Atmos. Chem. Phys. Discuss., 12, C12996–C13019, 2013
www.atmos-chem-phys-discuss.net/12/C12996/2013/

Atmospheric Chemistry and Physics Discussions

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

R.-J. Huang et al.

rujin@uni-mainz.de

Received and published: 28 February 2013

The authors thank the anonymous referees and S. Ball for their time to review our manuscript and particularly for their valuable comments and suggestions that have significantly improved the manuscript. We have made most of the changes suggested by the reviewers and have outlined these in detail below.

Anonymous Referee #1

General comments: Huang et al. present evidence in their study, that Fucus und Ascophyllum seaweeds are much stronger emitters of iodine than previously thought. This is an important finding since so far Laminaria has been considered the only significant contributor to coastal iodine emissions. Laminaria might still be the most important con-

tributor, but the authors show that the other species contribute similar high amounts of I2 when exposed to ambient air for longer periods of time. In future studies it will be important to investigate the biology and the release processes of these species in more detail, e.g. like Kuepper et al, 2008 did for Laminaria.

This paper provides important new results and I therefore recommend its publication with some modifications/revisions.

I am not sure if ACP is the best platform for such a biological paper, although it has implications for atmospheric chemistry and papers of this type have been published before in ACP. BG might be the better option, but that is something the editor has to decide.

Response: As pointed out by the reviewer that papers of this type have been published in ACP, we believe that ACP is appropriate because the implications of the paper speak directly to the source of iodine to the atmosphere and implications for atmospheric chemistry.

How are your values of I2 to be judged in the context of other observations, e.g. of IO, and how do they, or could they contribute to model simulations of the iodine chemistry? Accordingly you should also discuss the recent publication of Commane et al., 2011 in the introduction. Have simultaneous measurements of IO been taken?

Response: We did not take simultaneous measurements of IO during this campaign. However, our I2 measurements could provide a useful dataset to improve the current model for the MBL iodine chemistry, as discussed below. We discuss now the recent publication of Commane et al., 2011 in the revised manuscript.

A thorough error analysis is missing in this paper – see also comments below.

Response: We have included the error analysis in the revised version.

Specific comments:

ACPD

12, C12996–C13019, 2013

Page 25916, line 6: What are these values? Means? See comment below on Table 1.

Response: These values are the mean values of the I2 mixing ratio found above the macroalgae beds at nine different locations. We have clarified this in the abstract.

Page 25918, line 2-4: What are you indicating with the 3 arrows?

Response: Here we used 3 arrows to represent the multiple reaction pathways to form I2Oy.

Page 25918, line 24: Please explain FW – for a non-biologist this is not immediately clear.

Response: FW is the abbreviation of Fresh Weight. We have explained it in the revised version.

Page 25919, line 19: Please explain spp. - for a non-biologist this is not immediately clear.

Response: "spp." is the abbreviation of "species".

Page 25920, line 3 et seqq.: Why did you pick these sites? The reasoning/logic in this paragraph is not clear.

Response: We selected these sites because they are characterized by a high abundance (but discrete zonation) of brown macroalgae. Also, the macroalgal exposure time in these sites is representative of typical North Atlantic rocky seashores.

Page 25920, line 17 et seqq. and throughout section 2. Please list and explain your sources of error (precision and accuracy). All values given in the text and in the figures should have an error/show error bars (Fig. 2, Fig 3, Fig 5) – see also comments on Table 1.

Response: We have explained the lack of error bars (if applied) in Fig. 2, Fig. 3 and Fig. 5, respectively. The precision of the method for the determination of I2 is $< \pm 10\%$.

ACPD

12, C12996–C13019, 2013

Page 25921, line 20 et seqq.: Are there any other stress factors for the plants? Can they be ruled out?

Response: As discussed in Küpper et al. (2008), ozone is the stress factor governing the release of I2 from macroalgae when the species are exposed to air. When the plants are submerged in seawater, only aqueous oxidants (e.g., H2O2), in particularly in conjunction with biotic stress, will affect the level of iodine accumulated in the plants.

