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Interactive comment on "The effect of desiccation on the emission of volatile bromocarbons from two common temperate macroalgae" *by* E. C. Leedham Elvidge et al.

Anonymous Referee #1

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It is well established that seaweeds bio-accumulate bromine and iodine from sea water. Biological processes can then lead to the emission of halogen-containing, volatile compounds into the atmosphere with impacts on tropospheric chemistry and, potentially, stratospheric chemistry. Several studies have investigated the emission of iodine compounds from seaweeds (often considered to be the dominant flux of this element into the atmosphere in coastal regions). But there have been very few studies on bromine emissions. This work is therefore a welcome addition.

My one significant criticism of the work is that, in several places, it is qualitative rather than quantitative. I agree with the authors that sample-to-sample variability in biological systems sometimes makes it difficult to identify trends. However I also think there is

more quantitative information contained in their datasets than the authors have yet extracted. I suggest some areas where the work could be made more quantitative below.

Specific comments:

P 10675 line 5 "With many of the stress processes linked to exposure [,] it is the combination of several factor that may cause significant physiological effects." I'm not sure the cause-and-effect relationships are yet proven. True – there are many possible stress factors. But whether it is a combination of factors or one dominant factor that leads to halocarbon emissions isn't yet established.

P 10675 lines 11-16. Note that that agriculture has used seaweeds as a fertiliser/soil improver for centuries.

P 10676 line 9. It is also worth citing McFiggans et al (Atmos Chem Phys 10, 2975, 2010). This study observed peaks in bromo- and iodocarbons, molecular iodine and particle nucleation around low tides.

P 10676 lines 15-20 "Kupper et al 2013 found that there was no detectable bromine flux from Laminaria digitata under oxidative stress. . .. A better understanding of these processes is important. . . especially in intertidal regions where algae are exposed for several hours each day". L. digitata is not the best example to construct this argument. This species has often been studied because it is a prodigious emitter of iodine compounds; it is not unreasonable therefore that Kupper et al found it doesn't emit bromine (as in fact the authors note later on P 10687). Also L. digitata is a deeper-water species: it is typically exposed during only the lowest tides in the tidal cycle.

P 10677 section 2.1. Please provide more details about the seaweed collection(s). GPS co-ordinates for West Runton beach. Presumably seaweed samples were collected on several different visits – give dates (in Table 1?). Could seasonal differences affect the measured bromocarbon emissions and/or photosynthetic capacity?

P 10679 line 7. Samples were analysed by gas chromatography and electron impact mass spectrometry. Samples weren't analysed by an auto-sampler and a pre-concentration system.

P 10679 line 26. What is a "working air standard"? Is this a gas cylinder containing a calibration gas mixture (of what compounds and at what concentrations)?

Section 2.4, Table 1 & Section 3. It will help readers if the experiments are listed in Table 1 in the same order as they are discussed in the Results section. This would also mean re-ordering Section 2.4.

Section 3.1 is rather descriptive. It should be possible to fit a linear decay or (better) an exponential decay to each series in Fig 2 and thus deduce a decay constant characterising the mass loss from each sample. Section 3.1 could then assess whether the decay constants were consistent across the various samples in FM1 and FM2, and the extent that UM desiccates faster than FM. Is it possible to relate the FM/UM difference to the samples' surface areas?

Section 3.2. Again the discussion is qualitative: e.g. line 12 "Fv/Fm remained stable for some time.... began to decrease earlier but still remained fairly constant..." and line 20 "substantial water loss" – how much is substantial? As in Section 3.1, it might be helpful to fit the mass loss data in Fig 3 to extract decay time constants and thus make the discussion more quantitative. By eye, it looks like the mass loss is fastest in UP1 and slowest in UP2 with FP1 somewhere in the middle – the roll-off in Fv/Fm also seems to follow this trend.

