Interactive comment on "Probing the subtropical lowermost stratosphere, tropical upper troposphere, and tropopause layer for inorganic bromine" by B. Werner et al.

Anonymous Referee #2

Comments of the reviewer are given in black and our responses in blue

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We are grateful for the very detailed comments of the reviewer which certainly helped to improve the manuscript. Please see our detailed response below.

This study by Werner et al. presents DOAS measurements of bromine monoxide in the tropical and subtropical upper troposphere, tropopause region and lower stratosphere from the Global Hawk. These are important observations in a key region of the atmosphere. While the interpretation of the DOAS observations, and in particular the applied O3 scaling technique, has to rely on a number of assumptions, this may be the best technique available to measure bromine monoxide in this important atmospheric region. However, I suggest that more details on this method and the uncertainty due to the assumptions made are given here, rather than referring to the companion paper by Stutz et al.

In fact, in the first draft to report on the study, we tried to merge the contents of the Stutz et al., (2016) (http://www.atmos-meas-tech-discuss.net/amt-2016-251/) and the present manuscript. It turned out however, that reporting on (1) the new instrument, (2) the spectral retrieval, (3) a novel method to invert slant column amounts into absolute concentrations including sensitivity runs (see the supplement in Stutz et al., (2016), and (4) reporting on the bromine results would result in a manuscript in excess of 100 pages. So we decided to split it into two manuscripts, which unfortunately now requires some cross referencing. For the assumptions made in the scaling method and sensitivity runs aiming to test these assumptions see the manuscript of Stutz et al. (2016). If you are interesting in getting more insight into the novel scaling method and its sensitivity towards assumptions (e.g., mostly due to the relevant RT), we may additionally provide digital copies of the master theses of Raecke (2013), and Knecht (2015), the recent PhD theses of Werner (2015) and Hüneke (2016), as well as 4 recent bachelor theses, in which more facets and details of the novel scaling method and its sensitivity towards inevitable assumptions are investigated and discussed. For the reference see below.

The paper would clearly benefit from some rearrangement of the presented material, as further explained below.
Following the recommendations of reviewer 1, we rearrange the Figures, and added some text where necessary (see also below).

At parts also more detail is needed, as given in my specific comments below. With these modifications and after consideration of the other comments I recommend publication in Atmos. Chem. Phys.

Specific comments:
Abstract: The abstract is too long and should focus on the main findings.
We condensed the abstract by 8 lines.

p1, l1: why does this list here starts with CH4, O3 and NO2? I suggest using a similar statement as on page 4, where the list starts with BrO, as this is really the focus of this study.
The list somehow has to start with a given order of gases, since it is necessary to first understand changes in measured gases due to dynamics (CH4, O3), remaining uncertainties in method (comparison of measured and modelled NO2), before the photochemistry and budget of bromine in the LS and TTL can be discussed.

p2, l2: split: "...LS. In the TTL ..."
We accordingly changed the text.
p2, l9: how do these numbers relate to the reported range of BrO in the TTL?
Excellently. In fact as the text state, [Br_y^{inorg}] is calculated from measured BrO and the modelled [Br_y^{inorg}]/[BrO] (>1) ratio.
p2, l12: top of TTL defined to be 425K in line 3
We accordingly changed the text (…in the upper part…)
p2, l14: "chemical depletion": not clear what this means. 1/3 of observed global ozone trends (and if yes: over which period, which altitude region,...) or 1/3 of the chemical loss?
We accordingly changed the text (…global photochemical loss…)
p2, l16: what does "mostly by natural and anthropogenic" mean? Are there other sources than natural and anthropogenic? Or do you mean mostly by natural, but also some anthropogenic sources?
We accordingly changed the text (erased ‘ mostly’)
p2, l31: Maybe useful to include a sentence or two on observations of BrONO2 in the stratosphere (e.g., Höpfner et al.)
Thanks, we accordingly added a sentence (Further constraints on stratospheric Bry (range 20 - 25 ppt) were obtained by satellite-borne measurements of BrONO2 in the mid-IR spectral range at nighttime (Höpfner et al., 2009).
p5, l1: a few lines below, the phrase "a large number of species, including O3, NO2 and BrO" is used, which may be appropriate here as well. I suggest to give this list of possible species only once (and consistent) and refer to it.
We accordingly changed the text (….beside for some other species, see above)….)
p5, l1: maybe better move long list of references into section 2.1
We keep it.
p7, l29: "The received limb radiances ...": need a few more words that this refers to the mini-DOAS measurements. However, I suggest merging section 2.6 with 2.1, as this is an essential part of the mini-DOAS data analysis.
We accordingly changed the text (The measured limb radiances of the mini-DOAS instrument….) but we kept section 2.6, since it describes the tool (together with the modelled curtains) used in the interpretation of our measurements (section 2.1), rather than being a part of the DOAS method description.
p8, l4: Strange sentence: "Demonstrates that Earth sphericity, ...are relevant". I suggest to rather say, "...are relevant and taken here into account."
Thanks, we accordingly changed the text to ….The simulation indicates that correctly accounting for the Earth’s sphericity, the atmospheric refraction, cloud cover, ground albedo etc. is relevant for the interpretation of UV/vis/near-IR limb measurements performed within the middle atmosphere (Deutschmann et al., 2011).
p8, l23: "which together contain 1 ppt of bromine atoms" just repeats the first part of the sentence, or I don’t understand what is meant here.
We accordingly changed the text, i.e., erased (… , which together contain 1~ppt of bromine atoms.)
p8, l25: include explicitely that no sea salt aerosol source is assumed, in contrast to some other recent studies (e.g., Saiz-Lopez et al.)
Thanks a lot. We accordingly changed the text (see our detailed responses to reviewer 1)
p8, l28: "growth rate": why is the growth rate relevant? Because the CH4 content varies with age-of-air?
Yes, since present TOMCAT/SLIMCAT run is integrated from 1979 onwards, see P8, L27 of the revised manuscript.
p9, l1: How? By changing the BrONO2 photolysis, by changing the rate of BrO + NO2, or both?
By scaling k(BrO+NO2).
p9, l18: include "as well as“ after the reference to Jensen et al.

