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Atmospheric
Chemistry
and Physics
Discussions

Interactive comment on “Constraints on inorganic gaseous iodine in the tropical upper troposphere and stratosphere inferred from balloon-borne solar occultation observations” *by* A. Butz et al.

A. Butz et al.

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Reply to review 2

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« This paper reports upper limits of IO and OIO in the tropical upper troposphere and stratosphere inferred from balloon-borne solar occultation observations in Northern Brazil. Photochemical modeling is also used to estimate the compatible upper limits for the total gaseous inorganic iodine burden (Iy). Being clearly written and well structured, this paper is a relevant contribution for understanding and quantifying the ozone destruction by iodine species in the upper troposphere and stratosphere. I recommend

the paper for publication in ACP after addressing the following comments: »

We thank the reviewer for his comments and the appreciation of our work.

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« Specific comments page 14649, line 29: the authors should mention here the name of the station (Teresina).»

page 14649, line 1:

"(5.1°S, 42.9°W)"

-> "(Teresina, 5.1°S, 42.9°W)"

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« Page 14650, lines 2-7: At this stage, the authors should elaborate a bit more of the ground- based measurements. It is only when reading the legend of Figure 1 we learn that the long-path DOAS technique is used. Also the site of the ground-based measurements is located at the Brazilian coast at about 350 km from the balloon launch site. Did the 2005 and 2008 balloons fly in the direction of the coast ? This is an important point since the authors suggest that the sampling area is a source region of iodinated compounds.»

We supplement the main text by some more detail on the ground-based measurements.

We emphasize that we refer to these ground-based measurements in order to merely illustrate that iodine-bearing compounds are detectable in the boundary layer in the vicinity of the balloon launch site and that generally iodine-bearing air masses could be available for transport to the upper atmosphere. Obviously, we do not want to claim a direct link between the air masses sampled by our ground-based measurements in the lower troposphere and by the balloon-borne measurements in the upper troposphere and lower stratosphere at least half a year later. The balloon borne measurements were conducted in June during sunset and sunrise from around 5°S latitude, implying that the respective lines-of-sight (a more relevant measure than the balloon position) of the balloon-borne spectrometers pointed into north-western direction for sunset and north-eastern direction for sunrise, i.e. in parallel to or slightly toward the Brazilian coast. However, we argue in the manuscript (page 14664, 2nd paragraph) that most probably due to horizontal transport the entrainment area for the air masses sampled in the upper troposphere and particularly lower stratosphere is larger than the local distance between our measurement points and the Brazilian coast.

page 14650, line 2:

"Six months before the first balloon flight, we conducted ground-based measurements at the Brazilian coast approximately 350 km to the north-east of the balloon launch site. From the visible spectra recorded in a setup comparable to Peters et al. (2005), we infer IO abundances up to (0.82±0.31) ppt (Fig. 1) in the marine boundary layer suggesting that our sampling area is indeed a source region of iodinated compounds."

-> "Six months before the first balloon flight, we conducted ground-based measurements at the Brazilian coast (Alcântara, 2.4°S, 44.4°W) approximately 350 km to the north-east of the balloon launch site. From spectra recorded in the visible spectral range by a long-path DOAS setup comparable to the one described in Peters et al. (2005), we infer IO abundances along a 29 km absorption path in the marine boundary layer between the mainland and an island in the bay of Sao Marcos. IO concentrations up to (0.82±0.31) ppt (Fig. 1) suggest that our larger sampling area is a source region of iodinated compounds."

Figure 1, caption:

"Fig.1 Time series of IO measured by an active long-path DOAS setup along a 29 km absorption path in the marine boundary layer nearby Alcantara (2.4° S, 44.4° W), Brazil. The left abscissa shows inferred IO volume mixing ratio (boxes with error bars). The right abscissa correlates the local tides (blue line). The detection limit of the experiment is estimated 0.3 ppt (dotted black line). Nighttime is shaded grey."