Page 25924, line 26: apple, bump, mixed? I guess these distributions are not standard terms and can not be understood without knowing the Vana et al. publication.

Response: Like “banana”, the terms “apple”, “bump” and “mixed” have been used to describe the number size distributions of new particle formation events. These terms have been accepted by the community in recent years, see literature references such as Manninen et al., Atmos. Chem. Phys., 10, 7907-7927, 2010; Kyrö et al., Atmos. Chem. Phys. Discuss., 12, 32741-32794, 2012.

Page 25925, line 17/18: Why not naming the number of the site according to Fig.1?

Response: “at a fixed sampling site” is replaced by “at sampling site #1”.

Page 25925, line 28: Is one of these days the same day as for the measurements at this site? It is not clear from the text.

Response: We added “Figure 3 shows the 2-day temporal profile. . .”.

Page 25925, line 18 et seqq.: You write that: A lower mixing ratio was observed at the beginning of ebbing tide when the macroalgae were just exposed to the ambient air. Assuming a photolytical lifetime of I2 of 5s and taking your wind speed measurements of up to 11m/s, then one can speculate that the area from which you are gathering data might also change with ebbing tide, which on the other hand might partially be the reason for the increase of I2 over time. None of the locations looks like it is getting air from the open ocean. It’s not clear from the information given in the paper. A more thorough description is necessary. Somehow partial information is scattered around the

ACPD

12, C12996–C13019, 2013

paper, but not presented concisely at the places where needed. A plot showing, Time (UT), water level (and maybe resulting area of algae exposed to air), solar radiation and mixing ratios for each observation would be helpful.

Response: It is true that gradually more macroalgae were exposed to the air with decreasing water level due to the outgoing tide and therefore the total amount of I2 released to the air increased. However, the rapid photochemical destruction of I2 and its efficient dilution during transport will significantly minimize the contribution of nearby macroalgal sources to the I2 level at the sampling point. Moreover, our measurements were taken 5-10 cm above the macroalgal beds. Therefore, the data represent mainly the I2 level in the very small area. In the text, we added "Note that the contribution of nearby macroalgae sources to the I2 level at the sampling site is likely rather small due to the rapid photochemical destruction of I2, the efficient dilution during transport and the short distance (5-10 cm) between the denuder inlet and the macroalgal bed". Unfortunately, we did not measure the resulting area of algae exposed to the air considering the difficulties working on the rocky coast. However, in Fig 3 we plotted the exposure time, solar radiation and mixing ratios for site #1 which was most extensively studied during this campaign.

Page 25934, Table 1: Remove the details given in the Location column, e.g., 150 m away from MRI-Carna etc. I guess that is useful information only for people actually familiar with that site, but not for the general audience. In column 2, I2 (ppt), of that table it is not clear what you mean with the plus/minus values. Are these numbers the standard deviation? This would only be a useful quantity, if your samples were taken simultaneous under the exactly same conditions. Or a range?, which would not make sense, since it would be pure coincidence if the highest and lowest value would spread symmetrically around the mean. Or are these values the error of your measurement technique (precision and accuracy)? It's not clear from the text and the table – see also comment on errors.

Response: The details in the location column have been removed. The number in

ACPD
12, C12996–C13019, 2013

column 2 represents “Mean ± S.D.” of measurements at the same location.

Are all these measurements taken during daytime, or also during nighttime? I guess that during daytime I2 is photolysed fast enough, so that the area from which you are gathering data is localized and rather small, but during nighttime that would be different and transport processes could play a much more important role.

Response: The nearby macroalgal source may provide a negligible contribution to our “point” measurement during daytime considering the rapid photolytic destruction of I2 (during daylight) and the rapid dilution during transport. It is true that the ambient I2 level will build up during nighttime. However, our measurements were made very close to the source (i.e., 5-10 cm above the macroalgal beds) and the source concentrations were found to be at least 3-10 times higher than the ambient concentrations during low tide from our previous campaign (see Huang et al., 2010b).

Page 25935, Figure 1: Use higher resolution and different colours for the numbering and stations (red). Add a scale, so one can estimate distances. Acknowledge the source of the graph.

