

## ***Interactive comment on “Fucus and Ascophyllum seaweeds are significant contributors to coastal iodine emissions” by R.-J. Huang et al.***

**S. Ball**

sb263@leicester.ac.uk

Received and published: 7 December 2012

New measurements of iodine emission rates from fucus vesiculosus: T J Adams, S M Ball, C Leblanc & P Potin.

We have recently re-measured the iodine ( $I_2$ ) emission rates of several seaweed species collected in vicinity of the Station Biologique de Roscoff (SBR) in Brittany, France. This work extends our previous study of seaweed emission rates conducted at this site during the RHaMBLe field campaign in 2006 and reported in Ball et al. [ACP, 10, 6237, 2010]. We again used the spectroscopic technique of broadband cavity enhanced absorption spectroscopy (BBCEAS) to directly quantify gas phase iodine. We acknowledge the visitor access to SBR provided by the ASSEMBLE FP7 project “Association of European Marine Biological Laboratories”.

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Figure 1 shows a representative time profile of the emissions observed from a 1.05 kg sample of fucus vesiculosus collected from the beach in front of the SBR a few minutes before the experiment. The seaweed was initially submerged in sea water inside the sample vessel; the vessel was drained at time = 0 minutes; ambient room air was supplied into the sample vessel at 3.6 litres/min throughout the experiment, and the same flow of head-space gas was drawn from the vessel into the BBCEAS instrument.

Negligible amounts of  $I_2$  were detected in the head-space gas whilst the seaweed was underwater. (Apart from a brief “blip” whilst the water was drained at  $t = 0$  mins), the  $I_2$  emission rate remained low for some 30 minutes after the seaweed was exposure to air. It then increased fairly smoothly, reaching its maximum approximately 1.5 hours after exposure. Thereafter the emission decreased smoothly to establish a low (but non-zero) and approximately constant emission rate after 3 hours. Other fucus vesiculosus samples in our study exhibited similarly shaped emission profiles.

The profile's initial shape in Fig 1 shows some similarity with the fucus vesiculosus emission profile measured by Kundel et al. [Anal Bioanal Chem, 402, 3345, 2012; and Fig 5 in Huang et al.]. Both profiles start with low emissions and then reach a broad maximum 1.5-2 hours after exposure. The absolute value of the maximal emission rate here (0.042 pmol of  $I_2$  emitted per min per gramme fresh weigh of seaweed) is substantially smaller than the 1.3 pmol/min/gFW rate recorded by Kundel et al. This could be because Kundel et al. exposed their samples to 50 ppbv of ozone whereas our sample was exposed to room air (which, being indoors, likely contained less than the typical ambient 35 ppbv of ozone); this could also be due to natural plant-to-plant variability in emission rates of the same species.

The Kundel et al. time series stops after 2 hours, so it's not possible to use their data to comment on how/if emissions from fucus vesiculosus decline at long exposure times. Observations in the Huang et al. manuscript extend up to 6 hours after exposure and show emissions continuing to increase. This is different from our observation in Fig 1.

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For comparison in Fig 1, I have plotted the emission rates for fucus vesiculosus reported in Ball et al. [2010]. The duration of measurements with and without seaweed present inside the sample vessel are indicated by the horizontal error bars; the vertical errors are the standard deviation of the measurements averaged together to produce the data point. The older RHaMBLe measurement of 0.008 pmol/min/gFW in the first 10 minutes after exposure is broadly consistent with the initial phase of our new measurements. However because our older measurement lasted for only 10 minutes, it does not (it cannot) capture any later and possibly much larger emission maximum. Therefore I request that the authors rephrase the statement on p25924 of their manuscript that “This observation [the Huang et al. time series] is inconsistent with the macroalgae incubation experiments of Ball et al. (2010)”. (I much prefer the wording and emphasis of the ascophyllum and *F. vesiculosus* discussion on page 3351 of the original Kundel et al. paper). The authors should also rephrase their reference to an “apparent contradiction” a few lines later: I don’t see that there is a contradiction. (If anything, the “contradiction” is now that our new data show fucus vesiculosus emissions decaying back to low levels a few hours after exposure, whereas the Huang et al. data show emissions increasing for six hours, whilst the 2 hour duration of the Kundel et al. time series is too short to provide this information.) We note that both our older and new initial emission rates are an order of magnitude smaller than the ~0.1 pmol/min/gFW emission rates recorded for fucus vesiculosus by both Kundel et al. and Huang et al. in the initial 0-20 min sampling period (see Figs 5 and 4 respectively). There could be several reasons for this, including (as Kundel et al. stated in their original paper) “inter-plant variability”.

