Review for manuscript acp-2016-031

The manuscript of Navarro et al., reports on Cam-Chem **(**Community Atmosphere Model with Chemistry**)** modelling of the partitioning of inorganic bromine in the tropical tropopause layer (TTL) over the eastern and western Pacific Ocean. The modelling is compared with (averaged) observations of some key species, i.e. of the in-situ measured brominated source gases and O_3 from which to the partitioning of inorganic bromine is concluded. Comparisons of measured with and modelling in particular for the yet underexplored TTL are per-se important and interesting. However, based the already-published literature and state knowledge of this field, the paper has major flaw in its present state. My criticism of the present study is based on 5 major deficits (2 more general and 3 more specific comments including one related remark, #3), which are detailed in the following:

I.) Methodological deficits of the study

1. Using (spatial and temporal) averages for fast reacting species (radicals) in photochemical calculations:

   For the modelling of the bromine partitioning, averaged in-situ O_3 (together with bromine released from brominated VLSL) is used. Averaging over space and time of concentrations of photochemical reactive species (Figure 1) however is dangerous, since it may lead to incorrect and spurious results for the inferred quantities (for example concentration ratios). In order to see this please consider the rapidly established steady state of [Br] and [BrO] (both being a function of space x and time t) as well as of some (radical) species (e.g. O_3, OH, HO_2,..) at daytime, which is established through

$$J_{BrO}(x,t)\cdot[BrO(x,t)] = k(T)\cdot[O_3(x,t)]\cdot[Br(x,t)] + \ldots$$

or

$$\frac{[BrO(x,t)]}{[Br(x,t)]} = \frac{k(T)\cdot[O_3(x,t)]}{J_{BrO}(x,t)} + \ldots$$

   where in the present context irrelevant and missing terms are abbreviated by …. . Evidently in order for the equation to make sense k(T), $O_3(x,t)$, $J_{BrO}(x,t)$ need to be local (i.e. measured or calculated) quantities in the photochemical calculations. When using instead space and/or time-averaged quantities (the overbars denote either space or time averaging), the above mentioned equation would instead read as

$$\overline{J_{BrO}(x,t)}\cdot\overline{[BrO(x,t)]} = \overline{k(T)}\cdot\overline{[O_3(x,t)]}\cdot\overline{[Br(x,t)]}\cdot\overline{+\ldots}$$

$$\frac{\overline{[BrO(x,t)]}}{\overline{[Br(x,t)]}} = \frac{\overline{k(T)}\cdot\overline{[O_3(x,t)]}}{\overline{J_{BrO}(x,t)}} \overline{+\ldots}$$

   It can easily be seen, however, that the [BrO]/[Br] ratio calculated from averaged (space or time) quantities and from local quantities generally differ

$$\frac{\overline{[BrO(x,t)]}}{\overline{[Br(x,t)]}} = \frac{\overline{k(T)}\cdot\overline{[O_3(x,t)]}}{\overline{J_{BrO}(x,t)}} + \overline{\ldots}$$

$$\neq \quad \frac{[BrO(x,t)]}{[Br(x,t)]} = \left[\frac{k(T)\cdot[O_3(x,t)]}{J_{BrO}(x,t)} + \ldots.\right]$$

and accordingly only the latter gives the right answer for the photochemically established [BrO]/[Br] ratios in the atmosphere. In conclusion, when using space and time-averaged ozone concentrations (from the manuscript it is not clear as to whether (k(T), J_{BrO}, [Br] and [BrO] were also averaged in the same manner or not, but the answer is somewhat irrelevant to my argument), the modelled [BrO]/[Br] ratio may depart more or less from the actual atmospheric [BrO]/[Br] ratio.

Further when inspecting the ozone concentrations measured by the NOAA instrument in the TTL during ATTREX, it can be seen that actual ozone concentrations may vary by up to a factor of 10 (mostly with height, less in the horizontal in the TLL, see Figure 1) and so the [BrO]/[Br] should cover a similar dynamical range (keeping all the other parameters the same, see Figure 8 in Fernandez et al., (2014)), a behaviour not really recovered when using 1 km binned averages for ozone (Figure 1).

