Responses to reviewer #1 in black and comments of the reviewer in blue

General Comments

The paper reports results from the ATTREX campaign performed in the Eastern Pacific during 2013, which probed the UT, TTL and LMS. The experimental results are of high importance for determining the overall fraction of inorganic bromine injected to the stratosphere, i.e. capable of destroying ozone in the LMS. BrO measurements are compared with modelled output from the TOMCAT/SLIMCAT model, which runs at high resolution with the specific meteorology (i.e. ECMWF Era-Interim reanalysis) present during the ATTREX campaign.

Even when the presented results possess a notable scientific impact as they probe inorganic bromine species in a region of major importance for constraining stratospheric bromine injection, the presentation of results is in this reviewer´s opinion rather disordered, and the description of the model configuration/output used to interpret their measurements is rather confusing. Therefore, several issues, both structural/technical and scientific/descriptive, must be dealt with before this MS is ready for publication. I recommend the following major comments be addressed before this paper can be accepted in ACP.

We are very grateful for the time the reviewer spent on reviewing the manuscript. The comments will help us to improve the manuscript. Please find below our point-to-point responses to the comments and queries.

Major Comments:

1. The abstract is too long and contains unnecessary information such as i) the instruments used for probing the composition of the tropical atmosphere, ii) a description of the minor deficiencies in the modelled transport, iii) a reference to a paper with the definition of the TTL. Also, the most important information in the abstract is quite disordered and the main results (i.e., measured numbers which are the major findings of this work) are only given in the very last lines.

We agree that the abstract was too long and shortened it by 8 lines. However, we disagree that it contains unnecessary information since the description of i) is relevant for the interpretation of our measurements, ii.) is honest in that the modelled curtains need a (joint) vertical adjustment in order to match the observations, iii.) since conflicting definitions of the TTL (in particular its bottom) appear in the literature.

2. The authors used a quite simple proxy to separate tropospheric air from stratospheric air: the condition of [CH4] being larger or smaller than 1790 ppb. This selection is neither justified nor referenced within the MS, and its use should be clearly justified as many of the forthcoming results depend on the validity of this assumption. Indeed, the histograms shown in Fig. 13 seem to contradict the validity of the CH4 proxy in splitting tropospheric from stratospheric air for theta > 390 K. Also, within the abstract and text, the CH4 condition is defined both respect to 1390 and 1790 ppb, introducing an additional inconsistency to the definition.

The [CH4] = 1390 ppb criteria were typos. They should have read [CH4] = 1790 ppb. We corrected these mistakes in the text. Our intent was not to separate tropospheric from stratospheric air since only air from subtropical LMS and TTL was sampled. The [CH4] >< 1790 ppb criterion is used to (roughly) separate younger air sampled within the TTL from relatively older air from the subtropical LMS. No other more robust method was available from the aircraft observations.

3. In the abstract and methodology, the authors declare that the TOMCAT/SLIMCAT model was "constrained to the measured O3 and NO2 and adjusted to match the observed concentrations of some brominated source gases" (P2,L6-7). But no detail is given in the methodology about how this

special configuration was applied in the model. Later, many of the results are interpreted and discussed based on the output obtained from the global model. In light of the importance of the observations and conclusions drawn here, mostly the inferred Bryinorg, the authors should describe specifically how the model was constrained or adjusted.

The method how to match the observed O3 (and CH4) is described I detail in Stutz et al., (2016). In short, the following: TOMCAT/ SLIMCAT has a height resolution of about 1 km in the TTL. The GH on the other hand, mostly flies at altitudes located between the model grid points. Therefore, an interpolation is necessary to account for sub-grid trace gas concentrations and to allow for an accurate comparison between the model results and the measurements. Moreover, in order to compensate for the models small (and varying) inaccuracies in describing the vertical air motion in the atmosphere (c.f., due to transient gravity waves), the modelled concentration curtains of all chemical tracers are jointly shifted in the vertical (by typically less than modelled vertical grid) until measured and modelled O3 agree. Once this vertical adjustment is performed (e.g., see Stutz et al., 2016, compare Figure 12 with 13), the measured and modelled CH4 (a transport tracer measured by UCATS and HUPCRS) and NO2 (a photochemical active species measured by the DOAS instrument) largely agree (see Figures 4 to 9). As a consequence, it can be concluded that (a) the vertical adjustment is reasonable and justified (from the agreement seen in CH4), (b) that the scaling method works well for NO2 and hence for BrO, and (c) that the adopted NOx/NOy photochemistry is able to reproduce measured NO2 (see Stutz et al., 2016).

We changed the following parts of the manuscript in order to clarify :

P1 line 16 cont: Depending on the photochemical regime, the TOMCAT/SLIMCAT simulations tend to slightly under-predict measured BrO for large BrO concentrations, i.e. in the upper TTL and LS.

P11, line 16: The text now reads…… The panels (b), and (c) of Figs. 3 to 8 show comparisons of measured and modeled CH4, and O3 mixing ratios. Here the measured and modeled species reasonably agree within the given error bars, after the modeled curtains are altitude-adjusted by the same amount until measured and modelled O3 agree (for details see Stutz et al. (2016)). Noteworthy is, that in most cases the altitude adjustment is less than the grid spacing of TOMCAT/SLIMCAT (about 1 km in the TTL), thus mostly accounting for the altitude mismatches of the actual cruise altitude of the Global Hawk and the model output rather than deficits of the model to properly predict the vertical transport.

For example:
My major concern is about how removal/washout is considered in the model, mostly within the UT and TTL, as these processes will control the overall Bryinorg burden in that region of the atmosphere. The only reference to removal rates in the MS that I could found was on Page 15: L26 "…, and assuming no bromine is effectively lost in the troposphere, …" and L30-31 "Therefore effective loss processes for inorganic bromine, for example by heterogeneous uptake of inorganic bromine on aerosol and cloud particles, must act in the atmosphere". Detailed information on the removal processes considered here for brominated species should be given and also how they affect the BrO/Br ratios.

First, since the measurements were solely performed in the LMS and TTL, details in the budget and photochemistry of bromine in the troposphere only need to be considered in the model in as much as they are relevant to the budget of bromine in the TTL and LS. A description how the model is constrained to the budget of bromine in the troposphere and what processes are considered is given in section 2.7. In order to account for more complicated bromine sources (e.g., derived from sea salt and/or yet unknown minor organic brominated species), an additional 0.5 ppt of BrO is added to the near surface bromine, but only where TOMCAT/SLIMCAT predicts [BrO] < 0.5 ppt). Further, this modified BrO curtain is only used for the RT simulations, in order to better represent the BrO absorption introduced by the small fraction of light traveling through the lower troposphere before being analysed by the limb oriented telescope on the GH. This approach is justified based on (a) the findings reported in Stutz et al., Figure 8b, and 15, (b) the findings of Volkamer et al., 2015 on BrO in the tropical tropics, (c) Dorf et al., 2008, and our earlier work (Harder et al., (1998), Fitzenberger et al., (2000), (d) Chen et al. (2016), and (e) our measurements around Borneo during SHIVA. This assumption also appears to be justified based on recent modelling studies which argues that sea salt derived bromine might be delivered to the TTL (e.g., Schmidt et al., JGR, 2016 see also below).

However, we re-call here again that in the measurement/model inter-comparison (sections 4.1, 4.2 and 4.4) measured/inferred quantities are directly compared with the TOMCAT/SLIMCAT model output, except!!! that all modelled curtains are vertically shifted by the same amount until measured and modelled O_3 agree. The latter is necessary since (a) to avoid interpolation errors between the actual measurements altitude, the measurements themselves, and the model predictions provided in discrete step which do necessarily correspond to the altitude of the measurements, and (b) to compensate for small mismatches in the actual and modelled vertical transport. Mostly (> 98%), the necessary vertical shifted than the vertical spacing of the model (~1 km).

Accordingly, and to account for the omitted sea-salt source (and in order to avoid any confusion) we
(1) changed our text (page 8 line 25 cont.) to …

No other (cf., unknown organic or inorganic) sources of bromine for UT, LS, and TTL are assumed (e.g., Fitzenberger et al. (2000), Salawitch et al. (2010), Wang et al. (2015)). Omitting the release and heterogeneous processing of bromine from sea-salt aerosols (e.g., Saiz-Lopez et al. (2004)) in the model for the sake of saving computing time appears justified since (1) even though it is predicted to be relevant for bromine (~30% of the total Br_y^{inorg}) in the free troposphere (Schmidt et al. (2016)), its contribution to BrO in the TTL is at most of the order of the accuracy (~0.5 ppt) of our BrO measurements, (2) its time and space dependent sources (as for the brominated VSLS) are not well constrained, (3) in the modelled troposphere inorganic bromine only serve as boundary condition for bromine in the TTL, and (4) the additional BrO would not affect the BrO measurements-based calculation of Br_y^{inorg} for the TTL (see below).

(2) added the following in the discussion (section 4.4, page 14, line 35 cont.)

This gap could partly be closed by adjusting the CH2Br2 surface concentration and atmospheric lifetime, or by considering a detailed scheme for dehalogenation of sea salt, i.e. bromine activation (e.g. Saiz-Lopez et al. (2004), Fernandez et al. (2014), Schmidt et al. (2016)). Adjusting CH2Br2 would add 0.4 ppt of Br_y^{inorg} , or ~ 0.3 ppt to BrO, thus removing the flight-to-flight scatter in source gas concentrations (~ 0.8 ppt) in Br_y^{inorg} . This could for example be done by a detailed back trajectory and source appointment analysis to which a forthcoming study will be devoted. Likewise, release of sea salt halogens to the gas-phase could add another 0.5 ppt to BrO (or about 0.7 ppt of Br_y^{inorg}) in the upper TTL (Schmidt et al., 2016).

and
(3) changed text in the introduction (page 2, line 11 cont).

…(3) so-called very short-lived species (VSLS), and (4) inorganic bromine transported into the upper troposphere, e.g. previously released from brominated VSLS and/or sea salt (e.g., Saiz-Lopez et al. (2004), Fernandez et al. (2014), Schmidt et al. (2016)). This inorganic bromine is also transported into the stratosphere.

(4) On page 14, line 23 cont.: Therefore, effective loss processes for inorganic bromine, for example

by heterogeneous uptake of inorganic bromine on aerosol and cloud particles, must act in the atmosphere (e.g., Schmidt et al. (2016)).

b. Also, In the model description (P8,L21-23), the surface concentration of VSL is 1.00 pptv for CHBr3, CH2Br2 and other VSLS. Why at (P12,L12) a value of 1.05 pptv is informed?. Further on, in the conclusions (P17,L15) the 1.0 ppt value is mentioned again. It may simply be a typo? Even when a 0.05 ppt value will not make a difference, this point should be made clear and consistent. How were the surface emissions adjusted?

Thanks for finding this error, we corrected the typos on P12 and P17.

4. In relation with my previous comment about an improved description of the specific model configuration used in this study, the authors state that "No other (c.f., unknown organic or inorganic) sources of bromine for UT, LS, and TTL are assumed (e.g., Fitzenberger et al. (2000), Salawitch et al. (2010), Wang et al. (2015), and others), except that we add 0.5 ppt to the modeled tropospheric BrO in agreement with the finding discussed below (section 4.6)". Later in Section 4.6, no specific mention is given about this additional source of BrO.

The reviewer is correct this was not clearly stated. As explained already above, only in the simulated curtains used for the RT calculations BrO was set to 0.5 ppt in the lower troposphere when the modelled predicted lower BrO. This was done in order to better represent the BrO absorption introduced by the small fraction of light traveling through the lower troposphere before being analysed by the limb oriented telescope on the GH (at 14 to 18 km) (see Figures 14 and 15 in Stutz et al., 2016).

We accordingly changed the text in section 2.6 (page 8, line10 cont.) to: "Only in the RT simulations [BrO] is set to 0.5 ppt near the ground, where TOMCAT/SLIMCAT predicted lower BrO concentrations (see Figure 2 middle right panel), in agreement with the findings discussed in Stutz et al. (2016) and the recent study of Schmidt et al. (2016). "

As BrO is used to constrain inorganic bromine using TOMCAT/SLIMCAT, a clear description of this additional source of BrO must be given in the text.

No, TOMCAT/SLIMCAT is freely run with the sources of bromine as given in section 2.7.

b. Yang et al., 2005 and Ordoñez et al. 2012 show that an additional source of inorganic bromine from sea-salt in the MBL is required to reproduce observations. Fernandez et al 2014 highlighted the importance of the sea-salt contribution for Bry in regions of strong convection such as the tropical western-pacific. Is this additional source of BrO in this work related to sea-salt recycling?, if so, is it constrained as a boundary condition or explicitly calculated?

Please see our response to previous questions

Please expand the discussion about this important omission. In Section 4.6 (P16,L10-13) the impact of sea-salt (or any other additional source) on Inferred Brytotal should also be discussed.

The recent modelling study by Schmidt et al., JGR (2016) indicates that 30% of inorganic bromine in the free troposphere might be due sea to salt. Their model also simulates [BrO] concentration of about 0.5 ppt in the free tropical troposphere. We find [BrO] < 0.5 ppt from the down-looking observations (Figure 15 in Stutz et al., 2016), and that between 0.5 ppt to 5.25 ppt (mean 2.63 +/- 1.04 ppt) of inorganic bromine is transported through the bottom of the TTL. Consequently, our conclusion on contribution 4 (which includes sea-salt derived bromine) in the tropical troposphere appears to be fairly reasonable. Since SLIMCAT/TOMCAT is a more stratospheric centric CTM, omitting details of heterogeneous and microphysical processes of sea-salt derived bromine in troposphere, i.e. treating it as a model boundary condition, is justifiable to save computer time. Finally, since in our assessment on TTL bromine is based on measured BrO (CH4, O3, and NO2) and detailed photochemical modelling, no sizeable amount of bromine is omitted in the model, except that eventually some bromine (sub ppt, see below) might be tight to the TTL aerosol (which however is not really founded based on the findings of Murphy et al., 2016, (Halogen ions and NO+ in the mass spectra of aerosols in the upper troposphere and lower stratosphere, Geophys. Res. Lett., 27, 3217–3220, 2000 and our personal communication in 2000).

For the changes to the text see above.

5. In Section 2.1 (DOAS measurements of O3, NO2 and BrO), a companion paper (Stutz et al., 2016), describing the DOAS measuring technic used during the ATTREX campaign, is introduced. However, the current manuscript makes too many references to Tables, Figures and Sections within the Stutz et al. paper, which do not introduce additional clarification and in most cases difficult a direct reading of the main results. Please, revise the whole manuscript on this respect and keep the references to the Stutz et al., 2015 only when they are relevant for the results presented here.

In fact, we were trying to fit the entire material into a single manuscript, i.e. (a) a description of the instrument, (b) the spectral retrieval (DOAS), (c) the novel technique (scaling method) for the concentration retrieval, (d) the RT and CTM calculations and (e) the data interpretation. However combining (a) to (e) would have made a single manuscript too long and thus rather challenging to read. Consequently, we decided to split the study into two papers. We recommend to read the Stutz et al. (2016) paper in order to understand what information can be inferred from the measurements, and what information can not be obtained (c.f., averaged profiles of measured radicals, or a direct comparison to the Fernandez et al., 2014 and Saiz-Lopez and Fernandez, 2016 studies because they address a different atmospheric compartment or altitude range, see your comment below). Because the present manuscript often refers to the measurements, the underlying retrieval, and data interpretation, we feel it is rather necessary to frequently refer to the Stutz et al., (2016) manuscript. We would also like to add that the two manuscripts are linked to each other in the AMT/ACP environment and should be considered part 1 and 2 of the same study.

6. The results presented here somehow contrast with previously published measurements/modelling approaches. While the discussion respect to the findings from Wang et al., 2015 and Volkamer et al., 2015 are extensively discussed in section 4.3 (P13,L3-26), just a brief comment on the discrepancies respect to Fernandez et al., 2014 and Saiz-Lopez and Fernandez, 2016 is presented (Section 4.5, P15,L0-4).

The definition of the lower end of the TTL remains controversial, as already discussed above. We had several discussions with colleagues on this topic but no consensus could be reached. In fact, there is only little overlap (with respect to altitude, Θ, p) between the BrO measurements of Wang et al., (2015) Volkamer et al., (2015) and modelling presented by Fernandez et al., (2014) and Saiz-Lopez and Fernandez (2016) (which according to our preferred TTL definition based on Fueglistaler et al. (2009) addressed more the bromine photochemistry in the upper tropical troposphere) and our study. Since two different regimes are described it is not necessary to address them in greater detail (except to compare Wang et al., (2015) and Volkamer et al., (2015) with our BrO profile (see Figure 3a).

With regards to the [Br]/[BrO] ratio, the common pattern shown in Figs. 4-9 is that whenever BrO mixing ratios decrease, both HBr and atomic Br increase.
Yes, this is a consequence of the adopted JPL bromine photochemistry in TTL and LS and decreasing O3 concentrations towards the (our) bottom of the TTL.

When this inversion is observed, the flight altitude and O3 levels also decrease, indicating that the lower TTL is being probed. In most cases HBr surpasses Br, while at some points (e.g., Fig 5f, 23:00) [Br] dominates. Thus, the Br and HBr prevalence seems to depend on the height (and possibly temperature, not shown) at which the TTL is being probed. I would suggest further discussion and interpretation of those results. Particularly, if the absence of heterogeneous recycling is affecting the inferred BrO/Br ratio?.

We added two small paragraphs to clarify this issue.

P12, line 5 cont: Panels (e) in Figures 3 to 8 compare measured and modelled BrO. Again measured and modelled BrO mixing ratios reasonably compare for most of the flight, but sizable discrepancies are also discernible for some flight sections. Possible reasons for the latter, which are discussed in the following section, may be due to deficits in the models assumption of the sources of bromine (see section 4.2), and/or deficits in the adopted photochemistry (see section 4.4).

P14, line 5 cont: Overall this behavior is expected from arguments based on the amount and composition of the brominated organic and inorganic source gases, their lifetimes, atmospheric transport, and photochemistry (e.g., Fueglistaler et al. (2009), Aschmann et al. (2009), Hossaini et al. (2012b), Ashfold et al. (2012), WMO (2014), Fernandez et al. (2014), and Saiz-Lopez and Fernandez (2016), and others). In particular, for our measurements at daytime, it is observed that (a) BrO increases with O3 and available Bry^{inorg} and thus altitude, (b) the predicted BrO/Bry^{inorg} ratio decreases towards the bottom of the TTL, where (c) HBr and/or Br atoms may become as abundant as BrO, but HOBr does not play a major role in the Bry^{inorg} partitioning. While observation (a) is primarily due to the increased destruction of the short-lived Bry^{org} species and the efficient reaction of the released Br atoms with altitude dependent ozone concentrations, observations (b) and (c) are due to reactions of the Br atoms with CH2O, (and to a lesser extent H2O2) into HBr which is recycled to Br atoms through reactions with OH and on the available surface of aerosols and cloud particles, as predicted by Fernandez et al. (2014), and Saiz-Lopez and Fernandez (2016). Noteworthy is also the predicted minor role of HOBr formed by reactions of OH radicals with heterogeneously produced Br_2, or by the reaction HO2 + BrO. While the rate of the former reaction is small due to short photolytic life-time of Br2, the rate of latter reaction is small due to the small HOx concentrations in the TTL compared to photolysis of HOBr at daytime.

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7. In section 4.1 the authors directly start showing results for Figs. 4-9. Not a single description is given to Fig. 3. Thus, Fig. 3 should be moved further down in the text.
We agree. Figure 3 is now moved to become Figure 12.

In P11,L17-20 you state that "The excellent agreement achieved between measured and modelled CH4, and O3 lends confidence that the altitude-adjusted TOMCAT/SLIMCAT model fields reproduce well the essential dynamical and photochemical processes of the probed air masses.". The authors can only assure a sentence like this by means of a full vertical profile validation of the species, not only comparing data at a specific level.

In the core we agree, but as matter of fact our observations are covering largely different altitudes (for example during the dives), photochemical regimes (the LMS, and TTL), SZA's ranging from 0^o to 80^o degrees et cetera that at least we were really surprised how well the measurement and the model agree. Accordingly, we replaced excellent with …..astonishingly good …. in the text.

8. The works possess several informal phrases which may not fit well within a scientific work. I list below some of them (but certainly not all), that maybe should be rephrased to a more appropriate structure, justified by numbers/references or removed from the MS.

Abstract, P2,L4: "… and the expectation based on the destruction of brominated gases."

We accordingly changed the phrase to …. and the expectation based on the photochemical destruction of the brominated source gases.

P4,L1: "… indicating that some Bry_inorg (i.e. several ppt) is directly transported from the tropopause"

We accordingly changed the phrase to … "… indicating that variable amounts of Bryinorg (i.e. several ppt) from the troposphere into the stratosphere"

P9,L17: "…, some exciting observations and details"

We accordingly changed the phrase to "…, some observations, their details as well as some results"

P11,L4: "… we refrain from this much more complicated approach"

We keep it since as conclusion (using a personal pronoun) the phrase appears to be justified.

P11,L27: "… NO2 concentrations meet the expectations for NOx"

We accordingly changed the phrase to …."… NO2 concentrations meet the expectations with respect to it's a partitioning and total NOx"

P16,L24: "By far …"

We accordingly erased …By far …"

9. There are several other sentences that may benefit from revision. I list some of them below:

P8,L22: [CHClBr2,CHCl2Br,CH2ClBr,…]. What the three dots means? Please specify.

In English grammar it is called an astrophic continuation, see https://en.wikipedia.org/wiki/Glossary_of_literary_terms i.e. it stands for other not considered minor brominated organic source gases. In fact the native speakers in list of authors had no objection to use it, but it could be necessary to contact an Anglist on this.

P12,L3: NOy=(NOx,N2O5,HNO3,HO2NO2,…. What the three dots means? Please specify.

See above. Other, not considered minor NOy species for example ClONOy and BrONOy.

P17,L14: Once again [CHClBr2,CHCl2Br,CH2ClBr,…]

See above. Other, other not considered minor brominated organic source gases.

P18,L3: (Here: cite Hossaini 2016, acp when published)?

Thanks. We updated the references to Hossaini et al. (2016).

Figures Comments:

Fig. 1: All results shown in this paper are for the ATTREX Flights performed during 2013 in the Eastern Pacific. Then why do you show panel A with the ATTREX 2014 flights that are not used here?

We accordingly changed the Figure to only display the 2013 flights.

Fig. 3: This Figure should be moved down in the text to make it consistent with the presentation of results. Also, it may be unified into a 2 panel figure, with only 1 caption that distinguishes between the a) and b) panels. The same applies for Fig. 13.

We moved both Figures to become the new Figures 12a and b, and we merged them into a two panel plot. We also merged Figure 13a and b.

Fig. 4: A portion of the caption is completely missing.

Figure 3. Panel (a) shows the time-altitude trajectory of the sunlit part of the GH flight track (SF1-2013) on Feb. 4/5, 2013 (SF1-2013). Panels (b)-(e) show inter-comparisons of TOMCAT/SLIMCAT-simulated fields with observations of (b) CH4 (UCATS), (c) O3 (NOAA), (d) NO2 (mini-DOAS), and (e) BrO (mini-DOAS). The grey-shaded error bars of the mini-DOAS NO2 and BrO measurements includes all dominating errors, i.e. the spectral retrieval error, the overhead and the error due to a tropospheric contribution to the slant absorption, and the absorption cross section uncertainty. Panel (f) shows the SLIMCAT modeled Bry partitioning for the standard run #583. Panel (g) shows a comparison of inferred and modeled Br_y^{inorg}, including the errors as a grey band. The dashed vertical lines in Figures 4-9 separate different atmospheric regimes: (I) is the extra-tropical lowermost stratosphere, (IIa, IIb, ..) different mixing regimes of air from the extra-tropical lowermost stratosphere, and (III) from the tropical tropopause layer.

