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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Latitudinal distribution of reactive iodine in the Eastern Pacific and its link to open ocean sources" *by* A. S. Mahajan et al.

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Response to interactive comments by sources Anonymous Referee #1

We thank reviewer #1 for the helpful comments on our manuscript, which are now incorporated in the new manuscript. Detailed responses to each of the comments are given below.

R1.1) The manuscript by Mahajan et al. presents remote sensing observations of BrO and IO slant column densities take during a cruise in the Eastern Pacific from South to North America. The observations are converted to IO mixing rations using radiative transfer based retrievals and then converted to IOx (IO + I) with the help of model data. Using a correlation analysis of IOx vs a number of different parameters a positive

correlation of IOx with SST and salinity, and a negative correlation of O3 and Chl-a are identified. The authors also point to a disagreement between their observations and those made by satellite. The data set presented in this manuscript provides new insight into the latitudinal distribution of reactive iodine and possible sources of these species. Unfortunately the description of the analysis methods is, in many cases, not detailed enough to gain confidence in the observations. Details pointing out areas in which the manuscript needs to be improved are outlined below. The manuscript is worthy of publication in ACP after the detailed comments have been addressed.

RESPONSE: We thank the reviewer for the above comment and hope that the new version of the manuscript now details the analysis method to give confidence in the results and discussion.

Detailed Comments:

R1.2) Page 15545 lines 8-9 and Figure 3: Please explain how the inclinometer data was used to correct for the ship oscillations in the analysis routine. Do the colors of Figure 3 refer to discrete angles or is there variation in the elevation angles due to the ship?

RESPONSE: The inclinometer data, which has an accuracy of 0.01° was used to correct the elevation angles. The true elevation angle is given by the sum of the prearranged elevation angle and the inclinometer angle (positive or negative depending on the oscillation of the ship). The colours in figure 3 reflect angles within a variation of 0.2 degrees. This is now added to the manuscript.

R1.3) Page 15545 lines 23-25: Why was glyoxal not included in the fitting procedure (see Sinreich et al., 2010)?

RESPONSE: Glyoxal was initially included in the fitting procedure for the 430-459 nm spectral region (i.e., larger glyoxal absorption peaks), however, since it was not observed above the detection limit throughout the cruise, it was then excluded from the

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final analysis settings to avoid interferences. The glyoxal data analysis is presently the focus of another manuscript and will be discussed elsewhere.

R1.4) Page 15545 line 26: Please give more details on the BrO retrieval. Was HCHO included in the fit? Why was the Alliwell et al (2002) wavelength range not used?

RESPONSE: The referee is mistaken regarding the BrO analysis window - we have indeed used the Alliwell et al. (2002) suggested wavelength window, as was mentioned in the manuscript (Page 15546 line 6). HCHO was included in the analysis and retrieved levels match satellite estimates. Further details regarding the analysis of BrO/HCHO are not included considering it is not the focus of the current study and will be published elsewhere with the HCHO data.

R1.5) Page 15546, lines 10-15: As the instrument and the scanning geometry is different from the one used by Sinreich et al, please give more details on the cloud filtering algorithm, i.e. which elevation angles and wavelengths were used, what are the uncertainties, etc.

RESPONSE: These details are now included in the manuscript – 'A cloud index was used (0 – clear sky, 1 – cloudy sky) for estimating sky conditions. The filter was calculated using a ratio of radiation fluxes from the edges of the spectral window (420 nm and 459 nm) and elevation angles measured using the DOAS instrument in order to distinguish the predominant scattering conditions. This ratio was calculated between the zenith and 1°-elevation angles, with a low ratio indicating a cloudy environment. This ratio is used in conjunction with radiometer data, which were collected on board the cruise, and the DOAS retrieved O4 DSCDs. A threshold of 1.1 was calculated, above which the conditions were cloud free (cloud index of 0). It is difficult to compute the uncertainties on the cloud index; in fact, the filter is a stringent cutoff. This would mean that we are on the safe side, with a risk of disregarding some valid data near the threshold, but it ensures that only data from clear sky conditions was used for further analysis. A similar filter has been used previously by other groups for similar studies

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(Sinreich et al., 2010).'