As consequence, the modelled [BrO]/[Br] may not well represent actual [BrO]/[Br] ratio met in the atmosphere, and as thus may not really provide a meaningful information to reader.

Finally, the ozone measured by the NOAA instrument and plotted in Figure 1 (right panel) appears to be spikier (due to any reason, but this could also be visual illusion) than the same ozone plotted in Figures 3 to 8 (panel c) in Werner et al., (2017) for the Eastern Pacific.

2. Averaging (over the space and time domains) concentrations for longer lived species:

   For some selected measurements (which ones?) 6 O_3 averages and corresponding averages of $CHBr_3$, and CH_2Br_2 (out of in total 745 in-situ samples from the EP according to the information provided in Figures 2 and 3a) are inter-compared with the respective model predicted parameters. Averaging over time (or space) for species of different photochemical lifetimes is somewhat problematic.

   In order to see this let's consider species of different photochemical lifetimes τ_i (i = 1, 2, 3…) with a common timescale against atmospheric transport τ_m. Here remember that in general photochemical and dynamical time scales for individual air masses are distributed in space and time (e.g., Waugh and Hall, 2002; Waugh, 2009; for TTL distributions of O_3 see c.f., Pan et al., 2014). For the moment, however I skip these complications. Then the joint timescale for photochemical processing and transport is given by

$$\tau_{eff,i} = \left(\frac{1}{\tau_m} + \frac{1}{\tau_i}\right)^{-1}$$

   where for the sake simplicity, it is assumed that both photochemical and dynamical processes lead to exponentially decaying concentrations. With these simplifications in mind, the time averaged concentration is then obtained from

$$\overline{c(x)} = \frac{\int_0^\infty c(x,t) \cdot \exp(-\frac{t}{t_{eff,i}}) \cdot dt}{\int_0^\infty \exp(-\frac{t}{t_{eff,i}}) \cdot dt} = -\frac{1}{t_{eff,i}} \cdot \int_0^\infty c(x,t) \cdot \exp(-\frac{t}{t_{eff,i}}) \cdot dt$$

(which is a Laplace transform of c(x,t)). Averaging samples using an appropriate kernel (here exp(- $t/t_{eff,\,i}$) is of course different from the (geometrical) average taken over individual samples of $c_k(x,t)$, i.e.

$$\overline{c(x,t)} = \frac{1}{m} \cdot \sum_{k=1}^{m} c_k(x,t)$$

since in the latter calculation any kernel (whether appropriate, or not see below) to calculated averages is discarded.

While for photochemical processes an exponential decay is a reasonable assumption, for dynamical processes in the atmosphere, it is certainly not a good assumption due to the turbulent transport (2-D in the stratosphere). Accordingly, the kernel for dynamical averages (often also called probability density functions, or pdf) does not follow an exponential but rather a power law (e.g., Min et al., 1996; Pierrehumbert and Yang, 1993; Minschwaner et al., 1996; Seo and Bowman, 2000; and for the statistics of actual field data of O_3, ClO, and others e.g., see Tuck et al., 2003; Tuck, 2008; Pan et al., 2014). As a consequence, the resulting air mass age spectrum (from which the average age can approximately calculated) is then (approximately) represented by Γ-type functions for the concentrations, which again depend on the time and location in the atmosphere (Hall and Plumb, 1994, Waugh and Hall, 2002).

In consequence, the comparison of modelled and measured averages (for ozone in Figure 1 and 2, and ozone $CHBr_3$ and CH_2Br_2 shown in Figure 2) does not really make sense, if the pdfs for the atmospheric and modelled samples are not the same in a statistical sense. To put it into simple terms, when averaging over (limited) samples one has to prove that the sampling from the real atmosphere and from the modelled atmosphere are made from the same statistical distributed event in space-time manifold in order for comparisons to make any sense. So certainly the way that the measured and modelled parameters are averaged deserves much more attention in the manuscript.