This should be carefully controlled before submission. Also, following the equivalent figures for the rest of the flights (Figs. 5-9), no mention is given to what the vertical dashed lines represent. In addition, it would be very helpful to show a constant (dashed) line for O3 = 150 ppb and CH4 = 1790 pptv to distinguish the periods where the subtropical and TTL air was being probed.

Wouldn't it be a good idea to show the "mean temporal profile" measured by all of the ATTREX flights (i.e., for equivalent SZA)??

We thought about it and came to the conclusion that this is not really a good idea because the amount of BrO would also depend on total Br_y^{inorg}, O3, NO2, ….

Fig. 13: The large values of BrO at theta = 390-400 K within the freshly ventilated TTL (BrO > 7.5 pptv) shown during flight SF2 makes me doubt about the ability of the the CH4 < 1790 pptv as a good proxy for distinguishing stratospheric air.

Again it tentatively separates LMS from TTL air, for which unfortunately no strict horizontal barrier or criteria exists to distinguish both compartments.

Also, What is the meaning of showing Fig. 13b., for which most of the panels show no data at all??

Inferred total Br_y^{inorg} in the LMS. Unfortunately, due to operational constraints no measurements are available for $\Theta < 380$ K.

Fig. 14: Flights SF2 and SF4 are not shown. Why not?.

For SF2, GWAS did not measure VSL bromine and for SF4 a DOAS retrieval problem exists (see text).

(P14, L5) It would be a good idea to show the mean results for the campaign, and then highlight results for each of the flights.

Based on our experience we think averaging is often not a good idea. In fact, we provided comparable results once (for IO), which was then incorrectly used (by not properly considering the actual photolysis frequency during the measurements) in follow-on studies.

Fig. 11: I was surprised about the dispersion on the modelled/measured scatter plot for CH3Br. Being the bromo-carbon with largest lifetime, I would expect it to have an equivalent dispersion to the halons. No mention is given about this issue in the text.

Probably your surprise calms considered that the data range from 6 to 7.5 ppt for CH3Br and from 3 to 4 for Halon 1211, i.e. due to the scaling where the point (0,0) is truncated.

Additional Scientific Comments:

P2,L15: Is there a direct assignation of WMO, 2014 values specifically to year 2011?

It is assigned to year 2013, since only publications until 2013 are included in the report.

P3,L1: From which reference/s do you obtain the (2.5-4) ppt error on Bry inorg uncertainties within the inorganic method?

From our own experience (+/-2.5 ppt) and published literature (+/-4 ppt) (c.f., Parella et al., 2013)

P3,L4: UT, TTL and LMS should be defined independently in the abstract and introduction. There is no sense to introduce exactly which definition of the TTL you used in the abstract/introduction.

For the definition of the UT and TTL see the off-line discussion in which you were included. Even more complicated is the separation of the TTL and LMS since there exists no fixed barrier, even not with respect to PV. Since no dynamical variable were measured from aboard the GH, we decided to use the methane >< 1790 pptv criterion to separate both air masses as act of necessity.

P3,L32: Dorf et al., 2008 reported a contribution from VSL of (4.0 ± 2.5) for PG and (5.2 ± 2.5) for total (SG+PG). I do not find where you get the value of (2.5 ± 2.6) ppt. Also, there seems to be a confusion in the interpretation of contributions 3 and 4) from Dorf et al.

We checked our files, and accordingly changed to sentence to "The most direct information on contributions 3 and 4 came by the studies of Dorf et al. (2008), WMO (2011), and Brinckmann et al. (2012). They inferred 1.25± 0.16 ppt (VSLS-SGs, contribution 3) + 4.0±2.5 ppt (PGs, contribution 4) = 5.25±2.5 ppt (contributions 3 and 4) and 2.25±0.24 ppt (VSLS-SGs, contribution 3) + 1.68±2.5 ppt (PGs, contribution 4) = (3.98±2.5) ppt (contributions 3 and 4) from two balloon- borne soundings performed in the TTL and stratosphere over north-eastern Brazil during the dry season in 2005, and 2008, respectively."

P4,L4: Saiz-Lopez et al., 2012 also estimated the climatic impact of VSL sources within a CCM.

We added the reference.

P7,L10: Please describe which species were measured by the GWAS sampler, and which ones were used within this work.

We added a paragraph on P7, L7cont.

P7,L27: "The received limb radiances …". Do you mean the limb radiances measured with the mini-DOAS instrument? Please specify.

We accordingly changed the text to… The measured limb radiances of the mini-DOAS instrument…

P9,L3: Other works used this type of experimental data measurements on top of a model "curtains" (i.e Nicely et al., 2016). Some reference to any of these articles could be given here.

Using predicted curtains in the interpretation retrieval of UV/vis remote sensing data is not new at all. For example, we used it already in 2000 in the Harder et al., study (Figure 1), and later in studies, Weidner et al., 2005, Dorf et al., 2006….. and of course the IR community uses modelled curtains to forward guess their observations since the early 1990s.

P9:L20: What do you mean by "the NASA-ATTREX flights of the Global Hawk were strongly biased with respect to the sampled air masses". Please clarify.

The primary focus of NASA ATTREX mission was to study aerosol and clouds within the TTL (Jensen et al. 2015), and not to probe air of the subtropical LMS. So the flights went from EAFB base straight to the predicted coldest spot in the TTL on the highest possible cruise altitude (also because of air safety reasons, without losing fuel in performing dives in between at daytime). In addition, the GH has only two gears, either full thrust or no thrust on the engine (the latter used to perform the dive)

P11,L27-30: Please specify for which Flights the values for NO2 range between (70-170) ppt and were interpreted as belonging to the LMS.

For the separation of the LMS and TTL see above. The reminder is inferred from the data.

P12,L9: What do you mean by "even if the data is scattered from flight to flight"?

During the flight and from sortie to sortie the measured and modelled source gas data agree fairly well, but not perfectly.

P12,L17: Ordoñez et al. 2012 also describes the geographical and temporal variability of oceanic VSL sources.

….which was not implemented in the present simulation, primarily due to reasons given above (replies to queries 3 and 4). Also the Ordoñez et al. 2012 emission scenario is not undisputed for all VSLS species (see Hossaini et al., 2016).

P14,L6-7: Please explain better what you mean by "very young air" and "older air". Are you considering the [CH4] proxy given before?

We accordingly changed the text to ….. or comparable younger air based on measured [CH4].

P15,L5-7: A printed value of the overall Bryinorg error (and range) derived from the analysis shown on panel f of Fig. 4-9 would be helpful in the text.

Unfortunately, this poses a problem since the error changes from observation to observation due to the factors mentioned in the text. So addressing them in text would require an extended table. Individual errors bars are however given in Figure 14, i.e. for flight section when the WAS instrument sampled air for the brominated organic species.

P15,L22-26: All the analysis about the Bryinorg increment due to the decrease in VSLS is performed based on the "theoretical" dashed diagonal lines shown in Fig. 15. But the "modelled" diagonal lines are not shown for neither of the flights. Why? Including the modelled lines would strengthen the analysis, and justify the conclusions obtained here. Also, what do you mean by "…extrapolating the data points along lines of constant [VSLS]+[Bryinorg] (…) to [Bryinorg] = 0"? Do you mean getting the intercept of each of the (not shown) lines for each flight?

Naively speaking yes. However, the plot expresses something like a 'thought experiment' in that (by incorrectly) assuming that if there were no loss of bromine in the troposphere (which we know is not true), then near surface air would at least need to contain the amount of VSL bromine as indicated by the interpolation to [Bryinorg] = 0. Such a thought experiment is justified based on that (a) near surface VSL bromine measurements are much more frequent than VSLS plus inorganic bromine measurements (the latter virtually do not existing).

P16,L12: It is not clear how the range (0.5 to 5.25) pptv or uncertainty (± 1.04 pptv) of inferred Bry_{inorg} values is computed. Are these the maximum-minimum values modelled with SLIMCAT for all flights? Is this a model average within the Eastern Pacific region where measurements took place?

Yes, the range (0.5 to 5.25) ppt spans the minimum and maximum Bry_{inorg}, and the (2.63± 1.04 pptv) is the average over all inferred Bry_{inorg} at the bottom of TTL (according to our preferred definition). By the way, the mean amount of inferred Bry$_{inorg}$ compares very well with the model results (at 17 km) mentioned in Navarro et al, 2015 for the Eastern Pacific (i.e. compare Figure 13a the panel for 370 to 380 K results with concentration given in Navarro et al., 2015, Table 1 for the Eastern Pacific, i.e. 5.98 (VSL + Bry$_{inorg}$) minus 2.96 ppt (VSLS) versus 3.1+/-1.28 ppt (see Figure 13a) of the presented study.

P16,L19: The chemical loss rates were computed within the tropics (i.e, considering the 0º - 360º longitudes) or only within the Eastern Pacific region? It is important to make this clear, and in case of considering the whole tropics, a comparison to the values obtained within the EP is needed.

We re-run the model and accordingly changed first the sentence in the introduction to ….. Finally, for the Eastern Pacific (170_W - 90_W) the TOMCAT/SLIMCAT simulations indicate a net loss of ozone of - 0.3 ppbv/day at the base of the TTL ($\Theta = 355$ K) and a net production of + 1.8 ppbv/day in the upper part ($\Theta = 383$ K)……and second in section 4.7 to….. The chemical rates are averaged over the Eastern Pacific region (20° S - 20 °N, 170 ° W - 90 ° W) for the duration of the campaign.

P16,L22-27: The chemical loss analysis gets into details of which independent families and specific channels are the major contributor to the total (or bromine) ozone loss rate. I suggest including a table/sentence defining all the families considered, and which reactions are considered at least for the bromine channel.

We accordingly included an annex explaining which reactions where considered in the ozone loss calculations.

P17,L9: I do not agree that your results provide confidence in the modelled NOy photochemistry. You have only shown results for NO2 in this work. Much deeper analysis of nitrogen cycles should be given in order to perform this statement within the conclusions. Please see also text in P12,L3-4.

We partly concur based on that other NOy species were not measured! However, the NOy species would need extra-long atmospheric life-times since the shorter lived NOy species (N2O5, HO2NO2, HONO, ClONO2, BrONO2) are readily photolysed in the TTL at daytime, and would add to NOx, and ultimately to NO2 (being in steady state with NO). Even a longer lived NOy species, such as HNO3 need to be correctly modelled, because its life-time is certainly shorter than that of CH4. If not true, it would it again add to NOx.

Technical/Linguistic Comments:

P2,L11: It is not necessary to include a minus sign whenever you state that the value represent a net destruction. There are many other places in the MS when this also occurs.

Yes but nevertheless correct.

P2,L15: Within the text and figures, the terms Bry and Bry$_{Total}$ are both used to represent the same quantity. Please unify the criterion.

We changed Bry^{Total} to Bry where necessary (cf. Figure 14).

P2,L17. All halons must be written either with capital H or lower case h.

We changed all halon to Halon.

P2,L32: … several tenths of ppt.

We accordingly changed the text.

P3,L15: Colombia, not Columbia

We accordingly changed the text.

P5,L29: UAS acronym is not used at all in the paper, there is no sense to define it. Also, if the size is in Liters, then capital L should be used.

We accordingly changed the text.

P13, L3-7: Consider rephrasing.

We changed to text to…. Second, even though Wang et al. (2015) used a technique similar to ours and in particular they use the same radiative transfer code (e.g., McArtim see Deutschmann et al. (2011)), they inferred the BrO profiles using the optimal estimation technique (Volkamer et al., 2015).

P14,L17: What about BrCl? It is shown in Figs. 4-9 but not included in the definition of Bryinorg?

We accordingly changed the text.

P14,L19-20: Have you thought on including in a table the most important reactions that were changed between the three sensitivity runs?

No since the reaction are well known and are already tabulated in the JPL compilations.

P15,L35: Is the call to Fig. 15. correct?. If so, please explain.
Yes it is correct.
P17,L6: do you mean anti-correlated?
We accordingly changed the text.
Fig. 2: The altitude range should be given in between brackets.
We accordingly changed the text.
Fig. 15: Consider rephrasing the sentence starting with: “If all Bry …” for one in the form “The dashed diagonal lines indicate …”

We changed the text to “If all Bryinorg resulted from destroyed VSL bromine of the same air mass from near the surface, then all data points should follow individual diagonal lines.”

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).

Responses to reviewer #2

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

Received and published: 13 November 2016

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 ΔSZA = 0.2° 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.

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).

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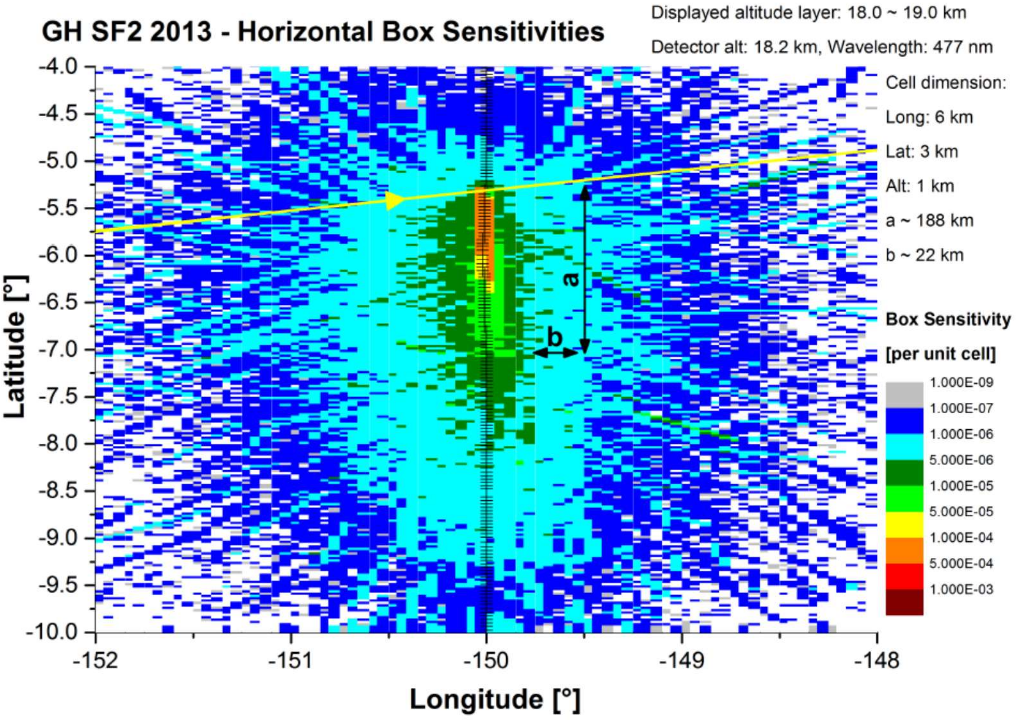

Figure 1: Horizontal sensitivity of DOAS measurements from the Global Hawk: Shown are horizontal box sensitivities in the altitude grid layer of flight altitude for a DOAS measurement with 0° telescope elevation angle at 18:24 UT, 27:1 ° N / 133:5 ° W, SZA = 57:2 °, SRAA = 102:2 °, detector altitude 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).

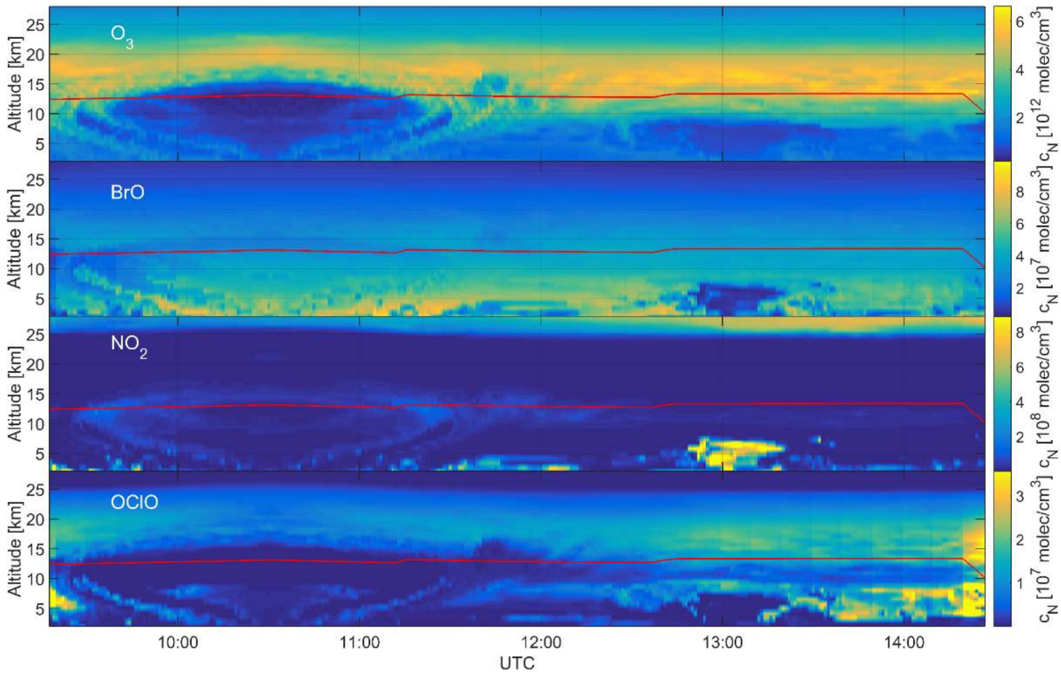

Figure 2: CLaMS predicted curtains of O_3, BrO and NO_2 and OClO for the Polstracc HALO flight from Kiruna on January 31, 2016 as function of flight time. The red lines indicate the flight trajectory of the aircraft. Please note that (a) the spatial and temporal structure of O_3, NO_2, BrO and OClO modelled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

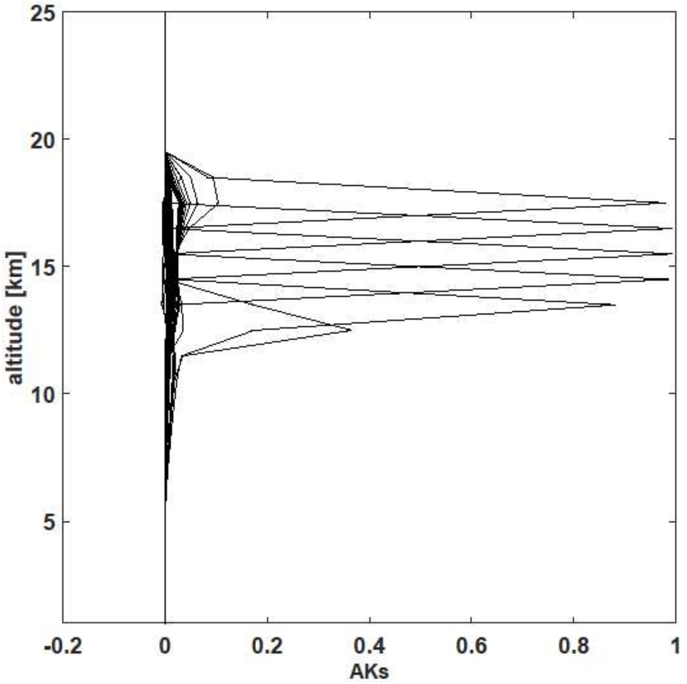

Figure 3: Averaging Kernels of the OE inversion of Fig. 3b (used in the comparison with the Wang et al., 2015 BrO profile.)

Probing the subtropical lowermost stratosphere, tropical upper troposphere, and tropopause layer for inorganic bromine

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Abstract. We report on measurements of CH_4 (in-situ measured by the Harvard HUPCRS and NOAA UCATS instruments), O_3 (in-situ measured by the NOAA dual-beam UV photometer) O_3, NO_2, BrO ~~and~~ (remotely detected by spectroscopic UV/vis limb observations, see (Stutz et al., 2016)) and of some key brominated source gases in whole air samples of the Global Hawk Whole Air Sampler (GWAS) instrument within the subtropical lowermost stratosphere (LS), tropical upper troposphere (UT) and tropopause layer (TTL) (14 - 18.5 km). The measurements were performed within the framework of the NASA-ATTREX (National Aeronautics and Space Administration - Airborne Tropical Tropopause Experiment) project from aboard the Global Hawk (GH) during 6 deployments over the Eastern Pacific in early 2013. ~~, , and were remotely monitored by analyzing limb scattered skylight in the UV and visible spectral ranges using the observations of the mini-DOAS (Differential Optical Absorption Spectroscopy) instrument (Stutz et al., 2016). was measured in-situ by the Harvard HUPCRS instrument and by the NOAA-UCATS instrument. was recorded at high precision by the NOAA dual-beam UV photometer, and some key brominated source gases were analyzed in whole air samples of the GWAS (Global Hawk Whole Air Sampler) instrument. All of these measurements are used for comparison~~ These measurements are compared with TOMCAT/SLIMCAT 3-D model simulations, aiming at improvements of our understanding of the bromine budget and photochemistry in the LS, UT, and TTL.

~~Potential changes~~ Changes in local O_3 (and NO_2 and BrO) due to transport processes are separated from photochemical processes in inter-comparisons of measured and modeled CH_4 and O_3. After ~~accounting for some minor deficiencies in the details of the modeled vertical transport,~~ excellent agreement is achieved among measured and simulated CH_4 and O_3, ~~indicating that in the subtropical LS and TTL concentrations mostly vary due to dynamical rather than photochemical processes. The TOMCAT/SLIMCAT simulations are further used for the interpretation of the measured and . In excellent agreement with the~~

~~model predictions,~~ measured and modeled [NO$_2$~~concentrations~~] are found to ~~range between~~ closely agree with $\leq$ 15 ppt in the TTL (which is the detection limit) and a typical range of 70 ~~-~~ to 170 ppt in the subtropical LS, and in the TTL ~~they are close to, or below the detection limit of 15 ppt in daytime. The measured BrO concentrations range~~ at daytime. Measured [BrO] ranges between 3 - 9 ppt in the subtropical LS~~, and in the TTLthey reach~~. In the TTL, [BrO] reaches 0.5 ± 0.5 ppt at the bottom ~~of the TTL~~ (150 hPa/355 K/14 km) and up to about 5 ppt at the top ~~of the TTL~~ (70 hPa/425 K/18.5 km, for the used TTL definition see Fueglistaler et al. (2009)), in overall good agreement with the model ~~simulation, and the expectation based on the destruction of brominated source gases.~~

~~The~~ simulations. Depending on the photochemical regime, the TOMCAT/SLIMCAT simulations tend to slightly underpredict measured BrO ~~depending on the photochemical regime studied, even when constrained to the measured and , and adjusted to match the observed concentrations of some key brominated source gases~~for large BrO concentrations, i.e. in the upper TTL and LS. The measured BrO and modeled BrO/$\mathrm{Br_y^{inorg}}$ ratio is further used to calculate inorganic bromine, $\mathrm{Br_y^{inorg}}$. For the TTL (i.e. when [CH$_4$] $\geq$ ~~1390~~1790 ppb), [$\mathrm{Br_y^{inorg}}$] is found to increase from a mean of 2.63 ± 1.04 ppt for θ's in the range of 350 - 360 K to 5.11 ± 1.57 ppt for ~~θ~~ θs $= 390 - 400$ K, whereas in the subtropical LS (i.e. when [CH$_4$] $\leq$ ~~1390~~1790 ppb), it reaches 7.66 ± 2.95 ppt for ~~θ~~ θs in the range of 390 - 400 K. Finally, ~~the~~ for the Eastern Pacific (170°W - 90°W) the TOMCAT/SLIMCAT simulations indicate a net ~~destruction~~ loss of ozone of - ~~0.5~~ 0.3 ppbv/day at the base of the TTL (θ = 355 K) and a net production of + 1.8 ppbv/day ~~at its top~~ in the upper part (θ = 383 K).