-> "Fig.1 Time series of IO measured along a 29 km absorption path in the marine boundary layer nearby Alcantara (2.4°S, 44.4°W), Brazil. The left abscissa shows inferred IO volume mixing ratio (boxes with error bars). The right abscissa correlates the local tides (blue line). The detection limit of the experiment is estimated 0.3 ppt (dotted black line). Nighttime is shaded grey."

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« Page 14651, lines 9-12: What are the assumptions used for the ray tracing (Earth sphericity, refraction, aerosols, ...) ? This should appear in the manuscript. Also the assumption is made that the absorber vmr is constant along individual lines-of-sight. Could the authors test the validity of this assumption ?»

We supplement the manuscript by more information on the ray-tracing method.

Concerning the assumption of constant volume mixing ratio along individual lines-of-sight, we refer to our reply to reviewer 1 where we justify the assumption in detail. Briefly summarizing, the assumption is acceptable since our solar-occultation measurements are mostly sensitive to one individual atmospheric layer, i.e. the tangent layer. Thus, the shape of the absorber profile plays a minor role. Further, the test runs with modelled IO and OIO profile shapes indicate that our assumption yields conservative estimates of the IO and OIO concentrations/upper limits i.e. upper limits of IO and OIO would be lower when using modelled profile shapes. Finally, we would like to keep the first part of our study free of any photochemical modelling given the uncertainties of the model parameters.

page 14651, line 11, added:

"Thereby, the ray-tracing model assumes a spherical, refractive, horizontally homogeneous, non-scattering atmosphere where ambient pressure and temperature are provided by the meteorological support of the balloon flight."

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« Page 14652, lines 12-15 and page 14653, lines 20-27: The authors have selected the IO and OIO absorption cross sections as in Bösch et al. (2003). However, new cross section sets have been published since then. This point merits a more detailed and quantitative discussion since this can have a strong impact on the IO and OIO SCDs and therefore on the inferred inorganic iodine burden Iy. A thorough error budget for IO and OIO SCDs including statistical and systematic errors would help.»

The inferred IO and OIO SCDs, e.g. shown in Fig. 2, have error bars that correspond to the 2-sigma statistical errors provided by a standard least-squares fitting routine. This is stated on page 14654, line 17-18, followed by a discussion on the interpretation of these errors as detection limits. Systemtatic errors are discussed from page 14655, line 18, to page 14656, line 28, covering errors originating from inaccurate removal of O3 and NO2 absorption signals, instrumental issues, deficiencies of the CLD correction term, unaccounted absorbers. Finally, we conclude that systematic errors affecting our retrievals cannot be excluded and thus, we refrain from claiming detection of IO even though retrieved SCDs are occasionally higher than the statistical 2-sigma error. When translating IO and OIO upper limits into upper limits of Iy, systematic errors of the photochemical parameters have to be considered. This is discussed in detail from page 14661, line 3, to page 14662, line 2, and illustrated by Fig. 5 and 6.

We concede that our study does not provide quantification of these systematic errors except for the photochemical modelling error which is easily accessible through sensitivity studies. However, we are not aware of any possibility to quantify the other error sources given that we do not dispose of a validation data set.

Concerning IO and OIO absorption cross section, the manuscript explicitly mentions the studies of Gomez-Martin et al. (2005), Spietz et al. (2005), and Dillon et al. (2005), Joseph et al. (2005), and Tucceri et al. (2005), Ingham et al. (2000) (page 14652, line 11, and page 14653, line 24) and also gives typical values for the vibrational bands

of IO at 427.2 nm and of OIO at 549 nm. Since our IO absorption cross section is significantly smaller than found by more recent studies, we explicitly state that "IO upper limits would be lower by a factor ∼0.75 when using absorption the cross section of Spietz et al. (2005)" and that the same applies to Iy upper limits derived from IO (page 14663, line 17). As a reply to reviewer 1, we explicitly mention the "factor ∼0.75" in section 2 of the revised version of the manuscript.

Given that the manuscript already includes quite substantial discussion on random and systematic errors as well as the employed absorption cross sections, we would like keep the text as is. However, we are grateful for any information on recent developments and for ideas on quantification of the systematic errors.