We accordingly changed the text.
p10, l1: closing bracked has to be after "tropical"
We accordingly changed the text.
p10, l6+l7: "optical“ -> "optimal“
We accordingly changed the text.
p10, l32: I couldn't easily find information on the integration time. Please organise the description in a way that all relevant information for the DOAS measurements can be easily found at one place of the manuscript. Currently this is distributed over Secs. 2.1, 2.6 and 3
On page 9, line 3 of the original manuscript is was already written (For all model levels and for the time resolution (~30 s) of the mini-DOAS measurements….). We accordingly changed the text (P9, l31) to "longer signal integration times (than the standard integration time which is 30 s), and are thus averaged "
p11, l1: Is really a higher spatial resolution required, or a finer temporal (or SZA) resolution?
A high spatial resolution is required, since the instrument probed air masses 1000 s ahead the aircraft (which for a cruise speed of 200 m/s corresponds to 200 km, see Stutz et al. 2016, Figure 10, which corresponds to a $\Delta SZA = 0.2^{o}$ during setting sun) and the time resolution of TOMCAT/SLIMCAT is already 30 s (or in terms of distance about 6 km).
Fig 7: Maybe it would make sense to indicate in the caption of Fig. 7 that DOAS data quality for SF4 is reduced?
We added the following to the legend of Figure 6 in the revised manuscript: Note that DOAS analysis of BrO for SF4-2013 is somewhat uncertain because the Fraunhofer reference spectra (taken via a diffuser) are affected by temporally changing residual structures likely due to ice deposits or some other residues on the zenith diffuser (see text).
Fig. 10: I assume for Fig. 10, model data are used as they are, i.e. not altitude adjusted?
All measured data are compared to the modelled data assuming the same altitude interpolation, i.e. all curtains are altitude shifted by the same amount until measured and modelled O_3 agree. Please note that the altitude shift is typically smaller than the vertical resolution of the model, which is about 1 km in the TTL.
p12, l4: The agreement between measured and modeled NO2 is indeed strong evidence for the validity of the approach, but be careful with the reasoning: It is not possible to validate both measurements and model at the same time from this comparison.
We agree, but since in-situ measured and modelled CH_4 is also found to largely agree (once all curtains are vertically shifted until measured and modelled CH_4 agree) a dynamical reason for an assumed fortuitous agreement can be ruled out. Further since NO_2 is a photochemical active species and air masses of quite different NO_2 mixing ratios were probed, an unrecoginzed major issue with the scaling method and/or adopted NOx photochemistry is highly unlikley.
p12, l7: better say "surface air mixing ratios"
We accordingly changed the text.
p12, l9: "data is " -> "data are“
We accordingly changed the text.
p12, l13: Not sure if you can draw this conclusion from this comparison. Does this not simply show that there is some spatial variability in CH2Br2 while the model assumes a constant mixing ratio at the surface? See next sentence.
You are right and we accordingly changed the text to… This is most likely due to an underestimation of the surface concentration (1 ppt), variable mixing ratios at the surface not correctly considered in the model, and/or errors in the atmospheric lifetime due to reactions of CH2Br2 with OH radicals in the model (e.g. Mellouki et al. (1992), Ko et al. (2013), WMO (2014)).
p12, l16: The sentence should finish before "... to be implemented in the model". Whether or not this should be implemented in a model is a totally different issue.
We accordingly changed the text.
p12, l27: I assume Wang et al and Volkamer et al use the same measurements, so better say "the TORERO measurements reported by Wang et al. and Volkamer et al."
We accordingly changed the text.

