Response (in red) to the comments of Barbara Dix, and Rainer Volkamer

We appreciate the response and the clarification on the results reported by Wang et al., and Volkamer et al., (2015). It was not our intent to question these results, but rather to put them in context to our findings, both from the methodology standpoint as well as with respect to the final results. Ultimately we believe that the disagreement between the observations motivates further study of bromine chemistry in the UTLS as well as more effort in ensuring the accuracy of high-altitude limb-scanning DOAS observations.

We have reformulated the respective paragraphs in the manuscript to avoid any a misunderstanding of our intentions:

"It is possible that the TORERO observations Wang et al. (2015) and Volkamer et al. (2015) off the western coasts of South and Central America, i.e. further south than the ATTREX region but during the same season, encountered an unusual meteorological situation that would have caused downward transport of bromine rich air from the lower stratosphere to the UT and the bottom of the TTL (up to about 14 km), or that sea salt released bromine played a role (e.g., Schmidt et al. (2016)). However, our study has identified possible problems when using optimal estimation technique with constraints based for example on measured O2-O2 for high altitude aircraft limb observations. The RT below the aircraft and in particular in the lower troposphere plays a crucial role for the observations, due to the much higher O2-O2 concentrations. Also since individual limb measurements already cover an area of typical 200 x 20 km in front of the aircraft (see Figure 5 in Stutz et al. (2016)), and even more crucial when applying optimal estimation for profile inversion a series of measurements taken during the ascent and descent of the GH are jointly inverted. Hence the radiative field and its time dependence needs to be known over a larger food-print (i.e., the RT is 2-D, or even 3-D plus its time dependence over the period of a single profile measurement)."

In the following we will provide some brief thoughts on the comments by Volkamer and Dix (in red).

We generally agree that "skylight analyzed for the O2-O2 absorption in limb direction may carry additional, or even predominantly information on the radiative transfer of lower atmospheric layers", but want to point out that BrO profiles published in Volkamer et al. (2015) and Wang et al (2015) were neither affected by underneath cloud cover, nor by cirrus above. Sections 2.10 and 3.1 in Volkamer et al. (2015) discuss explicitly the effect of aerosol and clouds, and make fully transparent that the presented RF12 and RF17 case studies are not affected by clouds. Furthermore, we show below HSRL data from these two flights (Fig. 1) that make transparent that no aerosols or thin cirrus layers were present above the aircraft.

It is our experience that cloud free conditions for the geometry of a limb-DOAS system, i.e. up to 200 km ahead and 20 km on the side, is quite rare, especially in the tropics and sub-tropics. In addition, the interpretation of the limb-observations requires 2-D (or even 3-D) radiative transfer calculation and information on the spatial 3D distribution of atmospheric scatters (e.g., Oikarinen, 2002; Figures 5 and 10 in Stutz et al., 2016; Raecke, 2013 see the Figure 1 provided below). In addition, radiative transfer condition can change during ascent or decent manoeuvres of an aircraft, which add another degree of complexity. Because, we did not have this information and clouds were nearly always present during ATTREX, we had to rely on a scaling technique with a trace gas that has a similar vertical distribution as BrO, i.e. ozone, to overcome the challenges of this radiative transfer challenge.
We agree with the comment that under cloud free conditions the combined radiative transfer and optimal estimation approach to retrieve vertical trace gas profiles should give reliable results.

Moreover, the authors are referred to Fig. 2 and Section 2.1 in Dix et al. (2016a), where it is shown that in cloud-free conditions measurements of O2-O2 are suitable to constrain RTM up to 15 km. The statement by the authors is too broad, and certainly does not apply to the Wang et al. and Volkamer et al. case studies. This should be corrected. Figure 1. Comparison of O4 ratios at 360 nm and 477 nm with HSRL particulate backscatter cross section data for TORERO RF04, RF12 and RF17 (Dix et al. (2016a); Volkamer et al. (2015); Wang et al. (2015)). Altitude resolved HSRL backscatter data is plotted and color coded along the flight track. Larger signals denote the presence of aerosol/clouds. HSRL is either measuring above or below the aircraft. The shading directly around the flight track seen in part of RF12 and RF17 is a near field effect that leads to erroneous large back scatter signals by HSRL. Green boxes in RF12 and RF17 mark data periods that were used for BrO, IO and NO2 optimal estimation profile retrievals as published in Volkamer et al. (2015). Regular HSRL upward scans show that for these time periods no aerosol or cloud layers were present above the aircraft. For more information see Dix et al. (2016a and b). p.13, line 22ff:

See our comments above. We should also add that the ATTREX mission included a downward looking LIDAR which provided information on clouds and aerosol below the aircraft. However, in most cases this information proved to be insufficient to constrain the radiative transfer with the required accuracy.

