BrO and inferred Br_y profiles over the Western Pacific: Relevance of Inorganic Bromine Sources and a Br_y Minimum in the Aged Tropical Tropopause Layer

Theodore K. Koenig[1,2], Rainer Volkamer[1,2], Sunil Baidar[1,2,#], Barbara Dix[1], Siyuan Wang[2,3], Daniel C. Anderson[4,†], Ross J. Salawitch[4,5,6], Pamela A. Wales[5], Carlos A. Cuevas[7], Rafael P. Fernandez[7,8], Alfonso Saiz-Lopez[7], Mathew J. Evans[9], Tomás Sherwen[9], Daniel J. Jacob[10,11], Johan Schmidt[12], Douglas Kinnison[13], Jean-François Lamarque[13], Eric C. Apel[13], James C. Bresch[13], Teresa Campos[13], Frank M. Flocke[13], Samuel R. Hall[13], Shawn B. Honomichl[13], Rebecca Hornbrook[13], Jørgen B. Jensen[13], , Richard Lueb[13], Denise D. Montzka[13], Laura L. Pan[13], J. Michael Reeves[13], Sue M. Schauffler[13], Kirk Ullmann[13], Andrew J. Weinheimer[13], Elliot L. Atlas[14], Valeria Donets[14], Maria A. Navarro[14], Daniel Riemer[14], Nicola J. Blake[15], Dexien Chen[16], L. Gregory Huey[16], David J. Tanner[16], Thomas F. Hanisco[17], Glenn M. Wolfe[17,18]

[1]Department of Chemistry & Biochemistry, University of Colorado, Boulder, CO, USA
[2]Cooperative Institute for Research in Environmental Sciences (CIRES), Boulder, CO, USA
[3]Department of Chemistry, University of Michigan, Ann Arbor, MI, USA
[4]Department of Atmospheric & Oceanic Science, University of Maryland, College Park, MD, USA
[5]Department of Chemistry & Biochemistry, University of Maryland, College Park, MD, USA
[6]Earth System Science Interdisciplinary Center, University of Maryland, College Park, MD, USA
[7]Department of Atmospheric Chemistry and Climate, Institute of Physical Chemistry Rocasolano, Spanish National Research Council (CSIC), Madrid, Spain
[8]Argentine National Research Council (CONICET), FCEN-UNCuyo, UNT-FRM, Mendoza, Argentina
[9]Wolfson Atmospheric Chemistry Laboratories (WACL), Department of Chemistry, University of York, York, United Kingdom
[10]John A. Paulson School of Engineering and Applied Sciences, Harvard University, Cambridge, MA, USA
[11]Department of Earth and Planetary Sciences, Harvard University, Cambridge, MA, USA
[12]Department of Chemistry, Copenhagen University, Copenhagen, Denmark
[13]National Center for Atmospheric Research (NCAR), Boulder, CO, USA
[14] Department of Atmospheric Science, Rosenstiel School of Marine & Atmospheric Sciences (RSMAS), University of Miami, Miami, FL, USA
[15]Department of Chemistry, University of California, Irvine, CA, USA
[16]School of Earth & Atmospheric Sciences, Georgia Tech, Atlanta, Georgia, USA
[17]Atmospheric Chemistry and Dynamics Laboratory, NASA Goddard Space Flight Center, Greenbelt, Maryland, USA
[18]Joint Center for Earth Systems Technology, University of Maryland, Baltimore County, Maryland, USA
[#]now at: National Oceanic and Atmospheric Administration (NOAA), Boulder, CO, USA
[†]now at: Department of Chemistry, University of Drexel, Philadelphia, PA, USA

Response to Reviewer 1; 02 December 2017

Black: Referee's comments
Blue: Author's reply
Green: sentence added/modified in the manuscript

We greatly appreciate Reviewer 1 for the review of our paper, including the both positive feedback and areas for improvement.

This paper describes airborne observations of bromine species (principally BrO) between the boundary layer and the lower stratosphere, over the tropical western Pacific. This is a region where there are very few observations, and so adds significantly to the global picture of bromine. The observations - mostly from airborne DOAS measurements - are compared with output from two global chemistry-climate models, and a chemical box model. There is thus a huge amount of data and careful analysis that has gone into the paper, making it quite a difficult paper to digest! In some respects it reads like several chapters of a PhD thesis, rather than a paper. Nevertheless, because the BrO levels are close to the instrument detection level, error analysis is very important and is discussed in detail, along with the actual location of the BrO retrieved from this remote sensing technique. The paper is extremely well written (with almost no typographical errors), and the diagrams are all appropriate and very clear, so the authors are to be congratulated on pulling together such a major undertaking.

