

Response to Referees and Comments

Iodine oxide in the global marine boundary layer

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We would like to thank both anonymous referees as well as Dr. Guzman for their constructive comments and also for their appreciation of our work. In the following we present our point-by-point answer (Authors Comment- AC) to each of their remarks on our manuscript (Referee Comment- RC, or Short Comment- SC).

Anonymous Referee #1

RC:

This is a very good paper which is suitable for publication in ACP, essentially as is. I did not find any substantive points to raise, but the authors may wish to consider one or two points made below.

The paper provides a very good synthesis of field data of IO measured by the MAXDOAS method during several marine cruises, spanning a good range of geographical locations worldwide. The observed levels are consistent with the source term for iodine being predominantly from the reaction of ozone with iodide in sea-water and subsequent chemical conversions and release of photolabile I, mainly in the form of HOI. Organic I (from measurements of RI species where available, otherwise estimated from global models) are a minor source of I – at least outside of the polar regions, and this study shows that the % contribution towards I production between inorganic and organic source gases varies from location to location. All the measurements are made using the MAX-DOAS method, which has a complex retrieval algorithm to generate slant column densities, and assumptions are then made regarding the sampling depth to convert to mixing ratios. In that regard including measurements using other methods based on fundamentally different principles of operation would be desirable in the future.

Perhaps the most important conclusion from this paper is that although the amounts of IO vary a little (0.4-1 ppt during the Malaspina cruise and other values close to this from other cruises), IO is present everywhere (polar regions not included in this analysis), demonstrating that iodine production from the oceans is a truly global phenomenon, and needs to be taken into account in Earth System Models, to properly calculate O₃, HO_x and other important intermediates which control, for example, the lifetimes and abundances of some non-CO₂ greenhouse gases (CH₄). The levels also show that the recently developed parameterisation for the release of inorganic I from the ocean is able to account for the typical levels observed (with the source rate varying owing to variations in O₃, SST, wind speed and sea-water I-). Direct measurements of HOI mixing ratios in the future though above the oceans would be highly desirable to confirm this.

AC:

We are grateful to Referee #1 for his/her comments and suggestions. We agree on his/her recommendations regarding objectives for future studies. We also consider that new measurements as well as a diversity of the employed measurement techniques would serve the purpose of a better understanding of the background chemistry despite the intrinsic uncertainties linked to each technique. We hope the scientific community will be encouraged by her/his suggestions. In the following we proceed to answer each of his/her comments referred to our manuscript.

Uncertainties are discussed in the supplementary material, and briefly in the main paper, but some mention of the uncertainty of the measurements should be given in the abstract following the range of values that are given. This will allow the reader to gauge how significant the observed levels of IO are compared with the instrumental uncertainties or detection limits (which will include the uncertainty in the mixing depths assumed to convert slant columns into mixing ratios, this depth varying from study to study).

AC:

As suggested, the measurement's uncertainty is now added also in the abstract ("30% uncertainty"). As the referee mentions, further details regarding uncertainties are already provided in the Supplementary Information (Sect. 1.1.2).

Page 22222, line 19, can the elevation angles also include the range of altitudes this corresponds to.

AC:

In general, the altitude sensed by a given MAX-DOAS elevation angle depends on diverse parameters like the physicochemical properties of the atmosphere, the ground albedo, the targeted wavelength and the particularities of the aimed trace gas itself. Since the MAX-DOAS technique has been widely used for years and there is a vast bibliography providing these sorts of details (e.g., Platt and Stutz, 2008 and references therein), we consider that including additional information regarding the technique itself could confuse the reader since in fact no vertical profile is intended in our work. If further information on the technique is needed, as suggested on our manuscript (Page 22222, lines 11-14) we recommend to refer to former works where detailed sensitivity studies were investigated for particularities such as the last scattering altitude for a given aerosol load and elevation angle (e.g., Hönninger et al., 2004). In the case of Malaspina and as stated in the manuscript (Page 8, line 5), photons gathered at an elevation angle of 2° referred to a mean last scattering altitude of 600 m.

