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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Iodine's impact on tropospheric oxidants: a global model study in GEOS-Chem" *by* T. Sherwen et al.

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Response to reviewers' comments

We thank the reviewers for taking the time to provide us with thorough set of reviews for the paper. We have made all of the changes that they have suggested as we believe that this has significantly improved the paper.

We address their comments in turn now.

Reviewer 1 (Rolf Sander).

"Section 5.2 provides a very interesting analysis of the ozone budget. Given the title of the manuscript, it is probably the most important section of all. Unfortunately, only two

model runs are compared here. Additional model runs are not mentioned until section 6. I'd like to make the following suggestions: [1] Present all model runs (including the sensitivity studies) in section 2, the model description section. [2] For clarity, it may be helpful to define and use concise names instead of the somewhat lengthy phrases currently used for the sensitivity runs, e.g.: "no hal" ! "NOHAL" "standard GEOS-Chem (v9-2)" ! "BROMINE" "just iodine" ! "IODINE" "iodine simulation" ! "BR+I" or "FULLHAL" [3] Add all simulations to Table A1, then move the table from the appendix into the main part. [4] Add the results of NOHAL and IODINE to Table 7 and analyze their ozone budgets also in section 5.2."

[1] We attempted to include the description of all of the simulations (including the sensitivity studies) in together in a single section. This created a very long and turgid section which ended up destroying the flow of the paper and would present the reader with a somewhat confused perspective of our work. We would argue that the clarity of the paper in better with the current arrangement which described the iodine simulation against what is now the standard GEOS-Chem simulation (ie with bromine) (Sections 3, 4, 5). We then have a section where we compare the impacts of bromine and iodine (Section 6). We then have a section where we investigate the sensitivity of the iodine simulation to various uncertainties in the iodine chemistry (Section 7). We have adopted the reviewer suggestions on naming of the simulation and have tried to improve the clarity of the document. [2] We have adopted this suggestion. [3] We have adopted this suggestion [4] We have adopted this suggestion.

"Abstract and elsewhere: "(350 < hPa < 900)"[.] This is incorrect. You probably wanted to write "(350 hPa < p < 900 hPa)" " We have adopted this through the manuscript.

"The term OX is used in the abstract already but not defined until section 5.2. Please define all acronyms when they are first used. Other expressions that must be defined are: IOX, CH2IX, PAN, PMN, PPN, and MPN." We have updated to the text to include these definitions.

" I think the introduction is much too long. For example, it contains [repetitions] like "The photolysis of O3 produces an electronically excited oxygen atom (O(1D)), which can react with a water molecule to produce two OH radicals." and "O3 is chemically lost in the troposphere predominantly through its photolysis in the presence of water to produce OH. " I suggest to shorten the introduction significantly and simply refer to the review by Saiz-Lopez et al. (2012) in Chem. Rev." We have reduced the size of the introduction.

"It is difficult to judge the model output without knowing the model input, i.e. the distribution of the emission fields. The text only states that inorganic iodine emissions are calculated using equations from Carpenter et al. (2013). In accordance with the ACP data policy (http://www.atmospheric-chemistry-and-physics. net/about/data_policy.html), I suggest to provide the emission fields as a supplement to this article."

A figures showing emission fields of inorganic iodine have now been added to the main section (Figure 1).

" Page 20973, line 22: ". . . approximately evenly sources. . . " Something seems wrong with this sentence." We have updated the text.

"Page 20974, line 13: "lowest most model level" Change to "lowermost"." We have updated the text.

"Section 5.2: Why are the numbers in the text different from the numbers in Tab. 7? The values are 748 vs 750 for iodine and 178 vs 184 for bromine." For iodine this was due to rounding issues and we have updated the text. For bromine this was a typo and we have updated the text.

"Page 20977: The calculation of the diurnal change is explained in the text as well as in the caption of Fig. 14. I don't think it is necessary to duplicate this." We have removed the explanation from the text and just have it in the caption.

(2.09) Summary and Conclusion sections

"It is unusual to have two separate sections called "Summary" and "Conclusions". Can they be combined?" The summary (section 7.7) solely considers the information presented in the sensitivity section, whereas the conclusion section provides a plenary to the whole paper. We have changed the title to "Summary of sensitivity simulations" for clarity.

"Being a persistent publication, I'd prefer that you cite my paper (doi: 10.5194/acp- 15-4399-2015) instead of my web page (Sander, 1999). The Henry's law data in the paper and on the web are the same." The citation has been update to Sander et al (2015) as requested.