Response: For Figure 1, we have used different colors for numbering and stations and added a scale. “Google earth” was acknowledged.

Page 25937, Figure 3: Why are the fit equation and the fit curve shown in Fig3 and not discussed anywhere? What does it tell us? Is it important? If yes, then please discuss in the text. If no, then remove.

Response: We removed the equation in the figure.

Page 25939, Figure 4: Why does the time series stop after 1 hour?

Response: Unfortunately, due to limit of the visit time at Helgoland, we stopped each measurement after 1-2 hour(s) to save time for studying also other macroalgal species.

Technical comments:

ACPD

12, C12996–C13019, 2013

Page 25915: Unify the details given in the affiliations, e.g. some have postcode, others don't.

Response: The postcode is not used in Ireland.

Page 25917, line 25: The Carpenter, 2003 reference is not listed in the back – only Carpenter, 2001.

Response: This reference has been added.

Page 25918, line 7: Saiz-Lopez et al, 2006 – 2006a or 2006b ?

Response: Saiz-Lopez et al., 2006a, b.

Page 25918, line 19: Kundel et al., 2012 – 2012a, or 2012b ?

Response: Kundel et al., 2012b.

Page 25926, line 18: Variable emissions between plants HAVE been found : : :

Response: "has" changed to "have".

Page 25931, line 22: Kundel et al., 2012b is not used in the text. In this case remove the 'a' in the preceding reference.

Response: now Kundel et al., 2012b is used in the text.

References: R.Commane, K.Seitz, C.S.E.Bale, W.J.Bloss, J.Buxmann, T.Ingham, U.Platt, D.Pöhler, and D.E.Heard, Iodinemonoxide at a clean marine coastal site: observations of high frequency variations and in homogeneous distributions: Atmos. Chem. Phys., 11, 6721-6733, 2011, www.atmos-chem-phys.net/11/6721/2011/doi:10.5194/acp-11-6721-2011.

Anonymous Referee #2

Strengths: Emissions from seaweed provide the strongest source of iodine into the atmosphere in coastal regions (as long as there are seaweeds growing in the re-

ACPD

12, C12996–C13019, 2013

gion). Atmospheric iodine perturbs tropospheric radical chemistry, affects ozone production/loss rates, and leads to the nucleation of ultra-fine aerosol particles that potentially affect the local climate. Several large, multi-institution field campaigns have focussed on the tropospheric chemistry of halogens in coastal regions. However large areas of uncertainty remain.

Most of the observational data to date has been for Laminaria digitata which is known to concentrate iodine in its tissues (probably as the iodide anion) and known to be a strong emitter of molecular iodine when exposed to air. By contrast relatively little is known about other seaweeds' ability to emit. Field measurements have observed iodine compounds in coastal atmospheres even when any nearby L. digitata beds remained covered by sea water and thus were unlikely to be emitting. This hints that other iodine sources exist, and this paper provide a possible (partial) answer. The observational data presented in this paper make a useful additional contribution to understanding the coastal sources of iodine.

The weaknesses of this paper fall broadly into three issues. ISSUE 1: the data trail. I found it difficult to follow how values/results quoted in the text arose from/corresponded with the observational data given in the figures and Table 1. Hence I also found it difficult to follow the logic of the authors' arguments (see Issue 2). In the simplest cases, the authors should give the readers signposts to follow:

Response: We have gone through the manuscript carefully again and added what the reviewer calls "signposts" in several instances.

25923.19 Table 1 shows the *denuder* results...;

Response: Change made as requested.

25923.21 the mixing ratios of I2 ranging from 104 ppt to 393 ppt *that are given in Table 1*...;

Response: Change made as requested.

ACPD

12, C12996–C13019, 2013

25924.01 The I2 mixing ratio of 547 ppt *(Fig 2)*... is one of the highest reported to data.;

Response: Change made as requested.