The discussion on p25927 of the manuscript says that “Leigh et al. [ACP,10, 11823, 2010] concluded that, in comparison to *Laminaria* spp, the contributions from *A. nodosum* and *F. vesiculosus* to the total I2 emissions were negligible in the coastal region around Roscoff by assuming... [the emission rates] taken from Ball et al (2010)”. The word “negligible” is inaccurate, and the authors may wish to finesse their text. It is certainly true that laminaria species dominate emissions source strengths in the model

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whenever the tide is low enough to expose these species. However there are other times e.g. around the minimum tidal amplitudes when shallow-water (*ascophyllum* and *fucus*) and medium-water species (*saccharina*) make comparable contributions. The detail of what happens at the RHaMBLe measurement site is even more complex – the laminaria beds are sometimes too far distant (the wind is too weak, or blowing in the wrong direction) for their emissions to reach the observation site. The model quite often predicts that significant amounts of the I2 measured at the RHaMBLe site derived from weakly-emitting but nearby shallow-water seaweeds. The Leigh et al. paper identifies some possible explanations for differences between the model and the RHaMBLe observations, including inaccuracies in the spatial distribution of seaweed species and small patches of seaweed (particularly those close to the measurement locations) not represented on the seaweed maps used in the model. In both cases, the missing component could be *fucus* and/or *ascophyllum*. If these species produce greater emissions than was assumed in the Leigh et al. model (as now seems probable from the present manuscript, from Kundel et al., and from our own new study), they are likely to bring the model into closer agreement with the measurements.

Let us not forget that the Leigh et al. model was operating with the best (the only!) emission rates available at the time. The heavy dashed line in Fig 1 of this comment shows the parameterised emission rate assumed for *fucus* species in the model (this was the average of the *fucus vesiculosus* and *fucus serratus* emission rates measured by Ball et al. (2010)). Within its limitations, the model’s parameterised emission rate provides a reasonably accurate representation of the emission rate for the first 30 minutes after our *fucus vesiculosus* sample was exposed to air, and for exposure times longer than 2.5 hours. I accept that if we were to adopt our new *fucus vesiculosus* emission rates, the Leigh et al. model would predict a greater role for *fucus* in the 0.5-2.5 hour period after exposure. However the increased role would not be as large as if the model were to assume the emission rates from the present Huang et al. manuscript.

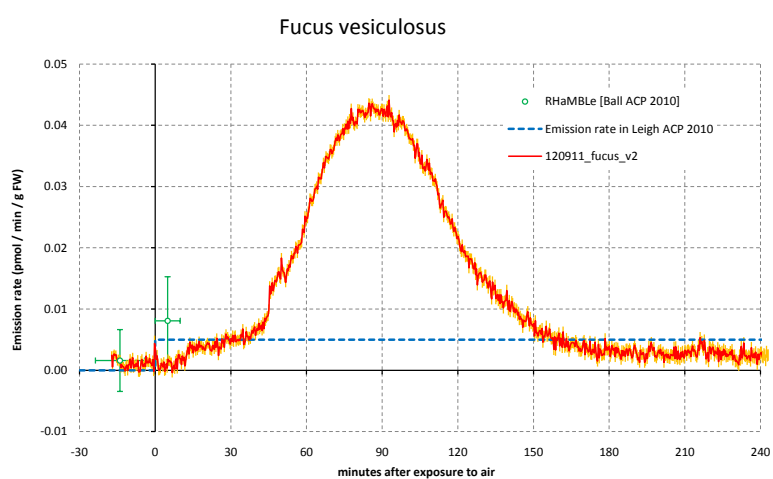
The picture for *ascophyllum* is more complex. Our new data show a lot of variability,

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both within a given time series and between time series recorded for different samples. That is a discussion for another day, once we've fully analysed our new data.

Interactive comment on Atmos. Chem. Phys. Discuss., 12, 25915, 2012.

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**Fig. 1.** Red data (yellow shading is measurement uncertainty): iodine emission rates from fucus vesiculosus (SBR, 11 Sep 2012). Previous RHaMBLe measured rates (green) and assumed in Leigh model (blue dashed).

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