Biogeosciences Discuss., 10, C766–C778, 2013
www.biogeosciences-discuss.net/10/C766/2013/

Biogeosciences Discussions

Interactive comment on "Emission of atmospherically significant halocarbons by naturally occurring and farmed tropical macroalgae" *by* E. C. Leedham et al.

E. C. Leedham et al.

e.leedham@uea.ac.uk

Received and published: 4 April 2013

Response to reviewers comments on: Emission of atmospherically significant halocarbons by naturally occurring and farmed tropical macroalgae

We thank the referees for their comments and provide our responses below. All page and line references and section numbers refer to the discussion manuscript. References (unless listed at the bottom of this reply) and abbreviations are also found in the original manuscript.

Response to anonymous referee #1

1) Page 484, line 16: insert “and elsewhere” before “South East Asia” Edit made.

2) Page 485, line 9-12: Halocarbons cannot act as antioxidants themselves, but they may be the reaction products of the antioxidant function of iodide or possibly also bromide, catalysed by haloperoxidase (this is what the papers by Palmer and Küpper say).

The original paragraph in the introductory chapter was written: “The broad suite of halogenated compounds found in, and released from, algae are thought to act as a defence mechanism. They help protect macroalgae from grazing; control bacterial, fungal and microalgal epiphytes; and limit fungal and bacterial infection (La Barre et al., 2010; Paul & Pohnert, 2010; Weinberger et al., 2007). Of these compounds, the volatile organic bromo- and iodocarbons, alongside inorganic iodine species such as molecular iodine (I2), act as antioxidants by removing harmful active oxygen species produced by macroalgae (Küpper et al., 2008; Palmer et al., 2005). This is consistent with previous work which suggests that environmental stresses such as desiccation, salinity and nutrient depletion influence halocarbon emission rates (Bondu et al., 2008; Mata et al., 2011; Nightingale et al., 1995).”

This has now been changed to: “Macroalgae concentrate halides from seawater (Küpper et al., 1998; Saenko et al., 1978) and it is believed that these halides act as antioxidants. In particular, iodine chemistry in phaeophytes as a response to oxidative stress at low tide has been well documented. A flux of internal iodine is observed during oxidative stress which can act as an antioxidant both within algal cells and also on the surface of the alga. Intracellular oxidation of iodine via haloperoxidase catalysed-reactions in the presence of H2O2 and other reactive oxygen species forms hypoiodous acids which may then react with nucleophilic acceptors such as ketones to produce halocarbons (Wever et al., 1991; Winter & Moore, 2009). Iodine may also be released onto the algal surface where it reacts with ozone (O3) to form molecular iodine (I2), which is now thought to be the dominant product from the iodine antioxidant response (Küpper et al., 2008; Palmer et al., 2005). A flux of bromocarbons as a product of a bromine antioxidant response has also been reported, incubation studies have

BGD

10, C766–C778, 2013

shown increased bromocarbon production with the addition of H2O2 to algal samples and decreases in bromocarbon production with the addition of peroxidase inhibitors (Collen et al., 1994; Pedersen et al., 1996; Wuosmaa & Hager, 1990). Halocarbon production as a product of an antioxidant response is consistent with previous work which suggests that environmental stresses such as desiccation, salinity and nutrient depletion influence halocarbon emission rates (Bondu et al., 2008; Mata et al., 2011; Nightingale et al., 1995). The broad suite of halogenated compounds found in, and released from, algae are thought to act as a defence mechanism. They help protect macroalgae from grazing; control bacterial, fungal and microalgal epiphytes; and limit fungal and bacterial infection (La Barre et al., 2010; Paul & Pohnert, 2010; Weinberger et al., 2007)."

3) Page, 486, line 29: Kelps occur in probably a large number of tropical locations, but in deeper waters (cf. Graham et al., 2007, PNAS).

