

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 I₂ 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 I₂ 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 I₂ 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 N₂ was sufficiently slow to ensure that evaporation of I₂ 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 I₂ vapour, produced by passing N₂ through a glass trap containing solid I₂ (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⁻¹ m⁻¹ 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 ~ 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 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 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 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 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 Ω 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 O_3 concentration used). The tungsten lamp showed high sensitivity for 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 I_2 and HOI independently.

Change p. 31448, l. 19 (experimental section): “The tungsten lamp showed high sensitivity for 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 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.

Response to comments by Anonymous Referee #2

This paper presents an interesting set of experiments on the mechanism of iodine release from the ocean. It is a problem that has been quite debated in the past few years and is not resolved yet, but has important potential implications for ozone photochemistry. The experiments presented here shed new light on this process and therefore I think the paper should be published in ACP, following some minor corrections and clarifications.

General Comments

A key issue is the reproducibility of the experiments and the reliability of the observations. The authors acknowledge poor reproducibility (page 31451) and _50% error in their determinations of the iodine fluxes. It is noted that iodine is detected using an indirect method (the accuracy of which should be discussed in section 2). As a consequence, the parametrizations derived from

these experiments likely suffer from rather large uncertainties, which should be addressed in section 4.5 together with the sensitivity analysis. I think that a longer discussion of the uncertainties involved in the experiments and the derived parametrizations is warranted. It might in fact help to explain the model-measurement discrepancies.

RESPONSE: The detection method is discussed in detail in the Carpenter et al. 2013 paper. The IOP detection of the I_2 and HOI fluxes is a relative technique and requires calibration. At low photolysis rates the IOP mass is a linear function of the I_2 concentration and accurate calibration coefficients can be obtained, typically with an uncertainty of $\sim 8\%$ encompassing the uncertainty of the iodine vapour pressure (Baxter, Hickey and Holmes, 1907) and the statistical uncertainty from the linear regression. An accurate calibration was important when comparing experimental iodine fluxes to the output of the interfacial model presented by Carpenter et al. 2013. Further experiments on the $I^- + O_3$ reaction were performed at the University of York using an entirely independent method for HOI and I_2 detection (Carpenter et al., 2013). The experimentally determined I_2 and HOI fluxes using both techniques compared well with the interface kinetic model results over a wide range of iodide and O_3 concentrations. Parameterised fluxes were then derived from the sea surface model using typical sea water conditions. As such, the uncertainties in the modelled fluxes will arise from the uncertainties of the kinetic model, and these include the parameterisations of the mass transfer coefficients for real seawater, which have an uncertainty around a factor of 2.

In the present paper the absolute calibration of fluxes is not as important as the relative variation of the IOP mass (proportional to the HOI or I_2 flux) as a function of other variables such as temperature or salinity. The detection method has enough precision as shown by the small scatter in the calibration plots and the reproducibility of calibrations under the same conditions. Even though the requirement of working under environmentally relevant conditions implies I_2 and HOI concentrations not far from the detection limits, the reproducibility of the room temperature data shows that detection precision is not a matter of concern. The major problem is the reproducibility of conditions in the experiment itself, i.e. in the cell containing the KI solution, and in particular in the experiments at low temperature (Figure 3). The implications for the uncertainty in the parameterised fluxes which arise from the relatively large uncertainty in the activation energies derived from the Arrhenius plots in Fig. 3, are discussed in detail in the revised manuscript as requested by the referee (see changes below). Note that due to the Arrhenius parameterisation of the iodide concentration, the effect of a potential variation of the surface emission processes with temperature will be superposed on the effect of varying iodide.

Finally, the 50% uncertainty mentioned by the reviewer arises from the parameterisation of the SSI concentration using SST (Eq. 1 and Fig. 5), not from the laboratory experiments. This parameterisation suffers from the scarce measurements reported in the literature and the lack of seasonal or long term studies. Geographical and seasonal/interannual variability of the surface ocean iodide is present in the data shown in Figure 5, spanning more than 25 years of measurements. The sensitivity of the model to iodide concentration is discussed in section 4.5 and potential explanations of the discrepancies between field and modelled data involving iodide are discussed in section 4.6.