More worrying is the lack of detailed explanation about the provenance/meaning of data given in Table 1 and the figures. How were the 13 observations at site #1 combined to produce the [I2] = 173.4 +/- 88.9 ppt entry in Table 1? What is the meaning of the +/-88.9 ppt uncertainty and how was it calculated? Why does the one observation at site #8 not have a +/- value? Are any of the data in Table 1 used to construct later figures: e.g. are the 13 data points plotted as circles in Fig 1 the same 13 observations at site #1 aggregated in Table 1? Are the two samples at site #3 in Table 1 the same data as the bar graph in Fig 2? The sampling site/sites must be identified in all figure captions.

Response: In Table 1, the number was given as mean $\pm$ s.d. for measurements taken at the same sampling location. We were trying to give a general idea that elevated I2 levels were present at the west coast of Ireland. We collected only one sample at site #8, therefore, the number has no +/- value. The sampling site has been identified in all figure captions.

A principal argument of this work is that emissions from different seaweed species vary with exposure time in different ways. Therefore some key information is missing from Table 1: the tidal height/exposure time when each measurement was taken. How is it possible to combine observations to create the site-specific values in Table 1, without also considering their presumably different exposure times? (c.f. site #1 and Fig 3; site #3 and Fig 2)

Response: This work is an extension of our pilot study in 2007 from which we found high levels of I2 above the intertidal macroalgae beds at one sampling site at Mweenish Bay. To explore whether elevated I2 concentrations are ubiquitously present above the macroalgae beds on the west coast of Ireland, we did a survey study at additional

ACPD

12, C12996–C13019, 2013

8 sites around the Mace Head Station in this study. However, careful consideration should be taken for the data shown in Table 1, i.e., they are not absolute values, but show the presence of elevated I2 levels when macroalgae beds are exposed to the ambient air (we have clarified this point in the revised manuscript). Following the survey we studied the temporal profile of I2 release to explain the observation of elevated I2 level.

25924.10 "...with an average of 134 ppt versus 301 ppt". Explain how these numbers were calculated from data given in Table 1.

Response: 134 ppt is the mean of those data observed at sites #1, 2, 4, 5, 6, 7 and 9 while 301 ppt is the mean of data from sites #3 and 8.

ISSUE 2: As I say above, the observational data presented in this paper make a useful additional contribution to understanding the coastal sources of iodine. However it is still a relatively limited dataset, with its own uncertainties. Yes, the authors have identified an area where current understanding is weak, and where the community might be missing something interesting. However I found the present dataset to be insufficient to justify many of the authors' "big picture" conclusions about the wider significance of the work; their dataset is still too sparse to constrain the uncertainties in current knowledge. Some comparisons with previous work were naively simplistic.

Response: We agree that the dataset is relatively sparse due to the short period of this campaign (2 weeks). However, we have taken field measurements at 9 sites and chamber studies of 3 different macroalgae species during this campaign. Also, this paper points to the incompleteness of current knowledge - i.e., a focus on Laminaria species to the exclusion of other iodine sources. Therefore, it advances our understanding of iodine sources in the coastal region, even if this is not the same as a careful characterization of the source strengths. Clearly, that would be appropriate for another study (see comments below from Dr. Ball as well).

25923.25 "the highest I2 mixing ratios were consistently observed above laminaria

ACPD
12, C12996–C13019, 2013

beds". If I have understood the data content of this paper, there are only two observations from the same time series over one particular laminaria bed (at 0-5 and 15-20 minutes after exposure, Fig 2), and one more observation over another site at an undisclosed exposure time (site #8 in Table 1). Three observations are insufficient to establish "consistency". Similarly 25925.12 "This time dependence was also observed in our field observations", and 25929 "In contrast the mixing ratio above the L digitata beds decreases with increasing exposure time": in both cases two data points in one time series are insufficient to establish a time dependence, let alone extrapolate the result from this one sample to establish the behavior of L. digitata generally. And 25925.21 "This emission profile is markedly different from that of L digitata": again there's only one digitata profile to compare against.

