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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Bromine in the tropical troposphere and stratosphere as derived from balloon-borne BrO observations" *by* M. Dorf et al.

M. Dorf et al.

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Author comment on review comment #2 for manuscript acpd-2008-0290

We are grateful to the referee's overall positive comments and suggestions. Please find below our point-to-point reactions in italic.

General comments:
The paper is written in a very compact manner and there are several places where the reader would be more interested in further details (a few sentences could be enough) than simply references. In particular:

1. BrO DOAS retrieval and profile inversion (Page 13001, lines 17-18)
The text was extended and now reads:
Bromine monoxide (BrO) is detected in the UV with the DOAS technique (Platt et al., 2008) in the wavelength range from 346 *nm to* 360 *nm as recommended by Aliwell et al. (2002). This wavelength range contains the UV vibration absorption bands (*$4-0$ *at* 354.7 *nm, and* $5-0$ *at* 348.8 *nm) of the A(*$^2\pi$*)←X(*$^2\pi$*) electronic transition of BrO. The set of reference spectra used contains a* NO_2 *reference spectrum for T=*207 *K, and two* O_3 *spectra at T=*197 *K and T=*253 *K, in order to account for temperature effects. All* NO_2 *and* O_3 *spectra were recorded with the balloon spectrograph in the laboratory. The BrO reference is the absolute cross-section measured by Wahner et al. (1988), with the wavelength calibration taken from own laboratory measurements.*

Profile information was obtained by a least-squares profile inversion technique (Maximum A Posteriori) Rodgers, 2000. A more detailed description of the DOAS profile inversion can be found in Butz et al. (2006). The SCD values were smoothed with a Gaussian filter of 1.0 km width, but since the altitude grid for profile inversion is 2 km, the results are not influenced significantly. Further details on the BrO DOAS-retrieval and the profile inversion can be found in Dorf et al. (2006).

Accordingly the following References were added:
Aliwell, S., Van Roozendael, M., Johnston, P., Richter, A., Wagner, T., Arlander, D., Burrows, J., Fish, D., Jones, R., Tornkvist, K., Lambert, J.-C., Pfeisticker, K., and Pundt, I.: Analysis for BrO in zenith-sky spectra: An intercomparison exercise for analysis improvement, J. Geophys. Res., 107, 2002.

Rodgers, C.: Inverse methods for atmospheric sounding, World Scientific, Singapore, New Jersey, London, Hongkong, 2000.

Wahner, A., Ravishankara, A., Sander, S., and Friedl, R.: Absorption cross section of BrO between 312 and 385 nm at 298 and 223 K, Chem. Phys. Lett., 152,

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507–512, 1988.

2. Photochemical calculations (Page 13001, lines 18-24): Which 1-D model is used ? Which photochemical data set is used ? JPL2006 ?
The paragraph was extended as follows:
A 1-D model was then used to reconstruct the diurnal cycle for comparison with the observations. The stratospheric photochemistry is modelled on 20 potential temperature (Θ) levels between Θ=323 K ($\simeq$9 km) and Θ=1520 K ($\simeq$42 km). The 1-D column model is initialised, at each height level, at 00:00 UT with 3-D CTM SLIMCAT model results. It is an updated version (using JPL-2006 kinetics; Sander et al. (2006)) of the model used by e.g., Butz et al., (2006) and includes a comprehensive set of all relevant gas-phase and heterogeneous reactions. Photolysis rates are interpolated with respect to pressure, temperature, overhead ozone and solar zenith angle (SZA) from a SLIMCAT lookup table where the actinic fluxes are calculated as recommended by Lary and Pyle, (1991).

Accordingly the following References were added:
Sander, S. P., Finlayson-Pitts, B. J., Friedl, R. R., Golden, D. M., Huie, R. E., Keller-Rudek, H., Kolb, C. E., Kurylo, M. J., Molina, M. J., Moortgart, G. K., Orkin, V. L., Ravishankara, A. R. and Wine, P. H.: Chemical Kinetics and Photochemical Data for Use in Atmospheric Studies, Evaluation Number 15," JPL Publication 06-2, Jet Propulsion Laboratory, Pasadena, 2006.

Lary, D. J. and Pyle, J. A.: Diffuse radiation, twilight and photochemistry, J. Atmos. Chem., pp. 373–392, 1991.

3. The whole-air-sampler BONBON (Page 13002, lines 2-6): The measured SGs should be listed here and not only on page 13004;
The SGs are listed now.

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What is the importance of the SG calibration scales since this could one explanation for the discrepancy between Bry-in and Bry-org (page 13004, line 24)? Please, develop a bit more
see the specific comments below.

