Atmos. Chem. Phys. Discuss., 12, C10127–C10134, 2012
www.atmos-chem-phys-discuss.net/12/C10127/2012/

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.

Anonymous Referee #2

Received and published: 4 December 2012

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 region). 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:

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

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

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

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.

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

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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)

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

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.

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

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

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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 downsteam 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.

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...

25924.11-25924.16 "This observation is inconsistent with the macroalgae 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.

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.

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.

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.

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 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.

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 experi-

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ments 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.

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].

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.

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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.

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

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 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.

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?

Technical corrections:

Please avoid imprecise comparative statements:

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

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.

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

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?).

Other technical corrections:

25925.18 beginning of [the] ebbing tide

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

25927.12 distinct I2 emission feature[s]

25928.26 “correlates positively with their exposure time”. You 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.

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