Finally, noteworthy is that averages over temporally and spatially distributed ‘fluctuations’ only give the same result for the inferred moments (averages, variance, et cetera) if the system is ergodic, which unfortunately in atmospheric dynamics is mostly not the case. Moreover, the samples need to be huge in order to fulfil one requirement of the central limiting theorem (CLT), that both samples (taken from the atmosphere and the model) converge to the same pdf (given they are the same which needs separately to be proven).

A remark

3. Comparing remotely sensed and modelled concentrations:

Moreover, the kernels to calculate averages (and used further on in inter-comparison exercises, see below) in remote sensing applications and in inverse modelling are strongly instrument and measurement-dependent (Rodgers, 2000). Fortunately, they often mask the above described effects due to their limited spatial or time resolution, i.e. their inherent averaging. In fact, in the latter applications these ‘kernels’ are called ‘averaging kernels

(AK)' of the observation and in colloquial English the averaging kernels can be called the 'glasses' by/through which the remote sensing observations were made. So the characteristics of 'the glasses' need to be considered in some way in inter-comparison exercises with modelled quantities (see below).

For some examples of actual AKs, please inspect Figures 5 and 10 (for the weighting of the probed concentrations in the horizontal) in Stutz et al., (2016), Figure 3.5 in Rodgers (2000), Figure 1 (below), or any other study on remote sensing. Chapter 3 in Rodgers, (2000) also discusses the different error sources of the traditional inversion methods used in remote sensing and inverse modelling. It also describes how remotely sensed quantities (here called $c_o(i)$, where i is the retrieval grid number somehow representing the vertical resolution of the measurement) need to be compared with modelled results ($c_m(i)$), i.e. by comparing the inferred $c_o(i)$ with the product AK· $c_m(i)$, where AK is a tensor, of which the columns (or rows) a filled with the individual averaging kernels, displayed for example in Figure 1.

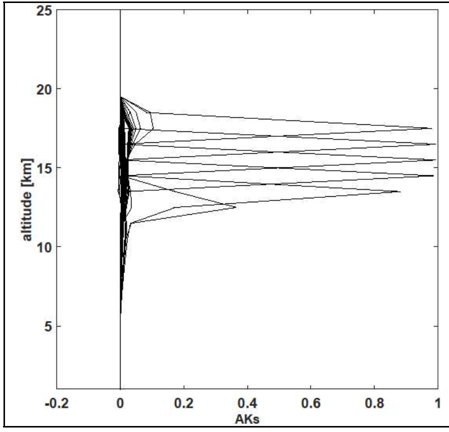

Figure 1: Calculated Averaging Kernels (AK) to infer BrO profiles (Rodgers, 2000) from limb observations during NASA ATTREX using optimal inversion (Stutz et al., 2016, and Werner et al, 2017).

In order to avoid these complications using traditional inversion methods for the interpretation of remotely sensed quantities (and in the particular case those arising from multiple scattering due to the a priori unknown spatial distribution and optical properties of aerosol and cloud particles), Stutz et al., (2016) describes a novel (scaling) method for the interpretation data. In effect, the scaling method uses additional information gained from simultaneously in-situ measured gases (i.e. O_3) in order to assist the interpretation of remotely sensed NO_2, and BrO in the TTL. Therefore, the scaling method has to be considered as a hybrid method (since it uses information collected by remote sensing and in-situ measurement), which comes with some advantages (and disadvantages) over traditional remote sensing methods. For example, it provides a higher accuracy than methods purely relying on remotely sensed information. Evidently the major disadvantage of the scaling method arises from the need of in-situ information of the probed air masses, i.e. it is suitable for applications from satellites, or high flying balloons. Further the scaling method still requires to carefully consider (by RT calculations simulating the observations) in order simulate how the information (the measured absorption) is obtained.