Line 25 to 29 previously read: "Different macroalgae species are found in different climatic regions, which could lead to differences in halocarbon production and emission rates. The ratio of rhodophytes (red algae) relative to phaeophytes (brown algae) and chlorophytes (green algae) is greater in tropical regions, and kelps, which are common in temperate regions, are absent in the tropics (Santelices et al., 2009)."

In response to the referee drawing our attention to the paper by Graham et al. (2007) we have updated this section accordingly: "The ratio of rhodophytes (red algae) relative to phaeophytes (brown algae) and chlorophytes (green algae) is greater in the tropics (Santelices et al., 2009). One example is the abundance of kelp species; whilst tropical kelp beds have been observed in deeper waters (from 10 m), warmer temperatures and lower nutrient concentrations mean kelps are not found in shallower coastal waters where they often dominante temperate macroalgal biomass (Graham et al. 2007). It therefore seems unlikely that tropical kelps contribute to tidal bursts of iodinated emissions (as seen over exposed kelp beds at low tides in temperate regions) and the associated burst in ultrafine particles (see Mäkelä et al., 2002)."

BGD

10, C766–C778, 2013

For continuity we also altered page 492, line 26 (additions in bold): “In temperate regions kelps and other phaeophytes often dominate the algal biomass in shallow coastal waters (de Vooys, 1979) but in tropical regions rhodophytes and chlorophytes are often more common (Santelices et al., 2009), potentially shifting the balance of emissions towards brominated species.”

4) Page 512, line 17: The author list of the reference of Carpenter et al. (2000, GBC) is incomplete. This has been corrected.

5) Table 3: The labeling is confusing / misleading! Halides were not actually measuring in this study. I would say, “halogens”.

Page 492, line 13 has been changed to (edits in bold): “To investigate further, the proportions of bromine, chlorine and iodine emitted as halocarbonsproduced by each species was calculated and Table 3 shows the results with species ranked in order of decreasing total halogen halide emissions”

The title of Table 3 now reads (changes/additions in bold): “Table 3. Total mass of halogens emitted as halocarbons during incubation and percentage contribution to this total from bromine, chorine and iodine. Species arranged in order of decreasing total mass of halogen emitted.” Table 3, column 2: Header changed from ‘halides’ to ‘halogens’. Response to anonymous referee #2

1) Page 491, line 20: Each production rate should be given with an error due to the variable incubation results. These have been added. An extra paragraph has also been added to compare our intra-species variability with those in the literature: this paragraph also collated discussion on differences between replicates from both Section 3.3 and Section 3.4 to make the flow of discussion clearer. The new paragraph is shown below.

“High intra-species variability was also seen amongst replicates in previous studies. Carpenter et al. (2000) saw replicate differences within a factor of 2, which they

BGD
10, C766–C778, 2013

attributed, in part, to fluctuations in light and temperature as their incubations were conducted outdoors. Fluctuations in environmental variables cannot explain all the variation, however, as our study was conducted under laboratory-controlled light and temperature, and variations of the magnitude reported by Carpenter et al. were observed in our study. Variability was also observed in other incubations conducted under controlled conditions, for example Collen et al. (1994) reported a percentage standard deviation on replicate incubations of up to 129%. This large variability is likely due to variations in both background seawater concentrations and biological variability between replicates. Giese et al. (1999) reported CHBr3 variations in their seawater controls of ∼10% and Laturnus et al. (1996) reported varying production rates from different sections of algal tissue, with, on average, blades producing more CHBr3 than stipes. Variability between replicates is discussed further in Section 3.4."

In Section 3.4 we referred back to the literature and added errors to several more of the production rates obtained from previous studies. This can be seen in an updated Fig. 6 in the final manuscript.

2) Page 493, line 26: "Fresh weights may provide a more accurate basis for scaling up emission estimates" – please state the reason for this.

This line has been altered to better reflect our meaning: "Fresh weight may provide an easier basis for scaling up biomass for emission estimates as they better represent natural biomass, whereas dry weight potentially provides easier comparisons between algal species as some algae contain much higher water content than others." 3) Page 495, line 11: "...the ratio of CHBr2Cl:CHBr3 decreases from 18:1 at t4 to 11:1 at t24" – with shorter lifetime of CHBr3 the ratio of CHBr2Cl:CHBr3 should increase with time.