P 10682 line 16 "different environmental histories". Were the three samples in e.g. UP1 collected at the same time and from the same position on the beach, thus implying they have similar histories? Were the three samples in UP2 collected at a different time/location from UP1? Is that why the three time traces within each group share some similarities, whereas there are larger differences between UP1 vs UP2? Please include collection data in Table 1.

P 10682 line 24. Have the authors generated plots of Fv/Fm versus mass loss? Do these plots show any consistent behaviour in terms of a mass loss threshold that must be reached before photosynthesis declines?

P10683 line 12 "varied considerably between... even those samples collected from the same location at the same time". Again, please include collection data in Table 1.

P 10683 line 13 "the maximum concentration [of what?] observed for replicate FL1a was around four times higher... than FL1b (100 pptv compared to 25 pptv, Fig 4)". Maybe I misunderstood Fig 4, but the 100 and 25ppt values seemed to be the peak CH2Br2 and CHBr3 concentrations observed for FL1b without any quantitative reference to what happened with FL1a.

P 10683 line 15 and Fig 4. The concentration time series in Fig 4 are interesting. But the more transferable quantity, in terms of comparisons between samples and for future studies, is the emission rate of the bromocarbons normalised for the sample's mass (moles per g fresh weight per unit time). See for example the iodine emission rates in the Ball 2010 reference cited a few lines later; also Kundel et al (Anal Bioanal Chem 402, 3345, 2012) for iodocarbon emission rates. There ought to be enough information in Fig 4, Table 1 and the flow rates to calculate emission rates from this study.

P 10684 line 18-21. Even within the sample-to-sample variability, the most consistent result in Fig 5 (and Fig 4 too) is that the CH2Br2 time series for each sample looks like its CHBr3 time series. It seems a pity to deal with this similarity in just two sentences. Have the authors tried constructing correlation plots of CH2Br2 emissions versus CHBr3 emissions? What are the emission ratios of these two compounds, and are the ratios consistent across the samples for each seaweed species?

P 10685 line 1 states that wetting with fresh water acts to impede emissions because some of the emitted halocrabons must first partition into the aqueous phase (a physical process). Fig 6 shows bromocarbon concentrations increasing after wetting due to the

osmotic stress (P 10688 line 11) induced in the biological sample by fresh water. Is it possible (how?) to separate these opposing physical and biological effects?

Section 3.4. It would have been good to see re-wetting experiments on Fucus too.

P 10686 line 6 “relatively linear patterns of water loss”. It’s not obvious that the loss is linear. See comment above re Section 3.1 about fitting for linear or exponential decays.

P 10686 lines 20-25 “commercial drying processes”. I didn’t get any sense of scale of the emissions due to commercial activity versus the emission that are taking place from natural tidal exposure. Or do the emissions from commercial seaweed farming only have effects local to the activity?

P 10687 line 7-9. It is important to note that Nitschke et al measured emission rates of iodine, not bromocarbons, and for a different species of seaweed from those examined here (L. digitata). The emission mechanisms could be very different!

P 10687 line 18 “a short-lived pulse of emissions” and “within the first few hours of exposure” are not consistent concepts. (See also “rapid” on P 10688 line 26). The seaweed may only be exposed for a few hours during the 12 hour tidal cycle. Moreover, the bromocarbon time profiles in Fig4-6 are markedly different from the immediate ($\sim$1 min) and very large iodine bursts emitted by L. digitata (Kupper 2008; Ball 2010; Nitschke 2011 etc), a species where iodine emission is a known stress response. If L. digitata is able produce a response within $\sim$1 min, why not also an “active” oxidative response of bromocarbon release from U. intestinalis or F. vesiculousus on the $\sim$1 hour timescale?

This is a compact, well-written paper. I only found two typographical errors: P 10675 line 17 “. . .evidence that [a] balanced. . .budget”. P 10684 line 5 “concentrations had reached [declined to]. . . control levels” i.e. concentrations going down, not up.

Interactive comment on Biogeosciences Discuss., 11, 10673, 2014.