1 Introduction

At present bromine is estimated to be responsible for roughly 1/3 of the ~~observed global chemical depletion in~~ photochemical loss in global stratospheric ozone (WMO, 2014). Past research has revealed that total stratospheric bromine (Br$_y$) has (in 2013) 4 major sources, or contributions: (1) CH$_3$Br which is ~~mostly~~ emitted by natural and anthropogenic sources with a present contribution of 6.9 ppt to Br$_y$, (2) 4 major ~~halons~~ Halons (CClBrF$_2$ or Halon-1211; CBrF$_3$ or Halon-1301; CBr$_2$F$_2$ or ~~halon-1202~~ Halon-1202 and CBrF$_2$CBrF$_2$ or ~~halon-2402~~Halon-2402) all emitted from anthropogenic activities with a present contribution of 8 ppt to Br$_y$, ~~and~~ (3) so-called very short-lived species (VSLS), and (4) inorganic bromine ~~of~~ transported into the upper troposphere~~which is~~, e.g. previously released from brominated VSLS and/or sea salt (e.g., Saiz-Lopez et al. (2004), Fernandez et al. (2014), Schmidt et al. (2016)). This inorganic bromine is also transported into the stratosphere. Together sources 3 and 4 are assessed to contribute 5 (2 - 8) ppt to stratospheric bromine (WMO, 2014). Previous assessments of total Br$_y$ and its trend revealed [Br$_y$] levels of $\approx$ 20 ppt (16 - 23 ppt) in 2011, which has been decreasing at a rate of -0.6 %/yr since the peak levels observed in 2000. This decline is consistent with the decrease in total organic bromine in the troposphere based on measurements of CH$_3$Br, and the ~~halons~~ Halons (WMO, 2014).

Estimates of stratospheric Br$_y$ essentially rely on two methods: First, the so-called organic ($\mathrm{Br_y^{org}}$) method, where all bromine from organic source gases (SG) found at stratospheric entry level is summed (Wamsley et al. (1998), Pfeilsticker et al. (2000), Sturges et al. (2000), Brinckmann et al. (2012), Navarro et al. (2015)). Second, total inorganic bromine ($\mathrm{Br_y^{inorg}}$) is inferred from atmospheric measurements (e.g., performed from the ground, aircraft, high-flying balloons, or satellites) of the most abundant $\mathrm{Br_y}$ species, BrO, assisted by a suitable correction for the $\mathrm{Br_y^{inorg}}$ partitioning inferred from photochemical modeling (e.g., Pfeilsticker et al. (2000), Richter et al. (2002), Van Roozendael et al. (2002), Sioris et al. (2006), Dorf et al. (2006a), Hendrick et al. (2007), Dorf et al. (2008), Theys et al. (2009), Theys et al. (2011), Rozanov et al. (2011), Parrella et al. (2013), Stachnik et al. (2013)~~, and others).~~). Further constraints on stratospheric $\mathrm{Br_y}$ (range 20 - 25 ppt) were obtained by satellite-borne measurements of $\mathrm{BrONO_2}$ in the mid-IR spectral range at nighttime (Höpfner et al., 2009). While the organic method is rather precise for the measured species (accuracies are several ~~0.1~~ tenths of a ppt), it suffers from the shortcoming of not accounting for any inorganic bromine (contribution 4) directly entering the stratosphere. Uncertainties in the inorganic method arise from uncertainties in measuring BrO as well as from modeling $\mathrm{Br_y^{inorg}}$ partitioning, of which the combined error amounts to $\pm(2.5-4)$ ppt, depending on the type of observation and probed photochemical regime.

Past in-situ measurements of $\mathrm{Br_y^{org}}$ were performed at different locations and seasons within the upper troposphere, TTL, and stratosphere. In the present context the most important were measurements performed within the TTL (for the TTL definition see Fueglistaler et al. (2009)) over the Pacific from where most of the stratospheric air is predicted to originate (e.g., Fueglistaler et al. (2009), Aschmann et al. (2009), Hossaini et al. (2012b), Ashfold et al. (2012), WMO (2014), Orbe et al. (2015)~~, and others~~). These include the measurements (a) by ~~Schauffler et al. (1993), Schauffler et al. (1998), and Schauffler et al. (1999),~~ Schauffler et al. (1993, 1998, 1999), who found [VSLS] = 1.3 ppt (contribution 3) at the tropical tropopause over the central Pacific (Hawaii) in 1996, (b) by Laube et al. (2008), and Brinckmann et al. (2012) with [VSLS] = 2.25 ± 0.24 ppt (range 1.4 - 4.6 ppt) and [VSLS] = 1.35 ppt (range 0.7 - 3.4 ppt) found within the TTL over ~~north eastern~~ northeastern Brazil in June 2005 and June 2008, respectively, and (c) most recently those by Navarro et al. (2015), who found [VSLS] = 2.96 ± 0.42 ppt and 3.27 ± 0.49 ppt at 17 km over the tropical Eastern and Western Pacific in 2013, and 2014, respectively. Information on contribution 3 was further corroborated by measurements performed in the upper tropical troposphere by (b) Sala et al. (2014) who found [VSLS] = 3.72 ± 0.60 ppt in the upper tropical troposphere over Borneo in fall 2011 and (c) by Wisher et al. (2014), who inferred [VSLS] = 3.4 ± 1.5 ppt for the CARIBIC flights from Germany to Venezuela/~~Columbia~~ Colombia during 2009 - 2011, Germany to South Africa during 2010 and 2011, and Germany to Thailand/Kuala Lumpur, Malaysia during 2012 and ~~2013, and others.~~ 2013.

Supporting information on brominated VSLS concentrations typical for the boundary layer of the Western Pacific came from measurements performed during the TransBrom ship cruise in October 2009 (median 2.23 ppt and range from 1.45 - 4.14 ppt, Brinckmann et al. (2012)) and the VSLS measurements made around Borneo during the SHIVA project (median 5.7 ppt and range from 3.9 - 10.7 ppt, Sala et al. (2014)). Corroborating model calculations to these field studies by (a) Tegtmeier et al. (2012) indicated that from the Western Pacific on average only 0.4 ppt and at maximum up to 2.3 ppt of the emitted VSLS bromine may reach the stratosphere, while (b) Liang et al. (2014) estimated that up to 8 ppt of VSLS bromine may enter the base of the TTL at 150 hPa, whereby the VSLS emissions from the tropical Indian Ocean, the tropical western Pacific, and off the Pacific coast of Mexico are suspected to be most relevant, and finally (c) the CAM-Chem modeling performed within the study of Navarro et al. (2015) which indicates that over the Eastern and Western Pacific contributions 3 and 4 (called [VSLS + $\mathrm{Br_y^{inorg}}$] in the study) amount to 6.20 ppt (range 3.79 - 8.61~~) ppt~~ ppt) and 5.81 ppt (range 5.14 ~~-6.48) ppt~~- 6.48 ppt), respectively.

Using the inorganic method contributions 3 and 4 have been indirectly estimated from measured BrO performed at the ground, high flying balloons, or satellites (e.g., Pfeilsticker et al. (2000), Richter et al. (2002), Van Roozendael et al. (2002), Sioris et al. (2006), Dorf et al. (2006b), Hendrick et al. (2007), Dorf et al. (2008), Theys et al. (2009), Theys et al. (2011), Rozanov et al. (2011), Parrella et al. (2013), Stachnik et al. (2013)~~, and others~~). All together these studies pointed to a range between 3 - 8 ppt with a mean of 6 ppt for contributions 3 and 4. The most direct information on ~~contribution~~ contributions 3 and 4 came by the ~~study~~ studies of Dorf et al. (2008), ~~who inferred~~ WMO (2011), and Brinckmann et al. (2012). They inferred 1.25 ± 0.16 ppt (VSL-SGs, contribution 3) + 4.0 ± 2.5 ppt ~~and~~ (PGs, contribution 4) = 5.25 ± 2.5 ppt (contributions 3 and 4) and 2.25 ± ~~2.6 ppt for~~ 0.24 ppt (VSL-SGs, contribution 3) + 1.68 ± 2.5 ppt (PGs, contribution 4) = 3.98 ± 2.5 ppt (contributions 3 and 4) from two balloon-borne soundings performed in the TTL and stratosphere over ~~north-eastern~~ northeastern Brazil during the dry season in 2005, and 2008, respectively. The inferred bromine was thus often larger than [VSLS] inferred using the organic method (contribution 3), indicating that ~~eventually some~~ variable amounts of $\mathrm{Br_y^{inorg}}$ (i.e. several ppt) ~~is~~ are directly transported from the troposphere into the stratosphere (contribution 4).

Based on these findings, Saiz-Lopez et al. (2012) and Hossaini et al. (2015) provided evidence for the efficiency of short-lived halogens to influence climate through depletion of lower stratospheric ozone (for contribution 3), but without explicitly considering the effect of inorganic bromine readily transported across the tropical tropopause (i.e. contribution 4). They concluded that VSLS bromine alone exerts a 3.6 times larger ozone radiative effect than due to long-lived halocarbons, when normalized to their halogen content. Moreover the benefit for ozone and UV radiation due to the declining stratospheric chlorine and bromine since the implementation of the Montreal protocol was quantified in a recent study by Chipperfield et al. (2015). Finally, in a recent study Fernandez et al. (2016) pointed out that bromine from contribution 3 and 4 contribute about 14% to the formation of the present antarctic ozone hole, in particular at its periphery. Further, they suggests a large influence of biogenic bromine on the future Antarctic ozone layer.

The present paper reports on measurements of BrO (and $\mathrm{NO_2}$, $\mathrm{O_3}$, $\mathrm{CH_4}$, and the brominated source gases) made during the ATTREX deployments of the NASA Global Hawk into the LS, UT, and TTL of the Eastern Pacific in early 2013. Corresponding data collected during the Western Pacific deployments in early 2014 will be reported in a forthcoming paper, primarily since most of the 2014 measurements were performed under TTL cirrus-affected conditions, for which the interpretation of UV/vis spectroscopic measurements is not straightforward (see below). The present paper further addresses the amount of inorganic bromine found in the TTL, and its transport into the lowermost tropical stratosphere (contribution 4), together with the implications for ozone.

Our study accompanies those of Navarro et al. (2015) and Stutz et al. (2016). While Stutz et al. (2016) discusses the instrumental details and the methods employed to remotely measure BrO, $\mathrm{NO_2}$, and $\mathrm{O_3}$, the study of Navarro et al. (2015) reports on the GWAS measurements of $\mathrm{CH_3Br}$ (contribution 1), the ~~halons~~ Halons (contribution 2), and the brominated VSLS (contribution 3) analyzed in whole air samples, which were simultaneously taken from aboard the NASA Global Hawk over the Eastern and Western Pacific during the 2013 and 2014 deployments, respectively.

The paper is organized as follows. Section 2 briefly describes all key methods used in the present study. Section 3 discusses the ~~major features how to infer absolute concentrations from measured slant column amounts from , , and , namely the~~

~~optimal estimation technique, and of our novel -scaling technique together with their sensitivity to various input and model parameters~~measurements and along with some (necessary) data reduction. In section 4, the major observations are presented and ~~discussed along with~~ they are compared with previous BrO measurements and our modelling results, along with their implications for the amount of inorganic bromine present within the TTL. Further implications of our measurements for the photochemistry of bromine and ozone within the TTL and lowermost subtropical stratosphere are discussed. Section 5 concludes the study.

2 Methods

The instruments of the NASA-ATTREX package most important for the present study ~~consists~~ consist of a fast UV photometer for measurement of ozone (Gao et al., 2012), a gas chromatograph (UCATS, Wofsy et al. (2011) and Moore et al. (2003)) as well as a Picarro instrument (HUPCRS, Crosson (2008), Rella et al. (2013), and Chen et al. (2013)) to measure CH_4, CO_2, and CO, a whole air sampler (GWAS, Schauffler et al. (1998) and Schauffler et al. (1999)) to analyze a large suite of stable trace gases, and a 3-channel scanning limb mini-DOAS instrument for spectroscopic detection of O_3, NO_2, BrO, OClO, IO, O_4, O_2, H_2O_{vapor}, H_2O_{liquid}, and H_2O_{solid} in the UV/vis/near-IR spectral ranges (e.g., Weidner et al. (2005), Platt and Stutz (2008), Kritten et al. (2010), Kreycy et al. (2013), Kritten et al. (2014), Stutz et al. (2016)~~, and others~~).

~~In following all~~ All instruments, techniques, methods, and tools are briefly described in the following.

2.1 DOAS measurements of O_3, NO_2, and BrO

The mini-DOAS instrument is a UV/vis/near-IR 3-channel optical spectrometer by which scattered skylight received from limb direction and direct sunlight can be analyzed for ~~a large number of atmospheric species, including~~ O_3, NO_2, and BrO (beside for some other species, see above). Since the instrument and retrieval methods are described in detail in the accompanying paper by Stutz et al. (2016) (for further details see Table 2 therein), only some key elements of the data analysis are described here.

The post-flight analysis of the collected data for the detection of O_3, O_4, NO_2, and BrO and concentration retrieval include (a) the spectral retrieval of the targeted gases using the DOAS method (Platt and Stutz, 2008) (for the DOAS settings see Table 4 in Stutz et al. (2016)), (b) forward RT-modeling of each observation using the Monte Carlo model McArtim (Deutschmann et al., 2011) (for further details see section 2.6), and (c) for the concentration and profile retrieval either the non-linear optimal estimation (Rodgers, 2000), or the novel x-gas scaling technique (for details see sections 4.2. and 4.3 in Stutz et al. (2016)). Typical errors are ± 5 ppb for O_3, ± 15 ppt for NO_2, and ± 0.5 ppt for BrO, to which possible systematic errors in the individual absorption cross section need to be added. These are for O_3-UV $\pm 1.3\%$, O_3-vis $\pm 2\%$, NO_2 $\pm 2\%$, and BrO $\pm 10\%$, respectively (for more details of error budget see Stutz et al. (2016)).

2.2 In-situ measurements of O_3

The NOAA-2 polarized O_3 photometer (Gao et al., 2012) is a derivative of the dual-beam, unpolarized, UV absorption technique described by Proffitt and McLaughlin (1983). Briefly, the ambient and O_3-free air flow is alternately directed into two identical 60 cm long absorption cells. The 253.7-nm UV light from a mercury lamp is split into two beams that are each directed into one of the absorption cells. Since O_3 strongly absorbs 253.7-nm photons, the UV beam passing through the cell containing ambient ozone is attenuated more than the beam passing through the cell containing O_3-free air. Knowing the O_3 absorption cross section ($\sigma(O_3)$) and the absorption path length (L), the O_3 partial pressure ($p(O_3)$) in the ambient air can be derived using Beer's law.

The instrument has a fast sampling rate (2 Hz at < 200 hPa, 1 Hz at 200 to 500 hPa, and 0.5 Hz at ≥ 500 hPa), high accuracy (3% excluding operation in the 300 - 450 hPa range, where the accuracy may be degraded to about 5%), and excellent precision (1.1×10^{10} O_3 molecules/cm^3 at 2 Hz, which corresponds to 3.0 ppb at 200 K and 100 hPa, or 0.41 ppb at 273 K and 1013 hPa). The size (36 l), weight (18 kg), and power (50 - 200 W) make the instrument suitable for many unmanned aerial vehicle systems ~~(UAS)~~ and other airborne platforms. In-flight and laboratory inter-comparisons with existing O_3 instruments have shown that measurement accuracy (3 %) is maintained in flight.

2.3 CH_4 measurements by UCATS

The Unmanned aircraft system Chromatograph for Atmospheric Trace Species (UCATS) measures atmospheric methane (CH_4) on one gas chromatographic channel along with hydrogen (H_2) and carbon monoxide (CO) once every 140 seconds. UCATS has two chromatographic channels with electron capture detectors (ECDs), two ozone (O_3) ultraviolet absorption spectrometers, and a water vapor (H_2O) tunable diode laser absorption spectrometer (TDLAS). The details of the CH_4 chromatography are similar to those on ~~our~~ balloon and airborne instruments described in (Moore et al. (2003) and Elkins et al. (1996)). The addition of 100 ppm of nitrous oxide to the make-up line of the ECD enhances the sensitivity to H_2, CO, and CH_4 (Elkins et al. (1996) and Moore et al. (2003)). The separation of these gases in air is accomplished with a pre-column of Unibeads (2 m × 2 mm diameter), and a main column of Molecular Sieve 5A (0.7 m × 2.2 mm diameter) at ∼ 110 °C (Moore et al., 2003). The precision of the CH_4 measurement during ATTREX was ±0.5% and is calibrated during flight with a secondary standard after every three ambient air measurements. Instrumental drift is corrected between the standard injections. UCATS measurements are traceable to the WMO Central Calibration Laboratory (CCL) and are on the CH_4 WMO X2004A scale (Dlugokencky et al. (2005), with update given at http://www.esrl.noaa.gov/gmd/ccl/ch4_scale.html).

2.4 CH_4 measurements by HUPCRS

The Harvard University Picarro Cavity Ringdown Spectrometer (HUPCRS) consists of a G2401-m Picarro gas analyzer (Picarro Inc., Santa Clara, CA, USA) repackaged in a temperature-controlled pressure vessel, a separate calibration system with 2 multi-species gas standards, and an external pump and pressure control assembly designed to allow operation at a wide range of altitudes. The Picarro analyzer uses Wavelength-Scanned Cavity Ringdown Spectroscopy (WS-CRDS) technology to make high precision measurements of greenhouse gases (Crosson (2008), Rella et al. (2013), and Chen et al. (2013)). HUPCRS reports concentrations of CO_2, CH_4, and CO every $\sim$ 2.2 seconds and the data are averaged to 10 seconds. In-flight precision for CH_4 is 0.2 ppb in 10 seconds.

Briefly, the analyzer uses three distributed feedback (DFB) diode lasers in the spectral region of 1.55 to 1.65 μm. Monochromatic light is injected into a high-finesse optical cavity with a volume of 35 cm^3 and a configuration of three highly reflective mirrors (~~$\leq$~~ $\geq$ 99.995%). Internal control loops keep the cavity at 140 ± 0.02 Torr and 45 ± 0.0005 °C in order to stabilize the spectra. The injected light is blocked periodically and when blocked, the exponential decay rate of the light intensity is measured by a photo-detector. The decay rate depends on loss mechanisms within the cavity such as mirror losses, light scattering, refraction, and absorption by a specific analyte. A sequence of specific wavelengths for each molecule is injected into the cavity in order to reconstruct the absorption spectra. A fit to the spectra is performed in real time and concentrations are derived based on peak height. High-altitude sampling (i.e. very low pressure and temperature) necessitated transferring the core components of the Picarro analyzer to a sealed tubular pressure vessel, which is maintained at 35 ° C and 760 Torr. The analyzer's components are isolated from the pressure vessel to provide vibration damping and decoupling from deformations in the pressure vessel caused by external pressure changes.

The sampling strategy for HUPCRS consists of bringing in air through a rear-facing inlet, filtered by a 2 μm Zefluor membrane, and dehydrating this air by flowing it through a multi-tube Nafion dryer followed by a dry-ice cooled trap prior to entering the Picarro analyzer. A choked upstream Teflon-lined diaphragm pump delivers ambient air to the analyzer at 400 Torr, regardless of aircraft altitude, via a flow bypass. A similar downstream pump, with an inlet pressure of 10 Torr, facilitates flow through the analyzer at high altitude and ensures adequate purging of the Nafion drier. Measurement accuracy and stability are monitored by replacing ambient air with air from two NOAA-traceable gas standards (low- and high-span) for a total of four minutes every 30 minutes. These standards are contained in 8.4 ~~liter~~ L carbon fiber wrapped aluminum cylinders and housed in a temperature-controlled enclosure. The total weight of the package is 97 kg.

2.5 The GH Whole Air Sampler (GWAS)

The Global Hawk Whole Air Sampler (GWAS) is a modified version of the Whole Air Sampler used on previous airborne campaigns (Heidt et al. (1989), ~~Schauffler et al. (1998), Schauffler et al. (1999),~~ Schauffler et al. (1998, 1999), and Daniel et al. (1996)). Briefly, the instrument consists of 90 custom-made canisters, Silonite-coated (Entech Instruments, Simi Valley, CA) of 1.3~~liter~~ L, controlled with Parker Series 99 solenoid valves (Parker-Hannifin, Corp., Hollis, NH). Two metal bellows compressor pumps (Senior Aerospace, Sharon, MA) allow the flow of ambient air through a custom inlet at flow rates ranging from 2 to 8 standard ~~liters~~L/minute, depending on altitude. The manifold and canister module temperatures are controlled to remain within the range of 0 - 30 °C. GWAS is a fully automated instrument controlled from the ground through an Ethernet interface. Parameters to fill the canisters, flush the manifold, and control the temperature, are pre-determined in the Data System Module (DSM) inside the aircraft, to fill the canisters automatically in case of failure of the aircraft networks. However, during the entire flight, the parameters are manually set with the ground laptop computer to improve the sampling collection at different altitudes. During the ATTREX campaign, the canisters were filled to $\sim$ 3 standard ~~atmosphere~~ atmospheres (40 psi) in about 25 sec at 14 km and 90 sec at 18 km. The samples are analyzed using a high performance gas chromatograph (Agilent Technology 7890A) and mass spectrometer with mass selective, flame ionization and electron capture detector (Agilent Technology 5975C). Samples are concentrated on an adsorbent tube at -38 °C with a combination of cryogen-free automation and thermal desorber system (CIA Advantage plus UNITY 2, Markes International). The oven temperature profile is -20 °C for 3 min, then 10 °C/min to 200 °C and 200 °C for 4 min, for a total analysis time of 29 min. Under these sampling conditions the precision is compound/concentration dependent, and ranged from $\leq$2% to 20%. Calibration procedures as well as mixing ratios calculations are described elsewhere (Schauffler et al., 1999).

During ATTREX 2013 the whole air sampler measured a variety of organic trace gases, including non-methane hydrocarbons, CFCs, HCFCs, methyl halides, solvents, organic nitrates, and selected sulfur species. For this work a range of long and short lived organic bromine gases are measured including $\mathrm{CH_3Br}$, $\mathrm{CH_2Br_2}$, $\mathrm{CH_2BrCl}$, $\mathrm{CHBrCl_2}$, $\mathrm{CHBr_2Cl}$, $\mathrm{CHBr_3}$, and Halon 1211 ($\mathrm{CBrClF_2}$) and Halon 2402 ($\mathrm{C_2Br_2F_4}$). Halon 1301 ($\mathrm{CBrF_3}$) is not measured and a constant value of 3.3 ppt is used to account for the bromine content from this compound.

2.6 Radiative transfer modeling

The ~~received limb radiances~~ measured limb radiances of the mini-DOAS instrument are modeled in spherical 1D, and in selected cases in 3D, using version 3.5 of the Monte Carlo radiative transfer (RT) model McArtim (Deutschmann et al., 2011). The model's input is chosen according to the on-board measured atmospheric temperatures and pressures, including climatological low latitude aerosol profiles from SAGE III (http://www.eosweb.larc.nasa.gov/PRODOCS/sage3/table-/sage3.htm), and lower atmospheric cloud covers as indicated by the cloud physics lidar measurements made from aboard the GH (see http://cpl.gsfc.nasa.gov/). In the standard run, the ground (oceanic) albedo is set to 0.07 in UV, and 0.2 in visible spectral range. The RT model is further fed with the actual geolocation of the GH, solar zenith and azimuth angles as encountered during each measurement, the telescopes azimuth and elevation angles, as well as the field of view (FOV) of the mini-DOAS telescopes. Fig. 5 in Stutz et al. (2016) displays one example of an RT simulation for limb measurements at 18 km altitude. The simulation ~~demonstrates that~~ indicates that correctly accounting for the Earth's sphericity, the ~~correct treatment of~~ atmospheric refraction, cloud cover, ground albedo etc. ~~are relevant in the context of the~~ is relevant for the interpretation of UV/vis/near-IR limb measurements performed within the middle atmosphere (Deutschmann et al., 2011). Even though the 3 (UV/vis/near-IR) mini-DOAS spectrometers are not radiometrically calibrated on a absolute scale, past comparison exercises of measured and McArtim modeled limb radiance provide confidence on the quality of the RT simulations (e.g., see Fig. 5 and Fig. 6 in Deutschmann et al. (2011) and Fig. 2 in Kreycy et al. (2013)).