Anonymous Referee #2

RC:

The manuscript by Prados-Roman et al. combines field observations of iodine monoxide with a 3D global model analysis of the most likely sources of reactive iodine in the marine boundary layer. The data originates from multi-axis DOAS measurements acquired during the Malaspina global circumnavigation in 2010. IO mixing ratios averaged in the lowest ~600m of the atmosphere are reported. In addition, IO data from earlier field experiments are included in the study. The global 3D atmospheric chemistry model CAM-Chem with various oceanic iodine source parameterizations was used to compare to the data. The parameterization including organic iodine precursors and an inorganic ocean surface source

of I2 and HOI, according to the parameterization of MacDonald et al., appears to match the data best. The authors thus conclude that an abiotic marine surface source, which accounts for 75% of the emitted iodine, is globally active.

This is a well written that presents interesting data and model results and carefully argues for the presence of an abiotic iodine source at the ocean surface. However, there are a number of issues that require more detailed explanations before the manuscript can be published in ACP:

AC: We kindly thank Referee #2 for his/her review which will help to improve our manuscript. We now proceed to answer her/his comments point-by-point.

1) A number of filtering procedures were applied to the data. It appears that after the filters have been applied, no IO DSCD observations below $\sim 1 \times 10^{13}$ molec. cm⁻² remain (Figure 3b). The insert in Figure 3b seems to indicate that all data with a 10° were excluded, even in scans where lower viewing elevation angles passed the filters. The exclusion of the larger viewing elevation angle data is rather counter-intuitive as MAXDOAS retrievals often lead to smaller, or at least similar, residual RMS for larger elevation viewing angles and no other filter should remove these data points if the smaller elevation angles passed the filters. This must be explained in more detail. While the reported IO mixing ratios were only derived from the 2° observations, the results in Figure 3b open the question on how appropriate the filtering procedures were. The fact that only 2° elevation angle data was used to derive the mixing ratios should be mentioned in the main text and not just in the supplement.

AC: We particularly thank this comment since, after having a closer look to the inset in Figure 3b addressed by the referee, we've realized there is an error in the colour of the empty squares (i.e., data below quality filters). By mistake the empty squares shown in the inset for the elevation angle of 10° presents the same colour code as for higher angles. This will be corrected in the new version of the manuscript. We do apologize for the mistake. Please bear in mind that the colour code for the main plot as well as for filled circles of the inset is correct. Indeed, as correctly stated by the referee and as shown in Fig. 3b by the filled circles (i.e., data above quality filters) not only in the main plot but also in the inset, there were times when measurements at high elevation angles were in fact statistically relevant.

Please note that, similarly to former studies (e.g., Mahajan et al., 2012), the quality filter applied to our measurements includes a diverse set of filters detailed in the SI such as the SZA, RMS, clouds, wind direction, etc., rendering this quality filter as a rather strict filter (necessary on the other hand given the size of Malaspina's dataset).

As suggested by the referee, besides the information that is already included in the SI, in the new manuscript the sentence (last paragraph of Sect. 3.1) "Therefore the values reported in Fig. 4 should be considered as the mean IO vmr in each of the aforementioned altitude ranges" will be completed with "linked to a given elevation angle (e.g., 2° in the case of Malaspina 2010)."

2) One of the main factors in converting MAX-DOAS column densities into mixing ratios is the assumption of the boundary layer height. The accuracy of the assumption of a 600m high boundary layer and the height of the boundary layer in the model merit a more detailed discussion. Ideally, the comparison between the observations and the model should be made using a vertical column density, perhaps in the lowest 1000m of the atmosphere, as this quantity would eliminate the boundary layer height uncertainty and thus be more closely related to the emissions.