"In Table 2, you correctly list the physical Henry's law constant of HI as 25 M/atm. However, the effective solubility, taking into account almost complete dissociation of HI into H+ and I-, is much larger. Is this considered in the model?" We do consider the effective solubility. We have included text to explain this and updated the table.

"In Table 2, you give Vogt et al. (1999) as the reference for H(INO2) = 3:00 10-1 M/atm. However, Vogt et al. (1999) assume infinity. Please check this discrepancy." This was a mistake. The the Henry's law for INO2 given in table is by analogy with BrNO2, not from vogt et al (1999). This has been updated in table 2.

"Table 3: I cannot see the reaction IO + ClO here. Is it not included in the mechanism?" We do not consider chlorine chemistry in this version of the model. We have future plans to include chlorine chemistry. (2.14) IO +_IO reaction

"Table 4: The reaction IO + IO [=>] I + OIO (T1) has no pressure dependence. Why is it listed as a termolecular reaction with "+O2" in the equation?" Tables 3 and 4 have been updated to be clearer as to how we calculate termolecular reactions when pressure dependences are not available.

"Figure 6 and 7: You show the species IONO and IONO2 in the plots. They are probably the same as INO2 and INO3 in the text. A consistent terminology should be used." We

have updated the text to be consistent.

“From the context, it becomes clear that Figures 7, 8, 9, 12, and 13 refer to the “iodine simulation”. Nevertheless, I think it would be helpful to mention this explicitly in the figure captions.” The manuscript has been updated so that simulation name (e.g. “Br+I”) is included in all figure captions

“Fig. 14: The calculation of the diurnal change seems to be inconsistent. If you subtract the maximum ozone value, then you should also divide by the maximum (not the daily mean). For example, if the maximum is 100 nmol/mol, and the mean is 50 nmol/mol, then a complete (100 %) ozone destruction would result in a diurnal change value of 200 % using your formula.” We have changed out data processing to follow this suggestion and updated the figures and text. There is no change in our conclusions.

“According to the IUPAC Recommendations (page 1387 of Schwartz & Warneck “Units for use in atmospheric chemistry”, Pure & Appl. Chem., 67(8/9), 1377-1406, 1995, http://www.iupac.org/publications/pac/67/8/1377/pdf) the usage of “ppb” and “ppt” is discouraged for several reasons. Instead, “nmol/mol” and “pmol/mol” should be used for gas-phase mole fractions. I suggest to replace the obsolete units.” “Page 20963, lines 22: “at high IO concentrations (> 2 pptv)” Change to: IO mixing ratios.”

“Page 20977, lines 14: “BrO concentrations (0.4 pptv)” Change to: BrO mixing ratios. ” Units have been updated to recommended IUPAC units throughout the text and we have used mixing ratio instead of concentration.

Reviewer 2.

“This is a long manuscript and provides a lot of information. I would recommend to re-write some parts of this manuscript with clear organization. However, saying this - there is potentially some really good useful science here, it is just lost beneath the overload of figures and tables.” Following both reviewer’s comments we have attempted to clarify the flow of the paper.

“Starting with the introduction section, 5 pages. It needs to be shortened. For example, the first paragraph could be a general explanation of the chemistry of the troposphere, including the main oxidants in the troposphere, OH and O3, and NO-NO2-O3 systems in the presence of organic compounds. The second paragraph, could start with the halogen chemistry and how it affects the ozone concentration.” Both reviewers make this comment so we have shortened the introduction.

“Page 20962, line 28: Moreover, the recent sea-to-air flux climatology of Ziska et al. (2013) could be also cited in the global organic halogen emissions part.” We have included this reference.

“I also agree with reviewer R. Sander that the model runs need to use concise names. Then section 2 and 6 would be clarified.” We have adopted this suggestion.

“Section 2, page 20966, lines 15-16: The model is run for “two years, (2004-2006)” (this is three years!) and use “the final year 2005”? Something seems wrong with this part.” This sentence has been updated to read “two years (2004 and 2005)” instead of “(2004-2006)”.

“I understand that in all the analysis, the model resolution is 2 x 2.5 and only the sensitivity studies are run with the model resolution at 4 x 5. I suggest to explain both model resolutions, 2 x 2.5 and 4 x 5, in section 2.” We have included text to make this clear.

“In section 2.1 the parametrization for the inorganic iodine compounds from Carpenter et al. (2013) is briefly described. I suggest to briefly describe how these monthly emissions of Ordóñez et al. (2012) are calculated. For example, in the abstract of Ordóñez et al. (2012) “Ocean emissions of (...) parametrized by a biogenic chlorophyll a (chl-a) dependent source in the tropical oceans (...)“ ” We updated the sentence on this within the text.