For the simulations of the trace gas absorptions measured in limb direction, the RT model is further fed with TOMCAT/SLIMCAT simulated curtains of the targeted gases simulated along the GH flight paths (see section 2.7). In the RT simulations [BrO] is set to 0.5 ppt near the ground, where TOMCAT/SLIMCAT predicts lower BrO concentrations (see Figure 2 middle right panel), in agreement with the findings discussed in Stutz et al. (2016) and the recent study of Schmidt et al. (2016).

2.7 Photochemical modeling

For the interpretation of our measurements, we use simulations of the TOMCAT/SLIMCAT 3-D chemical transport model (CTM) ~~(Chipperfield (1999), and Chipperfield (2006))~~(Chipperfield, 1999, 2006). More specifically, the simulations are used for inter-comparison with measured photochemical species, for assessment of the budget of $\mathrm{Br_y^{inorg}}$, and for sensitivity studies on the impact of our measurements on the photochemistry of bromine and ozone in the subtropical UT/LS, tropical UT, and TTL.

For the present study the TOMCAT/SLIMCAT model is driven by meteorology from the ECMWF ERA-interim reanalyses (Dee et al., 2011). The reanalyses are used for the large-scale winds and temperatures as well as convective mass fluxes (Feng et al., 2011). The model has a detailed stratospheric chemistry scheme with kinetic and photochemical data taken from JPL-2011 ~~Sander et al. (2011)~~ (Sander et al., 2011) with recent updates. The model chemical fields are constrained by specified time-dependent surface mixing ratios. For the brominated species, the following surface mixing ratios of stratospheric-relevant source gases are assumed: [CH_3Br] = 6.9 ppt, [halons]= 7.99 ppt, [$CHBr_3$] = ~~1.4~~1 ppt, [CH_2Br_2] = ~~1.05~~ 1 ppt, and Σ [$\mathrm{CHClBr_2, CHCl_2Br, CH_2ClBr}, ...$] = 1 ppt of Br. Organic bromine is thus [$\mathrm{Br_y^{org}}$] = 20.89 ppt at the surface, in agreement with recent reports (e.g., WMO (2014), Sala et al. (2014))~~, totalling = 21.19 ppt at the surface~~. No other (~~c.f.~~cf., unknown organic or inorganic) sources of bromine for UT, LS, and TTL are assumed (e.g., Fitzenberger et al. (2000), Salawitch et al. (2010), Wang et al. (2015)~~, and others) , except that we add~~). Omitting the release and heterogeneous processing of bromine from sea-salt aerosols (e.g., Saiz-Lopez et al. (2004)) in the model for the sake of saving computing time appears justified since (1) even though it is predicted to be relevant for bromine (∼30% of the total $\mathrm{Br_y^{inorg}}$) in the free troposphere (Schmidt et al. (2016)), its contribution to BrO in the TTL is at most of the order of the accuracy (∼0.5 ppt~~to the modeled tropospheric~~) of our BrO ~~in agreement with the finding discussed below (section 4.6) . The~~ measurements, (2) its time and space dependent sources (as for the brominated VSLS) are not well constrained, (3) in the modelled troposphere inorganic bromine only serve as boundary condition for bromine in the TTL, and (4) the additional BrO would not affect the BrO measurements-based calculation of $\mathrm{Br_y^{inorg}}$ for the TTL (see below). Further the surface concentration of CH_4 is specified based on observations of AGAGE (https://agage.mit.edu/) and NOAA, which reflect recent variations in its growth rate.

The standard model run (#583) is ~~initialised~~ initialized in 1979 and spun-up for 34 years at low horizontal resolution (5.6° × 5.6°) and with 36 unevenly spaced sigma-pressure vertical levels in the altitude range 0 - 63 km. Output from January 1, 2013 is interpolated to a high horizontal resolution (1.2° × 1.2°) and the simulation continued over the ATTREX campaign period using this resolution. The model output is sampled on-line along the Global Hawk flight tracks for direct comparison with the observations. Two further high resolution sensitivity experiments are performed from January 1, 2013 onwards. In run #584, the ratio of the photolysis frequency of $\mathrm{BrONO_2}$ and the three-body association rate reaction coefficient $\mathrm{k_{BrO+NO_2}}$ is increased by a factor 1.75 (e.g., Kreycy et al. (2013)). In run #585 the second-order rate reaction coefficient $\mathrm{k_{Br+O_3}}$ is set to the upper limit of its uncertainty range (Sander et al. (2011)).

For all model levels and for the time resolution (∼30 s) of the mini-DOAS measurements, 'curtains' of the targeted gases along the flight track are stored (e.g., see Fig. 6 in Stutz et al. (2016) and Fig. 2~~in this study~~). They are imported into the

~~radiative transfer~~ RT model McArtim for further forward simulations of the observations, and measurement versus model inter-comparison studies. The inclusion of simulated TOMCAT/SLIMCAT curtains in our study is particularly necessary for (a) the retrieval of absolute concentrations using the $\mathrm{O_3}$-scaling technique (see Stutz et al. (2016), section 4.3), (b) estimate of errors and retrieval sensitivities to various parameters (see section 4.4 and the supplement to Stutz et al. (2016)), (c) the separation of dynamical and photochemical processes in the interpretation of our data, (d) sensitivity tests for the assumed kinetic data, and (e) the assessment of total $\mathrm{Br_y^{inorg}}$ (see section 4).

Finally, details of how the loss in ozone is calculated is provided in appendix A.

3 Measurements and data reduction

Within the framework of the NASA-ATTREX project, the Global Hawk performed 6 flights into the subtropical LS, UT, and TTL over the Eastern Pacific in early 2013 (Fig. 1) and another 9 flights over the Western Pacific in early 2014. The present paper reports on the 2013 flights, since the 2014 flights were mostly performed into the cold TTL, where cirrus clouds mostly prevailed at flight level. Evidently due to the multiple scattering of light by the cirrus cloud particles, the interpretation of our UV/vis limb measurements is not straightforward. Accordingly the data collected in 2014 will be reported elsewhere in a future work. Details of the NASA-ATTREX 2013 instrument package, the flights, ~~some exciting observations and details~~ their details as well as some results on the collected data can be found in the articles of ~~Jensen et al. (2013) and Jensen et al. (2015),~~ Jensen et al. (2013, 2015), as well as on the project's website https://espo.nasa.gov/missions/attrex/content/ATTREX .

In February and March 2013, the NASA-ATTREX flights of the Global Hawk were strongly biased with respect to the sampled air masses, mostly because the scientific interest was primarily put on probing the TTL over the Eastern Pacific for aerosols and cirrus cloud particles during the convective season, rather than for the photochemistry of bromine in the LS, UT, and TTL (see Fig. 1). Therefore, and due to operational reasons typical flight patterns extended from Dryden/California into southern or south-western direction during daytime until a turn-point was reached and the back leg to Dryden in ~~north-eastern~~ northeastern direction occurred during the night, when the mini-DOAS instrument could not take measurements. The dives were mostly performed within the TTL, and occasionally within the subtropical lowermost stratosphere during the return legs at night but not during the out-going daytime legs. Finally the landings at Dryden were scheduled for the early local morning, mostly due to operational constraints. Therefore, no profiles of the targeted species could be obtained in the subtropical lowermost stratosphere at daytime, but a large number within the UT and TTL.

Furthermore, the latitudinal definition of the notations 'subtropical' LS and 'tropical' TTL need some clarification. According to the definition of Fueglistaler et al. (2009), the latitudinal boundary between the subtropics and tropics should be where the subtropical jet is located. However, since we do not infer dynamical parameters (such as the potential vorticity) from our data, we conveniently define the boundary according to proxies for (a) different air mass ages, i.e. $[\mathrm{CH_4}]$ concentrations $\leq$ ~~1390~~1790 ppb are labeled 'subtropical' and $[\mathrm{CH_4}] \geq$ ~~1390 ppb)~~ 1790 ppb are labeled 'tropical', and (b) photochemical regimes, i.e. $[\mathrm{O_3}]$ (subtropical when $[\mathrm{O_3}] \geq 150$ ppb, and TTL when $[\mathrm{O_3}] \leq 150$ ppb), which we find suitable from a visual inspection of our data (see below).

As mentioned above and outlined in detail in the study of Stutz et al. (2016), the processing of the mini-DOAS data included (a) spectral retrieval of the targeted gases from the mini-DOAS measurements (section 2.1), (b) forward modeling of the ~~radiative transfer~~ RT for each measured spectrum (section 2.6), and either applying ~~optical~~ optimal estimation or the novel x-gas scaling technique (see sections 4.1 and 4.2 in Stutz et al. (2016)). Comprehensive sensitivity simulations indicated that optical estimation based on constraints inferred from measured O_4 and/or relative radiance would not result in the desired error range (Stutz et al. (2016), section 4.2). Therefore we decided to apply the x-gas scaling technique (Stutz et al. (2016) and Raecke (2013)) with x being ozone measured in-situ by the NOAA-2 O_3 photometer (see section 2.2).

The O_3-scaling technique makes use of the in-situ O_3 measured by the NOAA instrument (Gao et al., 2012) and the limb measured O_3 total slant column amounts (SCD_{O3}) either monitored in the UV (for the retrieval of BrO in the 343 - 355 nm wavelength band) or visible wavelength range (for the retrieval of NO_2 in the 424 - 460 nm wavelength band) (see equation 12 in Stutz et al. (2016)). Here the ratio of the measured slant column and in-situ measured $SCD_{O3}/[O_3]$ can be regarded as a proxy for the (horizontal) light path length over which the absorption is collected. In fact in the paper of Stutz et al. (2016), it is argued that the so-called α factors account for the fraction of the absorption of the scaling gas x (e.g., x = O_3 in our study) picked-up on the horizontal light paths ahead of the aircraft relative to the total measured absorption. The sensitivity study on the α factors presented in Stutz et al. (2016) (e.g., in the supplement) indicates that for the targeted gases uncertainties in α factor ratios due to assumptions regarding the ~~radiative transfer~~ RT (for example due to Mie scattering by aerosols and clouds) mostly cancel out, while uncertainties in the individual profile shapes of the targeted and scaling gas are most relevant for the errors of the inferred gas concentrations. Therefore in the present study, profile shapes of the targeted and scaling gas predicted by the TOMCAT/SLIMCAT CTM are used in the ~~radiative transfer~~ RT calculations, aiming at the calculation of the α factors. The uncertainties in the profile shapes (assumed to be of the order of the altitude adjustment of the CH_4 and O_3 curtains, which are typically much smaller than the altitude grid spacing in the SLIMCAT/TOMCAT simulations) are then carried over to calculate the overall errors, as discussed in section 4.4 of the Stutz et al. (2016) study.

It should be noted that, for the flight on Feb. 21, 2013 (SF4-2013), the DOAS retrieval is much less robust than for all the other flights, most likely 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 entrance diffuser. Therefore the data of this flight are not analyzed in detail, but they are only reported for completeness here.

Finally, in our analysis only those data which are taken at a solar zenith angle (SZA) $\leq 88\,^\circ$ are considered, because for increasing SZAs the received skylight radiance requires increasingly longer signal integration times (longer than the standard integration time which is 30 s), and are thus averaged over longer distances ahead of the aircraft. Moreover, as the SZA increases the skylight is expected to traverse an increasingly inhomogeneous curtain of the probed radicals (e.g., inspect Figs. 5, and 6 in Stutz et al. (2016)). As consequence, the spatial grid of TOMCAT/SLIMCAT ($1.2 \times 1.2\,^\circ$) on which the photochemistry is simulated appeared too coarse for a useful interpretation of our measurements at large SZAs. Therefore for a tighter interpretation of our data, a model with higher spatial resolution than provided by TOMCAT/SLIMCAT would be required. Such an approach is for example followed in the balloon-borne studies of Harder et al. (2000), Butz et al. (2009), and Kreycy et al. (2013), and others. However, since both processes are likely to increase the error of our analysis, and since large SZA ($\geq 88^o$) measurements only constitute a minor part of all measurements, we refrain from this much more complicated approach.

4 Results and Discussion

In this section we first discuss how our mini-DOAS measurements of O_3, NO_2, and BrO, as well as of CH_4 (from ~~UCTAS~~ UCATS and HUPCRS), and of the organic brominated source gases (from GWAS) compare with the model predictions of the TOMCAT/SLIMCAT model (sections 4.1 and 4.2). Then measured BrO is compared with previous measurements in the UT/TTL/LS (section 4.3), and with the model predictions (section 4.4). Uncertainties and errors in the inferred $\mathrm{Br_y^{inorg}}$ are assessed (section 4.5), before implications of our measurements for total $\mathrm{Br_y}$ (section 4.6), and impacts of our measurements for TTL ozone are discussed (section 4.7).

4.1 Comparison with TOMCAT/SLIMCAT predictions

Figures 3 to 8 provide overviews on the measured data together with the TOMCAT/SLIMCAT modeled $\mathrm{Br_y^{inorg}}$ partitioning (panels f) and inferred total $\mathrm{Br_y^{inorg}}$ (panels g) as a function of universal time for each flight. The modeled values are obtained by linear interpolation of the curtain data (see Fig. 2) to the exact altitude of the GH.

The panels (b), and (c) of Figs. 3 to 8 show comparisons of measured and modeled CH_4, and O_3 mixing ratios. Here the measured and modeled species ~~agree excellently~~ closely agree within the given error bars, after the modeled curtains are ~~altitude-adjusted (~~altitude-shifted (i.e., interpolated) by the same amount until measured and modelled O_3 agree (for details see Stutz et al. (2016)). ~~The excellent~~ Noteworthy is that in most cases the altitude adjustment is less than the grid spacing of TOMCAT/SLIMCAT (about 1 km in the TTL), thus mostly accounting for the altitude mismatches of the actual cruise altitude of the Global Hawk and the model output rather than to deficits of the model to properly predict the vertical transport. The astonishingly good agreement achieved between measured and modeled CH_4, and O_3 lends confidence that the altitude-adjusted TOMCAT/SLIMCAT model fields reproduce well the essential dynamical and photochemical processes of the probed air masses. The quality of the dynamical simulations are further tested by comparing modeled and measured O_3 as a function of CH_4 (Fig. 9). For all flights the agreement of the observed and modeled O_3 vs CH_4 correlation is reasonably good, except for flights SF1-2013 and SF2-2013, where the UCATS measured CH_4 scatters around the simulated CH_4 concentrations. This scatter is most likely due to ~~calibration~~ precision errors of UCATS, rather than reflecting the real behavior of the atmosphere. Evidence for this conclusion is provided from the CH_4 comparisons for SF3-2013 to SF6-2013, in which the HUPCRS CH_4 data are taken; these data do not show such a scatter and compare reasonably well with the model predictions.

Panels (d) of Figs. 3 to 8 compare measured and modeled NO_2. Overall the measured (and modeled) NO_2 concentrations meet the expectations ~~for~~ with respect to its partitioning and total NO_x (= NO + NO_2 + NO_3) abundances in the LS, UT, and TTL over the pristine Pacific. Elevated NO_2 concentrations (range 70 to 170 ppt) are measured within the subtropical lowermost stratosphere, where aged air masses are probed, as indicated by depleted CH_4 concentrations and elevated O_3 concentrations (and presumably decreased N_2O concentrations). Note that N_2O is the primary source for stratospheric NO_x, and in the stratosphere CH_4 and N_2O destruction closely follow each other (e.g., Michelsen et al. (1998), Ravishankara et al. (2009)). Very low NO_2 concentrations ($\leq$ 30 ppt) are detected within the UT and TTL, indicating that the analyzed air does not originate from recently polluted, or lightning-affected regions. Further, the modeled NO_2 concentrations (red line in panel d) are found to fall into the given range of errors ~~of~~ in the measured NO_2 concentrations. This finding strongly indicates that, the NO_x and NO_y (= NO_x, N_2O_5, $HONO_3$, HO_2NO_2,...) budget and photochemistry of the LS, UT, and TTL are reproduced well in the TOMCAT/SLIMCAT simulations, and that overall the O_3-scaling technique works well for NO_2.

Panels (e) in Figures 3 to 8 compares measured and modelled BrO. Again measured and modelled BrO mixing ratios reasonably compare for most flight sections, but sizable discrepancies are also discernible for some flight sections. Possible reasons for latter are discussed in following, which may be due to deficits in the model's assumption regarding the sources of bromine (see section 4.2), and/or deficits in the adopted photochemistry (see section 4.4).

4.2 Comparison of measured and model organic bromine

Before measured and modeled BrO can be compared quantitatively, it is necessary to compare the measured amounts of different brominated source gases with the model predictions (Fig. 10). For the assumed (constant) surface ~~concentrations~~ mixing ratios (see subsection 2.7), measured and modeled CH_3Br (upper left panel), $CHBr_3$ (upper right panel), and for all other ~~halons~~Halons, for example H1211 (lower right panel), compare well, even if the data is scattered from flight to flight. For CH_2Br_2, however, TOMCAT/SLIMCAT run # 583 underpredicts the observed mixing ratio for high concentrations (by 0.1 ppt) and overpredicts it by up to 0.2 ppt for low concentrations (lower left panel). This is most likely due to an assumed too low surface concentration (~~1.05~~ 1 ppt), ~~and~~ variable mixing ratios at the surface not correctly considered in the model, and/or errors the atmospheric lifetime by reactions of CH_2Br_2 with OH radicals in the model (e.g. Mellouki et al. (1992), Ko et al. (2013), WMO (2014)).

The flight-to-flight and sample-to-sample scatter in CH_3Br, and $CHBr_3$ is mostly due to different source regions of the air masses probed during SF1-2013 to SF6-2013. This implies a spatially (and possibly time-dependent) varying source strength of the brominated natural source gases ~~to be implemented in the model~~ (e.g. ~~,~~ Hossaini et al. (2013), Ziska et al. (2013)~~, and others~~). In the present version of the TOMCAT/SLIMCAT simulations, this scatter introduces an estimated uncertainty of $\pm$ 0.8 ppt into Br_y^{org}, and potentially in the inferred Br_y^{inorg} available in the TTL. The systematic under-prediction of 0.1 ppt at high CH_2Br_2 concentrations, and its too long lifetime in the TTL leading to too large CH_2Br_2 concentrations in the model for old air (by up to 0.2 ppt) may cause an additional and systematic under-prediction of Br_y^{inorg} of up to $\leq$ 0.4 ppt in the model. Both contributions to the uncertainty in the Br_y^{org} are considered when comparing measured and modeled BrO, and Br_y^{inorg} (see below).

4.3 Comparisons of measured BrO with previous studies

Next, we compare our data with previous BrO measurements in the UT and TTL, i.e. the balloon measurements of Dorf et al. (2008), and the aircraft measurements of Wang et al. (2015) and Volkamer et al. (2015) during the TORERO campaign.

Overall the balloon-borne BrO profile measurements of Dorf et al. (2008) performed over tropical Brazil during the dry (i.e. the non-convective season) in June 2005 and June 2008 compare ~~excellently~~ well with the BrO profiles inferred from our measurements for the UT and TTL (i.e. typically [BrO] = 0.5 ~~-1.0~~- 1.0 ppt in the upper UT and base of the TTL, and up to 5 ppt at the cold point tropopause (e.g., compare Fig. 1 in Dorf et al. (2008) with Fig. 11).

The present study and the BrO profile measurement of Dorf et al. (2008) ~~are~~do, however, ~~in contrast to recent reports on the~~ not confirm the recently reported presence of BrO amounting up to 3 ppt in the tropical and subtropical UT, and around the bottom of the TTL (14 km) (Wang et al., 2015) (compare Fig. 2, panel A in Wang et al. (2015) with panel (c)in Fig. 11). ~~Here we emphasize again that we find no indications for~~ Sensitivity studies using the BrO profile of Wang et al. (2015) as the a priori of an optimal estimation concentration retrieval for the ATTREX measurements results in a kink of BrO around 12 km (Fig. 11). This behavior can be explained with the disagreement between the observed profiles above 13 km and the insensitivity of the ATTREX observation to BrO below this altitude.

While the geographical location of the observations by Wang et al. (2015) and those of the GH did not overlap, the ATTREX flights covered a wide geographic area over which we did not find indications of unexpected high or elevated BrO concentrations in the UT, and TTL, either from inspecting the UT from above (e.g., see Fig. 15 in Stutz et al. (2016)), nor when directly probing the TTL (see Figs. 11 to 8).

Several similarities and differences exist between the ~~Wang et al. (2015) and~~ TORERO measurements reported by Wang et al. (2015) and Volkamer et al. (2015) and our study. Using NSF/NCAR G-V HAIPER, Wang et al. (2015) probed the UT and the bottom of the TTL (up to about 14 km) for BrO over an adjacent part of the Pacific, i.e. mostly off the western coasts of South and Central America ~~, but~~ notably during the same season, but in area more to the south than probed during the present study~~, but notably~~ .

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~~. So it could be just a matter of chance, or due to the different regions probed in both studies that we missed detecting elevated concentration in the~~ , 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 ~~.~~

~~Second, even though Wang et al. (2015) use a technique similar to us in the present study, and in particular they use the same radiative transfer code~~ (up to about 14 km), or that sea salt released bromine played a role (e.g., ~~McArtim see Deutschmann et al. (2011))for the interpretation of their measurements, they were using the~~ Schmidt et al. (2016)).

However, our study has identified possible problems when using optimal estimation technique ~~to retrieve the profiles (Volkamer et al., 2015). It is known that the optimal estimation technique may deliver robust results if the region of interest is carefully sampled, and if the so-called forward model describes reasonably well the physical reality (Rodgers, 2000). Accordingly, Wang et al. (2015), and Volkamer et al. (2015) invested significant effort to constrain well their radiative transfer, for example by using information on the aerosol type and their optical properties gained by other instrumentation and/or by constraining the radiative transfer with measured information on the absorption of the~~ with constraints based for example on measured O_2-O_2 ~~collisional complex (see Fig. 3 in Volkamer et al. (2015)). Our study on the sensitivity of the~~ 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 O_2-O_2 ~~absorption measured in limb direction as function of the cloud cover underneath (see sections 4.2 and Fig. 7~~ 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))~~as well as the results presented by Volkamer et al. (2015) (in their Fig. 3) clearly demonstrates the limitation of the -method to constrain the radiative transfer for UV/vis studies above an altitude 10 km, mostly because the bulk of the -collisional complex is located near the surface.~~ , 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 single profile measurement).

We did not encounter conditions without (marine stratus cumulus) clouds in this footprint during any of the ATTREX flights. Therefore, any skylight analyzed for the O_2-O_2 absorption in the limb direction may carry additional, or even ~~predominantly~~ substantial, information on the radiative transfer of lower atmospheric layers (see Figure 7 in Stutz et al. (2016)), rather than of the targeted atmospheric layers. We acknowledge that Wang et al. (2015) and Volkamer et al. (2015) selected 'cloud-free' conditions at the location of their profile measurement, but the cloudiness in the large area ahead of their aircraft is less clear.

~~Furthermore, Wang et al. (2015) , and Volkamer et al. (2015) did not use a stratospheric CTM to study the potential influence of changing overhead~~ Another challenge we encountered was that of the overhead BrO ~~concentrations on their results. As result, the predominant occurrence of atmospheric~~ column, which can substantially contribute to the limb BrO signal. The large concentrations of BrO in the stratosphere at daytime, and its potential column changes mostly due to a changing tropopause height or intrusion of tropospheric air (e.g., at the subtropical or polar jet) may mimic the presence of BrO in limb the direction, or at flight altitude (e.g., Wang et al. (2015), and Volkamer et al. (2015) and Fig. 14 in Stutz et al. (2016)). We solved this problem by using a highly resolved stratospheric CTM to study the potential influence of changing overhead BrO concentrations on our results.