AC: During Malaspina 2010 the upper layer of the sensed "column" with the MAX-DOAS instrument (referred to as MBL in the manuscript) was defined by the mean last scattering altitude

(LSA) of the photon reaching the detector when the MAX-DOAS was measuring at an elevation angle of 2° . This LSA was calculated by means of sensitivity studies performed with the radiative transfer model NIMO (Hay et al., 2012). Thus, there was no need of estimating the height of the MBL per se. Instead, the LSA for the given elevation angle was modelled considering the measurements of O_4 at same elevation angle (note that the vertical distribution of O_4 in the atmosphere is a known parameter). This is now made clearer in the Supplementary Information (Sect. 1.1.2) by completing the sentence (line 26) “with 600 m as the mean last scattering altitude (LSA)” with “of the photon reaching the detector at that elevation angle defining the upper layer of the sensed “column” (i.e., MBL)”. As stated in the manuscript (Page 8, line 5), based on this mean LSA modelled during the campaign, the Malaspina’s IO mixing ratios presented were therefore regarded as representative of the first 600 m of the atmosphere (see also Fig. 1 below).

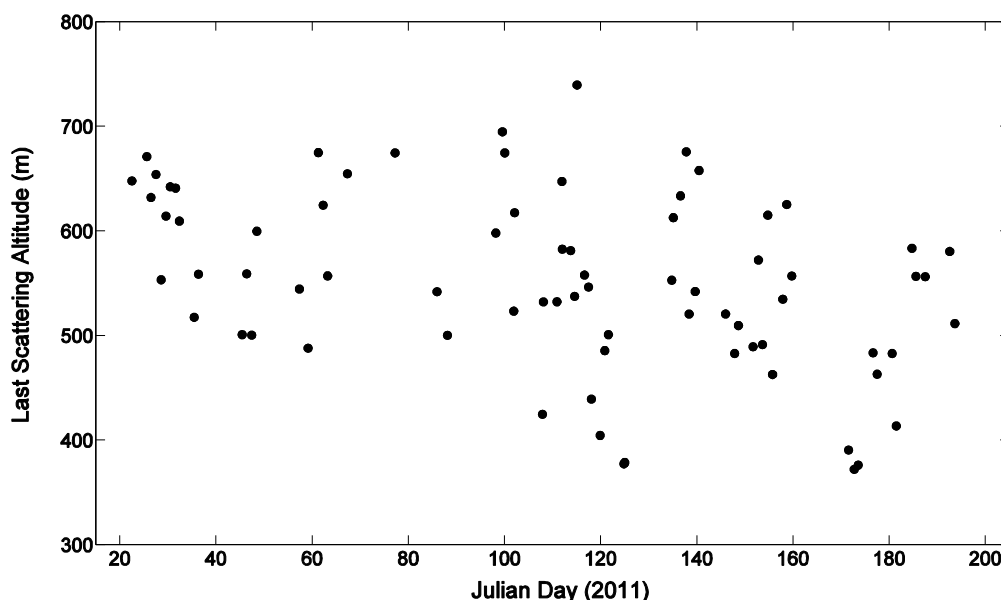


Fig. 1: Modelled mean last scattering altitude (2° elevation angle) during Malaspina’s expedition.

Note that this same altitude range was considered for the CAM-Chem output when comparing measured and modelled IO mixing ratios in the manuscript (i.e., 0-600 m). The same applies for the other campaigns bearing in mind that each campaign employed a different elevation angle for the retrieval of mixing ratios, yielding therefore a different intrinsic definition of the “column” sensed (MBL) for each campaign. This is now made clearer in the manuscript by completing the sentence (first paragraph of Sect. 3.2) “The performance of the model was evaluated by comparing modelled and observed IO mixing ratios in the MBL” with “for the aforementioned particular altitude range sensed during each campaign”.

3) Does the 3D model include clouds? If so, was model data filtered in the same way as observations? If not, could there be a bias in the model as cloudy days were excluded from the data? This needs a more detailed explanation.

AC: Generally speaking, the cloud formation, microphysics and precipitation schemes are indeed parameterised in CAM-Chem. The current version of the model includes improvements on the representation of deep convection, plume dilution and cloud fraction distributions by means of

introducing a Convective Momentum Transport scheme. As mentioned in the manuscript (Sect. 2.2), we recommend the reader to refer to the study of Lamarque et al., (2012) for further details on the model.

