., Müller, D. G., Peters, A. F., Kloareg, B., and Potin, P.: Oligoalginate recognition and oxidative burst play a key role in natural and induced resistance of sporophytes of *Laminariales*, J. Chem. Ecol., 28, 2057-2081, (2002).

McFiggans, G., et al.: Results from the field experiments in the reactive halogens in the marine boundary layer (RHaMBLe) project, Atmos. Chem. Phys. Discuss., in

ACPD

8, S9391–S9397, 2008

preparation.

Interactive comment on Atmos. Chem. Phys. Discuss., 8, 16501, 2008.

ACPD

8, S9391–S9397, 2008

Interactive Comment