In conclusion, ~~even though the reported~~ our sensitivity studies have shown potential problem with the O_2-O_2 constrained RT calculations used to retrieve vertical BrO profiles, as well as the need to accurately determine the stratospheric BrO column. With this in mind and the disagreement between our UTLS BrO profiles and TORERO flights 12 and 17 ~~were performed under clear-skies (Volkamer et al., 2015)~~Wang et al. (2015) and Volkamer et al. (2015), it is ~~unclear the extent to which unaccounted scattering due to aerosols and (probably) optically thin upper tropospheric clouds, lower level clouds, or changing overhead stratospheric contributed to the inferred (or by error attributed) elevated in the UT, and around the bottom of the TTL~~clear that future work is needed in reconciling the observations as well as the different retrieval approaches.

4.4 Comparison of measured and modeled BrO

Measured and modeled BrO are displayed in Figs. 3 to 8 (panel e), together with the modeled $\mathrm{Br_y^{inorg}}$ partitioning (panel f) and inferred $\mathrm{Br_y^{inorg}}$ (panel g). ~~Again elevated~~ Elevated BrO concentrations are measured within the LS (range 3 - 9 ppt), and lower BrO concentrations in the TTL (range 0.5 - 5 ppt), with the smallest BrO concentrations (0.5 - 1 ppt) occurring near the bottom of the TTL. Overall this behavior is expected from arguments based on the amount and composition of the brominated organic and inorganic source gases, their lifetimes, ~~and atmospheric transport~~atmospheric transport, and photochemistry (e.g., Fueglistaler et al. (2009), Aschmann et al. (2009), Hossaini et al. (2012b), Ashfold et al. (2012), WMO (2014), Fernandez et al. (2014), and Saiz-Lopez and Fernandez (2016)). In particular, for our daytime measurements it is observed that (a) BrO increases with $\mathrm{O_3}$ and available $\mathrm{Br_y^{inorg}}$ and thus altitude, (b) the predicted $\mathrm{BrO/Br_y^{inorg}}$ ratio decreases towards the bottom of the TTL, where (c) HBr and~~others).~~/or Br atoms may become comparable to BrO, but HOBr does not play a major role in the $\mathrm{Br_y^{inorg}}$ partitioning. While observation (a) is due to the increased destruction of primarily the short-lived $\mathrm{Br_y^{org}}$ species and the efficient reaction of the released Br atoms with increasing altitude and increasing ozone concentrations, observations (b) and (c) are due to reactions of the Br atoms with $\mathrm{CH_2O}$, (and less $\mathrm{H_2O_2}$) into HBr which is recycled back by reactions with OH and by variable amounts heterogeneously (depending on the available surface of aerosols and cloud particles) to Br atoms, as predicted by Fernandez et al. (2014), and Saiz-Lopez and Fernandez (2016). Noteworthy is also the predicted minor role of HOBr eventually formed by reactions of OH radicals with heterogeneously produced $\mathrm{Br_2}$, or by the reaction $\mathrm{HO_2 + BrO}$ and photolytic destruction of HOBr in the TTL. While the rate of the former reaction is anyway small due to short photolytic life-time of $\mathrm{Br_2}$, the rate of latter reaction is small due to the small OH concentration in the TTL as compared to photolysis of HOBr at daytime.

~~With these features in mind,~~ Fig. 12 compares measured and modeled BrO. For the majority of all flights (except flight SF4-2014, for which a DOAS retrieval problem exists which causes a ~~bias of~~ constant bias of about 2 ppt in inferred BrO), measured and modeled BrO ~~compare excellently~~ closely compare for low concentrations (i.e. close to bottom to the TTL), or ~~very young air~~ comparable younger air based on measured $\mathrm{CH_4}$. For larger BrO concentrations (and older air) good agreement between the measurement and model is found for SF1-2013, SF5-2013, and SF6-2013, when mostly air of low $\mathrm{NO_2}$ concentrations (and predicted low $\mathrm{BrONO_2}$ concentrations) is probed. For large BrO concentrations as encountered during flights SF2-2013, and SF3-2013, the measured BrO is up to 2 ppt, or 25% larger than what the model predicts. This gap could partly be closed by adjusting the $\mathrm{CH_2Br_2}$ surface concentration and atmospheric lifetime~~.~~, or by considering a detailed scheme for dehalogenation of sea salt, i.e. bromine activation (e.g. Saiz-Lopez et al. (2004), Fernandez et al. (2014), Schmidt et al. (2016)). Adjusting $\mathrm{CH_2Br_2}$ ~~thus~~ would add 0.4 ppt of $\mathrm{Br_y^{inorg}}$, or $\sim$ 0.3 ppt to BrO, thus removing the flight-to-flight scatter in source gas concentrations ($\pm$ 0.8 ppt) in $\mathrm{Br_y^{inorg}}$. This could for example be done by a detailed back trajectory and source appointment analysis to which a forthcoming study ~~well~~ will be devoted. Likewise, dehalogenation of sea salt could add another 0.5 ppt to BrO (or about 0.7 ppt of $\mathrm{Br_y^{inorg}}$) in the upper TTL (e.g., Saiz-Lopez et al. (2004), Fernandez et al. (2014), Schmidt et al. (2016)).

4.5 Uncertainties in estimating the inorganic bromine partitioning

Another reason for the gap in measured and modeled BrO may come from uncertainties in the used kinetic constants and how they affect the $\mathrm{Br_y^{inorg}}$ (= $\mathrm{Br + 2 \cdot Br_2 + BrO + BrONO_2 + HOBr + HBr + BrCl}$) partitioning. Our photochemical modeling, aimed at reproducing measured $\mathrm{O_3}$, $\mathrm{NO_2}$, and BrO (see the panels (f) in Fig. 3 to Fig. 8), indicates that at daytime HOBr and HBr contribute less than 10% to $\mathrm{Br_y^{inorg}}$. Therefore, we concentrate on the photochemical model errors due to the partitioning primarily among BrO, Br, and $\mathrm{BrONO_2}$. In this context, most important are the reactions $\mathrm{BrO + NO_2 + M \rightarrow BrONO_2 + M}$ followed by the photolysis of $\mathrm{BrONO_2}$, and the reaction $\mathrm{Br + O_3 \rightarrow BrO + O_2}$.

How uncertainties of the photolytic destruction (J) and three-body formation reaction (k) (together referred to as J/k) of $\mathrm{BrONO_2}$ propagate into BrO is tested in model run #584. Here, according to the finding of Kreycy et al. (2013) J/k was increased by a factor 1.7 (+0.4/-0.2) as compared to the JPL recommendation (Sander et al., 2011) (see the blue crosses in Fig. 12). Evidently increasing J/k helps to close the remaining gap in measured versus modeled BrO, which becomes particularly relevant to reproduce BrO when $\mathrm{NO_2}$ is large, i.e. in the subtropical LS.

Furthermore, Sander et al. (2011) estimate the uncertainty in the reaction rate coefficient $\mathrm{k_{Br+O3}}$ at low temperature (T = 190 K) to be ± 40% (see comment G31). When only considering the two studies which actually measured rather than extrapolated the reaction rate coefficient into the relevant temperature range (T = 190 - 200 K), smaller uncertainty (28%) is indicated (Michael et al. (1978) and Nicovich et al. (1990)). Therefore, in the following an uncertainty of 28% for $\mathrm{k_{Br+O3}}$ is assumed. Overall, increasing ~~k_{Br+O3}~~ $\mathrm{k_{Br+O3}}$ (model run #585) to the upper limit possible according to the JPL compilation (i.e. by factor of 1.28) changes the measured vs modeled correlation for BrO very little (see the red crosses in Fig. 12). It does change, however, the $\mathrm{Br_y^{inorg}}$ partitioning so that [BrO] is always largely prevalent over [Br] even at the lowest altitudes of the TTL (e.g., see panel (f) in Fig. 3 to 8). Our joint measurement of $\mathrm{O_3}$, $\mathrm{NO_2}$, and BrO and the supporting CTM simulations thus indicate $[\mathrm{Br}]/[\mathrm{BrO}] < 1$ for all probed regimes. Our finding is therefore in contrast to the simulations of Fernandez et al. (2014), and Saiz-Lopez and Fernandez (2016) who suggest that $[\mathrm{Br}]/[\mathrm{BrO}]$ may become larger than unity in the tropical UT and TTL at daytime. This conclusion is due mostly to the larger measured $\mathrm{O_3}$ concentrations than those modeled in the study of Fernandez et al. (2014) and Saiz-Lopez and Fernandez (2016), and the conclusion is irrespective of what (within the given error bars) is assumed for $\mathrm{k_{Br+O3}}$.

Gaussian addition of all uncertainties and errors (i.e. the errors of the retrieved BrO concentrations (in section 4.4 of Stutz et al. (2016)), the cross section error, and the uncertainty in the modeled $[\mathrm{Br}]/[\mathrm{BrO}]$, and $[\mathrm{BrONO_2}]$/[BrO] ratios), leads to the $\mathrm{Br_y^{inorg}}$ error, as indicated in the panel (f) of Figs. 3 to 8.

4.6 Inferred total $\mathrm{Br_y^{inorg}}$

Finally, we discuss the inferred $\mathrm{Br_y^{inorg}}$ (contribution 4) as function of potential temperature in the LS, UT, and TTL over the Eastern Pacific during the 2013 convective season (Figure 13). Here we discriminate between young air $[\mathrm{CH_4}] \geq 1790$ ppb, mostly found within the tropical UT and TTL (Fig. 13, left panel), and older air $[\mathrm{CH_4}] \leq 1790$ ppb (Fig. 13, right panel) mostly found in the subtropical lowermost stratosphere. The different histograms in Fig. 13 clearly indicate that ~~,~~ $\mathrm{Br_y^{inorg}}$ increases with increasing potential temperature, i.e. from 2.63 ± 1.04 ppt at θ = 350 - 360 K (at the bottom of the TTL) to 4.22 ± 1.37 ppt for θ = 390 - 400 K (just above the cold point tropopause). The inferred $\mathrm{Br_y^{inorg}}$ thus brackets well the model $[\mathrm{Br_y^{inorg}}]$ = 3.02 ± 1.90 ppt predicted to exist at 17 km in the TTL (Navarro et al., 2015).

The increase in $\mathrm{Br_y^{inorg}}$ with increasing potential temperature θ and decreasing $\mathrm{CH_4}$ concentration thus reflects the decrease in concentrations of brominated VSLS (contribution 3). The correspondence of decreasing $\mathrm{Br_y^{org}}$, and increasing $\mathrm{Br_y^{inorg}}$ concentrations is also found on a sample-to-sample as well as on a flight-to-flight basis. This correspondence keeps $[\mathrm{Br_y}]$ almost constant within the TTL during an individual flight, but $[\mathrm{Br_y}]$ varies from ~~flight-to flight~~ flight to flight in a range of $[\mathrm{Br_y}]$ = 20.3 ppt to 22.3 ppt (Figure 14).

Moreover, it appears that the increase in Br_y^{inorg} with θ mostly corresponds to a decrease in concentrations of the brominated VSLS, ~~however, only if~~ if only the same (young) air masses of large CH_4 concentrations are probed (Figure 15). For example for SF1-2013, SF5-2013, and SF6-2013 when mostly ~~TTL is~~ air masses of the TTL are probed, all data points fall into a band of about ±1 ppt in width, next to a flight-dependent diagonal line (not shown), but not for SF3-2013 when air masses of the LS (and thus older air) and TTL ~~is~~ are probed. When extrapolating the data points along lines of constant [VSLS]+[Br_y^{inorg}] bromine (grey dashed lines in Fig. 15) for SF1-2013, SF5-2013, and SF6-2013 to [Br_y^{inorg}] = 0, and assuming no bromine is effectively lost in the troposphere, then the apparent concentrations of brominated VSLS at the surface should range between 4 - 8.5 ppt. However, frequently larger concentrations of brominated VSLS (some 10 ppt) are measured in the boundary layer of the Pacific (e.g., Yokouchi et al. (1997), Schauffler et al. (1998), Wamsley et al. (1998) Yokouchi et al. (2005), Tegtmeier et al. (2012), Ashfold et al. (2012), Ziska et al. (2013), Sala et al. (2014)~~, and others~~). Further bromine released from sea-salt also contributes to Br_y^{inorg} in the marine boundary layer and may reach in variable amounts the bottom of the TTL (e.g., Saiz-Lopez et al. (2004), Fernandez et al. (2014), Schmidt et al. (2016)). Therefore effective loss processes for inorganic bromine, for example by heterogeneous uptake of inorganic bromine on aerosol and cloud particles, must act in the atmosphere ~~.~~ (e.g. Schmidt et al. (2016)).

Next, when subtracting from the given range (20.3 ppt to 22.3 ppt) of total Br_y, the almost constant contribution of CH_3Br and the ~~halons~~ Halons to total stratospheric bromine (14.6 ppt in 2013), a variable contribution from VSLS bromine (contribution 3), and Br_y^{inorg} (contribution 4) to total TTL bromine in the range of 5.7 ppt to 7.7 ppt (± 1.5 ppt) is calculated (Figure 15). We note that this range falls well into the range assessed in WMO (2014), or recently estimated by Navarro et al. (2015) (6 ppt~~range (~~; range = 4 - 9~~)~~ ppt) for contribution of 3 and 4 to the total stratospheric Br_y. It is, however, somewhat (up to 2 ppt) larger than ~~some of the earlier studies~~indicated in some earlier work, including our balloon-borne studies ~~, indicated~~ (for details see section 1).

Here one may wonder whether (a) this result is significant, or that (b) some Br_y^{inorg} is actually removed by heterogeneous processes in the TTL (e.g., Aschmann et al. (2011), Aschmann and Sinnhuber (2013)~~, and others~~), or (c) that, TTL Br_y shows some seasonality analogous to the tape recorder for H_2O (e.g., Levine et al. (2008), Krüger et al. (2008), Fueglistaler et al. (2009), Schofield et al. (2011), Ploeger et al. (2011)~~, and others~~).

Also remarkable are the the non-negligible amounts of Br_y^{inorg} (2.63 ± 1.04) ppt, range from 0.5 ppt to 5.25 ppt~~(~~, which is from close to zero to 25% of all TTL bromine) inferred for altitudes at the bottom of the TTL (θ = 350 - 360 K), of which 40 to 50% may consist of BrO. This finding clearly sets a range and an upper limit for the Br_y^{inorg} influx into the TTL due to entrained air masses of recent tropospheric origin (contribution 4). Again, the latter can most likely be attributed to different source regions (and thus emission strengths) of the brominated VSLS and bromine released from sea salt, and a varying degree of photochemical and heterogeneous processing of the air masses transported from the surface to the TTL. The increase in variance found for Br_y^{inorg}, which increases in absolute terms, but decreases in relative terms (i.e. from 0.4 for θ in the range 350 K to 360 K to 0.3 for θ = 390 K to 400 K) with increasing θ is also noteworthy. This may indicate a subsequent flattening-out of the air-mass-to-air-mass variability of Br_y^{inorg} in aging air due to the photochemical decay of the brominated organic source gases and atmospheric mixing processes.

4.7 Implications for ozone

The ozone budget in the TOMCAT/SLIMCAT simulation has been analysed based on the rate-limiting steps of the catalytic ozone destruction cycles, according to the concept of Johnston and Podolske (1978). The chemical rates are averaged over the ~~tropical~~ Eastern Pacific region (20°S - 20 °N, 170°W - 90°W) for the duration of the campaign. Within this domain, the net rate of ozone change varied from a loss of - ~~0.5~~ 0.3 ppbv/day at the base of the TTL (θ = 355 K, p = 150 hPa) to a production of + 1.8 ppbv/day at the top (θ= 383 K, p = 90 hPa). This increase of O_3 with height is due to the strong vertical gradient in the production rate of odd oxygen by O_2 photolysis. Within the catalytic ozone loss cycles in the TTL, the model indicates that those containing bromine contribute between ~~8~~12%(base of TTL) and ~~15~~22% (top of TTL) of the total (~~not shown). By far the~~ see appendix A). The dominant contribution to this is through the cycle involving BrO + HO_2 to form HOBr. Overall, the modeled ozone loss cycles which account for the majority of the destruction in this region are those with the rate-limiting steps of the reaction HO_2 + O_3 to form OH + $2O_2$ and the reaction of HO_2 + HO_2 to form H_2O_2, i.e. cycles involving HO_x species. Therefore, increases in the bromine loading of the TTL caused by possible/expected increases have the potential to deplete ozone, in a region where ~~climate is most sensitive to perturbations~~ ozone changes have the largest impact on radiative forcing (Riese et al., 2012).

Quantifying the radiative impact of the O_3 changes described above is the beyond the scope of this study. However, we can note that (i) recent work has highlighted the efficiency of brominated VSLS at influencing climate (through changed O_3), owing to their efficient breakdown in the UTLS (Hossaini et al., 2015), and (ii) a significant increase in Br_y in this region (from VSLS or other sources) could be important for future climate forcing. The latter could conceivably occur given suggested climate-induced changes to (1) tropospheric transport (e.g., Hossaini et al. (2012b)), (2) changes in OH, affecting VSLS lifetimes (3), and/or ~~oxidizing capacity due~~ an elevated bromine loading in the UT/LS and TTL to the expected increase in VSLS emissions from the rapidly growing aquaculture industry (WMO, 2014).

5 Conclusions

The subtropical lowermost stratosphere, upper troposphere, and tropopause layer of the Eastern Pacific are probed for inorganic bromine during the convective season (February and March 2013). The measurements of CH_4, O_3, NO_2, BrO, and some important organic brominated source gases are inter-compared with TOMCAT/SLIMCAT simulations. After the simulated TOMCAT/SLIMCAT curtains of O_3 are projected on the measured O_3 concentrations, measured and modeled CH_4 agree well. This agreement is not surprising, since O_3, and CH_4 are strongly ~~correlated~~ anti-correlated (see Fig. 9). ~~This~~ It thus provides evidence that the relevant dynamical processes are represented well in the TOMCAT/SLIMCAT simulations. When the simulated curtains of NO_2 are adjusted with the same parameters as inferred above, excellent agreement is again found between measured and modeled NO_2, thus providing further confidence in our measurement technique, in the modeled NO_y photochemistry, and in our overall approach.

The measured and modeled TTL concentrations of CH_2Br_2 ~~,~~ and $CHBr_3$ are found to compare reasonably ~~well after some adjustments~~ to the surface concentrations and atmospheric ~~life times~~ lifetimes of both species ~~are applied to~~ adopted in the model (~~e.g.,~~ [CHBr$_3$] = 1.4 ppt, [CH$_2$Br$_2$] = ~~1.05~~ 1 ppt at the surface). Further, the contribution to bromine in the LS, UT, and TTL by some other VSLS chloro-bromo-hydrocabrons (~~e.g.,~~ Σ [CHClBr$_2$, CHCl$_2$Br, CH$_2$ClBr, ...]) is accounted for by assuming a constant surface concentration of 1 ppt in the model. From flight-to-flight total organic bromine inferred from these VSLS species is found to vary by ± 1 ppt in the TTL over the Eastern Pacific in early 2013, which clearly ~~indicate~~ indicates different origins and possibly atmospheric processing of the investigated air masses.

The measured BrO concentrations range between 3 - 9 ppt in the subtropical LS. In the TTL they range between 0.5 ± 0.5 ppt at the bottom of the TTL, and about 5 ppt at ~~θ~~ θ = 400 K, in overall good agreement with the model simulations, and the expectation based on the decay of the brominated source gases, and atmospheric transport. In the TTL, the inferred $\mathrm{Br_y^{inorg}}$ is found to increase from a mean of 2.63 ± 1.04 ppt for ~~θ~~ θ in the range of 350 - 360 K to 5.11 ± 1.57 ppt for ~~θ = 390 – 400 K~~ θ = 390 - 400 K, respectively, whereas in the subtropical LS it reaches 7.66 ± 2.95 ppt for ~~θ'~~ θs in the range of 390 - 400 K. Also remarkable is the non-negligible $\mathrm{Br_y^{inorg}}$ found for the lowest altitudes of the TTL, i.e. 2.63 ± 1.04 ppt with a range from 0.5 ppt to 5.25 ppt (or close to zero percent up to 25% of all TTL bromine). This may indicate a sizable, but rather variable influx of inorganic bromine into the TTL, largely depending on the air mass history, i.e. source region, and atmospheric transport and processing.

Our findings on LS ~~,~~ and TTL $\mathrm{Br_y^{inorg}}$ are in broad agreement with past experimental and theoretical studies on the processes and amount of bromine injected by source gas and product gases into the TTL, and eventually into the extra-tropical lowermost stratosphere (Ko et al. (1997), Schauffler et al. (1998), Wamsley et al. (1998), Dvortsov et al. (1999), Pfeilsticker et al. (2000), Montzka et al. (2003), Salawitch (2006), Sinnhuber and Folkins (2006), Hendrick et al. (2007), Laube et al. (2008), Dorf et al. (2006b), Dorf et al. (2008), Sinnhuber et al. (2009), Salawitch et al. (2010), Schofield et al. (2011), Aschmann et al. (2011), Hossaini et al. (2012b), Ashfold et al. (2012), Hossaini et al. (2012a), Aschmann and Sinnhuber (2013), Sala et al. (2014), Wang et al. (2015), Liang et al. (2014), WMO (2014), Navarro et al. (2015), and many others). Our study, however, sets tighter limits than those previously existing on the amount of $\mathrm{Br_y^{inorg}}$ and $\mathrm{Br_y^{org}}$, the influx of brominated source ~~,~~ and product gases, and the photochemistry of bromine in the TTL and LS.

In particular, our study (re-)emphasizes that (a) variable amounts of VSLS bromine and (b) non-negligible amounts of $\mathrm{Br_y^{inorg}}$ are also transported into the TTL. While process (a) may strongly depend on the source region and season ~~(here: cite Hossaini 2016, acp-2015-822, when published),~~ (Hossaini et al., 2016), process (b) may depend on the efficiency of heterogeneous processing and removal of some $\mathrm{Br_y^{inorg}}$ by atmospheric (ice) clouds and aerosols (e.g., Aschmann et al. (2011), and Aschmann and Sinnhuber (2013)). Therefore it is not ~~suprising~~ surprising that TTL $\mathrm{Br_y}$ is rather variable (i.e. 20.3 ppt to 22.3 ppt) in the studied season.

We also note that the amount of $\mathrm{Br_y}$ over the Eastern Pacific during the convective season assessed here and in the study of Navarro et al. (2015) is somewhat (up to 2 ppt) larger than that presently found on average in the stratosphere (e.g., Dorf et al. (2006b), Hendrick et al. (2007), Dorf et al. (2008), and WMO (2014)). By assuming that this gap is significant, additional processes may come into ~~to~~ the focus of stratospheric bromine research, i.e. the seasonality and possibly long-term trend of the bromine transported into the stratosphere (e.g., Levine et al. (2008), Krüger et al. (2008), Fueglistaler et al. (2009), Schofield et al. (2011), Ploeger et al. (2011)~~, and others~~).

Conceivably adding some inorganic bromine (from contribution 4) to TTL bromine exerts an additional impact on ozone. For the for the Eastern Pacific (170°W - 90°W). Our model-based assessment ~~led to a loss of~~ indicate a net loss of ozone of -~~0.5~~ 0.3 ppbv/day at the base of the TTL (θ = 355 ~~),~~ K) and a net production of + 1.8 ppbv/day ~~at the top~~ in the upper part (θ = 383 ~~-~~K). Within the catalytic ozone loss cycles in the TTL (see appendix A), the model indicates that those containing bromine contribute between ~~8~~12% (at the base of the TTL) and ~~15~~22% (at the top of TTL) of the total.

