Response to reviewers

We thank both reviewers for taking the time to review our manuscript and for their helpful and positive reviews. Reviewer comments in blue, our responses in black. All page and line numbers refer to the discussion manuscript.

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.
We hope we have addressed this comment with our responses below, in particular see our responses to C9, C10, C17 and C20.

Specific comments:
C1. 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.
We have updated this section to clarify this point. We had meant to introduce the idea that many stress processes could be linked to exposure and these would not only act individually but could have combined effects. The sentence now reads: "Variation in environmental conditions during exposure may also combine to enhance the impact on the algae. For example…"

C2. P 10675 lines 11-16. Note that that agriculture has used seaweeds as a fertiliser/soil improver for centuries.
We do not claim that this process is recent. In a later section we also highlight that our particular, current, interest is due to growing interest in seaweed farming as a "source of chemical products and feedstocks, biofuels, food and for carbon sequestration (Schlarb-Ridley & Parker, 2013)." (page 10676, line 21) as these processes have the potential (or at least their potential is under discussion) to be upscaled.

C3. 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.
McFiggans et al. (2010) provides only a summary of the campaign results and cites halocarbon results from Jones et al. (2009). We have added a reference to Jones et al. (2009).

C4. 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.
This comment supports our rationale for this experiment in that there is little existing work on the bromocarbon oxidative stress response - the main study to date is the Küpper et al. (2013) study on *L. digitata*. To clarify, the Küpper et al. (2013) study was a dedicated study investigating bromine in *L. digitata* and, whilst brominated emissions are lower than iodinated emissions from kelps, they do still produce brominated emissions (Carpenter and Liss, 2000). *Laminiaria* spp., including *L. digitata,* have also been used to discuss tidally-mediated iodine emissions by Küpper et al. (2008). We have expanded this section to clarify some of these points. The updated section reads: ". A recent study by

Küpper et al. (2013) found that Laminaria digitata sequesters bromine from seawater (mostly as bromide) but its accumulation is far less pronounced than for iodine. It is a less suitable as an antioxidant and there was no detectable bromide flux under oxidative stress. This is perhaps expected: although Laminaria spp. do release volatile bromocarbons (Carpenter & Liss, 2000) they are known to be stronger emitters of iodinated compounds and to use iodide as an inorganic antioxidant (Küpper et al., 2008). However, the recent Küpper et al. (2013) study highlighted the complexity of the role bromine and bromocarbons may play in macroalgae and that this role is not yet fully understood, in particular from species that may release larger quantities of brominated compounds."

C5. 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?
We have added experiment dates to Table 1. On page 10677 line 19 we state that all samples were used within 1 week of collection. All halocarbon emission experiments were conducted between 31st Jan and 26th April and replicates (e.g. all Fucus desiccation experiments) within shorter time windows so it seems unlikely that seasonal differences could account for the biological variability in these emissions. All samples were kept in laboratory conditions for 24-48 hours prior to use to acclimatise them to identical light conditions (added to methodology) and all samples were further acclimatised to the experimental conditions prior to use (already in manuscript on page 10677, line 19).

C6. 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 preconcentration system.
Updated to read "Air samples were preconcentrated using…"

C7. 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)?
We have expanded our methodology to include this information.

C8. 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.
Done.

C9. 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?
We have increased the quantitative discussion in Section 3.1 in response to this comment and also C20 (below). See our response to C20 for a full description.

C10. Section 3.2. Again the discussion is qualitative: e.g. line 12 "F_v/F_m 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 F_v/F_m also seems to follow this trend.
We have improved this section, see our response to C13, by adding plots of F_v/F_m vs mass loss and increasing the discussion of this relationship. However, due to the fact that mass was measured roughly half the times that F_v/F_m was measured we have not attempted to fit the data or make assumptions based on this type of mathematical analysis.

C11. 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?
Wherever replicates were used (e.g FL1a and FL1b, FL2a and FL2b, UP1a and UP1b etc.) these replicates were always collected on the same date – we have clarified this in the methodology. Our methodology already specifies that samples were all collected from within the same 2m range of West Runton beach. During an individual collection period we always tried to collect samples from as close together as possible to minimise the chance of environmental history causing variation. However, even samples collected next to each other could have faced different levels of exposure, light and predation history, etc. UP1 and UP2 samples were collected on the same date, the only difference being the analysis date (19th and 21st June) which is provided in Table 1. So sampling dates cannot explain the differences between UP1 and UP2.

C12. Please include collection data in Table 1.
Dates included, see earlier response.

C13. P 10682 line 24. Have the authors generated plots of F_v/F_v versus mass loss? Do these plots show any consistent behaviour in terms of a mass loss threshold that must be reached before photosynthesis declines?
The photosynthesis experiments focussed on F_v/F_m measurements and, whilst mass measurements were made they were made for around half of the F_v/F_m measurements only. For this reason we do not have the data required to determine if there is a threshold or not. Our results suggest there may be: for FP1 and UP2 F_v/F_m remained relatively stable until around 50-60% of water had been lost, then began to quickly decline. However the decline in F_v/F_m was more constant over the entire experimental period for UP1. We have included Fv/Fm vs mass loss in Fig. 3. This point had already been discussed in Section 3.2, we have strengthened it and linked it to the updated Fig. 3.

C14. 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.
Done.

C15. 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 CH_2Br_2 and $CHBr_3$ concentrations observed for FL1b without any quantitative reference to what happened with FL1a.
We have clarified this. The section now reads: “Variation in the magnitude of emissions varied considerably between some algal specimens, even those collected from the same location at the same time. For example the maximum CH_2Br_2 concentration varied between 4 and 25 ppt for replicates FL1a and FL1b (Fig. 4).”

C16. 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.