Change p. 31448, l. 21: “At the low I_2 concentrations and photolysis rates of the experiments the IOP mass is a linear function of the I_2 concentration and accurate calibration coefficients can be obtained, typically with an uncertainty of ~8% encompassing the uncertainty of the iodine vapour pressure (Baxter et al., 1907) and the statistical uncertainty from the linear regression. The detection limits using laser photolysis are typically ~2 pptv for I_2 and ~50 pptv for HOI. In the $I^- + O_3$ experiments, the requirement to work at close to environmentally relevant concentrations of iodide and O_3 (within a factor of 10) results in a range of IOP numbers close to the detection limit of the particle counter, which may reduce the precision of the measurements. “

Change p. 31451, l. 18: “Even though the requirement of working under environmentally relevant conditions implies I_2 and HOI concentrations not far from the detection limit, the reproducibility of the room temperature data shows that the precision of the detection method is not a matter of concern. The major problem is the reproducibility of conditions of the experiment itself, i.e. in the cell containing the KI solution, and in particular in the experiments at low temperature, as shown by the error bars in Figure 3. A possible explanation is uptake and release of iodine species on the inner walls and the outlet of the temperature stabilised cell.”

Change p. 31456, l. 15: “Equations (2) and (3) are room temperature expressions, since Carpenter et al. did not consider the potential temperature dependence of any processes in the interfacial layer. As discussed above, a large temperature dependence of the $I^- + O_3$ reaction can be ruled out, but the modest experimental precision does not tightly constrain the activation energies of the iodine fluxes (see Figure 3). The interfacial layer model predicts activations energies for I_2 and HOI emission of -2 kJ mol^{-1} and 25 kJ mol^{-1} , respectively, which are within the experimental uncertainty of our measurements. Table 1 presents a summary of the relative error $(F_x(T)-F_x(293K))/F_x(293K)$ made when using the 293 K expressions (2) and (3) at 283 and 303 K using different values for the activation energies. For this exercise, an additional Arrhenius-type exponential factor is assumed in (2) and (3), and the experimental uncertainty limits for the activation energies (E_{up} and E_{low}) and the

activation energies derived from the interface kinetic model (E_{model}) are considered. The uncertainties in the HOI flux arising from the uncertainty in the activation energy are larger than for the I_2 flux, and since HOI this is the major inorganic species emitted, this must be kept in mind when modelling field data at SST other than 293 K.”

Table 1. Relative differences of the inorganic iodine fluxes at 283 K and 303 K with respect to the 293 K values, for the experimental confidence limits and the modelled values of the activation energies.

	I_2			HOI		
	E_{low}	E_{up}	E_{model}	E_{low}	E_{up}	E_{model}
	-25 kJ mol ⁻¹	11 kJ mol ⁻¹	-2 kJ mol ⁻¹	-33 kJ mol ⁻¹	67 kJ mol ⁻¹	25 kJ mol ⁻¹
303 K	29 %	-16%	3%	37%	-153%	-41%
283 K	-45 %	15%	-3%	-63%	63%	31%

If the ozone+iodide mechanism proposed in this paper does indeed occur everywhere on the ocean surface, it seems to me it should generate significant levels of I_2 during the night. These should be detectable especially in unpolluted and remote marine environments where concentrations of NO_3 are likely too small. However, I_2 was not reported in the Mahajan et al., 2012 or in the Grossman et al., 2013 papers. Can you comment on how to reconcile the mechanism with the apparent lack of I_2 observations?

RESPONSE: Using the highest predicted fluxes the maximum night time I_2 mixing ratio 5 m above the seawater is ~11 ppt and therefore should be detectable using currently available field measurement techniques. I_2 was not observed in Mahajan et al. 2012 or Grossman et al. 2013 as both campaigns used MAX-DOAS measurements and therefore were unable to make night time measurements.

Recently, Lawler et al. (Lawler, M. J., Mahajan, A. S., Saiz-Lopez, A., and Saltzman, E. S.: Observations of I_2 at a remote marine site, *Atmos. Chem. Phys.*, 14, 2669-2678, doi:10.5194/acp-14-2669-2014, 2014.) have reported I_2 mixing ratios of up to ~1.7 ppt measured by atmospheric pressure chemical ionization tandem mass spectrometry in two campaigns in Cape Verde in 2007 and 2009. Also measurements from a ship cruise in the South China and Sulu Sea have found significant I_2 at night using coupled diffusion denuder system, with a cruise average of ~2 pptv and night time maximum of 12 pptv – in good agreement with the modelled I_2 here (Heard, D., Walker, H., Ingham, T., Huang, R.-J., and Wittrock, F.: In situ measurements of IO and reactive iodine aboard the RV Sonne during SHIVA Geophysical Research Abstracts Vol. 15, EGU2013-10061, 2013 EGU General Assembly 2013).

Change p 31447, l. 29: “Very recently the first measurements of I_2 at a remote marine site (Cape Verde) have been reported (Lawler et al., 2014), with night time mixing ratios of up to 1.7 pptv.

These mixing ratios are not enough to sustain the levels of IO observed at Cape Verde (Mahajan et al., 2010), which concurs with our laboratory observations of HOI being the major species emitted from the ocean surface.”