Appendix A: **Ozone loss calculation**

The TOMCAT/SLIMCAT CTM contains a detailed description of stratospheric ozone chemistry, including radical and reservoir species in the odd oxygen, odd hydrogen, odd nitrogen, chlorine and bromine families. The model solves for the full ‘odd oxygen’ ($\mathrm{O_x = O_3 + O(^3P) + O(^1D)}$) continuity equation based on the relevant reactions involving the $\mathrm{O_x}$ species. However, in order to ascribe chemical ozone loss to particular catalytic cycles, it is useful to transform the odd oxygen continuity equation, using steady-state assumptions, so that loss terms can be associated with the rate-determining steps of identifiable cycles. The methodology to achieve this was outlined by Johnston and Podolske (1978).

In this study the modelled chemical ozone (or $\mathrm{O_x}$) changes are related to catalytic cycles using this methodology applied to the full chemical scheme and results are given in Section 4.7. In this appendix we describe this analysis for bromine (and some odd hydrogen) chemistry and show how the catalytic cycles are identified. An approach such as this is necessary in order to avoid overestimation (’double counting’) or underestimation of ozone loss, which could occur if catalytic cycles are extracted in isolation from the rest of the model chemistry scheme.

Table 1. TOMCAT/SLIMCAT reactions involving Br_y radical and reservoir species along with other reactions involving HO_x species. The numbering scheme follows that used in the model. Here O means $O(^3P)$.

8	$OH + O$	→	$H + O_2$
9	$O_2 + H + M$	→	$HO_2 + M$
10	$HO_2 + O$	→	$OH + O_2$
11	$OH + O_3$	→	$HO_2 + O_2$
12	$H + O_3$	→	$OH + O_2$
14b	$OH + OH$	→	H_2O_2
15a	$H + HO_2$	→	$OH + OH$
15b	$H + HO_2$	→	$H_2 + O_2$
24	$HO_2 + HO_2$	→	$H_2O_2 + O_2$
36	$HO_2 + O_3$	→	$OH + 2\,O_2$
120	$Br + O_3$	→	$BrO + O_2$
121	$BrO + O$	→	$Br + O_2$
123	$BrO + NO$	→	$Br + NO_2$
124	$BrO + OH$	→	$Br + HO_2$
125a	$BrO + ClO$	→	$Br + OClO$
125b	$BrO + ClO$	→	$Br + Cl + O_2$
125c	$BrO + ClO$	→	$BrCl + O_2$
127	$BrO + BrO$	→	$Br + Br + O_2$
128	$BrO + NO_2 + M$	→	$BrONO_2 + M$
130	$BrO + HO_2$	→	$HOBr + O_2$
131	$O + HOBr$	→	$OH + BrO$
134	$Br + CH_2O$	→	$HBr + CHO$
135	$Br + HO_2$	→	$HBr + O_2$
136	$HBr + OH$	→	$Br + H_2O$
137	$HBr + O(^1D)$	→	$Br + OH$
139	$HBr + O$	→	$Br + OH$
145	$BrONO_2 + O$	→	$BrO + NO_3$
146	$BrONO_2 + Br$	→	$Br + Br + NO_3$
147	$HBr + Cl$	→	$Br + HCl$

J_{BrO}	BrO + hν	→	Br + O
J_{BrONO2}	$BrONO_2$ + hν	→	Br + NO_3
J_{BrCl}	BrCl + hν	→	Br + Cl
J_{HOBr}	HOBr + hν	→	Br + OH
J_{H2O2}	H_2O_2 + hν	→	2OH

Based on the subset of the TOMCAT/SLIMCAT reactions listed in Table 1, the odd oxygen continuity (equation A1) would be written as:

$$\begin{aligned}\frac{d[O_x]}{dt} &= -k_8\cdot[OH]\cdot[O]-k_{10}\cdot[HO_2]\cdot[O]-k_{11}\cdot[OH]\cdot[O_3]-k_{12}\cdot[H]\cdot[O_3]-k_{36}\cdot[HO_2]\cdot[O_3]-k_{120}\cdot[Br]\cdot[O_3]\\ &\quad -k_{121}\cdot[BrO]\cdot[O]-k_{137}\cdot[HBr]\cdot[O(^1D)]-k_{139}\cdot[HBr]\cdot[O]-k_{145}\cdot[BrONO_2]\cdot[O]+J_{BrO}\cdot[BrO]\end{aligned}$$

This equation can be modified by assuming that short-lived species are in steady state. Based on the above reaction scheme, we can put Br in steady state to get the following:

$$\begin{aligned}\frac{d[Br]}{dt} &= -k_{120}\cdot[Br]\cdot[O_3]+k_{121}\cdot[BrO]\cdot[O]+k_{123}\cdot[BrO]\cdot[NO]+k_{124}\cdot[BrO]\cdot[OH]+k_{125a}\cdot[BrO]\cdot[ClO]\\ &\quad +k_{125b}\cdot[BrO]\cdot[ClO]+k_{127}\cdot[BrO]\cdot[BrO]-k_{134}\cdot[Br]\cdot[CH_2O]-k_{135}\cdot[Br]\cdot[HO_2]\\ &\quad +k_{136}\cdot[OH]\cdot[HBr]+k_{137}\cdot[O(^1D))]\cdot[HBr]+k_{139}\cdot[O]\cdot[HBr]+k_{146}\cdot[Br]\cdot[BrONO_2]\\ &\quad +k_{147}\cdot[HBr]\cdot[Cl]+J_{BrO}\cdot[BrO]+J_{BrONO_2}\cdot[BrONO_2]+J_{BrCl}\cdot[BrCl]+J_{HOBr}\cdot[HOBr]\\ &= 0\end{aligned}$$

We can derive similar equations for many other short-lived species. Johnston and Podolske (1978) also discussed placing the rate of change of longer lived species to zero in order to help simplify the odd-oxygen continuity equation. In practice the magnitude of these terms for odd oxygen loss would be very small. Using 'steady state' expressions of Br, $BrONO_2$, HBr, Cl, NO_2, OClO, OH, HCl, and H_2O equation (A1) can be converted to:

$$\begin{aligned}\frac{d[Br]}{dt} &= -k_{120}\cdot[Br]\cdot[O_3]+k_{121}\cdot[BrO]\cdot[O]+k_{123}\cdot[BrO]\cdot[NO]+k_{124}\cdot[BrO]\cdot[OH]+k_{125a}\cdot[BrO]\cdot[ClO]\\ &\quad +k_{125b}\cdot[BrO]\cdot[ClO]+k_{127}\cdot[BrO]\cdot[BrO]-k_{134}\cdot[Br]\cdot[CH_2O]-k_{135}\cdot[Br]\cdot[HO_2]\\ &\quad +k_{136}\cdot[OH]\cdot[HBr]+k_{137}\cdot[O^1D]\cdot[HBr]+k_{139}\cdot[O]\cdot[HBr]+k_{146}\cdot[Br]\cdot[BrONO_2]\\ &\quad +k_{147}\cdot[HBr]\cdot[Cl]+J_{BrO}\cdot[BrO]+J_{BrONO_2}\cdot[BrONO_2]+J_{BrCl}\cdot[BrCl]+J_{HOBr}\cdot[HOBr]\\ &= 0\end{aligned}$$

This is part of the transformed odd-oxygen continuity equation as used in the diagnosis of the full TOMCAT/SLIMCAT chemistry scheme. For the chemical scheme given in Table **??**, this equation can be further simplified by applying the steady state approximation to HOBr ($\mathrm{d[H_2O_2]/dt}$ = 0) and $\mathrm{H_2O_2}$ ($\mathrm{d[HOBr]/dt}$ = 0) to get:

$$\begin{aligned}\frac{d[O_x]}{dt} &= -2\cdot k_{10}\cdot[HO_2]\cdot[O]-2\cdot k_{12}\cdot[H]\cdot[O_3]-2\cdot k_{15a}\cdot[H]\cdot[HO_2]-2\cdot k_{24}\cdot[HO_2]\cdot[HO_2]\\ &\quad -2\cdot k_{36}\cdot[HO_2]\cdot[O_3]-2\cdot k_{121}\cdot[BrO]\cdot[O]-2\cdot k_{125b}\cdot[BrO]\cdot[ClO]-2\cdot k_{127}\cdot[BrO]\cdot[BrO]\\ &\quad -2\cdot k_{130}\cdot[BrO]\cdot[HO_2]-2\cdot k_{137}\cdot[HBr]\cdot[O(^1D)]-2\cdot k_{139}\cdot[HBr]\cdot[O]-2\cdot J_{BrCl}\cdot[BrCl]\end{aligned}$$

As discussed in Section 4.7, the dominant terms for ozone loss due to bromine chemistry are those involving the formation of HOBr ($2\cdot \mathrm{k_{130}}\cdot[\mathrm{BrO}]\cdot[\mathrm{HO_2}]$). Overall, the $\mathrm{HO_x}$ cycle represented by $2\cdot \mathrm{k_{36}}\cdot[\mathrm{HO_2}]\cdot[\mathrm{O_3}]$ dominates the ozone loss with a minor contribution from reactions involving $\mathrm{H_2O_2}$ production ($2\cdot \mathrm{k_{24}}\cdot[\mathrm{HO_2}]\cdot[\mathrm{HO_2}]$).

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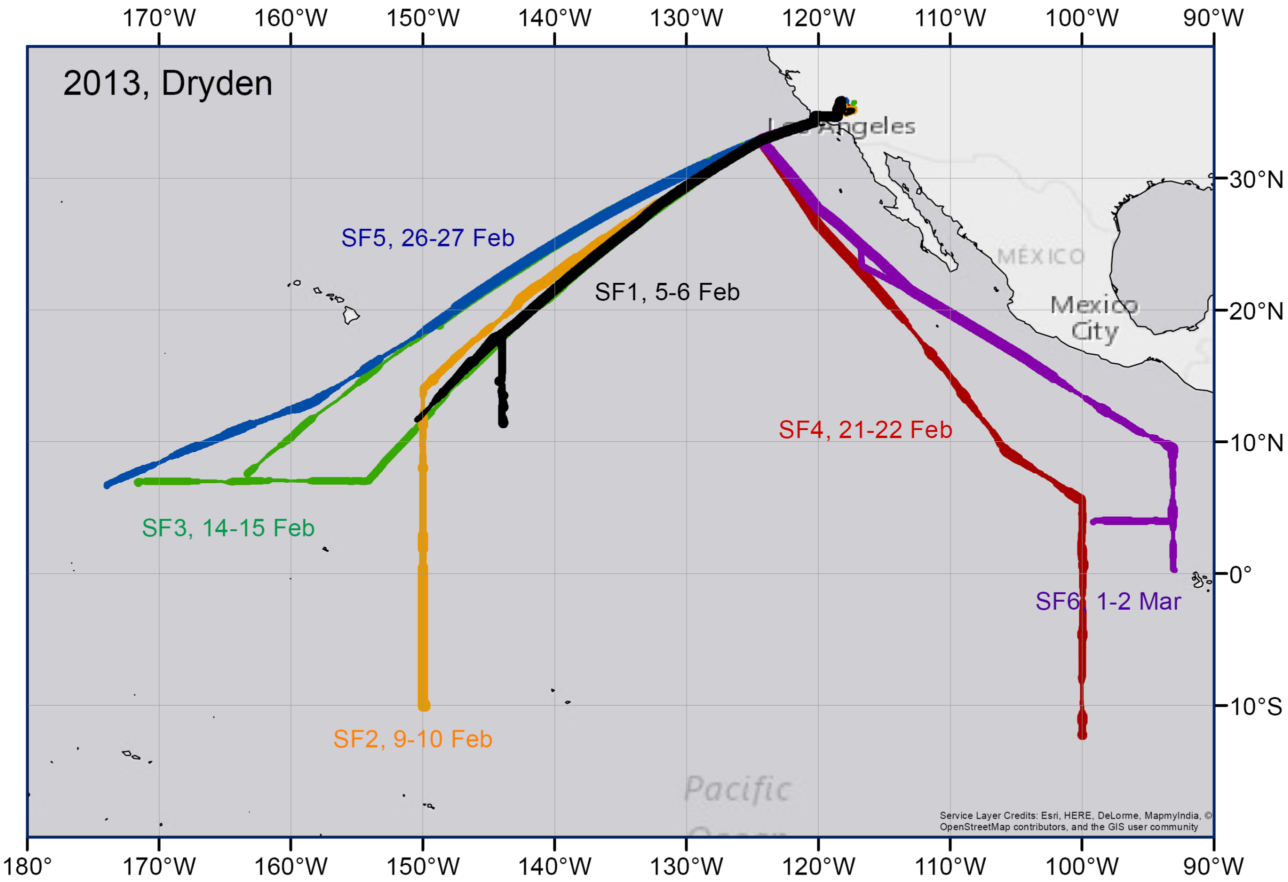

Figure 1. Overview of the NASA Global Hawk ATTREX flights ~~; for (left) the Guam 2014 campaign and (right) the Edwards Air Force base (EAFB) 2013 campaign.~~ conducted from Dryden in 2013. The thickness of the lines ~~correspond~~ corresponds to flight altitudes, where the thinnest line is for an altitude of around 14 km and the thickest line for around 18 km.

~~Comparison of profiles retrieved using the optimal estimation method (black), using the -scaling technique (green), and predicted by the TOMCAT/SLIMCAT model, which is used as a priori to constrain the optimal estimation inversion retrieval (blue), and for comparison published by Dorf et al. (2008), which was measured over northeastern Brazil in June 2005 (red). 0.5cm~~

~~Comparison of profiles using the optimal estimation method (black), using the -scaling technique (green), and from Wang et al. (2015) (re which is also extrapolated to 20 km (blue). These profiles are both used as a priori in the optimal estimation. Since in the probed altitude range the inferred profile (black) tend to the profile obtained from the -scaling technique (green), the unexpected kink around 12 to 13 km in the inferred profile when the inversion is constrained to the Wang et al. (2015) profile indicates that our and the Wang et al. (2015) profiles are not compatible (for further details see section 4.3).~~

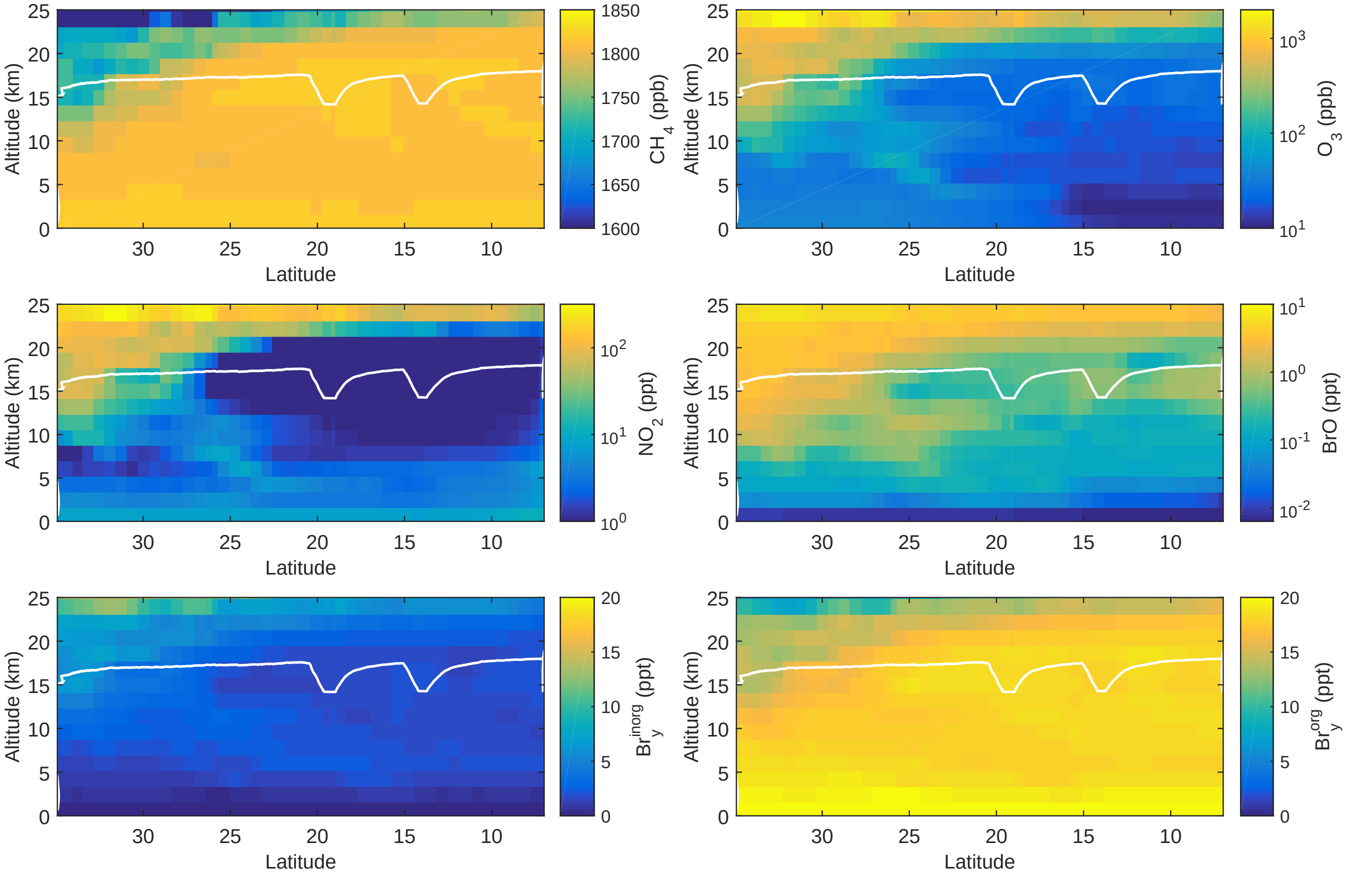

Figure 2. TOMCAT/SLIMCAT predictions of mixing ratio curtains of $\mathrm{CH_4}$ (upper left), $\mathrm{O_3}$ (upper right), $\mathrm{NO_2}$ (middle left), BrO (middle right), $\mathrm{Br_y^{inorg}}$ (bottom left), and $\mathrm{Br_y^{org}}$ (bottom right) for the sunlit part of SF3-2013 (Feb. 14, 2013). Note the different color scale ranges. The white line is the flight trajectory of the Global Hawk. For better visibility, the simulated mixing ratios are shown for the altitude range 0 - 25 km, although the TOMCAT/SLIMCAT simulations cover the range of 0 - 63 km altitude

~~Comparison of the inferred profiles for the ascent after dive # 2 of the flight on Feb. 5/6, 2013 with previously published (modeled and measured) profiles.~~

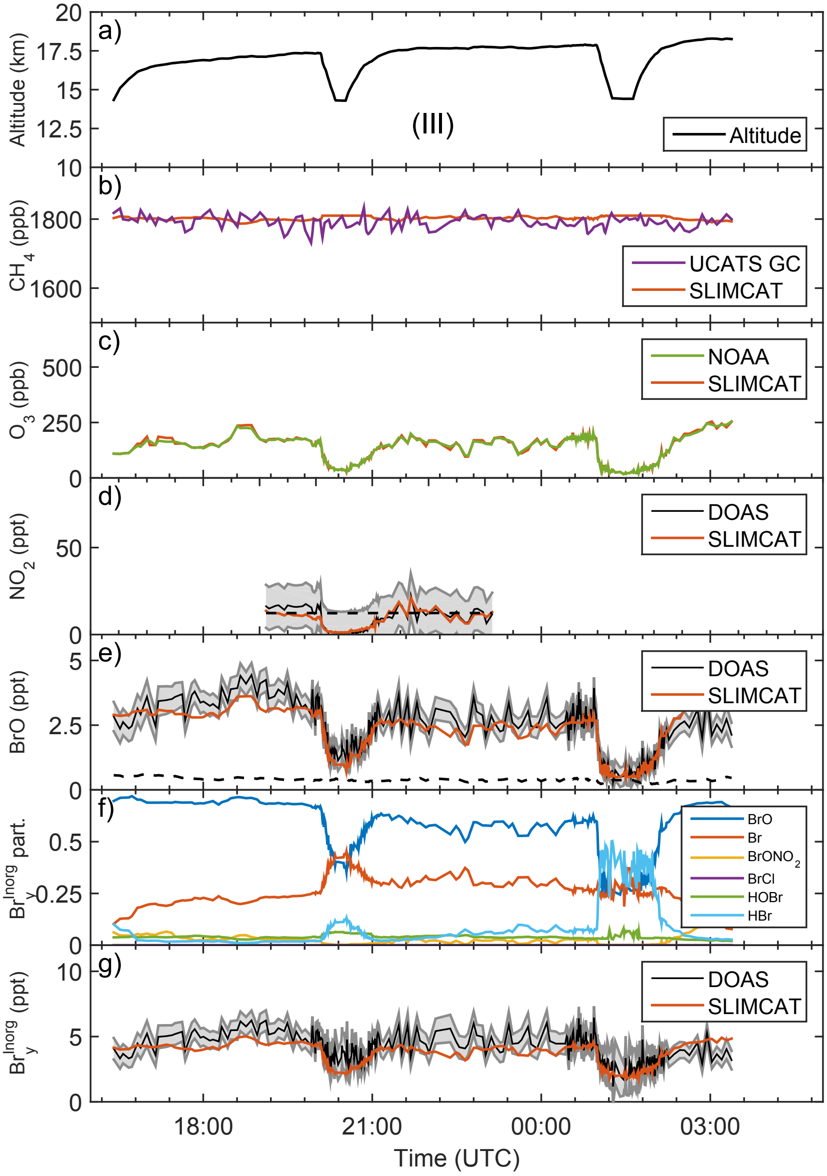

Figure 3. Panel (a) shows the time-altitude trajectory of the sunlit part of the GH flight track (SF1-2013) on Feb. 4/5, 2013 (SF1-2013). Panels (b)-(e) show ~~intercomparisons~~ inter-comparisons of TOMCAT/SLIMCAT-simulated fields with observations of (b) CH_4 (UCATS), (c) O_3 (NOAA), (d) NO_2 (mini-DOAS), and (e) BrO (mini-DOAS). The grey-shaded error bars of the mini-DOAS ~~measurements of~~ NO_2 ~~,~~ and BrO measurements includes all ~~dominating~~ significant errors, i.e. the spectral retrieval error, the ~~overhead and the~~ error due to a ~~tropospheric~~ contribution to the slant absorption from above the aircraft and from the troposphere, and the absorption cross section uncertainty. Panel (f) shows the SLIMCAT modeled Br_y partitioning for the standard run #583. Panel (g) shows a comparison of inferred and modeled Br_y^{inorg}, including the ~~errors~~ uncertainty as a grey band.