I have two substantive comments. First, section 3 is labelled "Results", but actually contains a lot of discussion of the observational and modelling results which should really be in section 4 - "Discussion".

We agree, and have renamed Section 3 "**Results and Atmospheric Modeling Context**", and Section 4 "**Discussion and Atmospheric Implications**". We have synergized text throughout the manuscript according to these section headings, to avoid duplication, and to assure the information concerning Figures is in one place.

More general statements that did not belong to Sects. 3.1 and 3.2, but are needed to understand Sect. 3.3 have been moved to Sect 3.3, and were edited to read as follows:

Broadly, for case 0 in the lower FT (< 6.5 km), aged TTL and stratosphere the SA is high enough to remove HBr in the box model. As a consequence, Br_y estimates are insensitive to further increases in SA, and the BrO/Br_y ratio is rather robust, i.e., primarily determined by gas-phase chemistry. In contrast, between 6.5 and 13.5 km the inferred Br_y is sensitive to assumptions about the available SA and heterogeneous chemistry.

Second, there is a very nice summary in Section 1 about the possible ways in which bromine could impact on tropospheric chemistry. I was therefore hoping to see a bit more discussion in the Conclusions about how the understanding gained from this study affects the assessment of these impacts. The authors conclude that the sea-salt source of bromine is not well described by the two global models, and these models also do not capture well the minimum in Bry in aged upper tropospheric air - so, is this an important result in terms of impacts on the troposphere?

This summary in Section 1 is based on model results that do not consider SSA sources for bromine, and provides important context to the discussion of impacts. We have synergized all text related to impacts into a new subsection 4.5 "**Chemical Implications of Findings**". The partly new/partly synergized text reads as follows:

4.5 Atmospheric Implications

4.5.1 Relevance of halogens for atmospheric composition

Bromine is important for the oxidation of atmospheric mercury (Coburn et al., 2016; Goodsite et al., 2004; Holmes et al., 2006; Parrella et al., 2012), the destruction of ozone (von Glasow et al., 2004; Read et al., 2008; Saiz-Lopez and von Glasow, 2012; Schmidt et al., 2016; Simpson et al., 2015; Wofsy et al., 1975), and oxidative capacity. Recent first simultaneous measurements of BrO and IO over the entire height of the tropical troposphere (Volkamer et al., 2015) suggest that bromine and iodine together account regionally for 34% of column integrated ozone loss over the tropical Eastern Pacific Ocean (Wang et al., 2015). Globally, the impact of bromine and other halogens reduces the ozone burden between 10 and 18%, which is comparable to the ozone sink from the $HO_2 + O_3$ reaction (Saiz-Lopez et al., 2012, 2014, Sherwen et al., 2016, 2017b). Bromine oxidation of NO_x is an important NO_x sink, and contributes to ozone reduction by reducing the photochemical formation of ozone (Schmidt et al., 2016). Halogen chemistry is responsible for a 11% reduction in global average OH radical concentrations (Schmidt et al., 2016), and increases the atmospheric lifetimes of methane from 7.47 to 8.28 years (Sherwen et al., 2016). However, the most recent papers (Schmidt et al., 2016; Sherwen et al., 2016) do not consider the SSA source when estimating the impacts of bromine and other halogens in the troposphere. This suggests that the above impacts may be lower estimates, as our results strongly support the need for a SSA source in the lower marine atmosphere.

Knowledge about heterogeneous/condensed phase reactions is rapidly evolving. Recent work has found that an improved implementation of the condensed phase reaction of HOBr with S(IV) significantly inhibits recycling of HOBr and lowers the global gas phase Br_y burden by 50% (Chen et al., 2017). Our models are not optimized to include these condensed phase reactions, and including these sinks for Br_y would lower Br_y estimates from global models in Fig. 6 (and Table 5), and bring near surface Br_y in global models with SSA source into better agreement with the inferred Br_y. Moreover, recent laboratory observations of surface active BrO_3^- (primary ozonide) (Artiglia et al., 2017) support the important role of O_3 reactive uptake for the heterogeneous recycling of gas-phase Br_y, which is most relevant in the upper troposphere, where SSA is proportionally a larger source of Br_y (Schmidt et al., 2016). The surface activity of the primary ozonide also suggests that recycling of Br_y to the gas phase may be in competition with bulk accommodation of HOBr and subsequent S(IV) chemistry, which would reduce the efficiency of Br_y washout. Furthermore, the role of organic surfactants is unclear. If organics reduce the rate of heterogeneous recycling our Br_y estimates could be lower limits; if surfactants are neutral/accelerate heterogeneous reactions, our box-model inferred Br_y would be rather insensitive since HBr is only a very minor reservoir species already. The impact of uncertain heterogeneous chemistry is transparent from Figs. 5 (and Fig. S4), and most relevant in the altitude range between 6.5km and 14.5km, where Br_y inferred from BrO observations is sensitive to assumptions about heterogeneous chemistry, and estimated conservatively here. Uncertain heterogeneous chemistry is less relevant for our Br_y estimates in the aged TTL and LS (where the BrO/Br_y ratio is flat in Figs. 5 and S4). Future development of chemical transport and climate models needs to refine the representation of heterogeneous/multiphase reactions of halogens, which is currently highly simplified, yet important to assess the impacts of tropospheric halogens for atmospheric composition and climate.

