

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 mode 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 activation 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 $(F_x(T) - F_x(293\text{K})) / F_x(293\text{K})$ 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%
283 K	-45%	15%	-3%	-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 $\sim 11\text{ ppt}$ 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 I_2 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 I_2 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 I_2 flux estimated by Jones et al. 2010 is 2.2×10^8 molec. $\text{cm}^{-2} \text{ s}^{-1}$. Mahajan et al. 2010 calculated a diurnally varying I_2 flux, peaking at 5.7×10^8 molec. $\text{cm}^{-2} \text{ s}^{-1}$ or a constant flux of 5×10^7 molec. $\text{cm}^{-2} \text{ s}^{-1}$ (in this scenario the post-sunrise peak is also observed). Grossman et al. 2013 estimated an I_2 flux of 1.8×10^8 molec. $\text{cm}^{-2} \text{ s}^{-1}$. The maximum (total I) flux predicted by our parameterisation is $\sim 5.4 \times 10^8$

molec. $\text{cm}^{-2} \text{ s}^{-1}$, therefore 2.7×10^8 molec. $\text{cm}^{-2} \text{ s}^{-1}$ equivalent for I_2 , and the minimum is $\sim 1 \times 10^7$ molec. $\text{cm}^{-2} \text{ s}^{-1}$, 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 I_2 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