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« Page 14666, lines 3-24: The impact of IO and OIO on stratospheric ozone is an important outcome of the present study but in the current version of the manuscript, it is mainly a short summary on what it has been discussed in Bösch et al. (2003) and WMO-2006. Could the authors elaborate a bit more on this with respect to their own findings and photochemical model, e.g. discussing the impact of using the JPL-2006 kinetics, which a major change with respect to Bösch et al. (2003) and WMO-2006.»

In reaction to a similar comment by reviewer 1, we extended the discussion on implications for ozone loss in the manuscript.

Our model does not use JPL-2006 for iodine-involving reactions but does use "Table 2 in Bösch et al. (2003) unless stated otherwise" (page 14667, line 12). Exceptions, for which JPL-2006 is indeed used, are reactions (R2 - IO photolysis), (R4 - IONO2 formation), (R6 - HOI photolysis), and (R7 - IONO2 photolysis) (page 14658, line 17). All other reactions not involving iodine are also implemented according to JPL-2006 (page 14657, line 8).

We point out that recommendations of Bösch et al. (2003) and JPL-2006 concerning iodine chemistry are mostly equivalent. Some reactions listed by Bösch et al. (2003) are (partially) missing in JPL-2006, the reactions listed above have been updated by JPL-2006. In detail, the differences between our study and Bösch et al. (2003) concerning iodine photochemistry are the following:

- (R2 - IO photolysis): Bösch et al. (2003) used the IO absorption cross section of Harwood et al. (1997) which is higher than the compilation recommended by JPL-2006. Our study assumes 30% uncertainty of the IO photolysis rate according to Bösch et al. (2003).

- (R4 - IONO2 formation): Bösch et al. (2003) refers to JPL-1997 which recommends $\sim$10% slower reaction rate for IO + NO2 than JPL-2006. We adopt the JPL-2006 uncertainty factor 1.3 (at room temperature increasing to higher and lower temperatures).

- (R6 - HOI photolysis): Bösch et al. (2003) used the absorption cross section of Rowley et al. (1999). JPL-2006 recommends the average values of Rowley et al. (1999) and Bauer et al. (2000) which are in "reasonable agreement" (JPL-2006, page 4-196). Our study assumes 50% uncertainty of the HOI photolysis rate according to Bösch et al. (2003).

- (R7 - IONO2 photolysis): The recommendations of Bösch et al. (2003) and JPL-2006 are equivalent. Thus, our statement that reaction (R7) was updated with JPL-2006 is not appropriate. We change the manuscript accordingly.

The differences between the photochemical kinetics used by our study and by Bösch et al. (2003) are well within the uncertainty range adopted for our sensitivity runs that estimate the overall photochemical modelling error. We conclude that the estimates for iodine-induced ozone loss calculated by Bösch et al. (2003) are valid for our study as well within the photochemical modelling uncertainty.

References:

Rowley, D. M., J. C. Mössinger, R. A. Cox, and R. L. Jones; The UV-visible cross section and atmospheric photolysis rate of HOI, J. Atmos. Chem., 34, 137– 151, 1999

Bauer, D., T. Ingham, S. A. Carl, G. K. Moortgat and J. N. Crowley: J. Phys. Chem., 102, 2857-2864,1998

Harwood, M. H., J. B. Burkholder, M. Hunter, R. W. Fox, and A. R. Ravishankara: Absorption cross sections, and self-reaction kinetics of the IO radical, Phys. Chem. A, 101, 853–863, 1997.

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« Technical corrections

Page 14670, line 33: 2 should be in subscript in IONO2.»

Done.

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Further modifications:

We update the reference Gomez Martin et al., 2008: Gómez Martín, J. C., S. H. Ashworth, A. S. Mahajan, and J. M. C. Plane: Photochemistry of OIO: Laboratory study and atmospheric implications, Geophys. Res. Lett., 36, L09802, doi:10.1029/2009GL037642, 2009

page 14666, line 16:

fractional contribution of iodine

-> fractional contribution of 0.1 ppt iodine

Interactive comment on Atmos. Chem. Phys. Discuss., 9, 14645, 2009.