Response: Due to a miscommunication between the participating groups during the preparation of the manuscript, we made a wrong statement about "the highest I2 mixing ratios were consistently observed above Laminaria beds". This sentence has been removed in the revised paper. The I2 release profile of L. digitata, characterized by a decreased concentration with increasing exposure time, has been found in a number of laboratory studies. In this study, we found that a similar release profile occurs under natural conditions. It is true that we should include/cite those laboratory studies when we draw a conclusion about the I2 release profile of L. digitata and have done so. 25925.12 In the revised text the phrase "This time dependence was also observed in our field observations" has been replaced by "This phenomenon was also observed in our field observations". 25925.21 In the revised text the phrase "This emission profile is markedly different from that of L. digitata" has been replaced by "This emission profile is markedly different from that of L. digitata observed in the present and previous studies (e.g., Ashu-Ayem et al., EST, 2012). 25929 In the revised text the phrase "In contrast the mixing ratio above the L. digitata beds decreases with increasing exposure time" has been replaced by "In contrast the mixing ratio above the L. digitata beds decreases with increasing exposure time, as observed in the present and previous studies."

ACPD

12, C12996–C13019, 2013

25924.03 The present observations were made 5-10 cm above seaweed beds, whereas previous in situ measurements made at, for example, O Grove (Spain) were approx 10 m away from the seaweed (Mahajan 2011) and measurements at Roscoff (France) were 1 km away from the Laminaria beds (McFiggans 2010; Leigh 2010). Horizontal and vertical dilution make it highly problematic to generate direct comparisons between observations from different geographical locations, especially where observations were obtained at different distances downstream of highly localised emission sources. Photolytic destruction of iodine (and potentially chemical recycling of I2) between the source and detection adds further complications, especially for the more distant measurements. See the modelling work of Leigh et al (2010) and Mahajan et al (2009, 2011). The current text ignores these complications.

Response: We were not trying to make comparisons between our measurements and those published in the literature. Instead, we combined our data with those published to emphasize the current consensus that Laminaria spp. are very strong emitters of I2. Of course, we agree with the reviewer that observations are not directly comparable. Therefore, in the revised text we added the following "Although it is difficult to compare observations made at different geographical locations, in particular where observations were obtained at different distances downstream of highly localized emission sources, considering the dilution effect, the short photolysis lifetime and potential chemical recycling of I2, these measurements are consistent with the current consensus. . ..".

Similarly 25918.09 "The observations of I2 at Roscoff and O Grove are thought to be a consequence of large I2 emissions from... L digitata and L hyperborea which are the dominant species at these measurement sites." As above, this all depends on which seaweed species are exposed, on the biomass of seaweeds growing at these sites, on the sunlight levels, wind speed and direction etc...

Response: We share the opinion of the reviewer in terms of the factor which could influence the I2 concentration in the coastal marine boundary layer. Here, we were trying to express that macroalgae are the major source of I2 in the coastal marine

ACPD
12, C12996–C13019, 2013

boundary layer.

25924.11-25924.16 “This observation is inconsistent with the macroalgal incubation experiments of Ball et al. (2010)... we attribute this apparent contradiction...” If I’ve understood correctly, Ball et al only measured for the first 10 minutes after the seaweed was exposed to air. They measured a small I2 emission rate; just like the present data also show a small initial emission rate. That is not inconsistent or an apparent contradiction. Be sure to compare like with like.

Response: We have changed the following “This observation is inconsistent with the macroalgae incubation experiments of Ball et al. (2010) which showed that I2 emissions from A. nodosum and F. vesiculosus were several orders of magnitude lower than those from Laminaria spp.. Their measurements were carried out over a short initial exposure period ($\sim$10–17 min), and we attribute this apparent contradiction to the distinct time-dependent emission characteristics of these species discussed below”. See below the reply to S. Ball.

25924.20 “...A nodosum and F vesiculosus could be the main sources of I2 in the vicinity of Mace Head during most low tides”. Whether I agree with this statement depends how the authors define “vicinity”. Their statement may well be true for Mweenish Bay. However my memory of the Mace Head Atmospheric Research Station (where many previous atmospheric chemistry field observations have been sited [Saiz-Lopez et al. 2004, 2006 etc]) is that the rocky coastline drops away quickly into the sea, and that there are not extensive beds of A nodosum or F vesiculosus nearby. The authors later cite Ehn et al (2010) 25925.01 “the inhomogeneous distribution of these two macroalgae species [ie ascophyllum and fucus] (whose habitat is restricted to A SMALL NUMBER OF areas around Mace Head)...” I’m still unclear therefore what the authors are saying about the seaweed distribution at the Mace Head Atmospheric Research Station, its ability to emit iodine and any consequences for previous measurements based at that site.