This ratio had been written the wrong way round – what was meant was: "Some evidence for the formation of CHBr2Cl from CHBr3 may be seen in this study; although both compounds are present at t4 and t24 the ratio of CHBr3:CHBr2Cl decreases from ∼18:1 at t4 to ∼11:1 at t24. This could be indicative of conversion occurring during this

BGD
10, C766–C778, 2013

time."

4) Page 495, line 17: The lifetime of CH2I2 in the seawater is reported to be only 14 minutes (Jones and Carpenter, 2005). Are you sure the decomposition is negligible in your 24-h incubation under constant illumination?

Jones and Carpenter (2005) reported lifetimes of CH2I2, CH2BrI and CH2ClI of 10 mins ($\pm$1 min), 4.5 hours ($\pm$40 mins) and 9 hours ($\pm$2 hours) respectively. These photolysis lifetimes do fall within our incubation times. However, the Jones and Carpenter photolysis loss rates were conducted in UV-transparent quartz flasks which were left outside in natural sunlight. They attribute breakdown to absorption of tropospheric levels of UV radiation at 290 nm or below.

Incubations reported in this study were conducted in glass flasks in an incubator under artificial light (Philips fluorescent tubes) set to 130 μmol photons s-1 m-2. UVA and UVB light in this incubator were measured (see Keng et al., 2013) and no UVA or UVB were detected from this light source at light level similar to those used during our incubations. Hughes et al. (2006) reported that no photolysis of CH3I, CH2I2, CH2BrI and CH2ClI was observed under conditions similar to those used in our study (glass flasks under artificial illumination). We therefore conclude that UV-related photolysis is likely to be limited in our incubations (supported by high levels of CH2I2 seen in some incubations, see Fig. 3). However, we have added a sentence to the methodology to make this clear for future readers.

"Jones and Carpenter (2005) reported UV photolysis of CH2I2, CH2BrI and CH2ClI with lifetimes of 10 minutes ($\pm$1 min), 4.5 hours ($\pm$40 mins) and 9 hours ($\pm$2 hours) respectively, lifetimes that could be significant within the 4 and 24 hour timescales of our incubations. However, no UVA or UVB light was measured in the incubator (Keng et al., 2013) and we therefore conclude that UV photolysis is negligible." 5) Page 497, line 5: "Of these, 5 papers expressed results only per gram of DW and so were removed." Why do you remove those data? You also have the production rates on DW to be

BGD
10, C766–C778, 2013

compared (p. 489 line 8).

For the brevity and clarity of this manuscript we did not wish to provide two separate comparisons, one comparing our fresh (FW) biomass production rates to those in the literature and one comparing our dry (DW) biomass production rate. We opted to compare FW production rates a) as there was more data in the literature that expressed their production rates per gram FW and b) as we use FW production rates in Section 3.5.

However, following the process in Carpenter et al. (2000) where they converted DW production rates to FW production rates using a DW-to-FW ratio we have included several extra studies from the literature to Fig. 6., using DW-FW conversion ratios provided in Baker et al., 2001 and Bravo-Linares et al. (2010).

6) Page 498, line 2: "The percentage standard deviation was similar for both halocarbons". Please show the number of percentage standard deviation for each halocarbon.

Page 498, line 2 has been updated to show these values: "The percentage standard deviation across the whole CH3I and CHBr3 datasets were similar for both halocarbons at 393 (CH3I) and 328 (CHBr3)."

7) Page 501, line 14 "...for these reasons, our ability to use local biomass data is of distinct benefit to the following estimates." Is this true in the scale up to the whole south east Asia?