This is incorrect, and a misleading reflection of the literature. First, Volkamer and Wang et al. (2015) used a stratospheric model (RAQMS) to study the influence of changing BrO concentrations above, and show that potential changes in the stratospheric BrO VCD, or apparent changes in the measured limb dSCDs due to a changing tropopause altitude do not affect the results. Second, the authors are referred to section 2.10 in Volkamer et al. (2015), and Fig. S4 in the SI text of Wang et al. (2015) for the excellent agreement with the aircraft microwave temperature profiler measurements and the location of the thermal tropopause in the model. Third, the supplement of Volkamer et al. (2015) shows that the stratospheric profile above the aircraft is accurately corrected. Finally, Dix et al. (2016a) used RAQMS BrO profiles for the correction of stratospheric BrO contributions to the limb dSCD measurement, and confirms excellent agreement with the optimal estimation case study profiles from Wang et al. (2015) and Volkamer et al. (2015) using a parameterization method within low error bars.
p.13, line 27ff:

We acknowledge that Wang et al. (2015) and Volkamer et al. (2015) considered the overhead BrO column and that there results rely on model calculations. However, as our study points out, even a sophisticated and well-tested stratospheric CTMs, such as SLIMCAT, have problems accurately simulating the details of the vertical BrO profile at flight altitudes in the UTLS. To our knowledge, RAQMS is not a CTM in which the stratosphere is represented very well, which would worsen this problem.
In particular, certain dynamical processes are often not properly resolved by CTM's (see Figure 2 below). These may include mixing of air masses across the UTLS around the subtropical and polar jet, transient vertically and horizontal propagating gravity waves, Kelvin waves in the tropics, planetary wave in the sub-tropical surface zone and / or those acting at the edge of the polar vortex (Figure 2).
We also show in Stutz et al. (Figure 11) that only a fraction α (= 0.15 - 0.6) of the measured BrO absorption in the TTL/LS is due to line-of-sight absorption, but the majority of the absorption is due to the overhead BrO (and eventually due to light being back-reflected from the troposphere below). Therefore, potential spatial and temporal changes of both contributions to the total absorption have to be carefully considered in the data analysis of the limb observations.

This conclusion is incorrect in all aspects listed. See our above responses. TORERO flight RF12 and RF17 are neither affected by aerosol/cloud extinction above, nor lower level clouds below, nor changing stratospheric BrO.
Please see our responses on the relevant RT (above) and the necessity to properly resolve the (mostly dynamics related) spatial structures of the stratospheric composition in the scale relevant for our method.

We respectfully disagree, and show below that the results presented in Fig. 3b of Werner et al. (2016) and Wang et al., (2015) are in fact quite compatible. Werner et al. show that optimal estimation (OE) profile retrievals in Figs. 3a and b yield within error bars the same results for the altitude range between 14.5 and 18.5 km, regardless of a priori profile choice. This shows that the OE inversion is well constrained by measurements for these altitudes. However, below 14.5 km, the measurements by Werner et al. are not well constrained, and essentially follow the a priori in both cases shown. The "unexpected kink around 12 to 13 km" is therefore not unexpected at all, but to the contrary, it is the expected result of the OE solution that transitions from 'constrained by measurements' (above 14 km) to reproducing the a priori profile at lower altitudes (below 12 km). This behavior is likely reflected in the averaging kernel that are not shown, and should be included in the manuscript. Also, is the OE based on limb spectra only or are downward scans included? This information is missing in the paper.

We run more than 100 test inversions to study the sensitivity of the OE, for example to different a priori profiles, internal and external constraints et cetera. Because of the large sensitivity of the inferred profile on the a priori information for the atmospheric part not directly probed during the limb observation (and due other constraints which are not well-defined), we avoided this approach in our analysis and rather used the newly developed O_3 scaling technique (see the green profile in Figure 11 in the revised manuscript).

The kink is because our measurements are not compatible with the findings of Wang et al. BrO profile. As the comment correctly indicates our measurements are barely sensitive to BrO below ~13 km and therefore the retrieved profile is "pulled" towards the a priori BrO profile (Wang et al.). The altitude range 13 – 18 km the average kernels (AK) are around 1 indicating that the inferred BrO is predominately determined by the observations (see Figure 3). We did not include the AK in the paper as we ultimately we do not use the OE approach.