Various previous studies in different oceanic regions (eg, Jones et al. 2010, Mahajan et al. 2010, Grossman et al. 2013) have estimated that an I₂ flux may be required to match the IO observations in addition to measured iodocarbons fluxes. How do the fluxes reported in those papers compare to those calculated with the parametrization presented here? And can the salinity, organics and temperature dependences explain the differences in the I₂ fluxes estimated for different regions - as highlighted in the previous studies? A brief comment on these points could be an interesting addition to the paper.

RESPONSE: Our parameterised flux expressions result in reactive iodine concentrations which are in reasonable agreement with the IO observations during the HALOCast-P cruise. In addition, parameterised fluxes were shown in our previous paper (Carpenter et al., 2013) to replicate well the IO levels at Cape Verde. Note that this is a superior exercise to adjusting the iodine flux in a model to match the observed IO.

The I₂ flux estimated by Jones et al. 2010 is 2.2×10^8 molec. cm⁻² s⁻¹. Mahajan et al. 2010 calculated a diurnally varying I₂ flux, peaking at 5.7×10^8 molec. cm⁻² s⁻¹ or a constant flux of 5×10^7 molec. cm⁻² s⁻¹ (in this scenario the post-sunrise peak is also observed). Grossman et al. 2013 estimated an I₂ flux of 1.8×10^8 molec. cm⁻² s⁻¹. The maximum (total I) flux predicted by our parameterisation is $\sim 5.4 \times 10^8$ molec. cm⁻² s⁻¹, therefore 2.7×10^8 molec. cm⁻² s⁻¹ equivalent for I₂, and the minimum is $\sim 1 \times 10^7$ molec. cm⁻² s⁻¹, in reasonable agreement with previous measurements.

Note however that according to our laboratory findings (Carpenter et al., 2013) the major species emitted from the ocean surface under environmentally relevant conditions should be HOI. Indeed Lawler et al. 2014 show that the night time I₂ mixing ratios observed at Cape Verde (up to 2 pptv) are not sufficient to sustain the IO levels measured at the same location by LP-DOAS (Mahajan et al., 2010). High mixing ratios of HOI have been detected in the Sulu sea during the SHIVA campaign (unpublished results reported at the EGU general assembly 2012 and 2013).

The reviewer is right in pointing out that the iodine fluxes from the ocean must be different at different locations depending on the local values taken by the relevant variables. This in turn could be the explanation of the different mixing ratios of reactive iodine observed in the MBL, e.g. in the Eastern Atlantic (Mahajan et al, 2010), the Eastern Pacific (Mahajan et al., 2012; Gomez Martin et al., 2013) or the Western Pacific (Grossmann et al, 2013; Heard et al.; 2013). However a discussion of

geographical (i.e. longitudinal) differences in the sea-to-air iodine fluxes or the reactive iodine mixing ratios observed is beyond the scope of the paper. The objective of our work (Carpenter et al, 2013, and this paper) is providing for the first time a parameterisation of the iodine flux from the ocean surface based on laboratory experiments where all known environmentally relevant variables have been considered, and showing that such parameterisation yields reasonable estimates of the reactive iodine mixing ratios when compared with a dataset spanning a wide range of oceanic conditions such as the HaloCAST-P dataset. Currently several groups are working on alternative parameterisations of the surface ocean iodide field and on the implementation of our parameterised flux expressions in global models. Discussion of the geographical differences on sea surface iodide and MBL reactive iodine is warranted in these upcoming papers.

Specific & Technical Comments

In section 3.2 is not clear whether you tried to reproduce the Hayase et al. experiments with fulvic acid and/or the Reeser/Donaldson experiments with octanol.

RESPONSE: Our intention was not repeating the Hayase/Reeser experiments, but using similar organic reagents to investigate whether similar effects could be observed with our experimental set up using realistic seawater concentrations, as stated in p. 31450. In fact the Hayase paper was published after these experiments were performed. SDS was used as an example surfactant which is also commonly found in seawater.

I don't understand whether ozone was measured or not during the cruise. It would appear it was not from section 4.4, but figure 6 seems to suggest it was. Can you please clarify.

RESPONSE: O₃ was not measured during the cruise (as stated in p. 31455, l. 9) but was modelled using CAMChem as described in section 4.4. This has been clarified in the Figure 6 legend.

On page 31457 (line 10) change "ws" to "wind speed (ws)"

RESPONSE: Wind speed (ws) appears earlier in p 31456, line 14.

On page 31461 explain the acronym SSS

RESPONSE: The acronym is explained earlier in p 31447, l. 24.

Please add the parameters of the linear fits to figures 3 and 7

RESPONSE: Done