Little data is available on natural biomass distributions of seaweed species in this region. A University of Malaya monograph (Phang et al. (eds.), 2008): 'Taxonomy of southeast Asian seaweeds' suggests that similar genera are found in coastlines around this region. However, our knowledge of the distribution around much of south east Asia is poor, and so we have rephrased this sentence (edits in bold): "For these reasons, our ability to use local biomass data is of benefit to estimates made around Malaysia and, assuming similar species are found throughout south east Asia (Phang et al., 2008), to

BGD
10, C766–C778, 2013

a wider regional estimate as well."

A discussion of errors associated with biomass estimates is also made as part of our response to comment 10.

8) Page 501, line 25: "We averaged production rates for phaeophytes, rhodophytes and chlorophytes. . ." – please give the error estimates for the averages. This has been answered as part of comment 10.

9) What is the point of conclusion 3? The paragraph could be more concise.

We have altered conclusion 3 to read: "Nonetheless, data from previous studies were compared to our tropical data and the range of production values was similar. As the tropical dataset is considerably smaller than for polar and temperate species, only preliminary conclusions may be drawn at this time. However, from our dataset it seems that tropical species are, on average, not individually stronger producers of halocarbons than their temperate and polar counterparts. Differences in species distribution may, instead, drive geographical differences in regional coastal halocarbon emissions; for example, a higher propensity toward stronger-producing rhodophytes (natural or farmed) in tropical regions."

10) Conclusion 4 – Is this true after all errors are considered?

Our response to this question also refers to the introductory comments made by the referee: "My major criticism of the paper is that the emission estimates of CHBr3 and CH2Br2 from the coastlines of Malaysia and South East Asia are based on rather uncertain values and many assumptions, and so the conclusion is questionable. First of all, the production rates of CHBr3 and CH2Br2 from tropical macroalgae (supplementary Table 1) are highly variable in each class of phaeophytes, rhodophytes and chlorophytes. However, the authors use their average to calculate a production rate per unit area (378 nmol CHBr3 m−2 h−1) without any statistic evaluation. From supplementary Table 1, I calculate the relative standard deviations for CHBr3 production

BGD
10, C766–C778, 2013

at t24 to be as high as 81%(rhodophytes), 147% (phaeophytes) and 146% (chlorophytes). The errors could be larger, taking the effect of incubation time (t4 and t24) into consideration. Since the value (378 nmol CHBr3 m−2 h−1) is used in all the scenarios, the following calculation illustrates the problem."

In the discussion of our emission estimates (Sections 3.5 and 3.6) we had tried to draw attention to assumptions made wherever possible. However, these comments are valid and lead us to distinguish between our assumptions and potential uncertainties in our calculations, as follows: 1. Potential uncertainty in calculations are associated with values taken from our (or others) experimental data and will have an error attached. The main examples in this section are the calculated production rates from incubations discussed earlier in this paper and the biomass measurements from Keng13. 2. An assumption is a value we have had to assume to assist with calculations, for example that seaweed beds are found around 40% of Malaysian coastlines, or that seaweed beds extend out to 200 m from the shore. These assumptions are based on knowledge of the local area or previous studies. A discussion of these assumptions was made in the previous copy of the manuscript, and we used based our comparison with the existing literature on a range of annual emission estimates based on three scenarios, hopefully accounting for some of the uncertainty associated with our assumptions. With respect to potential uncertainties in calculations we hope to improve our emission estimates by adding in a further discussion of potential uncertainties in calculations, namely the uncertainty on the calculated point source emission rate of 378 nmol CHBr3 m−2 h−1 as raised by referee #2 in their opening remarks.

Uncertainty on the calculated emission rate of 378 nmol CHBr3 m−2 h−1 Referee #2 quotes percentage standard deviation (%SD) errors from Supplementary Table 1 of 81%(rhodophytes), 147% (phaeophytes) and 146% (chlorophytes). This is the percentage standard deviation (%SD) on the mean production rates at t24 for each species within a class (e.g. rhodophyte). This is, we assume, meant to represent the fact that uncertainty in species distribution leads to variation in a flux per square metre.

