Atmos. Chem. Phys. Discuss., 12, C7942–C7948, 2012
www.atmos-chem-phys-discuss.net/12/C7942/2012/

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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Received and published: 10 October 2012

Response to interactive comments by sources Anonymous Referee #2

We thank the anonymous reviewer #2 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.

R2.1) The paper by Mahajan et al. describes observations of iodine monoxide and methyl iodide in the Eastern Pacific. These measurements are used for model and correlation studies indicating non-biological mechanism for the emission of iodine precursors. In general the paper is well written and an interesting piece of work and therefore mer- its publication in ACP. In particular observations presented here are very sparse

and possibly provide new insight into the distribution of reactive iodine over the oceans. However, like referee 1 I have serious concerns about the analysis presented in this study and I therefore suggest a major revision of the paper before publication.

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:

R2.2) Abstract: Please add LOS information for which slant columns up to 5*1013 molec/cm2 have been retrieved (corresponding to 1 ppt in which layer?). Avoid comments on the comparison with satellite instruments since this has not really proofed with the data set presented here (see comments below).

RESPONSE: The LOS is now added in the abstract. We feel that comparison with satellite observations is important and this is discussed further in the last comment.

R2.3) Introduction: Some studies are missing, Puentedura et al., 2012 (IO profile retrieval from Tenerife) or Oetjen, 2009 (IO observations from several sites, e.g. from the Maldives).

RESPONSE: Citation for Oetjen (2009) is now included. Puentedura et al. (2012) observations were made in the free troposphere and are hence not comparable to this study.

R2.4) At least a brief introduction to the MAX-DOAS technique is needed since not all readers of ACP are aware on this. Give references like Hönninger et al., 2004, Wittrock et al., 2004, Roscoe et al., 2010.

RESPONSE: A brief description is now added- 'A MAX-DOAS instrument was set up on the second deck of the research vessel. The instrument makes use of scattered sunlight along different elevation angles and by combination of several lines of sight including the zenith, the concentration of an absorber in the boundary layer can be

obtained either, in a first approximation by a simple geometric approach or alternatively, by simulating the light path with a radiative transfer model taking into account also multiple scattering effects and the correct treatment of the aerosol loading in the atmosphere (Hönninger et al., 2003; Platt and Stutz, 2008; Wagner, 2004)'.

R2.5) What is the time for one measurement cycle (all elevation angles in one wavelength region)? "The data were then averaged between 10 to 30 min". Is this for one angle? How often the instrument was switched between UV and Vis? What about wavelength stability while doing this?

RESPONSE: These details are now added to the manuscript – 'A complete cycle of elevation angles took $\sim$30 s to measure and the instrument focused on each wavelength window specified (see below) for one hour. There was no appreciable wavelength shift (<0.1 nm) noticed in the spectra and the spectra were recalibrated before analysis using the Fraunhoffer absorption lines. The data were then averaged for 30 min to improve the signal to noise ratio.'

R2.6) The IO was retrieved using the HITRAN 2003 cross section for H2O. Why not using the 2009 data set, which accounts also for small water vapour features in the area of the strongest IO band? In fact, the residual shown in Figure 2 of this study exhibits strong variation around 427 nm.

RESPONSE: Our analysis setup did include the HITRAN 2003 data and we thank the referee for bringing the 2009 dataset to our notice. We will ensure to use this in the future, however, for the current dataset, with the interference from the H2O lines being an order of magnitude smaller than the IO absorption, we do not feel it necessary to reanalyse all the data using the HITRAN cross-section from 2009.

R2.7) Why the authors have not included inelastic Vibrational Raman Scattering by oceanic water in their retrieval? Recent studies (Vountas et al., 2003, Dinter et al., 2005) have shown that this is relevant for open water bodies with low chlorophyll.

RESPONSE: Use of the raman scattering by oceanic water is needed for satellite spectra looking at the water surface. However, it is unlikely to have a major effect in spectra where one does not look at the water surface and has a very small fraction of photons due to scattering from the ocean surface. This is the reason it is not commonly used for MAX-DOAS retrievals.

R2.8) It is absolutely not clear to me, how the cloud index is calculated. Which wavelengths have been chosen? You have only 40nm in one spectrum, or not? Or do you have compared UV and Vis spectra not recorded simultaneously? What is the time resolution for the values?

RESPONSE: This has now been expanded on 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 (Sinreich et al., 2010).'