R1.6) Page 15546, line 15 ff. Please add more detail on the uncertainties of the CH3I observations.

RESPONSE: Added. The precision for the CH3I measurements was approximately 8%.

R1.7) Page 15547, equation 1: How was kw determined?

RESPONSE: It is stated in the manuscript that kw was determined using the gas exchange parameterization from Sweeney et al (2007), which is an update of the Wanninkhof (1992) parameterization.

kw = 0.27 (u10)2 (Sc/660)-0.5

where u10 is the 10 meter wind speed (m/s) and Sc is the Schmidt Number which is a function of the diffusivity of the gas and the kinematic viscosity of the water. These details can easily be checked in the cited publication.

R1.8) Page 15548, lines 19-21: Which method was ultimately used to determine the IO mixing ratios? The manuscript states that an optimal estimation retrieval using a radiative transfer model was used, while the SI gives the impression that the method from Sinreich et al (2010), i.e. using O4, was used. Also there needs to be a discussion how the uncertainty of the retrieval propagates though to the IO mixing ratios.

RESPONSE: Both methods were used to retrieve the surface mixing ratios and the absolute mixing ratios matched closely. We used the O4 method throughout the cruise and the NIMO radiative transfer model on some days to retrieve the surface mixing ratios and validate the O4 method. Both methods gave similar results, and hence, the O4 method retrieved mixing ratios were considered for analysis. This is now made clear in the manuscript. As the referee would be aware, estimation of uncertainties on mixing ratios is difficult for the O4 method. It is possible that the errors, which include the DOAS fitting errors, are underestimated. However, the errors calculated

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are similar to uncertainties in the optimal estimation method. This is mentioned in the supplementary text. Further details on the radiative model are published by Hay et al. (2012).

R1.9) Page 15548, lines 21-22: This sentence states that IO vertical concentration profiles were retrieved. Why are they not shown?

RESPONSE: The vertical profiles were retrieved on the few days that the radiative transfer calculations were made. However, they not shown as they do not add further information to the context of the study, which focuses only on the surface IO response to bio-geophysical oceanic parameters. Whether the IO is confined to the lowest 50 m or 500 m would not change these variation correlations or the conlcusions, as they do not depend on the absolute mixing ratios. IO being low even at the surface, it is difficult to retrieve any more than a surface mixing ratio value. The a priori profile shape would mostly influence any retrieved vertical profile with little information coming from the measurements. Hence we have not included this in the manuscript.

R1.10) Page 15548, line 24: Why was the NO2 from the MAX-DOAS not used to constrain the calculations? Please state that NO2 was indeed measured.

RESPONSE: NO2 is listed as one of the species fitting in the IO spectral window. We have not done any radiative transfer calculations for NO2, to retrieve surface mixing ratios, which would in any case be under the DOAS detection limit in the remote boundary layer. Hence it is not possible to use DOAS observations as a constraint in the remote environment.

R1.11) Page 15549, line 4: The use of the model to determine the IOx correction factor needs to be explained further. For example, the authors talk about observed surface IO, while my understanding is that the IO mixing ratios are more representative of the MBL average. Why can a daily average be used for this approach, doesn't the IO/I ratio change throughout the day? As the MAX-DOAS can be used to retrieve vertical profiles, why was not the entire profile compared with the model?