ACPD
12, C12996–C13019, 2013

Response: We have added “in the vicinity of Mace Head (see Fig. 1)...” and “whose habitat is restricted to A NUMBER OF SMALL areas around Mace Head, e.g., Mweenish Bay, Glinsk and Roundstone) in the revised text to clarify the “vicinity”.

25926.03 Not comparable! The data in Fig 3 are for A nodosum and F vesiculosis whereas the Ashu-Ayem (2012) incubation study is for L digitata.

Response: We have removed “as Ashu-Ayem et al. (2012) have also observed in incubation studies”.

25927.13-17 All references to prior work are missing from the discussion about seaweed’s different physiological adaptations depending on their habitat in the littoral zone, and the probable link between their short/long exposures at low tide and their I2 source strengths. Neither of these topics are novel to the present work.

Response: We have expanded this section which makes the point now perfectly clear:

"It is beyond the scope of the present work to investigate the biochemical mechanism governing the distinct I2 emission feature between different macroalgal species, but it is tempting to hypothesize that it is linked to different physiological adaptations of Ascophyllum, Fucus and Laminaria to their differing positions in the littoral zone. Ascophyllum and Fucus are intertidal species and get exposed at every low tide, while Laminaria is a mostly submerged-living species, only getting exposed during stronger spring tides."

The different position of Fucus, Ascophyllum and Laminaria in the coastal zonation is very well-established, de facto textbook and natural history book knowledge - this does not require further referencing.

ISSUE 3: The Kundel et al. (2012) data in Fig 5 have already been published elsewhere. I absolutely agree that the present work’s new observations need to be discussed in the light of Kundel’s work. However I didn’t feel that Kundel’s work needed to be re-presented in the level of detail it was in this paper (it had its own method section

ACPD

12, C12996–C13019, 2013

Interactive Comment

2.4), or to share equal billing with the new observations in the abstract and discussion. The juxtaposition of the Kundel work with the new work confused the flow of the paper. I suggest introducing the Kundel study at the discussion stage at 25926.26. There needs to be a clear statement in the text that Fig 5 is part of something previously published elsewhere. Section 2.4 could be deleted in favour of a very brief description of Kundel's method in the discussion section, whilst referring the interested reader to the original publication.

Response: We completely agree with the reviewer that there is a certain overlap of the online measurements with Kundel's work. Therefore, we have removed Section 2.4 and restructured the relevant discussion at 25926.26 in the revised text. We already stated in the caption of Fig. 5 that it is modified from Kundel et al. 2012.

25926.26 The Kundel et al time profiles support this paper's observations that A nodosum and F vesiculous emissions increase with exposure time. But there are two significant caveats: (i) the Kundel experiment was performed at 50 ppb of ozone, somewhat higher (x1.5) than ambient levels – there isn't enough observational data to yet know how/if ozone levels affects these species' emission rates. (ii) the Kundel experiments were performed on only one or two samples of each species – insufficient to test for intra-species variations. In particular, the first-10-minute and first-hour-integrated I2 emission values calculated in 25928.05-08 need to carry the above warnings. Additionally the Kundel data extend for 1 hour for A nodosum and 2 hours for F vesiculosus, so it's unclear how these seaweed species behave over a "typical" 6 hour tidal exposure.

Response: We agree with the reviewer that there are different experimental conditions applied in Kundel's work, i.e., slightly higher ozone concentrations and shorter exposure time compared to the natural conditions. However, our offline chamber experiments carried out at Mweenish Bay (see Fig. 4) also support the field observations. In the revised text, we have added "Note that the emission rate is calculated based on one or two samples of each species."