In the end this exercise confirms that our observations and those by Wang et al. above 13km are different and that this difference is likely not due to an OE problem.

Furthermore, section 4.4 in Stutz et al. (2016) states that GH measurements during SF3 are compatible with up to 1.5 pptv of BrO directly below flight altitude. This is quite compatible with the TORERO campaign average BrO vertical profile, which shows a significant decrease of BrO above 14 km, with a mean of 1.86 ± 0.16 pptv at 13.5 km, and 1.38 ± 0.16 pptv at 14.5 km (Dix et al., 2016b).

This upper limit is based on the residual noise of the DOAS retrieval, i.e. [BrO] < 1.5 ppt, and is thus not a proof of the presence of this much BrO. Then interpretation of BrO levels on these scales will depend crucially on the fine-scale dynamics and vertical profiles. It is thus nearly impossible to determine if our observations are compatible with those by Dix et al.

The TORERO average profile is compared with model predictions in Fig. 5 in Schmidt et al., (2016), and is shown with a better resolution in Fig. 10 of Dix et al. (2016b) (included as Fig.2 here). Notably, the case studies in Volkamer et al. (2015) and Wang et al. (2015) are 100% consistent within low error bars (5%) with the parameterization retrieval (Dix et al., 2016a), if the same data subsets are compared. These case studies had probed primarily air masses influenced by convection over oceans. The lower mean BrO for the complete TORERO data set is mainly reflecting different air mass histories, consistent with the variability in Bry noted in Wang et al. (2015), and our hypothesis that sea-salt derived Bry is a source for BrO in the upper free troposphere downwind of marine convection.

We agree that an unrecognized source of bromine is required in the tropical UT/TTL (> 12 km) to explain the TORERO results. Whether this source is sea salt will need to be further investigated as supporting reports are somewhat contradictory. For example Froyd et al., (2009) found in the air analysed from aboard the NASA WB-57 southwest of Central America during the Pre-AVE and CR-AVE campaigns in February 2004 and 2008 that the fraction of sea salt containing aerosols strongly decreased from < 5% in the 4 - 12 km region to virtually zero above 12 km (Figure 4 in Froyd et al., 2009). Schmidt et al. (2006) modelled a total Br*y* of ~3 ppt in the middle troposphere of the tropics (Figure 2). Accordingly, about 1 ppt might due to bromine released by sea salt given the 30% statement cited above. Therefore, it is hard to see how sea salt may give rise to 2 ppt of [BrO] at 13.5 km in the tropics during daytime. Nevertheless, it is difficult to rule out this source for a particular observation and thus it seems prudent to further investigate the possibility of a sea salt source.

In the end we think the overreaching question is why the two studies disagree and which of the two observations is more representative of the TTL. This is a question that will only be answered through further observations.

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

Refs:

1. Hueneke T., The scaling method applied to HALO measurements: Inferring absolute trace gas concentrations from airborne limb spectroscopy under all sky conditions, PhD thesis, Institut für Umweltphysik, Universität of Heidelberg, Heidelberg, Germany, 2016.
2. Froyd, K. D., D. M. Murphy, T. J. Sanford, D. S. Thomson, J. C. Wilson, L. Pfister, and L. Lait (2009), Aerosol composition of the tropical upper troposphere, *Atmos. Chem. Phys.*, *9*(13), 4363–4385, doi:10.5194/acp-9-4363-2009.
3. Murphy, D. M., Thomson, D. S., and Mahoney, M. J.: In Situ Measurements of Organics, Meteoritic Material, Mercury, and Other Elements in Aerosols at 5 to 19 Kilometers, Science, 282, 1664, doi:10.1126/science.282.5394.1664, 1998.
4. Murphy, D. M. and Thomson, D. S.: Halogen ions and NO+ in the mass spectra of aerosols in the upper troposphere and lower stratosphere, Geophys. Res. Lett., 27, 3217–3220, doi:10.1029/1999GL011267, 2000.
5. Murphy, D. M., Cziczo, D. J., Hudson, P. K., and Thomson, D. S.: Carbonaceous material in aerosol particles in the lower stratosphere and tropopause region, J. Geophys. Res., 112, 4203, doi: 10.1029/2006JD007297, 2007. Oikarinen, L.: Effect of surface albedo variations on UV-visible limb-scattering measurements of the atmosphere, J. Geophys. Res., 107, 15 1–15, doi:10.1029/2001JD001492, 2002.-
6. Raecke 2013; Atmospheric Spectroscopy of Trace Gases and Water Vapor in the Tropical Tropopause Layer from the NASA Global Hawk, Master Thesis, University of Heidelberg, Heidelberg, 2013. Upon request we can provide a digital copy of the thesis.
7. Schmidt, J. A., Jacob, D. J., Horowitz, H. M., Hu, L., Sherwen, T., Evans, M. J., Liang, Q., Suleiman, R. M., Oram, D. E., Le Breton, M., Percival, C. J., Wang, S., Dix, B., and Volkamer, R.: Modeling the observed tropospheric BrO background: Importance of multi-phase chemistry and implications for ozone, OH, and mercury, Journal of Geophysical Research: Atmospheres, 121, 11,819–11,835, doi:10.1002/2015JD024229, http://dx.doi.org/10.1002/2015JD024229, 2015JD024229, 2016.

