**Atmospheric
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Discussions**

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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.

a.butz@sron.nl

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« The study by Butz et al. addresses an important issue in research on stratospheric ozone, namely the question what the impact is of iodine catalyzed chemistry on stratospheric ozone depletion. The measurements presented provide new information on the upper limit of the stratospheric iodine burden deduced from recent balloon-borne measurements. »

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

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« I suggest that the paper should discuss in more detail the importance of the new upper limits of stratospheric iodine on ozone loss estimates. »

The manuscript addresses implications for ozone loss estimates on page 14666, starting with "Implications for stratospheric ozone have been discussed in detail by Bösch et al. (2003) and WMO- 2006." (l. 3), followed by a summary of the quoted studies. Further, abstract and conclusions state "that iodine-mediated ozone loss plays only a minor role for stratospheric photochemistry." (p.14647, l.12, cf. p. 14667, l.13). Since the photochemical scheme employed here, is not significantly different from Bösch et al., (2003) and WMO-2006, we decided not to re-do an explicit modelling study concerning ozone loss estimates, but to refer to previous studies. We believe that a new study would not add significant insight and further load the manuscript.

However, we concur with the reviewer's opinion that the impact of our findings on ozone loss estimates is the most important implication of our study. Thus, we put more emphasis on the respective statements in abstract and conclusions and extend the above quoted discussion in section 6.

Abstract, p. 14647, l.12:

"Our findings imply that the amount of gaseous iodine transported into the stratosphere through the tropical tropopause layer is small and that iodine-mediated ozone loss plays only a minor role for stratospheric photochemistry." -> "Our findings imply that the amount of gaseous iodine transported into the stratosphere through the tropical tropopause layer is small. Thus, iodine-mediated ozone loss plays a minor role for contemporary stratospheric photochemistry but might become significant in the future if source gas emissions or injection efficiency into the upper atmosphere are enhanced."

Section 6, p. 14666, l.3:

"[Implications for stratospheric ozone have been discussed in detail by Bösch et al.

(2003), WMO- 2006, and Li et al. (2006).] As briefly outlined by the introduction, reactive iodine can undergo several catalytic ozone loss cycles either self-catalytically (Reactions R1 and R12) or through coupling with reactive hydrogen (Reaction R5), reactive nitrogen (Reaction R4), reactive chlorine (Reaction R8) or bromine (Reacton R10). Based on a photochemical scheme that involves these cycles, Li et al. (2006) found that the ozone depletion efficiency of inorganic iodine in the tropical lower stratosphere is up to 500 times greater than the one for inorganic chlorine owing to the large fraction of Iy being reactive iodine (see also figure 4). The relative importance of the iodine-involving ozone loss cycles strongly depends on the availability of the respective reaction partners. Li et al. (2006) inferred that in the mid-latitude UT/LS all cycles contribute with IO+HO2 being most important in the upper troposphere and the interhalogen and selfcatalytic cycles being dominant in the lower stratosphere. [WMO-2006 point out ... ... tends to maximize the impact of iodine on ozone.] Overall, the inferred upper limits for total gaseous inorganic iodine in the tropical UT/LS allow for a minor contribution of iodine to catalytic loss of ozone. It is unclear to what extent reactive iodine has contributed to the observed declining trend of lower stratospheric ozone which is estimated roughly -3% between 1979 and 2004 (WMO-2006). [Thereby, reactive iodine could have amplified the effect of reactive chlorine and bromine through coupled catalytic cycles.] In a future climate, emission of iodine-bearing source gases and transport efficiency into the upper atmosphere might increase or other iodine-containing gases such as CF3I (considered for replacement of halons in aircraft) might be directly injected into the upper atmosphere (Li et al. 2006, WMO-2006). Thus, monitoring of reactive iodine abundances in the lower stratosphere seems warranted."

Conclusions, p. 14667, l.13:

"[...] the amount of gaseous iodine-bearing compounds transported into the tropical lower stratosphere is low and that iodine does not play a major role in catalytic destruction of ozone in the lower stratosphere." -> "[...] the amount of gaseous iodine-bearing compounds transported into the tropical lower stratosphere is low. These upper limits

allow for a minor contribution of iodine-involving catalytic cycles to total ozone loss, but it remains unclear whether reactive iodine contributes - possibly through coupling with chlorine or bromine - to the observed trend of declining ozone in the lower stratosphere. In the future, the importance of iodine-mediated ozone loss could grow if source gas emissions or transport efficiency to the upper atmosphere increase or if iodine-bearing gases such as CF3I are directly injected into the lower stratosphere."

References, added:

Li, Y., Patten, K.O., Youn, D., and Wuebbles, D. J.: Potential impacts of CF3I on ozone as a replacement for CF3Br in aircraft applications, Atmos. Chem. Phys., 6, 4559-4568, 2006

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« p. 14647, l. 24: "much more": How much more? This statement should be better quantified. »

We change the manuscript:

p. 14647, l.24

"Thereby, iodine is - on a per atom basis - much more efficient at destroying ozone than bromine and chlorine" -> "Thereby, iodine is - on a per atom basis - a few hundred times more efficient at destroying ozone than chlorine."

p. 14666, l.3ff: added

"the ozone depletion efficiency of inorganic iodine in the tropical lower stratosphere is up to 500 times greater than the one for inorganic chlorine"

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« p. 14651, l. 11-12: What is the justification for this assumption? And what is the impact on the deduced IO and OIO values should this assumption be violated? I suggest

a more thorough discussion here (see also below). »

We infer upper limits for IO and OIO in concentration units under the assumption that the absorber volume mixing ratio is constant along individual lines-of-sight.