p13, l3: I suggest to discuss similarities and differences to the results of Wang et al and Volkamer et al., but limit the speculations about possible discrepancies.
We accordingly changed the text.
My impression is that too much weight is given on explaining possible differences to the TORERO results, while other studies are not mentioned.
We are not sure about this regarding (1) our concerns towards TORERO BrO profiles reported in Wang et al., (2016), (2) our findings on BrO in the TTL reported in the present study (3) previous BrO measurements in the TTL (Dorf et al. 2008), (4) not yet published BrO data (e.g., collected during different HALO missions during the past 4 years), and (5) the comments of Dix&Volkamer to the present manuscript.
p13, l3: spell out the name of the aircraft
We accordingly changed the text.
p13, l6: rephrase sentence, avoid the double use of "but"
We accordingly changed the text.
p13, l6/7: This sentence does not contain any solid information and could be removed:
It is trivial that any two measurements that are not performed at the same place at the same time could differ just by chance.
We accordingly changed the text (erased the sentence).
p13, l8-12: I find this statement problematic: What do you want to imply?
We accordingly changed the text to …. they inferred the BrO profiles using the optimal estimation technique with constraints based on measured O2-O2, in-situ measured aerosol parameters and remotely measured Mie extinction Volkamer et al. (2015). However, we strongly feel that a 1-D treatment of the RT used in the interpretation of UV/vis/NIR limb measurements is not justified, if OE is used for the mathematical inversion (see also our response to the comments of Dix&Volkamer).
We also changed to text (P13, L29 -34). In conclusion, even though the reported TORERO flights 12 and 17 were performed under clear-skies (Volkamer et al.,2015), the extent to which the 2-D (and under cloudy sky 3-D) dimensionality of the underlying radiative transfer problem, in particular relevant when using optimal estimation for profile inversion, impacts the results. In particular, unaccounted scattering due to aerosols and (probably) optically thin upper tropospheric clouds, lower level clouds, or changing overhead stratospheric BrO could have contributed to the reported elevated BrO in the UT, and around the bottom of the TTL.
p13, l33: remove "Again“
We accordingly changed the text.
p14, l3: remove "and others" - already contained in "e.g."
We accordingly changed the text.
p14, l4: What does this mean: "with these features in mind"?
We accordingly changed the text (we erased "with these features in mind"?).
p14, l5: Probably misleading formulation: if you really know there is a bias of 2ppt you could correct for it.
Essentially you are right, but without a physically consistent explanation for the processes, we feel a correction is inappropiate. Consequently we leave this formaulation as is.
p14, l6: "bottom to“ -> "bottom of“
We accordingly changed the text.
p14, l10: Not sure what you mean here. Increasing CH2Br2 in the model would be easy, and does not require a detailed back trajectory study.
Yes, for the constant low bias in assumed CH2Br2. Adjusting it in the model would need another, computer intensive, model run from 1979 onwards. However, it is fair to assume that Bry levels would linearly follow the assumed CH2Br2, so this effort is not really necessary.
This would likely not "remove flight to flight scatter". However, including a more detailed source parameterization (i.e., time and space dependent) likely would.
p14, l14: "well be“ -> "will be“
We accordingly changed the text.
p14, l15: "gap in“ or "gap between“ ?

We checked the correct usage. Both versions are possible.
p16, l26: "climate is most sensitive": maybe better say more carefully "where ozone changes have the largest impact on radiative forcing"
We accordingly changed the text.
p16, l33: "oxidizing capacity due to expected increase in VSLS emissions" is probably not what you mean. There are actually three possible processes at work: (1) changes in atmospheric transport, (2) changes in OH, affecting VSLS lifetimes and (3) changes in VSLS emissions due to aquaculture.
We accordingly changed the text.
p17, l4: "some" -> "important" (?)
We accordingly changed the text.
p17, l12: what kind of "adjustments“ are performed here? Please give more details and justify!
We accordingly changed the text to … The measured and modeled TTL concentrations of CH2Br2, CHBr3 are found to compare reasonably well to the surface concentrations and atmospheric life times of both species adopted in the model.
p18, l3: Hossaini et al., 2016 is now published
We accordingly changed the text.
p18, l9: remove extra "to"
We accordingly changed the text.

In the acknowledgment, we added the following sentence: The authors are grateful to the comments given by two anonymous reviewers, and the comments of Barbara Dix and Rainer Volkamer (CU, Boulder, USA).

Additional references:

1. Knecht, M.: Simulation of radiative field modification due to tropical clouds, Master thesis, Institut für Umweltphysik, Universität of Heidelberg, Heidelberg, Germany, 2015.
2. Hueneke, T., The scaling method applied to HALO measurements: Inferring absolute trace gas concentrations from airborne limb spectroscopy under all sky conditions, PhD thesis, University of Heidelberg, Heidelberg, Germany, 2016.
3. Raecke R., Atmospheric Spectroscopy of Trace Gases and Water Vapor in the Tropical Tropopause Layer from the NASA Global Hawk, Master thesis, Institut für Umweltphysik, Universität of Heidelberg, Heidelberg, Germany, 2012.
4. Werner, B., Spectroscopic UV/vis limb measurements from aboard the NASA Global Hawk: Implications for the photochemistry and budget of bromine in the tropical tropopause layer, PhD thesis, University of Heidelberg, Heidelberg, Germany, 2016.