Accordingly, when applying the scaling technique to their remotely sensed data, Stutz et al., (2016) and Werner et al., (2017) actually simulated each individual observation by modelling the actual RT (and the predicted absorption of the targeted species) by considering instrumental and other details of the measurements as well as predicted curtains of the targeted species, obtained from CTM modelling (TOMCAT/SLIMCAT). This approach (as in any traditional remote sensing application) thus carries over to the analysis any relevant instrumental and observation-related features in the forward modelling of the observation. Evidently, the scaling method (as any traditional inversion method) then allows very close inter-comparisons of the predicted quantities (e.g. trace gas concentrations) with the observations, including a correct attribution of the fraction of the measured absorption (or slant column) to parts of the atmosphere not directly probed by the observation, however only if the averaging kernels are appropriately considered.

Here please also note that the latter approach to inter-compare remotely sensed data and CTM modelling is not new at all, but e.g., it has been used by our group for more than 2 decades. Further using the scaling method, the calculation of absolute concentrations is achieved using a simultaneously in-situ measured and remotely sensed gas (e.g., O_3), together with an appropriate consideration (by RT modelling) of the different sensitivities for detection of the targeted and scaling gas (see equation 14 in Stutz et al., 2016). In effect, the accuracy of the inferred quantities is arguably much better (Stutz et al., 2016) than only relying on remotely sensed quantities for the retrieval of concentrations. Accordingly check your statement on page 6 (lines 14 and 15) for correctness.

II.) Comparison with available measured data

Further, I'm really curious why the authors did not attempt to compare their modelling work with actual measured NO_2 and BrO data (potentially) available to the first author for more than a year and which now have been published (Werner et al, 2017). However, when using remotely sensed data in inter-comparison exercises, the kernel for horizontal averaging (see Figure 10 in Stutz et al. (2016)) has to be appropriately taken into account for the modelled data (see my remark #3 above). Further, given that the Werner et al., (2017) manuscript (which the first author of the present article co-authored) was submitted earlier (July 17, 2016) than the present manuscript (Nov. 18, 2016), the statement on page 4 (line 18) is not well based. By being more specific, the lack of a tight comparison of the modelled results with existing measured data give rise to some more deficits of the present study:

4. Simulated NO_2:

   For the Eastern Pacific TTL, the CAM-Chem model predicts NO_2 between 0.7 – 343 ppt at daytime (Table 1 and Figure 6). No reasons are provided for the elevated NO_2 in the TTL over the EP, except that modelled air masses are affected by 'pollution'. However, no other indication (neither from, for example, measured CO during NASA-ATTREX (UCATS) nor any further evidence inferred from the model) is provided that in fact polluted air masses were reaching the TTL over the EP in early 2013. In fact, the NO_2 mixing ratios reported by Werner et al., (2017) were < 20 ppt in the TTL, and they agree well (within the error bars +-/10 ppt) with the predictions of the TOMCAT/SLIMCAT simulations assuming no contribution from 'pollution'. In all these respects, and in particular with respect to the discussion provided above under point #3, the statement on page 6 (lines 14 and 15) is not well founded.

   Accordingly, in any further study information has to be provided why for the EP TTL the Cam-Chem model predicts NO_2 concentrations much large than observed. In addition, coherent evidences both from observations and modelling has to be provided (for example from CO/O_3 and $CH4/ O_3$) that indeed the TTL over the EP is affected by 'pollution'.