R2.9) Definitely the weakest part of the paper is the description of the steps leading from measured DSCDs to mixing ratios. What is finally used in the further analysis: results from the OE or those from simple geometric assumptions with just one elevation angle? As reviewer 1 I do not see any serious error propagation in the results presented here. What about systematic errors (e.g. cross sections), forward model errors (e.g.

a priori, aerosol load), smoothing errors, different wavelength regions used for aerosol and trace gas retrieval?

RESPONSE: Please check the detailed response to (R1.8). Further details on the errors are included in the supplementary text.

R2.10) p15548,l21: "The retrieved IO is confined within the boundary layer, with a steep gradient showing maximum mixing ratios at the surface." This statement has to be proven by showing profiles e.g. for one day with low and one with higher aerosol load.

RESPONSE: The DSCD gradient for clear sky conditions shows that this is clearly the case. For further discussion on this comment, please refer to comment (R1.9).

R2.11) Looking to Figure 3 I would see only 6 to 7 days where DSCDs for all LOS are well separated. This might have two reasons: Either on the other days the IO is not in the lowest layer or the aerosol load is much higher. For the latter one I would assume that the profile retrieval compensate for this effect calculating similar results for the mixing ratio on all days. In fact, IO values shown in Figure S1 are between 20âŮęS and 30âŮęN in the same range even with the (too?) small error bars given here. Therefore the statement on [p15549,l22] that "the estimated amplitude of the change in IOx around the equator is different to that of the IO DSCDs mainly because of the low O3" is not supported by the data set.

RESPONSE: Although subjectively the angle separation might not seem similar on most days in figure 3, only the data that passed the cloud filter, i.e., only DSCDs with strong angle separation were included for correlational analysis. Figure 3 is only to show the entire dataset and the variation in the DSCDs. The sentence in the manuscript regarding the IO and IOx variation is now corrected as the referee suggested.

R2.12) At least in the supplement I would like to see the aerosol load retrieved from the

O4 observations and a comparison between modelled and retrieved O4 slant columns. The time series for the IO mixing ratio has to be shown as well in Figure 5, not only in Figure S1.

RESPONSE: Using the O4 method ensures that the aerosol loading is not of direct importance and hence we have not shown them. Additionally, they are not central to the focus of the paper, which is on the correlation of IOx, rather than only the MAX-DOAS observations. The IOx mixing ratios are better suited to figure 5 considering the total iodine loading is the important parameter for correlational analysis rather than the IO concentrations since using only the IO mixing ratios does not take into account the change in O3. The IO mixing ratios are shown in the supplementary text.

R2.13) When IO mixing ratios used for the further analysis in this paper just based on 1âŮę measurements: How sure are the authors that these measurements are not affected by reflection from the water surface (in particular on days with higher wave acitivity)? The FOV of the instrument is 1âŮę which means that just 0.5âŮę uncertainty in the LOS is needed to hit the ground.

RESPONSE: We have now mentioned the errors on the line of sight in the manuscript. The angles are filtered for errors beyond 0.2 degrees, which ensures that we are not using spectra that hit the ground.

R2.14) The authors claim that there results are inconsistent with the paper published by Schönhardt et al., 2008. I'm quite critical about that for several reasons. First of all there is a clear statement in Schönhardt et al. that enhanced values seen above the tropical Western Pacific over or close to upwelling regions have to be treated with caution, since the signal-to-noise ratio of the retrieval is poorer than for other regions like the Antarctic. For that reason they never calculated mixing ratios or did other further analysis using the results for low latitudes. Furthermore the cruise track does not really match areas where the satellite (might) see enhanced IO. Most of these regions are closer to the continents. Possibly a minor point: Schönhardt et al. report on observa-

tions from September to November while the cruise was in April. I suggest to remove any statements on the comparison to satellite observations or at least rephrase the paragraph taking into account the uncertainties of both data sets. As already mentioned above the statement on [p15552, l27] that the MAXDOAS data set of IO peaks around 20âŰęS is not supported by the data when taking into account the error bars.

RESPONSE: We feel that one of the most important aspects of this study is the lack of an increase of IOx in the biologically active region as suggested by Schönhardt et al., 2008. Indeed the peak for the satellite data ranged between September - November but the satellite still sees elevated levels even in April, which is distinctly different from our dataset. The uncertainties on the satellite data, as the referee mentioned are indeed higher in this region, and our dataset helps constrain better the upper limits for the satellite, which is directly useful for further satellite retrievals. We have now added a sentence regarding the low signal-to-noise in the satellite observations above the open ocean. The peak in our dataset is indeed at 20 degrees S, although the referee is right in saying that it is not very different. This is now mentioned in the text.

Interactive comment on Atmos. Chem. Phys. Discuss., 12, 15541, 2012.