BGD

10, C766–C778, 2013

However, this is better represented by propagating together the error on each individual species' production rates (see Supplementary Table 1 where SD is provided for each species) and the error associated with the biomass study conducted over 18 months. From this we calculate a %SD error on the emission rate per square metre of 61%. This is mainly associated with high variability in calculated production rates for several of the rhodophytes (e.g. Gracilaria sp. - refer back to Section 3.2) and also a patchy distribution of rhodophytes observed during the Keng13 biomass studies.

We have included this calculation in our discussion as follows: Starting from the beginning of Section 3.6 (Page 501), we have made the following alterations: âĂć Page 501, line 23: A1. We added "Errors on biomass studies (Keng13) were included in the error associated with our flux rate, see A2." âĂć Page 501, line 25: A2. We added "The main errors associated with this flux rate come from the calculated production rates and the estimations of regional biomass from Keng13. To account for this, the individual standard deviations on species' production rates (Supplementary Information Table 1) were propagated with the standard deviation error associated with the biomass studies over an 18 month period to give a percentage standard deviation (%SD) error on our flux rate of 61%. This rate is similar to the $\sim$70% error on global CHBr3 annual emission from macroalgae given by Carpenter and Liss (2000). A large proportion of this error is due to intra-species variability observed in the incubation experiments (see Section 3.2) and the patchy distribution of rhodophytes at the Port Dickson sampling site. This error is discussed further in the following sections as we use this flux rate to determine regional emission estimates."

In response to the query by referee #2 that we base conclusion 4 on uncertain emission estimates we draw our readers' attention to the fact that the annual emissions from our study that we compare to the existing literature are based on three scenarios due to the fact we made various assumptions on tidal flushing, tidal exposure of macroalgae etc. The range of annual emissions from these three scenarios for Malaysia was estimated at 1-7 Mmol Br yr-1 and 17-140 Mmol Br yr-1 for SEA. Using the 61%SD from our

BGD
10, C766–C778, 2013

calculated emission rate per square metre of coastline to calculate emission of ∼610 nmol m-2 hr-1, and applying this value to scenarios 1-3 would result in: a) A flux rate range of 17-610 nmol CHBr3 m-2 h-1 (previously, 45-378, see page 505, line 7). This is still similar to the range given by Quack & Wallace (2003). Our upper limit now exceeds their upper limit, however our upper limit is based upon all emissions from macroalgae reaching the atmosphere, which is likely to be an overestimate due to seawater loss processes, as discussed in A5 (page 502, line 5). b) Maximum annual emissions from Malaysia and SEA of 12 and 224 Mmol Br yr-1 respectively. These values are still at the lower end of emission estimates discussed on page 506 and in Supplementary Information Table 3. Therefore our conclusion 4 remains valid.

We have also added the following to Page 502, line 19 (A5) to improve our discussion of potential sources of errors. To: "The range of CHBr3 concentrations measured was 0.9–6 ppt." we added: "A sensitivity analysis showed that high seawater concentrations (see scenario 1) dominate the flux and that altering the atmospheric concentration within the range observed during SHIVA has little effect on the calculated flux rate."

On page 503, line 17: to "...similar to that which would be seen after 6 hours of constant emissions into the seawater." we added: "This may be somewhat of an overestimate due to a larger tidal range in Car2000; 3 m at Mace Head compared to 1.7 m at Port Dickson."

On page 509, line 5: to "It is assumed that air-sea gas exchange processes are equal for natural and farmed algae and that the rate of these processes will not change in the future." we added: "Many factors, some unique to the coastal region, mean determining coastal flux rates are difficult. These processes include wave damping, drag (in shallower waters the ocean floor will exert a greater effect), higher wind speeds, thermal stratification (increased warming by light on shallower waters), changes in salinity due to precipitation and increased surfactants (Upstill-Goddard, 2006 and references herein)."