In our work, as stated in the manuscript (last paragraph of Sect. 2.2.1) and similarly to the study of Saiz-Lopez et al. (2014), we considered a specified dynamic mode based on the meteorological fields from a previous climatological simulation representative of the 2000-2010 decade. Therefore the geographical and temporal evolution of the cloud fields and precipitation rates used were climatological (i.e., not representative of the particular meteorology of any specific year). Thus, the model cloudiness cannot be compared directly to the specific conditions of the Malaspina 2010 cruise. Instead, based on that climatology (i.e., the most probable situation from a statistical point of view), we applied a temporal mask when computing the monthly model averages to consider only day-time mixing ratios at any given latitude and longitude in the same way as for the experimental data. It is worth mentioning that, within all the unknowns and uncertainties related to the implementation of the iodine chemistry into a 3D global model, the presence of clouds are only a minor component and, in any case, their stronger impacts are associated to the washout efficiency by in-cloud and below cloud scavenging of inorganic iodine species (Lamarque et al., 2012; Saiz-Lopez et al., 2014). Note that our work shows that, independently of the absolute levels that could be affected by unaccounted clouds in the model, both modelled and measured mixing ratios are compatible and indicate the ubiquitous presence of IO in the MBL.

In summary, this manuscript is well suited for publication in ACP. I recommend publication after the issues described above have been addressed.

AC: We appreciate Referee#2's recognition. We consider with this answer we have covered all the issues addressed by the referee.

Dr. Guzman

SC:

The manuscript “Iodine oxide in the global marine boundary layer” by Prados-Roman et al. presents multi-axis DOAS measurements of IO radical mixing ratios (< 1 pptv, altitude ≤ 600 m) performed over the marine boundary layer (MBL). A combined analysis with other field data suggests that iodine driven chemistry is of global importance over the oceans. A 3D CAM-Chem model discerning the contribution of organic and inorganic emissions (specifically hypoiodous acid and molecular iodine), and their associated geographical dependence, estimates that 75% of the total iodine oxide budget is of abiotic origin in the global MBL. This manuscript is an important contribution to understand the oxidizing capacity of the atmosphere and presents new data to support an abiotic mechanism is operative over open ocean waters. However, it would be important to consider in this manuscript a recent laboratory study by Pillar et al. (Environ. Sci. Technol., 2013, 47, 10971–10979, <http://dx.doi.org/10.1021/es401700h>) that indicates how sea spray aerosol production and in-situ oxidation produces hypoiodous acid and molecular iodine. Guzman et al. (J. Phys. Chem. A, 2012, 116, 5428–5435, <http://dx.doi.org/10.1021/jp3011316>) studied the enrichment of halides during aerosolization of seawater mimic samples providing new insights about how concentration effects could be included in a model. More importantly, it would be

interesting to discuss in the final version of the manuscript to be published in ACP how reactions at the air–water interface of sea spray, followed by transfer of reactive products to the gas-phase (Environ. Sci. Technol., 2013, 47, 10971–10979, <http://dx.doi.org/10.1021/es401700h>) contributes to the model presented. In addition, it would be important to connect the manuscript with Pillar et al. previously proposal indicating that 1) the actual source of reactive iodine species will vary geographically., 2) the production of sea spray will be sensitive to local conditions, particularly surface winds, 3) the production of iodine will depend on factors such as temperature, humidity, and the concentration of halogen species, and 4) 3D models should be chosen over 1D models to approach this problem.

AC: We thank Dr. Guzman for his appreciation of our work and comments. Note that the references Dr. Guzman addresses relate to the heterogeneous chemistry behind marine aerosol. Our work focuses on the measured ubiquity of IO in the MBL and on modeling the oceanic inorganic vs. organic contribution to the emitted iodine. Although the model used in our work included recycling of HOI, IONO₂ and INO₂ in aerosols (see also Saiz-Lopez et al., 2014), getting into the particularities of the different pathways such as the mechanism proposed in the study of Pillar et al. (2013) is actually out of the scope of our current study. Nevertheless, in agreement with Dr. Guzman, we also consider the interactions of halides and sea spray a very interesting topic worth looking at in future works where both measurements and model studies could be combined.