

Response to interactive comments by anonymous Referee # 1:

The comments of the Referee are printed in usual black font and our answers are printed in **bold font**. New passages of the revised manuscript are printed in *italic*.

Comment 1

Referee # 1: This is an important paper which adds significantly to our understanding of iodine chemistry over the remote low-latitude oceans, in this case the western Pacific. The important conclusions are: 1) that the IO radical is present at levels which produce significant ozone depletion; 2) the IO is highest in the tropical (warmest) part of the cruise; 3) there is no correlation with chlorophyll; and 4) the observed IO cannot be accounted for with the measured iodocarbon flux i.e., an additional source of iodine (postulated here to be I₂) is required. As the paper points out, these conclusions have been tentatively reached in other recent studies (e.g. a ground-based campaign at Cape Verde, and a cruise in the eastern Pacific). However, this study confirms the earlier work, and extends our knowledge of the global distribution of IO (which it seems cannot be achieved from satellite observations over the ocean).

Authors: We thank Referee # 1 for the above summary and the positive comments on our manuscript. We considered the overall comments and the minor points in the revised manuscript (see comments below).

Comment 2

Referee # 1: My criticism of the paper is the length of the discussion devoted to the Max-DOAS technique for measuring IO, compared with the detail devoted to discussing the science, which leaves the paper unbalanced (I note that Dr Gomez Martin makes the same point in a comment).

Authors: We have discussed the MAX-DOAS technique for measuring IO, and in particular the vertical profile retrieval in detail. A detailed description of the analysis is very important, as the IO dSCDs as well as the signal-to-noise ratio are relatively low. Therefore, we feel that it is necessary to discuss the uncertainties of the retrieval, i.e. the errors and the averaging kernels, in detail, in order to give the reader information on the limitations of the method. Dr Gomez Martin has a few suggestions for improving the discussion of the data, but does not criticise the length of the MAX-DOAS evaluation.

Comment 3

Referee # 1: Max-DOAS is basically not a very good technique for making vertical profile measurements – which the authors demonstrate quite openly. In spite of all the correction factors which are applied, there is very little vertical

information contained in the signal (the averaging kernels in Fig. 3 demonstrate this, as well as the text on page 27488, lines 8-10). All one can do is show that most of the IO is close to the surface, and use the lowest elevation angle measurements to estimate a mixing ratio. Of course, until some other measurement method is available, Max-DOAS is all we have so this is not a criticism of using the technique per se.

Authors: We disagree that MAX-DOAS is not a very good technique for making vertical profile measurements, as numerous publications have already shown, e.g., Frieß et al. (2011), Wagner et al. (2011), Irie et al. (2011). The problem here is that the signal-to-noise ratio of the IO measurements is low compared to other trace gases with stronger optical density (e.g., NO₂ in polluted areas).

Comment 4

Referee # 1: The comparison between the Bremen and Heidelberg dSCDs in Figure 6 shows how sensitive the spectral deconvolution is to the various spectra that are included in the fit. It is not quite clear why this figure is included, since no further details are given about the Bremen instrument. Is this figure supposed to increase one's confidence in the technique – for this reader it had the opposite effect?! If the Bremen IO data is used subsequently in the paper, this is not made clear.

Authors: Figure 6 is included in the manuscript to confirm the IO dSCDs measured by the IUP Heidelberg. The data sets from Bremen and Heidelberg are in a good agreement and have a similar diurnal variation, although the retrieval settings are slightly different (see page 27492, line 5-11). The Bremen instrument is described in Peters et al. (2012). We inserted the following sentences in the revised manuscript for an explanation:

- page 27492, line 2: The inferred IO dSCDs were also compared to the measurements simultaneously taken with the Bremen instrument (*for instrument description see Peters et al. (2012)*) for 14 October 2009 (Fig. 6).
- page 27492, line 11: *Since both data sets showed an overall good agreement, for further analysis only the Heidelberg IO dSCDs were used.*

Comment 5

Referee # 1: The modelling part of the paper complements the measurements very well. The method used to convert the modelled vertical profiles into the “degraded” vertical profiles that a Max-DOAS would measure is a clever approach to deal with the lack of vertical resolution in the Max-DOAS. One interesting thing that this exercise reveals is that the relatively higher IO observed early in the morning during part 3 of the cruise is consistent with I₂ emission being a substantial iodine source. Overall, this is an impressive piece

of work which should be published after the authors consider the balance of the paper (see above), as well as the (mostly minor) points listed below.

Authors: We thank Referee # 1 for this encouraging comment. We have considered the balance of the paper in Comment 2. The minor points are addressed below.

Minor points

- page 27480, line 1: complemented, not corroborated
Authors: The change to *complemented* has been included in the revised manuscript.
- page 27489, line 5: unstable, not instable
Authors: The change to *unstable* has been implemented in the revised manuscript.
- page 27491, lines 24-28: this is an interesting observation, which should be discussed again later on in the modelling discussion.
Authors: The enhanced IO dSCDs as well as the O₄ dSCDs (not shown here) seen in the morning of 19 October 2009 are most likely caused by radiative transfer effects. On overcast days the length of the light path reaching the MAX-DOAS instrument changes a lot due to multiple scattering within clouds. The following sentence has been added to this paragraph in the revised manuscript: *The enhanced IO dSCDs as well as the O₄ dSCDs (not shown here) seen in the morning of 19 October are most likely caused by radiative transfer effects. On overcast days the length of the light path reaching the MAX-DOAS instrument changes a lot due to multiple scattering within clouds.*
- page 27492, line 26-27: this is another interesting finding. Is the interpretation that even elevated CH₃Cl emission does not compete with I₂? This should be discussed.
Authors: From the model calculations shown in Fig. 8, one can infer that the additional CH₂ClI in cruise part 3 causes an increase in IO VCD of about 1×10^{12} molec/cm² compared to cruise part 2, whereas I₂ contributes with about $(0.5 - 1) \times 10^{12}$ molec/cm². The following sentence has been added to the revised manuscript on page 27495, line 3: *The additional CH₂ClI observed in cruise part 3 causes an increase in the modelled IO VCDs of about 1×10^{12} molec/cm² compared to cruise part 2, whereas I₂ contributes with about $(0.5 - 1) \times 10^{12}$ molec/cm².*
- page 27497, line 7: the reaction of O₃ with DOM does not self-evidently make iodocarbons; need to explain where the iodine comes from.
Authors: The reaction of O₃ with DOM as a possible source for volatile organoiodine compounds at the ocean surface has been suggested by Garland and Curtis (1981) and Martino et al.

(2009) as stated in the manuscript. To make this reaction mechanism clear to the reader, the following passage is included in the revised manuscript on page 27493, line 13:

At the same time reactions of ozone with dissolved organic matter (*DOM*) at the ocean surface could have initiated the release of iodocarbons into the atmosphere. *When ozone reacts with dissolved iodide, hypoiodous acid (HOI) and molecular iodine (I₂) are formed at the ocean surface Garland et al. (1980). HOI and I₂ further react with DOM to produce dissolved organic iodine (DOI). Iodocarbons can then be produced from the oxidation of iodide by ozone and the reaction of HOI with organic molecules (Garland et al., 1980; Garland and Curtis, 1981; Martino et al., 2009).*

Bibliography

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