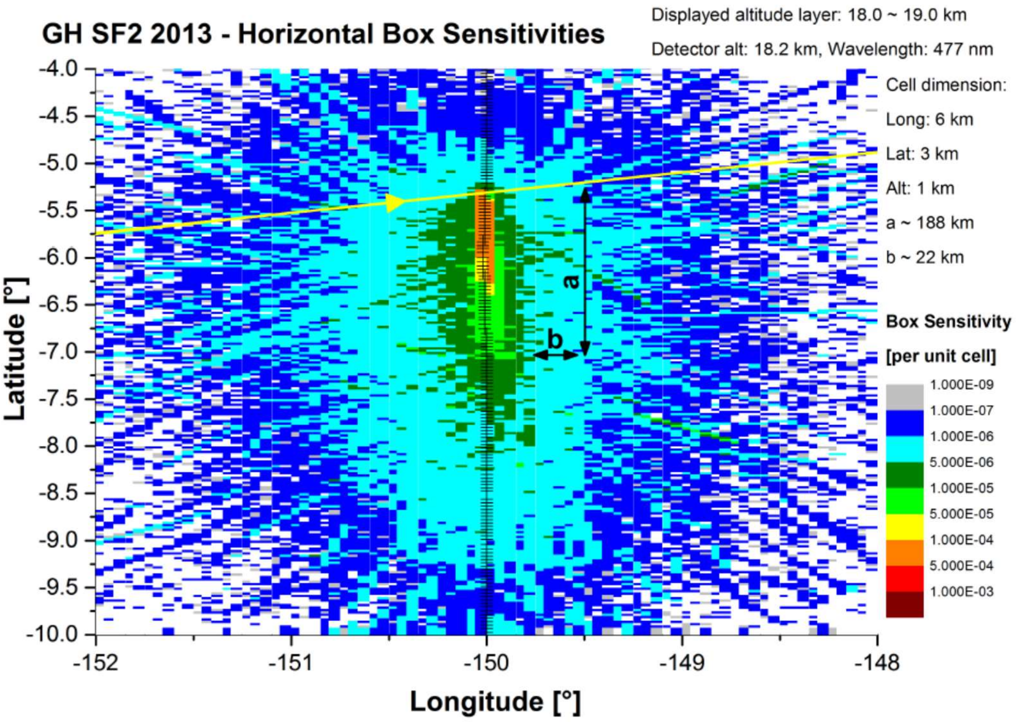

Figure 1: Horizontal sensitivity of DOAS measurements from the Global Hawk: Shown are horizontal box sensitivities in the altitude grid layer of flight altitude for a DOAS measurement with 0° telescope elevation angle at 18:24 UT, 27:1 ° N / 133:5 ° W, SZA = 57:2 °, SRAA = 102:2 °, detector altitude 17.1 km (top), and for a DOAS measurement at point P, 02:03 UT, 5:3 ° S / 150:0 ° W, SZA = 57:2 °, SRAA = 77:9 °, detector altitude 18.2 km (bottom). The yellow arrow line denotes the incident direction of photons from the sun. The intersection with the black line (flight path) describes the model detector position. Every tick on the black line describes a 0 ° DOAS measurement (from Raecke, 2013).