4.5.2. Inorganic Bromine Sources

The choice by recent global models (Schmidt et al., 2016; Sherwen et al., 2016), to estimate halogen impacts based only on organic bromine sources, i.e., without considering the SSA source, is justified by the ability to approximate the vertical profiles of BrO over the tEPO (Volkamer et al., 2015; Wang et al., 2015) reasonably well without a SSA source; and by the lack of any measurable BrO in the remote MBL over the tEPO (see Sect. 4.4). A key difference between profiles over the tWPO and tEPO is that significant BrO is measured in the MBL over the tWPO. This strongly supports the need for a SSA source. It also raises questions whether models used to rationalize previous measurements accurately represent all atmospheric processes. Figure 6 illustrates that a SSA source is needed to explain inferred Br_y in the MBL, and that this source impacts atmospheric composition up to at least 3.5 km. The amount of inferred Br_y is well within the range predicted by two global models; but models that include SSA sources predict Br_y amounts that vary by a factor of 3-10 over this altitude range. In the mid FT, the data remains inconclusive; there is no pressing need for SSA source, but the range of inferred Br_y is not inconsistent either. Above 9.5 km the inferred Br_y increases with altitude. A Wilcoxon-Mann-Whitney rank test shows that the inferred Br_y in the upper FT and convective TTL is higher than that in the mid FT with 98% confidence, supporting a C-shaped profile of inferred Br_y. Models generally do not predict this increase, and profiles remain either flat, or even decrease with altitude. This observation supports the speculation by Wang et al. (2015) that marine convection over the tWPO is a source for inorganic bromine. Our data provide previously missing evidence that support the widespread impact of inorganic bromine sources on the upper troposphere.

The mechanism driving the gas-phase Br_y minimum in the aged TTL is currently not well known, and could have dynamical or chemical reasons. The contribution of bromine to ozone destruction is largest in the vicinity of the tropopause (Fernandez et al., 2014; Salawitch et al., 2005; Schmidt et al., 2016; Sherwen et al., 2016), and the observed reduction in gas-phase Br_y in the aged TTL is likely to have a significant impact on ozone and OH that is relevant for the lifetime of brominated VSLS. The lifetime of VSLS in the TTL affects the ratio at which CBr_y is injected into the stratosphere as organic source gases or inorganic product gases (Gao et al., 2014; Nicely et al., 2016; Rex et al., 2014). Since the complex structure of Br_y in the TTL is only partially captured by a model like CAM-Chem suggests the need for further development and testing of models that dynamically couple the troposphere and the stratosphere.

We have also added a brief statement in the conclusions to reflect this:

The most recent modeling estimates of the global impact of bromine do not include an SSA source and are likely lower limits as a result. Further modeling studies will be necessary to determine the magnitude of revised impacts which account for SSA derived Br_y.

The novelty of the aged TTL minimum makes it more difficult to assess impacts without speculation, we have added the following statement to the conclusions:

It is currently unknown how much Br_y is transported into the stratosphere as aerosol bromide and whether this bromide is available for ozone destruction in the lower stratosphere. The proportional contribution of bromine to ozone destruction is largest in the vicinity of the

tropopause (Fernandez et al., 2014; Salawitch et al., 2005; Schmidt et al., 2016; Sherwen et al., 2016). A reduction in available bromine could thus have a significant impact on ozone in the TTL.

Minor points:

page 2, line 2: are found

Corrected

page 5, line 21: add a clause or reference to explain what the Kurucz spectrum is

Added original and most recent references for Kurucz solar spectrum

Chance and Kurucz, 2010; Kurucz et al., 1984

page 21, line 11: CONTRAST

Corrected

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