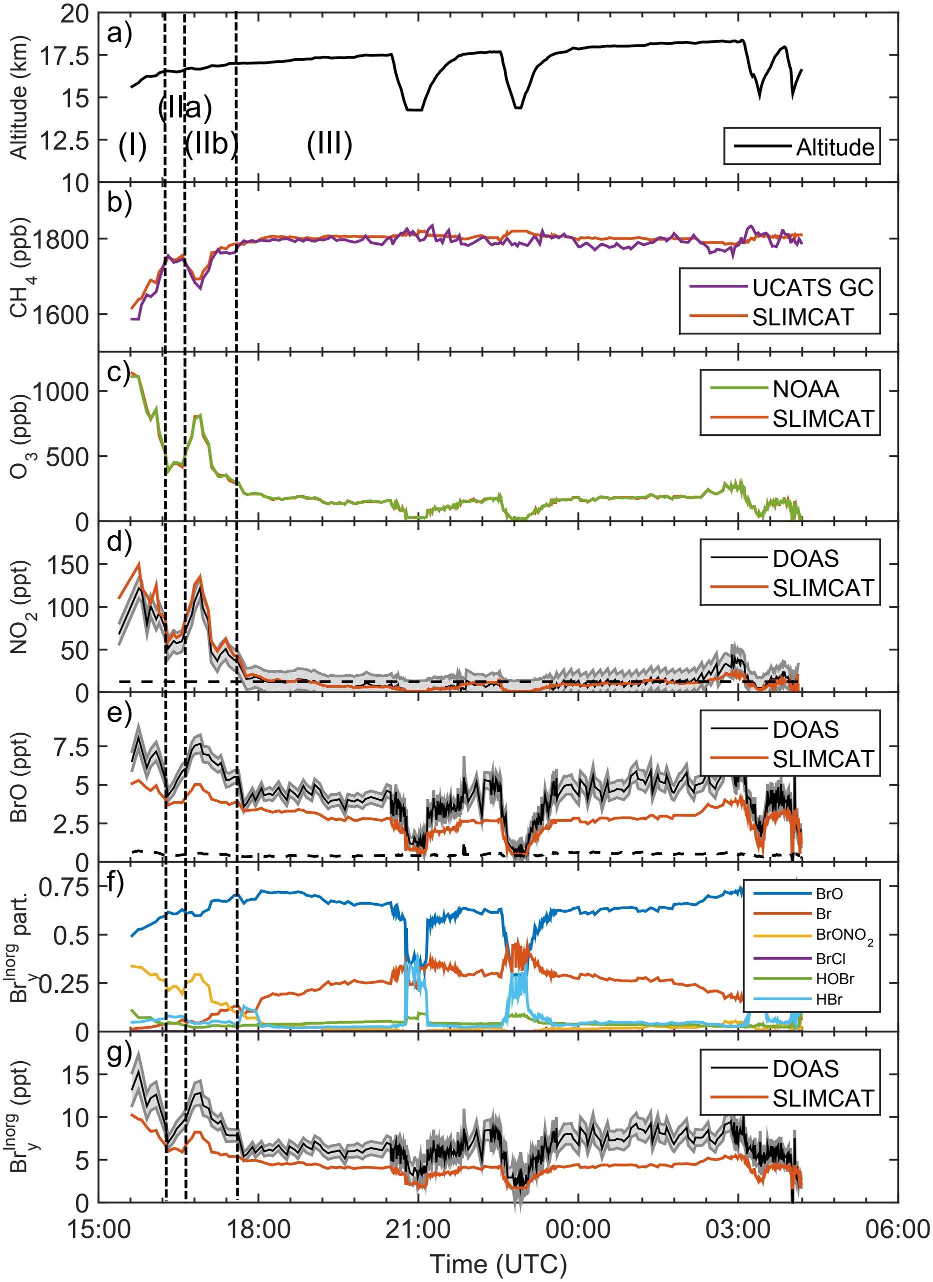

Figure 4. Same as figure 3 but for the research flight on Feb. 9/10, 2013 (SF2-2013). The dashed vertical lines in Figures 4-9 separate different atmospheric regimes: (I) is the extra-tropical lowermost stratosphere, (IIa, IIb, ...) different mixing regimes of air from the extra-tropical lowermost stratosphere, and (III) from the tropical tropopause layer.

~~Same as figure 3 but for the research flight on Feb. 9/10, 2013 (SF2-2013).~~

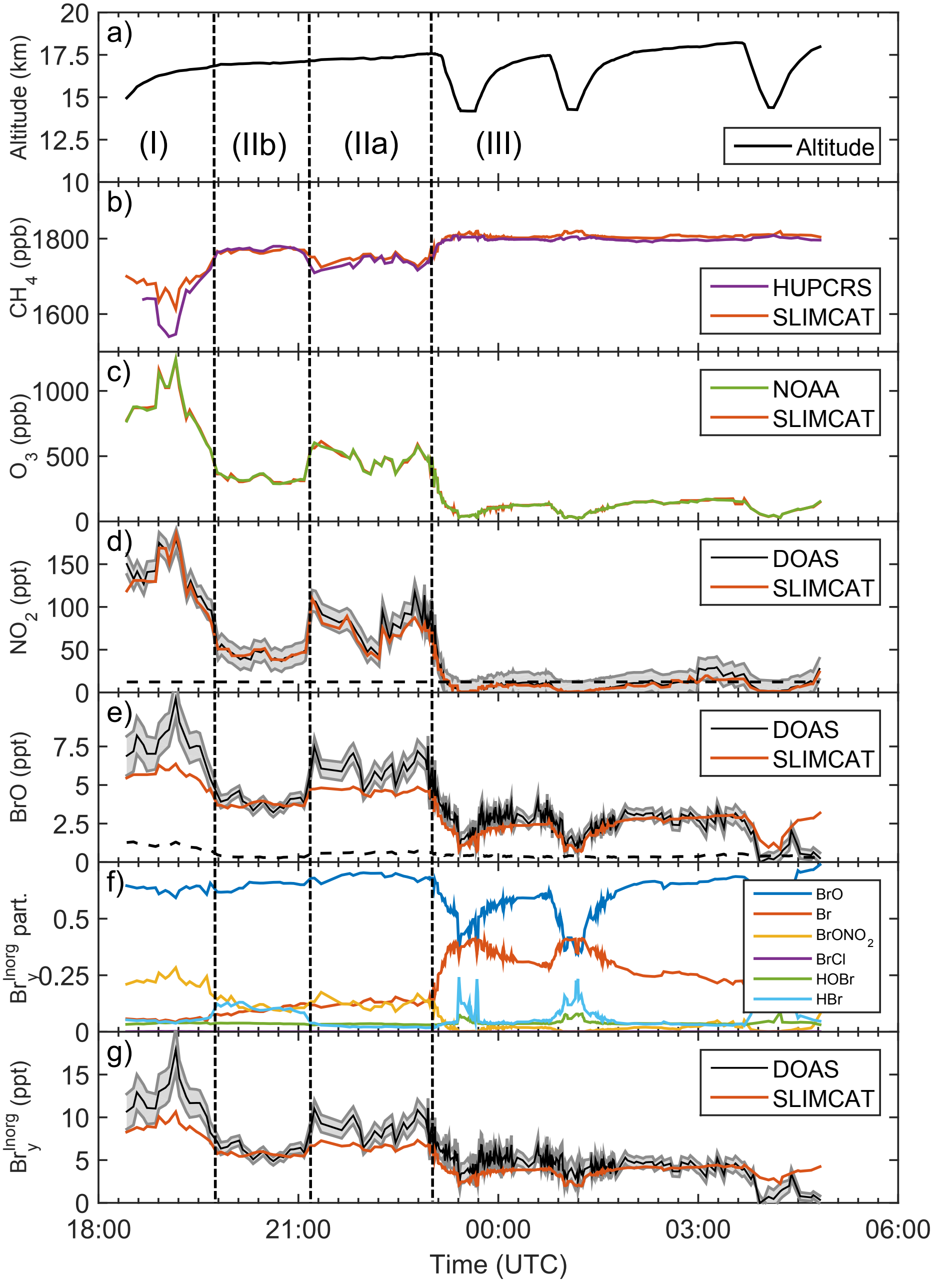

Figure 5. Same as figure 3 but for the research flight on Feb. 14/15, 2013 (SF3-2013).

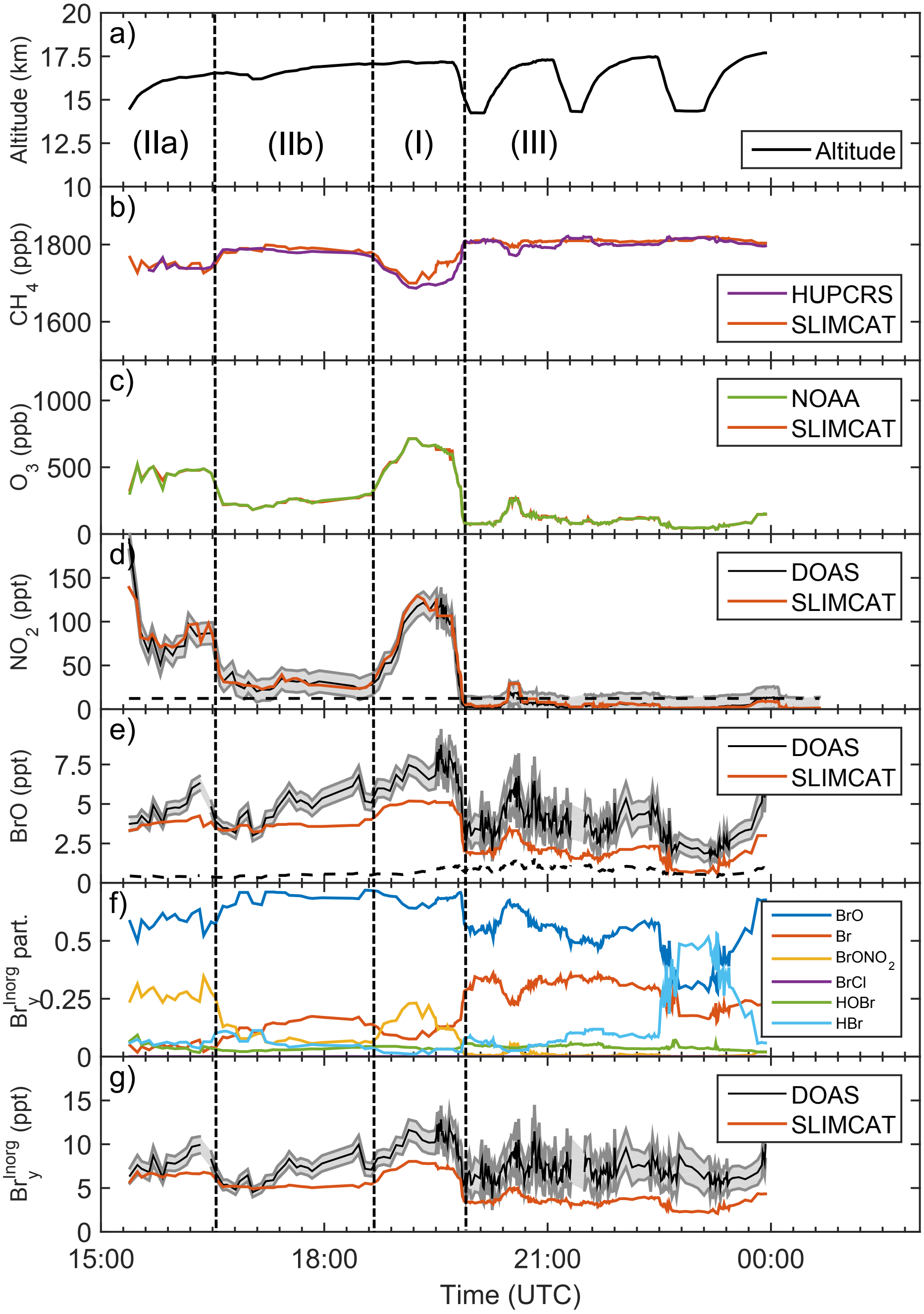

Figure 6. Same as figure 3 but for the research flight on Feb. 21/22, 2013 (SF4-2013). Note that DOAS analysis of BrO for SF4-2013 is somewhat uncertain because the Fraunhofer reference spectra (taken via a diffuser) are affected by temporally changing residual structures likely due to ice deposits or some other residues on the entrance diffuser (see text).

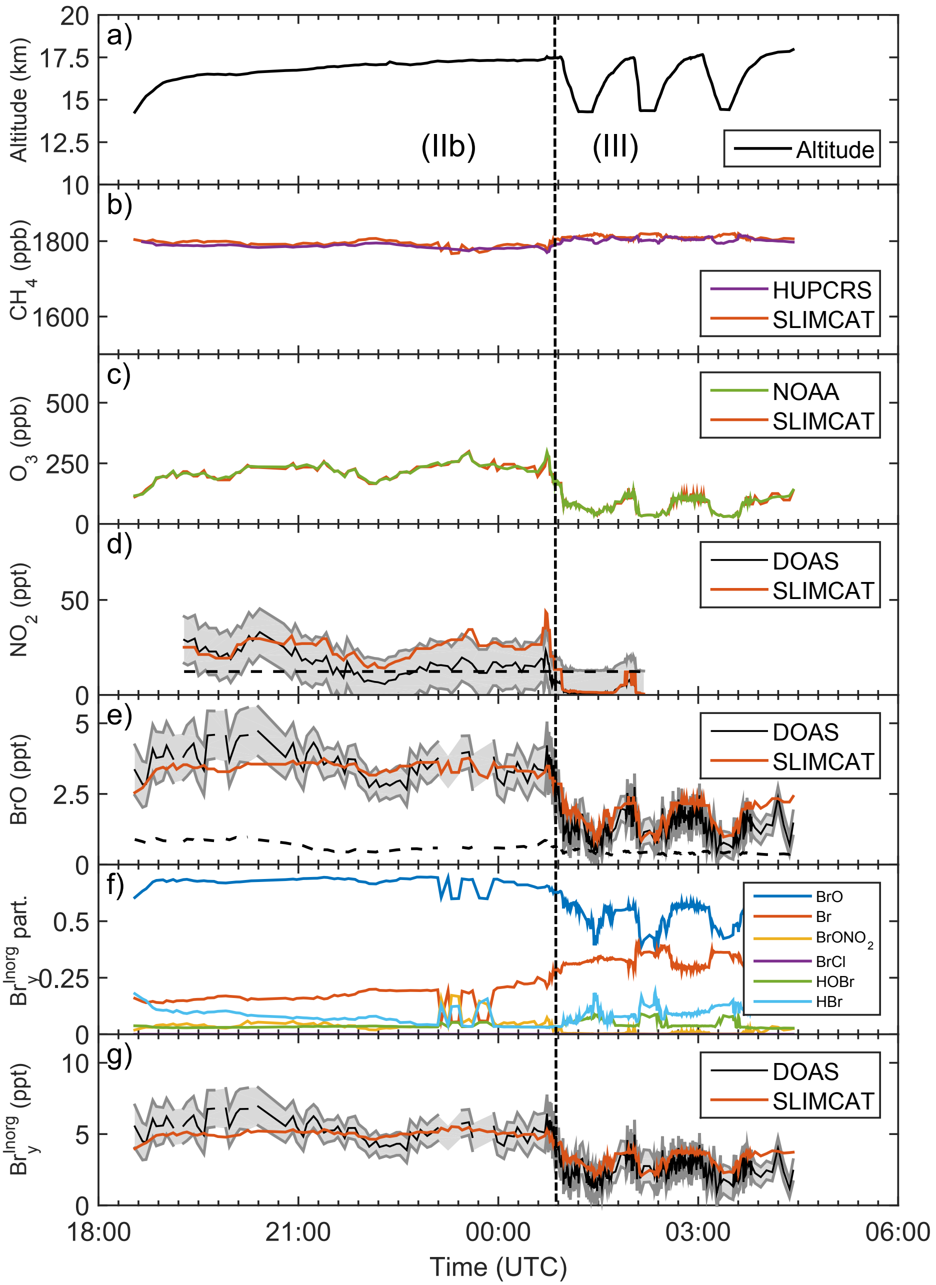

Figure 7. Same as figure 3 but for the research flight on Feb. 26/27, 2013 (SF5-2013).

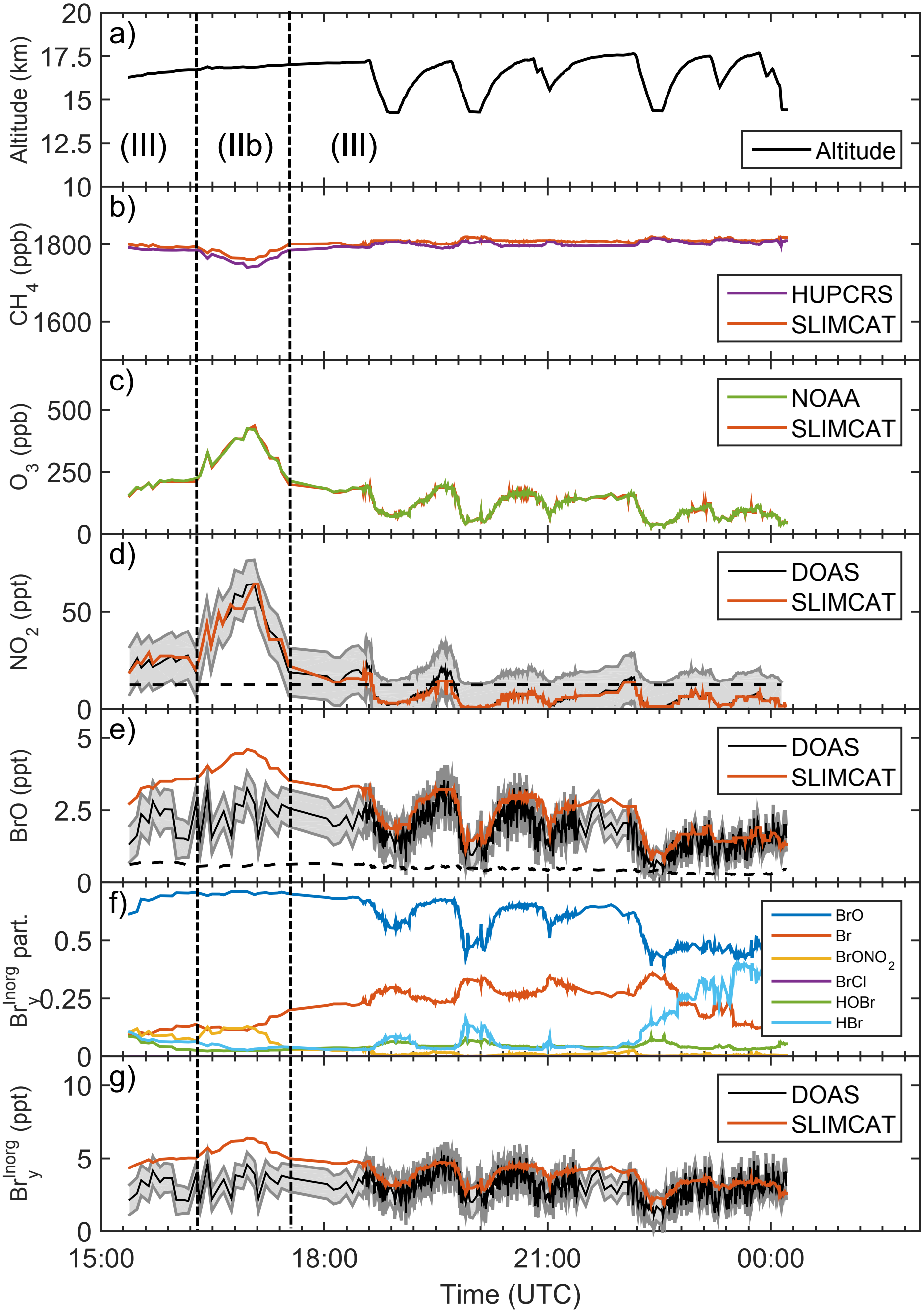

Figure 8. Same as figure 3 but for the research flight on Mar. 1/2, 2013 (SF6-2013).

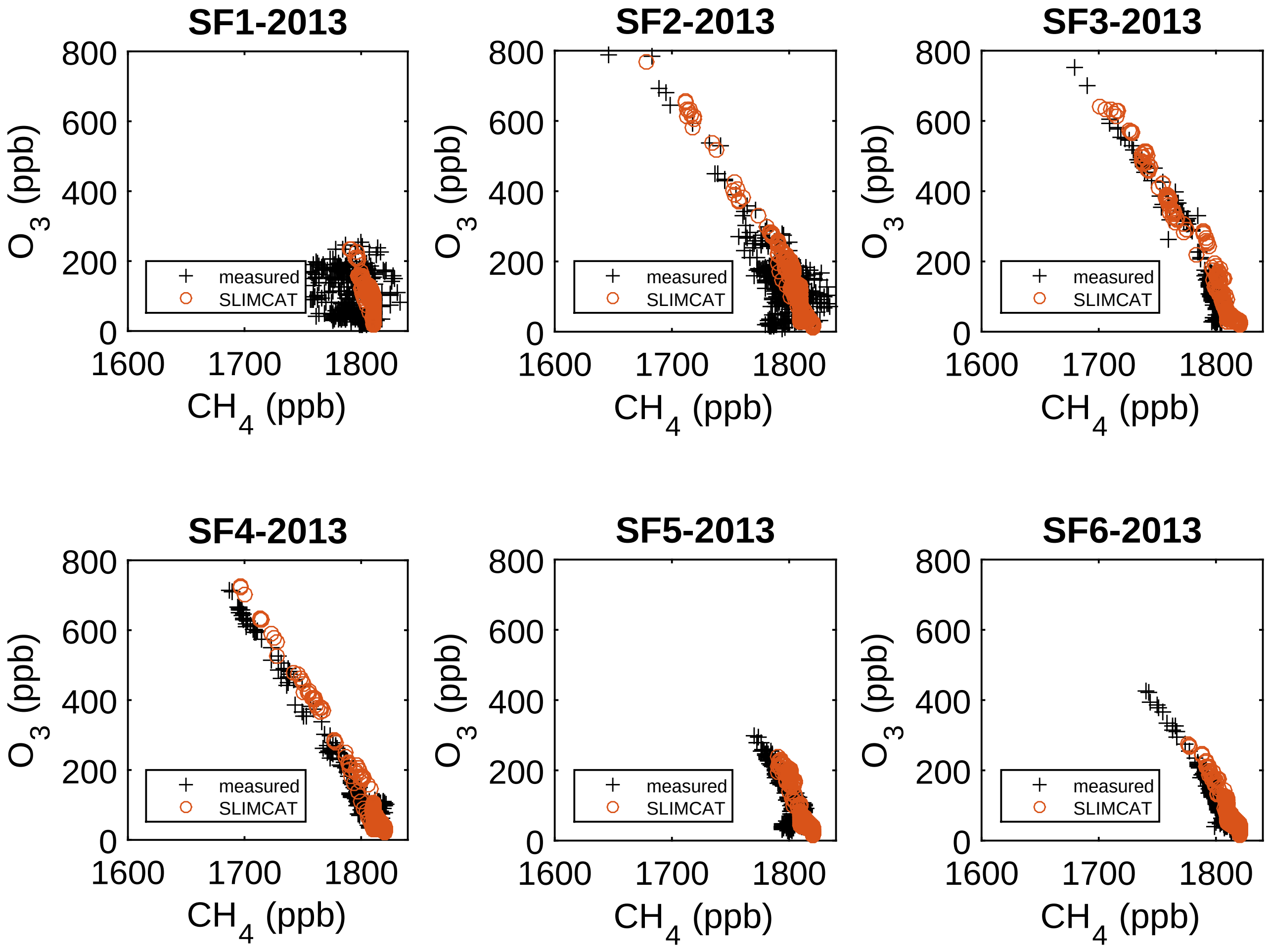

Figure 9. Correlation of observed CH_4 (UCATS SF1-2013 and SF2-2013; HUPCRS SF3-2013 to SF6-2013) and O_3 (NOAA) for the 6 NASA-ATTREX science flights in 2013. Also shown are the equivalent correlations from the TOMCAT/SLIMCAT simulation.