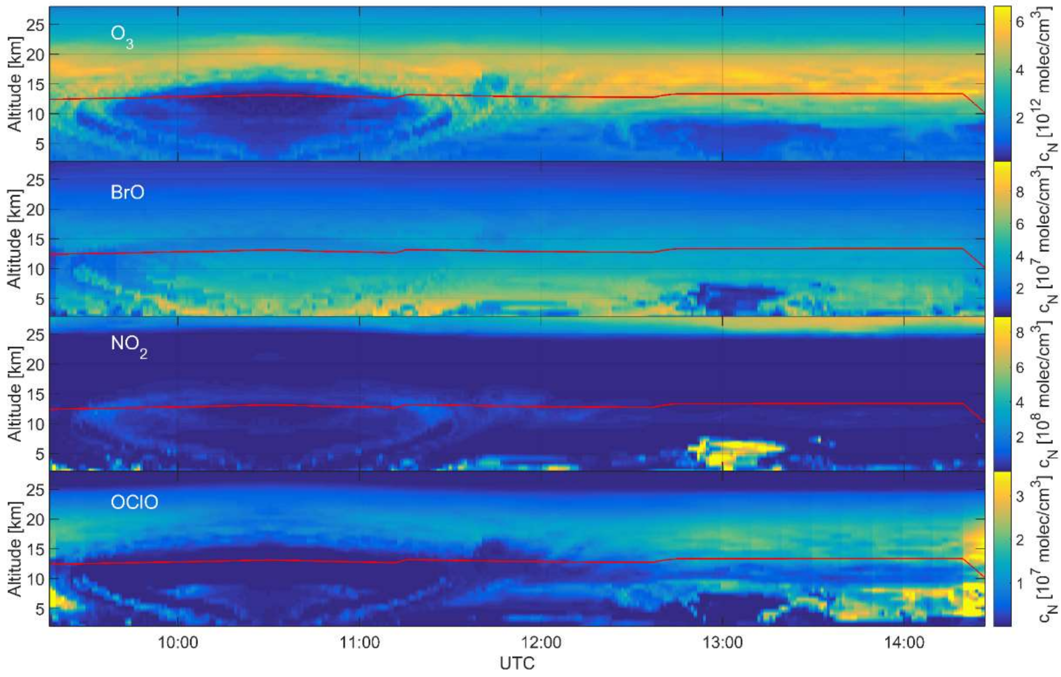

Figure 2: CLaMS predicted curtains of O_3, BrO and NO_2 and OClO for the Polstracc HALO flight from Kiruna on January 31, 2016 as function of flight time. The red lines indicate the flight trajectory of the aircraft. Please note that (a) the spatial and temporal structure of O_3, NO_2, BrO and OClO modelled by

CLaMS in the stratosphere (c.f., mixing around the the polar jet at around 11:45 UTC and less around 9:45 UTC), which show the challenge in assuming a constant overhead slant column for DOAS based concentration retrievals, and (b) that CLaMS is not not very skillfull in modelling BrO in the troposphere, due to missing bromine sinks derived from borminated hydrocarbon degradation. The figure was kindly provided by J.U. Groß, Forschungszentrum Jülich, Jülich Germany.

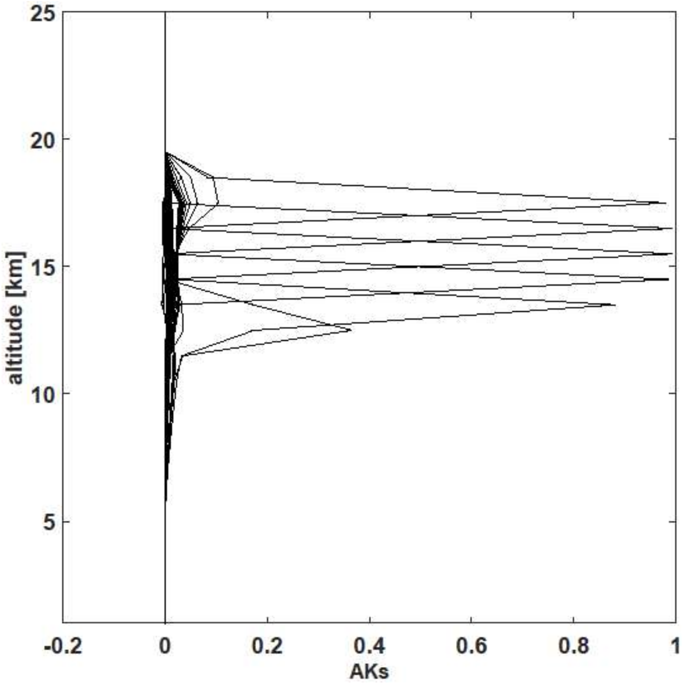

Figure 3: Averaging Kernels of the OE inversion of Fig. 3b (used in the comparison with the Wang et al., 2015 BrO profile.)