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RESPONSE: Yes, the reviewer is right to suggest that the IO/I ratio changes according to the time of day (although there is not a large variation for SZA<60 degrees) and this has been taken into account in the model. (Now mentioned in the manuscript). As referred to in the manuscript, the THAMO model has been used extensively in the past for studying iodine chemistry and we do not feel its necessary to explain it in further detail than presented for this study and have cited the previous studies with full model descriptions. The correlation we have presented is however with daily average values due to the fact that not all the parameters taken into consideration are available at sub-daily resolution. Hence, although it would be interesting to study diurnal variations in the future, for a first study of its kind, we felt it was more important to study longer temporal resolution changes in order to avoid effects of diurnal changes in other parameters, which would not be considered. In the future, we hope to be able to study the shorter timescale correlations.

R1.12) Page 15549 line 4: Since the O3 was not measured, how does the uncertainty in the O3, i.e. the potential difference between true and modeled O3, affect IOx.

RESPONSE: As mentioned, the IO:I $\sim 0.12 \times$ [O3]. This means that for 1 pptv of IO, a two-fold change in O3 from 20 ppb to 40 ppb would cause IOx to decrease by 0.24 pptv – which is smaller than the variation observed in the IOx over the study. This is now added in the manuscript.

R1.13) Page 15549, line 10 -12: There is no supporting analysis for this statement. Also, because only modeled NOx and O3 were used, the question is whether this actually reflects what is happening in the atmosphere or rather what happens in the model. The statement would be more convincing if actual NO2 data from the MAX-DOAS were used.

RESPONSE: As mentioned in response number (R1.10), the NO2 values from the MAX-DOAS cannot be used as constrain. Even though modelled NO2 values are used, it is well known that marine boundary layers are O3 destroying regimes due to

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low NO2 concentrations – typically less than 20 pptv. Changing the NO2 mixing ratio from 5 pptv to 20 pptv changes the IOx by ∼7%. This is now added to the manuscript.

R1.14) Page 15549, lines 15-17: As already mentioned above, which IO mixing ratios were used, those from the optimal estimation or those from scaling IO DSCDs with O4?

RESPONSE: Changed.

R.115) Figure 5: Please explain what the error bars in Figure 5 mean. The IOx mixing ratio error bars seem very low considering the errors of the IO DSCDs and the complex calculations that are needed to convert DSCDs into mixing ratios followed by the calculation to determine IOx. A detailed explanation of the error calculation, including all uncertainty terms is needed to convince the reader that the authors truly know IOx mixing ratios to within 0.1-0.2 ppt. Figure 5: What are the error bars for CH3I air and water? If these are statistical uncertainties, is it even possible to calculate a statistically significant CH3I flux? If the flux can indeed be calculated, please add the data to Figure 5.

RESPONSE: As mentioned in response to (R1.8), the error estimation for the O4 method is tricky. A description of the error propogation included is included in the supplementary text. However, it should be noted that the total errors in the calculation of IOx are indeed less that the variation observed through the cruise, which ranges from 0.4 to 1.2 pptv – almost a three fold change. The fluxes for CH3I were calculated and the correlation to the IOx is included in the figure 6 and discussed in the manuscript. We felt that the inclusion of the flux in figure 5 is not necessary considering we show the CH3I in air and water in the already crowded figure.

R1.16) Page 15552, line 7-9: The authors could test this hypothesis with CH3I, for which water concentrations and fluxes have been measured.

RESPONSE: We have now made correlation calculations for CH3I with SST and salin-

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ity as suggested. This is now added to the manuscript.

R1.17) Page 15552, line 19: I disagree with the authors that the parameters used in the correlation analysis do not co-vary. Figure 5 shows that SST and salinity do, to a certain extent, co-vary. Consequently the statement in line 19 needs to be backed up with a cross-correlation analysis of the different parameters. Should this analysis find a correlation between any of the parameters, the correlation analysis of IO with the respective parameters would need to be revisited.

RESPONSE: The referee is right to suggest that SST and salinity co-vary and indeed some other parameters also do. We meant that although some of the parameters may co-vary, not all of them do, indicating a complex mechanism, which can only be understood using a multivariate analysis. This has been changed in the manuscript.

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