

## **Response to comments by Anonymous Referee #1**

**This manuscript is concerned, in general terms, with trying to understand and model the observed iodo emissions from ocean surfaces. As such it is interesting, and certainly takes an ambitious stance. However, as written, it is two quite different papers, put together into a single MS. The two - a laboratory exploration of the influences exerted by various parameters on the emission, and a modelling study, using a new parameterization of HOI and I<sub>2</sub> emissions - are quite unconnected in almost every way. I suggest they be disentangled, and published separately.**

RESPONSE: We thank Referee #1 for his comments. However, we strongly disagree with the statement that the two parts of the paper are “unconnected in almost every way”. The objective of our paper is to report a parameterisation of the inorganic iodine flux from the ocean surface based on laboratory experiments where a wide range of environmentally relevant variables have been considered, and showing that this parameterisation yields reasonable estimates of the reactive iodine mixing ratios when compared with a dataset spanning a wide range of oceanic conditions. The referee has provided no substantial comments to back up his/her suggestion of splitting the paper in two. We would therefore prefer to keep the structure of paper as submitted.

**Some comments I can make on the MS follow.**

**Page 31448, lines 20-21: I think you must assume the I<sub>2</sub> is at its equilibrium vapour pressure here. This should be made explicit, as well as any checks done to ensure this was so.**

RESPONSE: Yes, it is assumed that the I<sub>2</sub> is at its equilibrium vapour pressure. The iodine crystals within the cell were allowed to equilibrate for some time before the experiments were started, and it was established that the entraining flow of N<sub>2</sub> was sufficiently slow to ensure that evaporation of I<sub>2</sub> was fast enough to maintain the equilibrium vapour pressure.

Change in p. 31448, l. 19-21: “The experimental setup was calibrated using a known flow of I<sub>2</sub> vapour, produced by passing N<sub>2</sub> through a glass trap containing solid I<sub>2</sub> (Sigma Aldrich) in equilibrium with its vapour phase, for each of the light sources used.”

**Page 31449, lines 17-19: What absorption coefficient(s) and wavelengths were used to extract the [HA] from the absorbance?**

RESPONSE: Extinction coefficients and molecular weight are not available for HA; instead a specific absorbance (SUVA) value for humic acid of 5 L mg<sup>-1</sup> m<sup>-1</sup> at 254 nm was used (Weishaar, J. L.; Aiken, G. R.; Bergamaschi, B. A.; Fram, M. S.; Fujii, R.; Mopper, K. Evaluation of specific ultraviolet absorbance

as an indicator of the chemical composition and reactivity of dissolved organic carbon. Environ. Sci. Technol. 2003, 37, 4702–4708.) Absorption due to HA at 254 nm was  $\sim 0.1$  therefore, this gives a DOC concentration of  $\sim 2 \text{ mg L}^{-1}$ .

Change in p. 31449, l. 18: “The concentration of humic acid was determined by UV/Vis spectroscopy to be around  $2 \text{ mg dm}^{-3}$ , using a specific absorbance of  $5 \text{ L mg}^{-1} \text{ m}^{-1}$  at 254 nm (Weishaar et al., 2003)”.

**Page 31450, lines 3-8: Please either show the trace impurity result, or state quantitatively how much  $\text{I}_2$  was associated with the impurity in the NaCl.**

RESPONSE:  $< 50 \times 10^{-9} \text{ M}$  iodide so at least 20 times smaller than the concentration used in the salinity experiments. The equivalent in terms of  $\text{I}_2$  flux would be  $< 6 \times 10^8 \text{ molecule cm}^{-2} \text{ s}^{-1}$  at 0.5 M NaCl, i.e. well within experimental error ( $\pm 4 \times 10^9 \text{ molecule cm}^{-2} \text{ s}^{-1}$ ).

Change p 31450, l. 8: “The equivalent in terms of  $\text{I}_2$  flux would be  $< 6 \times 10^8 \text{ molecule cm}^{-2} \text{ s}^{-1}$  at 0.5 M NaCl, i.e. well within experimental error ( $\pm 4 \times 10^9 \text{ molecule cm}^{-2} \text{ s}^{-1}$ ).”

**line 21: the monolayer-forming conc for SDS seems very high.**

RESPONSE: This concentration (6.2 mM) was taken from the reference cited (Hore et al. 2005) “SDS (Aldrich) was dissolved in 18.2 M $\Omega$  Nanopure water to achieve a bulk concentration of 6.2 mM. At this concentration, a well-ordered monolayer forms at the interface.” They also reference Gragson et al. 1997 (J Am Chem Soc) who gave bulk concentrations necessary to form a well-ordered monolayer ranging from 4-8 mM SDS.

**Page 31451: How did the results of experiments done with the different photolysis sources compare? What was the advantage of having the 3 sources?**

RESPONSE: The three sources showed varying detection limits (hence the necessary changes in the  $\text{O}_3$  concentration used). The tungsten lamp showed high sensitivity for  $\text{I}_2$  but did not allow measurements of HOI. The xenon lamp was used for measurements of HOI, however, the sensitivity and selectivity using this light source was poor and therefore the laser was employed to measure  $\text{I}_2$  and HOI independently.

Change p. 31448, l. 19 (experimental section): “The tungsten lamp showed high sensitivity for  $\text{I}_2$  but did not allow measurements of HOI. The xenon lamp was used for measurements of HOI, however, the sensitivity and selectivity using this light source was poor. The laser was employed to measure  $\text{I}_2$  and HOI independently and enabled high sensitivity for both species and back-to-back operation.”

**Page 31452, line 20-21: I think it was Tobias and Jungwirth who should be credited here.**

RESPONSE: This information was taken from the Gladich et al. (2011) reference cited. We have added the reference to Tobias and Jungwirth, 2006.

**Page 31454, lines 20-25: I do not follow how a lack of T-dependence gives rise to an activation energy, as proposed here.**

RESPONSE: The lack of temperature dependence applies only to the  $I^- + O_3$  reaction, the overall temperature dependences are for the flux of HOI and  $I_2$  out of solution. These arise from the various temperature dependences of parameters in the model, including the respective Henry's law constants, diffusion constants, mass transfer velocities etc.

**Page 31456, line 1 AND Fig 5: Could there be 2 different dependences here?**

RESPONSE: Note first that the open ocean surface iodide concentrations plotted in Fig. 5 are sparse, were recorded in separate cruises at different locations and different seasons of the year, and span more than 2 decades. The variability of iodide may result from a number of different processes which are not fully understood. However, a clear pattern emerges when plotting the available open ocean iodide concentration data vs. SST or latitude. In particular  $\ln(SSi)$  vs  $1/T$  provides a convenient parameterization which accounts for this general trend. An upcoming paper by Chance et al. (submitted) discusses the global ocean iodide field in detail.