“In the last paragraph of section 3.1 is discussed the model overestimation of I2 con-

centrations. However, the parametrization for the inorganic iodine (I2, HOI) from Carpenter et al 2013 is not mentioned in this section. Could be any limitation in this parametrization that also contribute to the overestimation of I2? This parametrization depends on 1/wind speed. What happen at low wind speeds? I also agree with reviewer R. Sander that the emission fields need to be included as a supplement to this article." We have added a plot of the inorganic emissions to the paper (figure 1) and have indicated that the IX emissions ratio may also contribute to this in the text. We have updated the text to clarify the wind speed limits.

"Table 7 gives a lot of information, however only a few results are discussed in section 5.2. In addition, I couldn't find the global tropospheric OX loss of "184 Tg yr-1 from bromine chemistry" in Table 7. I suggest to rewrite this section in a clear way and thinking that the reader needs to find easily the information from Table 7 in Section 5.2." We discuss key point in this table rather than going through all of the results which would become fairly turgid and boring. The table is designed to allow for a comprehensive comparison to other global model. We reviewer has noted a typo in our Ox loss for BrO which we have updated in the text.

(4.08) Clarity of boxplots

"Boxplots in the manuscript are confusing. For example lets take a look at Figure 4. From first glance its appears that the model and observations data are made at different latitudes or times stamps, and I assume this is not the case. The same for Figure 5 with the altitude. I suggest to plot both model and observations at the same time and latitude, instead of one next to the other, or explain in more detail what these boxplots show us."

"I suggest to give more information about the axis of each figure. Figures 5 and 11 miss the names of the species "IO" and "O3" in the x-axis. In addition, I suggest to use the same structure in the axis. For example in the axis of Fig. 4 " IO concentration (pptv)" and in the axis of Fig. 10 " O3 / ppbv"." We have adopted the reviewer suggestions

here and have attempted to improve the aesthetics of the plots as suggested and have included more information in the figure captions.

"Page 20960, second paragraph: I suggest to add after "to produce two OH radicals" that this process is dominated by the tropics." This comment was considered with other reviewer comments when re-structuring the introduction, and broader description is now present within the introduction.

"Page 20966, line 3: Are there a lot of species that have linearized chemistry in the stratosphere as an upper BC for the troposphere? If there are only a few I suggest to specify these species." In excess of thirty species are treated this way, therefore this have not been included within the text.

"Page 20966, line 19: "spun-up" Change to: spin-up" Updated.

"Page 20967, Section 2.2: The last sentence in the first paragraph is repeated in the second paragraph." These two paragraphs describe wet and dry deposition respectively. The final sentence of each paragraph states the treatment of iodine aerosol in the model. The sentence has been amended to state whether it is referring to dry or wet deposition.

"Pages 20969-20970: Surface mixing [ratios] of IO, IO, OIO, HI, IONO and IONO2 from Figures 1 and 2 are not discussed in the document. It might be useful some discussion in sections 4.1 and 4.2." A Sentence has been added following the reviewers request. Due to limited or nonexistent measurements of these species in the remote marine boundary layer, these species offer limited ability to constrain the modelled values. Focus was given to comparing against the relative large, but still limited, dataset of observations IO in the literature.

"Page 20970, lines 13-14: "Concentrations of CH2ICl appear to be better simulated (Fig.3)". We could say that CH2ICl is better simulated in the MBL. However, there is a lack of observational data above the MBL. A more detailed discussion is lacking here."

The sentence describing CH2ICl observations has been updated from “Concentrations of CH2ICl appear to be better simulated (Fig 3)” to “Concentrations of CH2ICl appear to be better simulated in marine boundary layer where measurements are available (Fig 3).”

“Page 20970, line 22 : “over estimate” Change to: overestimate” Updated.

“Page 20971, line 7: “over estimate”. Change to: overestimate” Updated from “under and over estimates” to “under- and over- estimates”

“Page 20974, line 8: “tropspheric” Change to: tropospheric” Updated.

“Page 20976, line 23: the word “O3” needs to be added after “Global tropospheric burdens of”” Updated.

“Page 20977, line 7: “fractional diurnal fractional”. Something seems wrong with this sentence. The manuscript has been updated to remove the word repetition.

“Page 20980, first paragraph: The “I2Ox exp. X-sections” simulation is not defined in the manuscript.”

This was a typo and has been updated in the draft.

“Figure 11: The pressure needs to be turned in these plots. 1000 hPa should be in the surface and not in the top of the atmosphere.” This had been updated.

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