ACPD
12, C12996–C13019, 2013

Specific comments: Abstract: “We suggest that A. nodosum and F. vesiculosus may provide an unaccounted and important source of photolabile iodine... and that their impact on...should be reevaluated...” Something can’t be “reevaluated” if it was previously “unaccounted”. In fact an attempt to evaluate the iodine contributions from these two species was made by Leigh et al (ACP 2010) using emission rates from Ball et al (ACP 2010). The authors may disagree with the conclusions of Leigh et al, but they do need to acknowledge its precedence. Similarly 25928.16-19 “Fucales... may provide an unaccounted and important source... and their impact on... should be reevaluated”. Again the reason the contribution from Fucales is “unaccounted” is because there are so few observations –beyond the present/Kundel work, I only know of Ball et al 2010 and an early study by Sellegri et al [Env Chem, 2, 260, 2005].

Response: Better knowledge about the emission rate of A. nodosum and F. vesiculosus can be used to better model and understand the contribution of these two species to the ambient I2 concentration and local/regional iodine chemistry, as discussed by S. Ball (see below his comment). We of course acknowledge the precedence of the work from Sellegri et al., Leigh et al. and Ball et al.. We have removed “unaccounted” from the text.

25917.16 “The nucleation events generally occur around low tide during day light...” It would help the authors to strengthen their case that additional important iodine sources exist if they would review the observational evidence for/against any ultrafine particle nucleation events occurring (i) at times other than the tidal minimum, and (ii) at low tides that aren’t low enough to uncover laminaria seaweed beds, but that do uncover other seaweeds types. Similarly at 25919.18 the authors argue that the different emission characteristics of A nodosum and F vesiculosus “may provide an explanation for the frequently observed new particle events at the west coast of Ireland” but fail to discuss the frequency/distribution of such events, or whether their new observations help explain previously unexplained/poorly-explained events.

Response: Our long-term observations at the Mace Head Station show that the new

ACPD
12, C12996–C13019, 2013

particle formation events occur on more than half of the days and that the events occur as well when the water level is not low enough to uncover the Laminaria beds. Moreover, the new particle bursts typically last for some hours before and after the tidal minimum. It therefore suggests additional iodine sources. We added the following at 25919.21, "For example, during a field campaign in 2007 enhanced nucleation events were observed in 14 out of 23 days of measurements at Mweenish Bay where A. nodosum and F. vesiculosus are dominant species. The ultra-fine particle bursts typically last for about 4-6 h, which is closely related to the diurnal variation of the exposure period of these two species (Huang et al., 2010c).

25917.18 "numerous studies have shown that the coastal particle bursts are closely linked to iodine emission from low tidal macroalgal exposure (Huang et al, 2010c; McFiggans et al 2010)." The studies are more numerous than the two sited in the text. The authors should also reference McFiggans 2004 and Saiz-Lopez 2006; indeed there are other studies, probably some that pre-date these well-known examples I've given here. For the authors to first (immodestly!) cite their own paper implies (wrongly!) that they were the first group to account for this observation. 25918.06: The authors also immodestly cite their own 2010 papers ahead of the earlier pioneering work of Saiz-Lopez who was the first to observe molecular I2 at Mace Head.

Response: We have cited the work of McFiggans et al. 2004 and Saiz-Lopez et al., 2006. We have also changed the order of citation.

25919.16 "This finding would likely apply to numerous other brown algae species". This sounds like speculation. What is the authors' evidence?

Response: Yes-this is a hypothesis based on the results received. Therefore, we use "...would likely apply...".

25921.16 "detection limit was below 1.0 ppt for a 15 liter sample volume". Please be clear: is this for sampling at the denuder flow rate of 500 ml/min (25922.04) for 30 mins? If so, why quote detection limits for 30 mins when elsewhere the sampling

ACPD
12, C12996–C13019, 2013

period is 20 mins (25922.05 and Fig 4) and 5 mins for L. digitata (25924.01) – what are the corresponding values for shorter acquisition times? Also what is the accuracy of the technique? The data in Fig 4a and 4b have error bars – presumably these are the uncertainties due to variability between several seaweed samples? How do the variability errors compare with the accuracy errors of the technique itself? An indication of accuracy error should be given on the bar graphs in Fig 2 and Fig 4c. The data points in Fig 3 need vertical error bars for their accuracy and horizontal error bars indicating the 30 minute duration of each measurement.