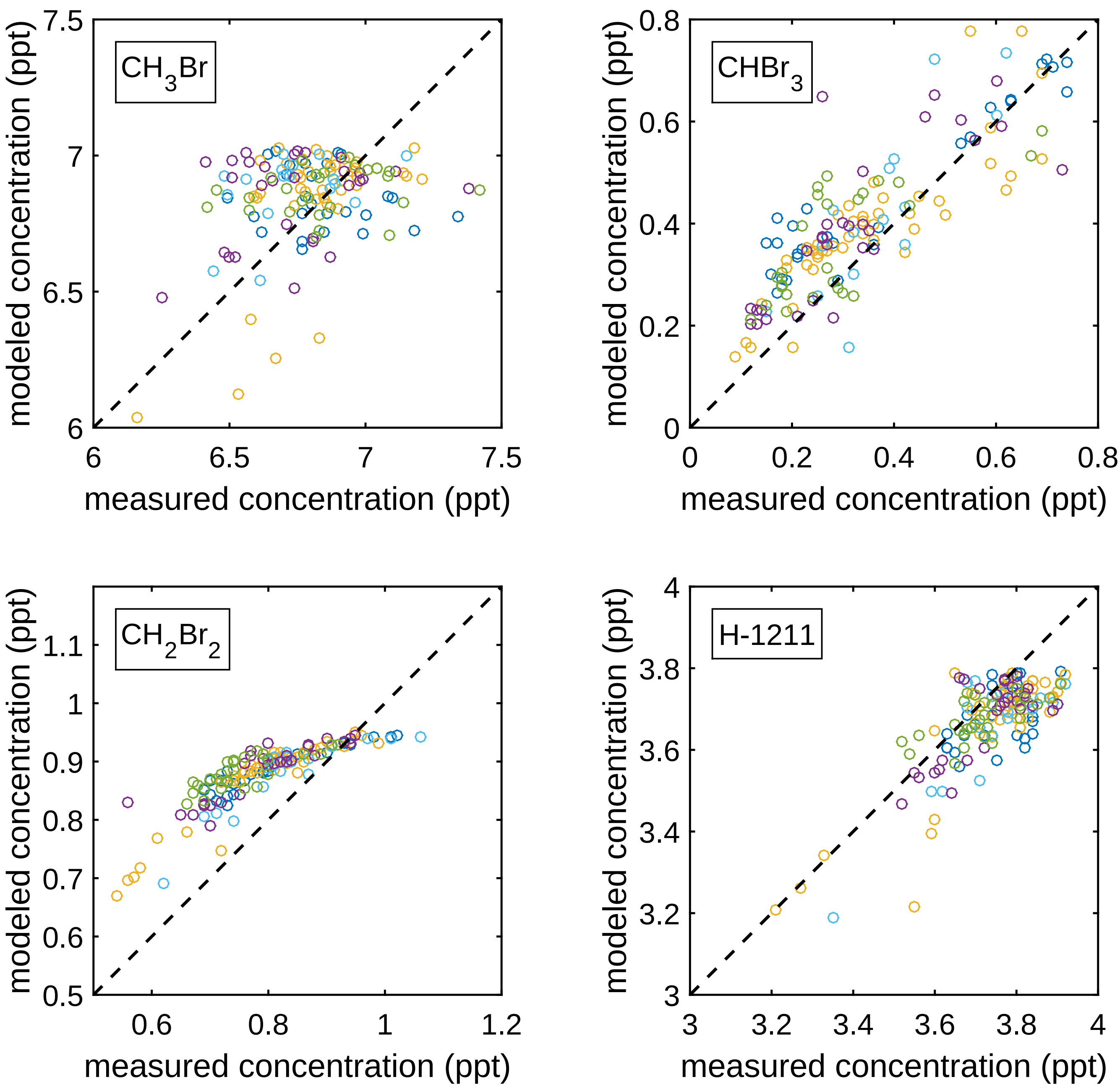

Figure 10. Correlation of GWAS measured and TOMCAT/SLIMCAT modeled major brominated source gases. Upper left panel for $CHBr_3$, upper right panel for $CHBr_3$, lower left panel for CH_2Br_2, and lower right panel for ~~halon H1211.~~ Halon 1211. The concentrations for different flights are color-coded; SF1-2013 in blue, SF3-2013 ~~in~~ yellow, SF4-2013 light blue, SF5-2013 ~~in~~ purple, and SF6-2013 ~~in~~ green.

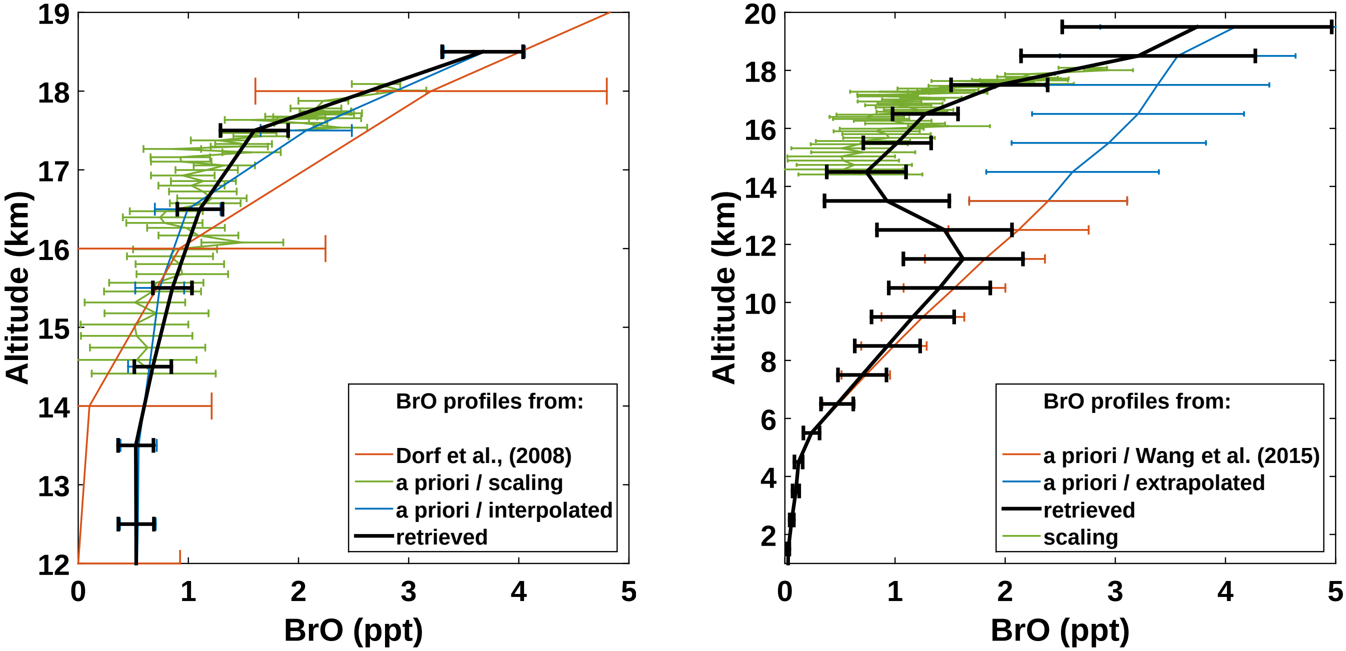

Figure 11. Comparison of the inferred BrO profile for the ascent after dive # 2 of the flight on Feb. 5/6, 2013 with previously published (modeled and measured) BrO profiles. Please note the different altitude range in the two panels. BrO profiles retrieved using the optimal estimation method are shown in black and those using the O_3-scaling technique are shown by green symbols, error bars and lines. In the two panels different a priori information is used to constrain the optimal estimation retrieval. Left panel: TOMCAT/SLIMCAT model predictions are used as a priori (blue). Also shown for comparison is the BrO profile published by Dorf et al. (2008), which was measured over northeastern Brazil in June 2005 (red). Right panel: The BrO profile of Wang et al. (2015) (red) and its extrapolation to 20 km (blue) are used as a priori in the optimal estimation. The kink in the retrieved BrO profile (black) at about 12 km strongly indicates that BrO profile of Wang et al. (2015) is neither compatible with the BrO profiles inferred using O_3-scaling technique (green) nor from optimal estimation (black) (for further details see section 4.3).

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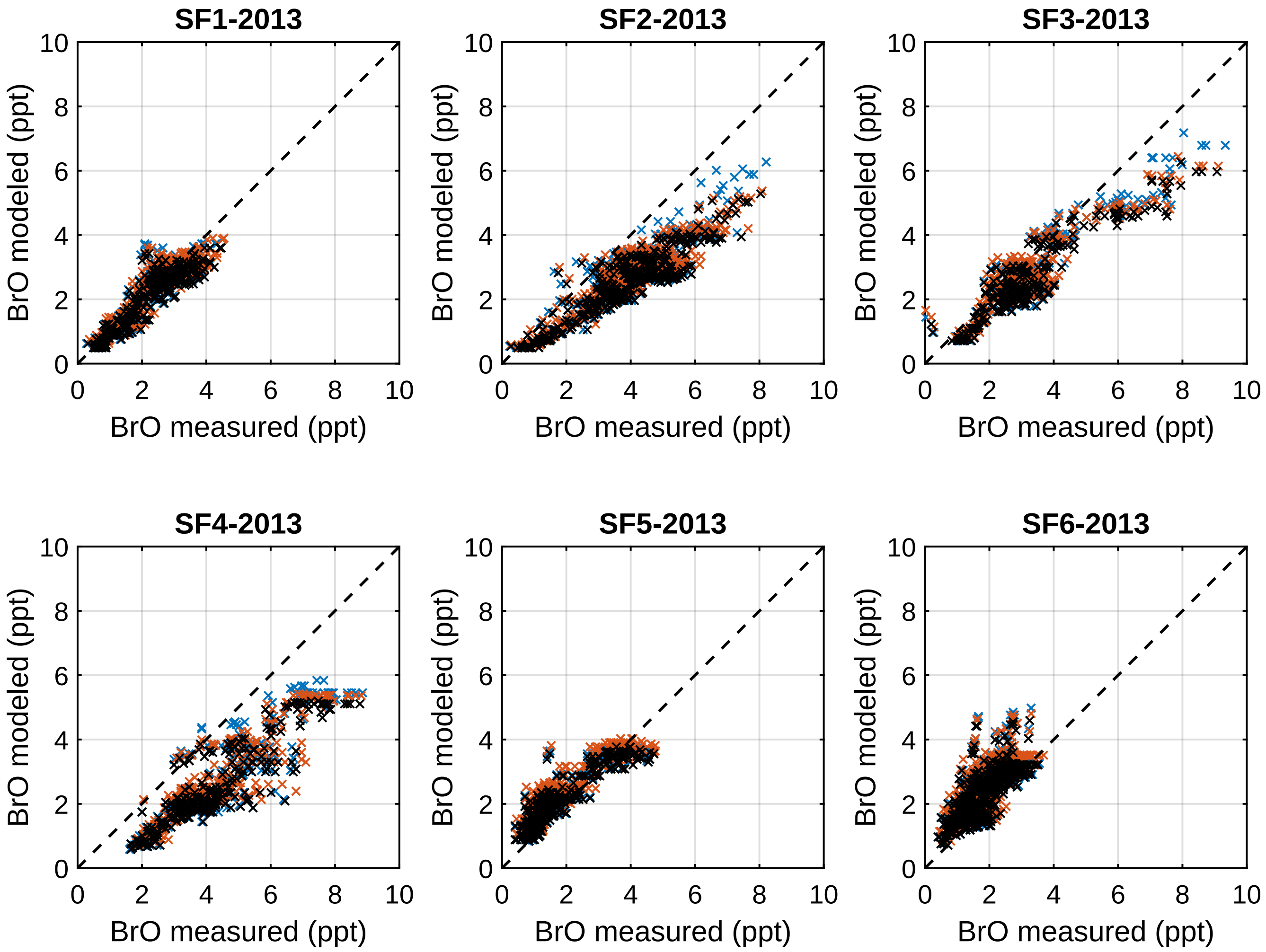

Figure 12. Comparison of measured and modeled BrO for the NASA-ATTREX science flights 1 to 6 in 2013. Black crosses are for model run # 583, blue crosses for # 584, and red crosses # 585.

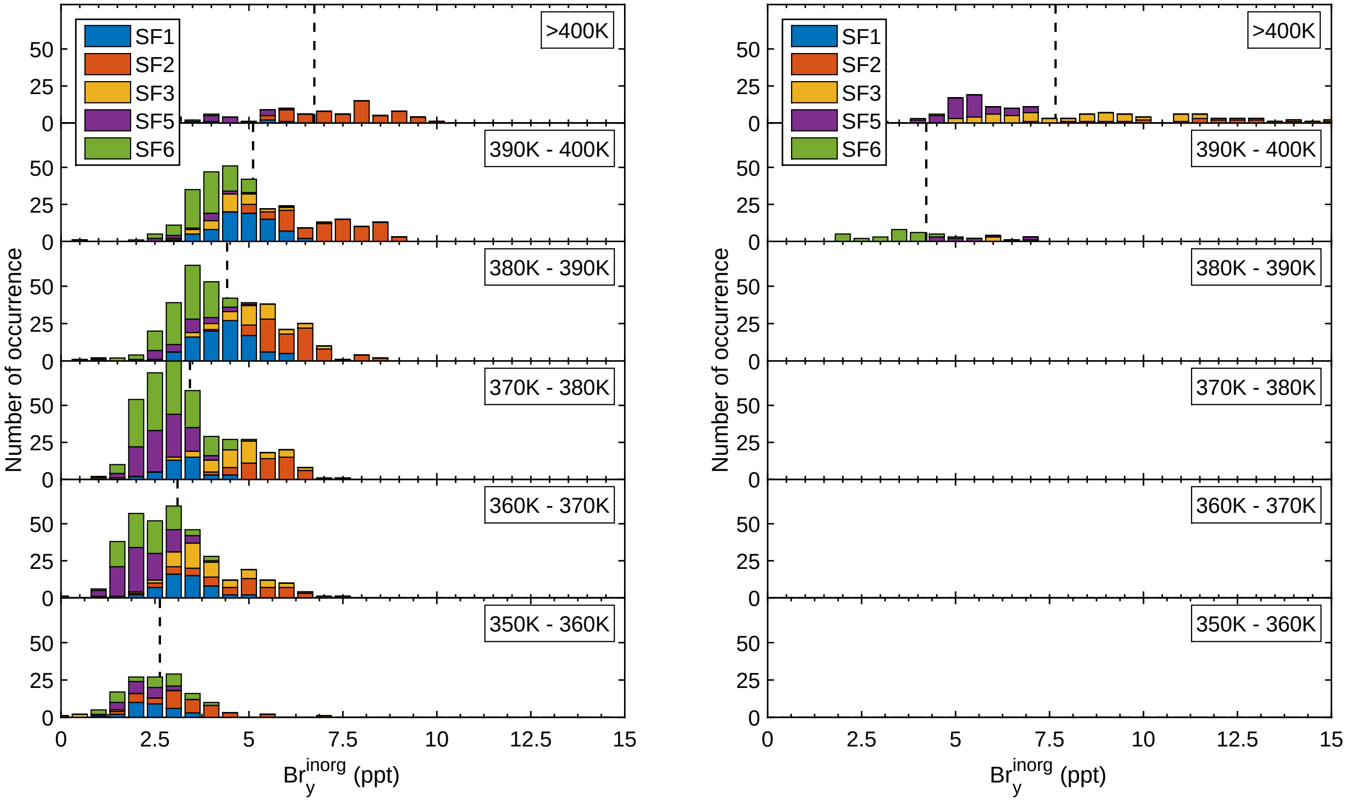

Figure 13. Histogram of $\mathrm{Br}_y^{\mathrm{inorg}}$ occurrence as a function of potential temperature for [CH$_4$] ≥ 1790 ppb (~~as indicated in the panels~~left panel) ~~, which~~ and [CH$_4$] ≤ 1790 ppb (right panel). High [CH$_4$] can be considered as a marker for young air mostly found in the freshly ventilated TTL while low [CH$_4$] can be considered as a marker for aged air mostly found in the subtropical lowermost stratosphere. The mean and the variance of $\mathrm{Br}_y^{\mathrm{inorg}}$ for young air (left panel) are: for θ = 350 - 360 K, 2.63 ± 1.04 ppt; θ = 360 - 370 K, 3.1 ± 1.28 ppt; θ = 370 - 380 K, 3.43 ± 1.25 ppt; θ = 380 - 390 K, 4.42 ± 1.35 ppt; θ = 390 - 400 K, 5.1 ± 1.57 ppt, and θ ≥ 400 K, 6.74 ± 1.79 ppt. Aged air (right panel): for θ = 390 - 400 K, ~~respectively~~4.22 ± 1.37 ppt, and θ ≥ 400 K, 7.67 ± 2.72 ppt.

~~Histogram of occurrence as function of potential temperature for ≤ 1790 ppb, which can be considered as a marker for aged air mostly found in the subtropical lowermost stratosphere. The mean and the variance are for = 390 - 400 K, 4.22 ± 1.37 ppt, and ≥ 400 K, 7.67 ± 2.72 ppt, respectively.~~

~~Histogram of occurrence as function of potential temperature for all NASA-ATTREX flights in 2013. The dashed lines mark the mean concentration for each potential temperature range.~~

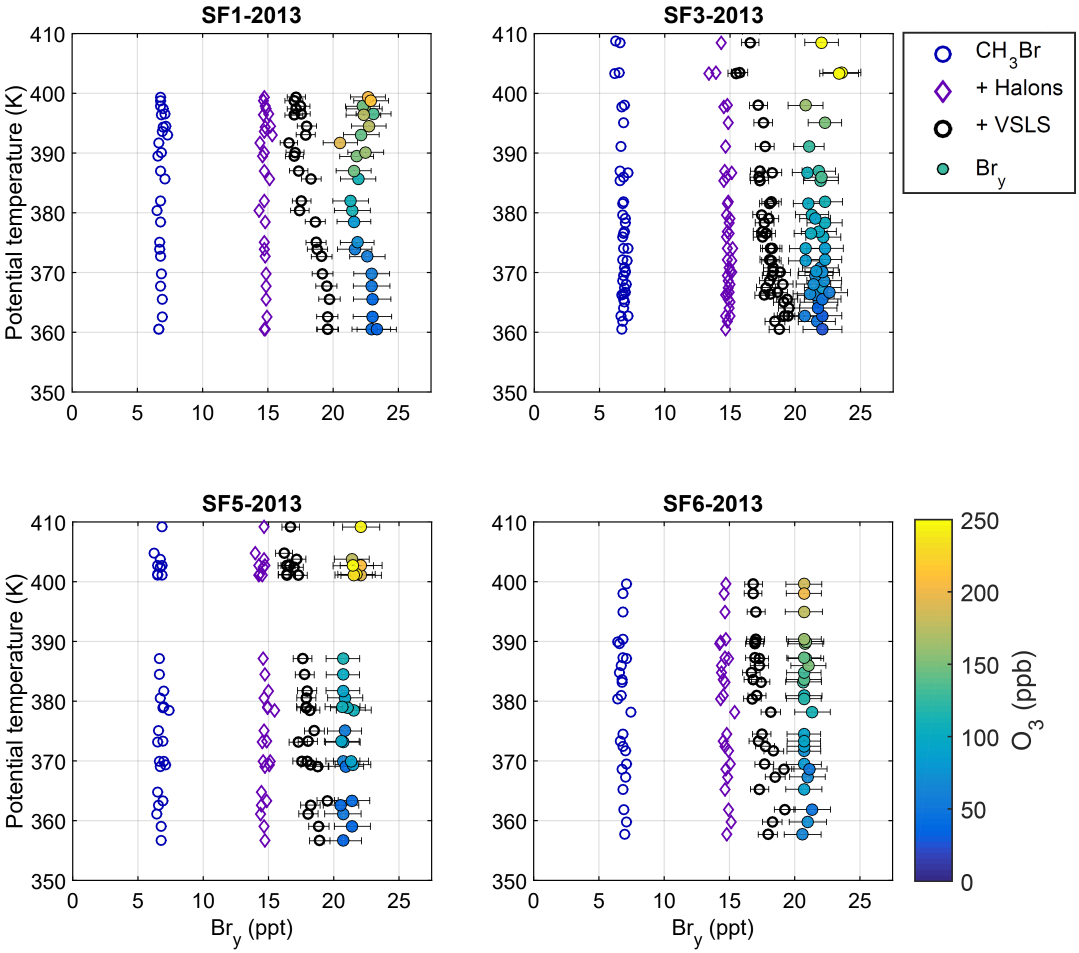

Figure 14. $\mathrm{Br_y}$ as a function of potential temperature (θ) for all dives during the 2013 NASA-ATTREX flights, when joint measurements of $\mathrm{Br_y^{org}}$ and $\mathrm{Br_y^{inorg}}$ are available.

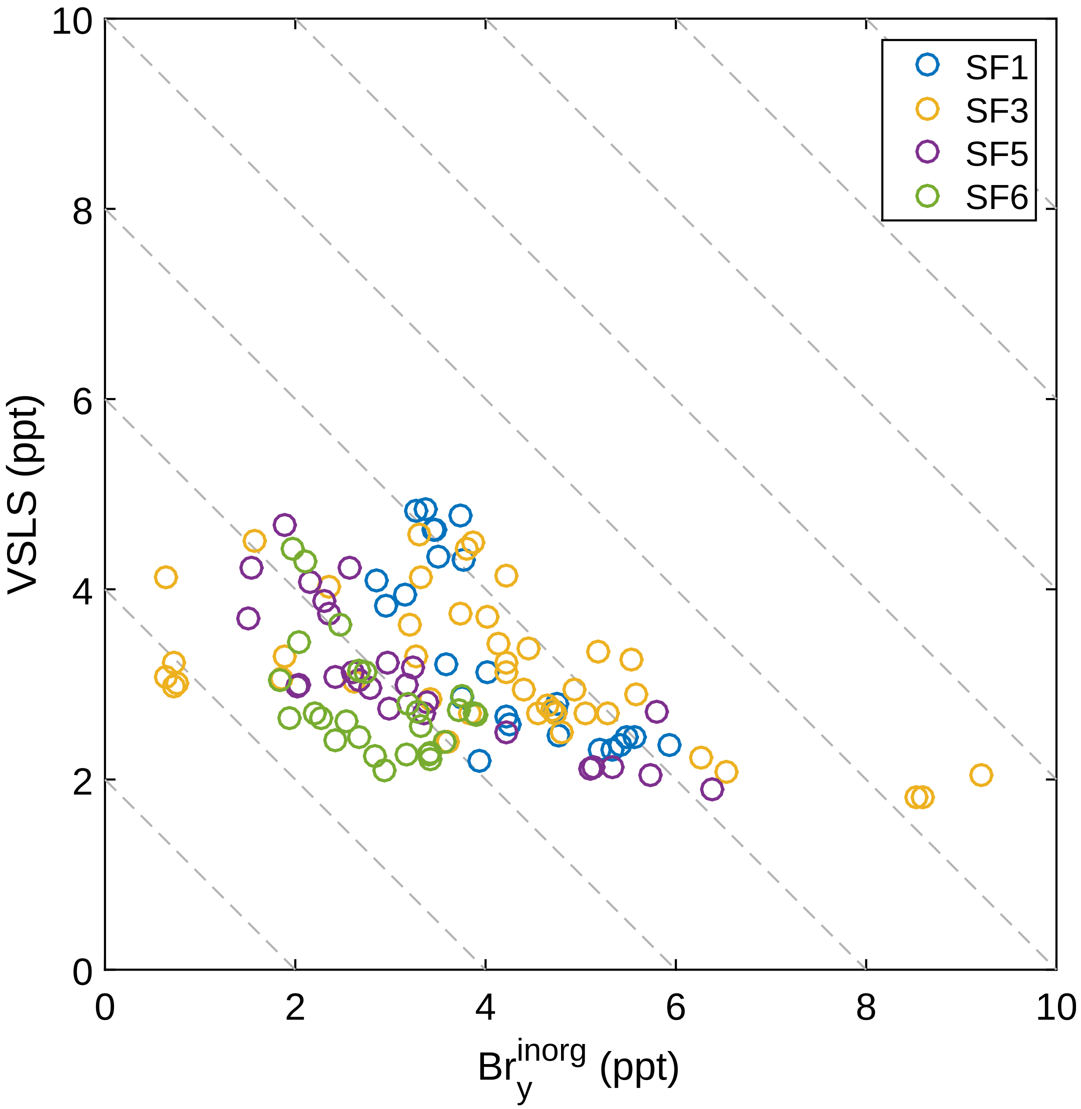

Figure 15. $\mathrm{Br}_y^{\mathrm{inorg}}$ as a function of the sum of all brominated VSLS using the same color code as in figure 10. If all $\mathrm{Br}_y^{\mathrm{inorg}}$ ~~was produced~~ resulted from destroyed VSL bromine of the same air ~~masses with~~ mass from near the ~~same amount of brominated organic VSLS concentrations available at the~~ surface, then all data points should follow individual diagonal lines.