The weighting function (box air mass factor) for our solar occultation viewing geometry is strongly peaked in the tangent layer, i.e. the lightpath in the tangent height layer by far dominates the entire lightpath and individual lines-of-sight are mostly sensitive to the respective tangent height. Weighting functions below the tangent layer vanish identically, weighting functions above the tangent layer decrease steeply with altitude. Thus, our measurements are mostly sensitive to the tangent layer and marginally sensitive to layers above and the assumed shape of the absorber profile does not impact our conclusions substantially.

Further, the model runs indicate that the IO and OIO mixing ratio profiles rather increase than decrease from the tropopause up into the mid-stratosphere (under the assumption of a constant Iy burden). Thus, in the UT/LS, a constant mixing ratio profile attributes more absorber molecules to the tangent layer than the modelled profiles would. Hence, the inferred upper limits for IO and OIO represent conservative estimates, i.e. upper limits in the lower stratosphere would be lower when using modelled IO and OIO profile shapes.

Our intention is to keep the first part of the study (section 3) free of any modelling results since modelled iodine chemistry exhibits substantial uncertainties (as shown in sections 4 and 5). Further, if we used modelled IO and OIO mixing ratio profiles, we would have to assume a vertical profile of the Iy burden which can only be an equally speculative estimate in particular in the lower stratosphere.

Therefore, we believe that our assumption is an acceptably accurate, yet clear and transparent choice.

We add the following statement to the manuscript:

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p. 14651, l.12

"This yields an approximate estimate of the absorber concentration at the respective tangent height since, for our solar occultation viewing geometry, the lightpath through the tangent layer dominates the entire lightpath."

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« p. 14652, l. 15: "lower upper limits": quantify how much lower upper limits. »

See p.14664, l.14.

We add the following statement to the manuscript:

p. 14652, l.15

"(factor ∼0.75)"

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« p. 14656, l. 8-12: First the word "aerosol" should not be used synonymously with "ice particles". The papers cited here are referring to ice particles, not to aerosol particles. »

We replace "aerosol" by "particles", and "layered aerosol" by "particulate layer" (p.14656, l.9, l.10).

« Second, the issue should be discussed in more detail. Is it only extinction that is relevant here? Could multiple scattering play a role?»

The effect which we describe in the manuscript is an interference between the IO spectral retrieval and the empirical CLD correction term. The reason is a deficiency of the CLD correction term which extinction by particles could possibly reveal. There is no direct correlation of broadband particulate extinction with the narrow-band IO spectral retrieval. We do not see how multiple scattering - although probably negligible at subvisible optical thickness - could impact our reasoning here.

« Further, for the tropics, it was recently reported that events of enhanced ice water content are observed which are related to recent impact of convection. (Schiller, C., et al. (2008), Ice water content of Arctic, mid-latitude, and tropical cirrus, J. Geophys. Res., 113, D24208, doi:10.1029/2008JD010342). Is it possible that in this way injections of iodine into the lower tropical stratosphere are masked and are not detected in the measurements reported here?»

Our method can only detect gaseous iodine species. If ice particles inject iodine into the lower tropical stratosphere, we cannot detect it before gaseous IO or OIO is released. For aerosols, this is discussed in detail in the manuscript p.14665, l. 20 ff.

We replace "aerosols" by "aerosols or ice particles" (p.14665, l.25).

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« p. 14657, l. 27: is it correct to say that "all" reactions relevant are incorporated? Isn't it possible that the chemistry of non-methane hydrocarbons becomes important at these altitudes? »

The findings of our modelling study are largely driven by photochemistry of inorganic iodine and the uncertainties of iodine photochemical kinetics. Further, the model is constrained by measured O3 and NO2. While non-methane hydrocarbons could play a role for upper tropospheric photochemistry in a general sense, we doubt that our findings for Iy and the Iy partitioning are contingent on the consideration of NMHCs in the model. Admittedly we did not explicitly test this.

We change the manuscript:

p. 14657, l.27

"since all geseous and surface reactions relevant to the upper troposphere are incorporated." -> "since all gaseous and surface reactions relevant to our study are incorporated."

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« p. 14660, l. 3: It is unclear what the numbers 0.007 and 0.15 mean. If there are dimensionless numbers, which quantity are they describing? If they are reaction rates, what is the unit? »

The numbers 0.007 and 0.15 refer to the OIO photolysis yield and thus, are dimensionless.

We clarify the manuscript:

p. 14660, l.3

"with the upper limit of 0.007 for Reaction (R16) and 0.15 for Reaction (R17)" -> "with an upper limit fractional yield of 0.007 for Reaction (R16) and an upper limit fractional yield of 0.15 for Reaction (R17)"

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« Section 5: The assumption inherent in the retrieval of IO and OIO is that the mixing ratio is constant along the line of sight. This assumption could be tested here against the model results. In how far do the model results support the assumption of a constant mixing ratio along the line of sight? »

See comment above.

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« Conclusions: The impact of the new upper limits for Iy on estimates of the contribution of iodine to observed ozone loss is only mentioned in Section 6. It is an important issue and should also be (briefly) discussed in the Conclusions (and likewise in the abstract).»

See comment above.

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