Response: Yes-the detection limit varies with the sample volume. The detection limit is 0.17 ppt at 500 ml/min for 30 min, 0.25 ppt at 500 ml/min for 20 min and 1.0 at 500 ml/min for 5 min. We have changed the sentence to "detection limit was generally below 1.0 ppt during this campaign". The precision of the method for the determination of I2 is $< \pm 10\%$. We have added this piece of information in the revised text.

25937/Fig 3 What is the significance of the -279.4 intercept? Would it not be better to force the best-fit line through the origin, on the basis that one doesn't expect to observe any iodine until the seaweed has been exposed?

Response: We have redrawn Fig 3 by forcing the best-fit line through the origin.

Technical corrections: Please avoid imprecise comparative statements:

25920.11 "exposed... for a much shorter period". How long? Give a typical duration.

Response: "for a much shorter period ($\sim$ 20-30 min)."

25921.02 "the relatively low solar flux... implies a lifetime that is several times longer". How low? How long? Fig 3 reports observations of solar radiation, so the authors ought to be able to make quantitative statements about iodine's photolytic lifetime under their conditions.

Response: Saiz-Lopez et al. (2004) calculate a lifetime of I2 of about 8 s at a solar irradiance of 1100 W m-2. The low irradiance (< 200 W m-2) during most of our mea-

ACPD
12, C12996–C13019, 2013

surements implies a much longer I2 lifetime of over 40 s. In three of the measurements the I2 lifetime is shorter and around 12-15 s.

25925.17 “Fig 3 shows... at a fixed sampling site...” Which site?

Response: We have changed “at a fixed sampling site” to “at sampling site #1”.

25927.21 “Due to measurement limitations, we have not yet been able to...” Explain what the limitations are. (One point every 20 minutes? Only two points in the profiles in Fig 2 and Fig 4?).

Response: We have changed “due to measurement limitations” to “due to a relatively limited dataset”. Ideally, one can get the detailed release profile if more measurement points are taken with a relatively higher time resolution.

Other technical corrections:

25925.18 beginning of [the] ebbing tide

Response: This has been changed as suggested.

25926.25 ...and would be expected to emit more [after correction for its grams fresh weight].

Response: This has been changed as suggested.

25927.12 distinct I2 emission feature[s]

Response: This has been changed as suggested.

25928.26 “correlates positively with their exposure time”. You mean “increase with exposure time”?

Response: Yes-we mean “increase with exposure time”.

Fig 2 Use “0-5 min” and “15-20 min” instead of 1st and 4th 5 min intervals to match the convention in Fig 3.

ACPD

12, C12996–C13019, 2013

Interactive Comment

Response: This has been changed as suggested.

Comments from S. Ball

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 (I2) emission rates of several seaweed species collected in the 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".

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 I2 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 I2 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 nonzero) 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

ACPD

12, C12996–C13019, 2013

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 I2 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. 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

ACPD
12, C12996–C13019, 2013

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".

Response: We have changed the following "This observation is inconsistent with the macroalgae incubation experiments of Ball et al. (2010) which showed that I2 emissions from A. nodosum and F. vesiculosus were several orders of magnitude lower than those from Laminaria spp.. Their measurements were carried out over a short initial exposure period (∼10-17 min), and we attribute this apparent contradiction to the distinct time-dependent emission characteristics of these species discussed below" to "This observation is somehow different from the macroalgal incubation experiments of Ball et al. (2010) which showed that I2 emissions from A. nodosum and F. vesiculosus were several orders of magnitude lower than those from Laminaria spp.. We attribute the enhanced I2 emissions of A. nodosum and F. vesiculosus to the longer exposure period in our study and the distinct time-dependent emission characteristics of A. nodosum and F. vesiculosus discussed below".

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 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 –

ACPD
12, C12996–C13019, 2013

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.

Response: We agree with Dr. Ball and have changed “negligible” to “relatively small”.

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, 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.

ACPD
12, C12996–C13019, 2013

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

ACPD

12, C12996–C13019, 2013

Interactive Comment