We have updated Fig. 4 and Fig. 5 to include emission rates. We have provided emission rate per gram dry weight (as in Kundel et al., 2012) rather than fresh weight as the fresh mass changed during desiccation. We have also discussed this addition in the manuscript.

C17. 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 CH_2Br_2 time series for each sample looks like its $CHBr_3$ time series. It seems a pity to deal with this similarity in just two sentences. Have the authors tried constructing correlation plots of CH_2Br_2 emissions versus $CHBr_3$ emissions? What are the emission ratios of these two compounds, and are the ratios consistent across the samples for each seaweed species?

We did not discuss the similarity between CH_2Br_2 and $CHBr_3$ emission patterns further as this result has been seen in most, if not all, previous studies investigating bromocarbon emissions from macroalgae. We have made the following updates to expand on this:

1. Provided references to previous studies where this result was also observed, and discussed in further detail (Carpenter & Liss, 2000; Leedham et al., 2013).
2. We have calculated a range of emission ratios (slope of CH_2Br_2 vs $CHBr_3$ for each experiment) and compared it to values from the literature.

C18. 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?

As discussed in our introduction the impact of tidal exposure (and subsequent desiccation) is complex due to the variety of factors, both physical and biological that are involved. When investigating rewetting it would be difficult to separate these opposing effects.

C19. Section 3.4. It would have been good to see re-wetting experiments on Fucus too.

We were limited by time available for experiments and so selected *Ulva* due to the fact it emitted higher levels of bromocarbons. Future experimentation on *Fucus*, as well as other species, would be useful and we mention possible future experiments throughout our manuscript.

C20. 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.

Fig. 2 did not clearly show the water/mass loss patterns – we have updated Fig. 2 so this is clearer. 5 *F. vesiculosus* replicates were desiccated as part of the water/mass loss experiments, 3 during FM1 (FM1a, FM1b and FM1c) and 2 during FM2 (FM2a and FM2b) (Table 1). Of these 5 replicates 3 showed a relatively constant loss of water, with rates of 0.22 (SD=0.06), 0.18 (SD=0.03) and 0.18 (SD=0.06) % min^{-1} respectively. Corresponding linear fits (now shown in Fig. 2) for these 3 replicates had R^2 values of 0.995, 0.994 and 0.981 respectively. The final two replicates did not show a linear decay. However, the change in loss rate occurred around the time that the experimental procedure switched from ~ 3 samples an hour to ~ 1 sample an hour. The experimental procedure and the rationale behind it was discussed on page 10681 lines 23-26. For this reason we have not added a fit to these two replicates and have added a marker to Fig. 2 to show where the experimental change occurred. Water loss in *U. intestinalis* slowed toward the end of the experiment as the amount of water available within the algae decreases substantially. *U. intestinalis* lost water faster and to a larger extend than *F. vesiculosus* (as discussed in our existing manuscript) - at the end of the experiment *U. intestinalis* weighed between 31-68 % more than its dry mass compared to 66-82% for *F. vesiculosus*. As a consequence of the reduction in rate of water loss in the last few measurements exponential fits have been applied to the *U. intestinalis* mass loss plots in Fig. 2. All the above has been discussed further in the main body of the manuscript.

C21. 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?
Our discussion in this section does not attempt to discuss differences in scale between commercial drying processes and natural tidal exposure. The point we make is that we had seen differences between our experiment, where *U. intestinalis* was spread out in a thin mat, and previous studies where *U. intestinalis* was found to trap water between fronds (so one assumes it was piled up/overlapping to allow water to be trapped between fronds). We linked this to differences between commercial and natural desiccation as follows: “…artificial desiccation, for example during drying of harvested algae to create a market product, may vary from natural tidal desiccation. During commercial drying processes the algae are often spread into thin mats to increase the speed of drying and ensure drying occurs before onset of decay. This will increase the rate at which the algal biomass dries and so increase the rate of exposure to stress.”. This section aimed to discuss differences in technique, not a comparison of quantity. We discuss potential increases in aquaculture in our introduction and conclusion.

C22. 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!
We have clarified this point. We believe this reference is still worth including being the only other study of this type.

C23. P 10687 (1) 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). (2) 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 (_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 _1 min, why not also an “active” oxidative response of bromocarbon release from U. intestinalis or F. vesiculousus on the _1 hour timescale?
(1) one can have a short-lived pulse of emissions within the first few hours of exposure. This comment is a general one and shows that the pulse may not occur at exactly the same time for all specimens, but always occurred within the first few hours and was short-lived. We have updated this sentence to read “In many of the experiments the bromocarbon response to desiccation was a short-lived pulse of emissions **that occurred within the** first few hours of exposure.”
(2) We proposed the idea that this **may** not be linked to a direct oxidative stress response based on the fact that during this time we had not seen a significant decrease in F_v/F_m (as discussed in the previous paragraph) and link it to other research that (Küpper et al., 2013) that found that bromine was not a major antioxidant in the brown algae *L. digitata* (also explaining that this was research on one brown algal species and discussing why our results may differ for *U. intestinalis*. We have made some alterations to this paragraph to make this clearer.

C24. This is a compact, well-written paper. I only found two typographical errors: (1) P 10675 line 17 “: : :evidence that [a] balanced: : :budget”. (2) P 10684 line 5 “concentrations had reached [declined to]: : : control levels” i.e. concentrations going down, not up.
(1) Done
(2) Done

References
All references can be found in the *Discussions* manuscript except:

Jones, C. E., Hornsby, K. E., Dunk, R. M., Leigh, R. J., & Carpenter, L. J.: Coastal measurements of short-lived reactive iodocarbons and bromocarbons at Roscoff, Brittany during the RHaMBLe campaign. Atmospheric Chemistry and Physics, 9, 8757–8769, 2009.