5. Simulated inorganic bromine, its partitioning and spatial patchiness:

   A major part of the study is devoted to model the bromine partitioning. First, I found it hard understand why the model does not really reproduce the increase in total inorganic bromine with increasing height (potential temperature) within the TTL, mainly caused by the destruction of brominated VSLS. This is somehow curious since the bromine concentrations at the lower boundary reported by Navarro et al., (2015) (page 3, line 18 and 19; VSLS; 3.84 ± 0.64 and 3.18 ± 1.49 ppt from WP and EP, respectively, and inorganic bromine 3.02 ± 1.90 ppt of Bry over the EP and 1.97 ± 0.21 ppt over WP) are in reasonable agreement with the data for the EP TTL, reported by Werner et al., (2017). Moreover, in the Cam-Chem model inorganic bromine (in gaseous form) barely increase from ~2 ppt (from the lower boundary at 14 km) to ~3 ppt at 18 km (Figures 4 and 8), in stark contrast with the observations presented in the Werner et al., study for the upper levels of the TTL over EP. Here, depending on the flight, inorganic bromine ranges from (2.63 ± 1.04) ppt (range from 0.5 ppt to 5.25 ppt) to 5.1 ±1.57 ppt (at Θ = 390 - 400 K) to 6.74±1.79 ppt (at Θ > 400 K), in agreement with the measured destruction of brominated VSLS species (Navarro et al., 2015, and Figure 14 in Werner et al., 2017). So the obvious question is: Does the model either not efficiently destroy the brominated VSLS, and/or does the missing bromine reside in/on particles? If the latter is the case, the bromine up-taken by particles need to be rather large (2 – 3 ppt) in order close the bromine budget. So some information has to be provided how the bromine budget is closed in the model, and in particular on how much bromine is up-taken by the particles.

Next even though the modelled absolute amount of gaseous inorganic bromine likely may not affect the Br_y partitioning, the modelled [Br]/[BrO] (cited: (1) …. the modelled Br/BrO maximizes at 17 km from page 7, line 7 to 17 and in Figure 7 and (2) …..that Br/BrO may become as large as 2 in the TTL of the EP, see Figure 7) deviates from expectations based on the amount of ozone and its increase with height (see Figure 1 left panel, and Figure 3 to 8 in Werner et al., 2017), and the modelled bromine partitioning in the TTL as function of ozone (Fernandez et al., 2014, Figure 8). In fact, these findings largely contrast with early findings based on the Br/BrO ratio in TTL (at 17 km) during daytime c.f., by Fernandez et al., 2014 (Figure 1, left panel where Br/BrO < 0.6 at 17 km during tropical noon), Schmidt et al., (2016) (Figure 1), or lately the model results presented in Werner et al., (2017) (inspect Figure 3 – 8, Br/BrO < 0.6 at 17 km). Reasons for this discrepancy, including a discussion how the averaging of the ozone and the source gas concentrations and of other quantities impacts the modelled Br/BrO ratio (see points 1 and 2 above) certainly need to be addressed in any future study.

Finally, the model predicts a certain patchiness (on spatial scales of some hundred kilometres) of the modelled Br/BrO ratio at 17 km for the EP (and WP), with [Br]/[BrO] ratios ranging from below < 0.5 to about 2. No further reason for this patchiness is provided in the manuscript. If air masses entrained by mesoscale convection into the TTL are responsible for this patchiness, then it also needs to be seen in other gases (e.g. CO, CH_4…), but again no evidence for this is provided in the manuscript. The predicted patchiness also contrasts with measured O_3, NO_2, and BrO, in particular since the remote sensing measurements can easily resolve horizontal variations of the measured quantities on the hundreds of kilometre scale (e.g., Stutz et al., (2016) figure 9, and Werner et al., (2017), figures 3 to 8). Further, since at daytime a rapid steady state is established between Br and BrO (see above) as function of the solar illumination and O_3 concentration, it is difficult to infer from measured data any reason for the predicted patchiness in the [Br]/[BrO] ratio.

6. Error and uncertainties:

Finally, as an experimentalist who devotes 85 % of his efforts in the interpretation of data to get a handle on a reliable (thus justifiable) errors and uncertainties of the measured quantities, I always find it curious if studies lack a proper discussion of errors and uncertainties of the presented results. In modelling studies, this could for example be done by (1) inspecting respective Jacobians of the relevant quantities, (2) investigate differences in the modelled fields from 'on and off' runs, and (c) perform ensemble runs et cetera. So also in this respect, the present study largely lacks this requirement for robust science.

Summary

Given the above described methodological deficits (points 1 and 2), the lacking comparison of the modelled results with actual measured data (points 4 and 5), and the lacking discussion of errors and uncertainties (point 6), unfortunately it is impossible to recommend the manuscript for publication in the present form.

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