BGD
10, C766–C778, 2013

We would also like to draw attention to a basic sensitivity analysis done on the biomass data on page 507, line 9 onwards: "...One example is the percentage of total macroalgal biomass comprised of phaeophytes, rhodophytes and chlorophytes. Data from Keng13 suggests rhodophyte biomass is <1% of total seaweed biomass per square metre, yet rhodophytes were the dominant halocarbon producers during our incubation studies. For example, increasing rhodophyte biomass to 10% in Scenario 1 leads to a doubling of the scenario 1 mean flux rate from 45 nmol CHBr3 m-2 h-1 to 93 nmol CHBr3 m-2 h-1.

Finally: âĂć All the above comments and calculations have been updated in the main text as well as the Supplementary Information Tables where appropriate. âĂć They have also been repeated for CH2Br2 and the manuscript and Supplementary Information updated as appropriate.

11) The authors first calculate the average production of bromoform from incubated macroalgae, then estimate its concentration in the water, and finally its sea-to-air flux. I wonder why the authors don't measure bromoform concentration in the water, which should give more direct and reliable estimate for the flux. The water data should also be useful to evaluate the appropriateness of the assumptions for macroalgal biomass and potential bromoform production in the tropical coastal water.

Whilst direct in situ seawater measurements would have been an ideal addition to the study presented in this paper logistical issues prevented these measurements during our field campaign. The main logistical problem was that the need to analyse seawater samples soon after collection could not be met due to the distance between the sampling site and the laboratory and the time required to extract and analyse multiple samples upon return to the lab. Preliminary research at UEA showed that even seawater samples that had been filtered (Whatman™, GF/F) and stored at 4 °C in the dark were susceptible to some changes in measured halocarbon concentrations over time periods of less than 24 hours. On page 503 (lines 18-25) we provide a comparison between our estimated seawater concentration and those taken from the literature for

BGD
10, C766–C778, 2013

other regions. We hope that the data provided in this study provides a basis for future research in this area. We have added the following sentence to conclusion 6 to highlight this: “In particular, a need for in situ measurements of halocarbon concentrations in SEA coastal seawater would help strengthen estimates of fluxes and annual emissions from this region.”

Additional references: Graham, M. H., Kinlan, B. P., Druehl, L. D., Garske, L. E. and Banks, S.: Deep-water help refugia as potential hotspots of tropical marine diversity and productivity, PNAS, 104(42), 16576-16580, 2007. Mäkelä, J., Hoffman, T., Holzke, C., Väkevä, M., Suni, T., Mattila, T., Aalto, P. P., Tapper, U., Kauppinen, E. I. and O’Dowd, C. D. Biogenic iodine emissions and identification of end-products in coastal ultrafine particles during nucleation bursts, Journal of Geophysical Research, 107, D19, 2002. Phang, S.-M, Lewnamomont, K. and Lim, P.-E. (eds.): Taxonomy of Southeast Asian Seaweeds. University of Malaya Monograph Series 2, Institute of Ocean and Earth Sciences (IOES), University of Malaya, Kuala Lumpur, 2008. Saenko, G. N. , Kravtosova, Y. Y., Ivanenko, V. V. and Sheludko, S. I.: Concentration of iodine and bromine by plants in the seas of Japan and Okhotsk, Marine Biology, 47, 243-250, 1988. Upstill-Goddard, R.C.: Air-sea gas exchange in the coastal zone, Estuarine, Coastal and Shelf Science, 70, 388-404, 10.1016/j.ecss.2006.05.043, 2006. Wever R., Tromp, M. G. M., Krenn, B. E., Marjani, A. and van Tol, M.: Brominating activity of the seaweed Ascophyllum nodosum: Impacts on the biosphere, Environmental Science and Technology, 25(3), 446-449, 1991. Winter, J. M. and Moore, B. S.: Exploring the chemistry and biology of vanadium-dependent haloperoxidases, The Journal of Biological Chemistry, 284(28), 18577-18581, 2009. Wuosmaa, A. M. and Hager, L. P.: Methyl chloride transferase: a carbocation route for biosynthesis of halometabolites, Science, 249, 160-162, 1990.

Interactive comment on Biogeosciences Discuss., 10, 483, 2013.