Specific comments:
Page 13002, lines 23-25: a negligible BrO content is found in the lower and middle troposphere. This is an important result since it challenges most previous estimates, except those from Schofield et al. (2004 and 2006). Therefore, I think it merits a full discussion here in Section 3 than only in the Conclusions and Summary. Possible reasons are given by the authors to explain these contrasting findings.
The discussion was moved from the Conclusions and Summary. The paragraph starting on page 13002, line 23 was extended as follows:
In the lower and middle troposphere BrO concentrations are compatible with zero within the uncertainties (around 1 ppt, depending on altitude – see Fig. 1). The very low, or even negligible, BrO concentrations (<1ppt) for the lower, middle and upper troposphere agree with recent studies of Schofield et al. (2004 and 2006), but largely challenges other findings Richter et al. (1998),Fitzenberger et al. (2000),Roozendael et al. (2002), Salawitch et al. (2005), Hendrick et al. (2007), Fietkau et al. (2007), Theys et al. (2007). With regard to these contrasting findings, it is not clear whether the bromine released during the breakup process of the VSLS in the troposphere either (1) quickly reacts into less reactive forms of bromine (HBr, HOBr, and $BrONO_2$) without being efficiently activated on particle surfaces Glasow et al. (2004), Iraci et al. (2005), or (2) is permanently taken-up by particles and eventually washed-out, or (3) whether the reverse is true and we (and others) simply missed probing the right air-masses in the tropics, in which the brominated PGs can efficiently become activated into BrO.

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Accordingly the Conclusions and Summary section was changed , page 13006, line 19:
Our result on reactive bromine and the PG abundance in the troposphere is inconclusive. Tropospheric BrO is compatible with 0 ppt and <1 ppt within the uncertainties. This is in agreement with studies of Schofield et al. (2004 and 2006), but contradicts other findings e.g., Richter et al. (1998), Fitzenberger et al. (2000), Salawitch et al. (2005), Theys et al. (2007). Future research is needed with more sensitive instrumentation and sophisticated models in order to reveal the role that bromine plays for the photochemistry of the troposphere and UT/LS region.

Something which is puzzling me is the discrepancy between the Teresina tropospheric BrO profile (no BrO in the free troposphere) and the Kiruna summer 1998 profile (Fitzenberger et al., 2000; 2+/-0.8 ppt BrO at 5 km altitude). Did you investigate the impact of the reanalysis of the BrO-SCDs (see lines 14-16 on page 13005) on the Kiruna Summer 1998 and Winter 1999 tropospheric BrO profiles? If not, I think this should be done since your reanalysis seems to give lower BrO concentration values (stratospheric Bry is 2ppt smaller with the reanalysis for the Kiruna Winter 1999 flight).

We have not investigated the impact on the BrO profiles for the high-latitude (Kiruna) summer 1998 and winter 1999 in detail yet. We agree that the reanalysis of the BrO-SCDs will have an impact on the profiles, and we are planning to perfom such an analysis in a separate study. In our opinion such a study should be more extensive, than just reanalysing Kiruna 1998 and Kiruna 1999 measurements, but should also include recent tropospheric BrO balloon observations from 2001, 2003, and 2004.

Page 13004, lines 2-10: Modelled BrO values during solar occultation (SZA larger than 90^o) are up to 15% larger than the measured ones. It would be interesting to test the impact of the uncertainties on the photolysis rates (BrO, $BrONO_2$, HOBr) at

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such large SZAs. Maybe this could help to reconcile the model with the measurements.

We agree that one could reconcile the model with the measurements if pushing the photolysis rates of relevant species like (BrO, $BrONO_2$, HOBr) to their uncertainty limits. The puzzling thing that remains is, that for mid and high-latitudes we have always perfect agreement between the model and the measurements for the same SZA range (occultation measurements). With recent balloon observations during sunrise and sunset performed in June, 2008 at the same tropical location (Teresina), we will try to resolve this issue in a follow-up investigation, including observations of relevant trace gases from other balloon payloads.

Page 13004, lines 24-25: I think the authors should give more details on what is a calibration scale for the SGs and why this scale depends on the laboratory (see also the general comment). This could help the reader.

It is hard to give absolute numbers here. Laube et al. (2008) state that: 'their observations and calculations are mainly based on the NOAA calibration scale and that, e.g., the other large global monitoring network AGAGE found 0.72 ppt higher bromine from H1211 and H1301 in 2004, probably reflecting differences in absolute calibration scales.'
Different inter-calibration studies are currently ongoing and have to be done for all species, to resolve this issue, especially for the VSLS.
The word 'absolute' has been added on page 13004, line 25 - '...the SG absolute calibration scales...'

Page 13004, lines 26-28: The discrepancy between Bry-in and Bry-org could be at- tributed to a contribution of VSLS changing with time and location. A way to verify this possibility is to perform trajectory calculations in order to determine if the air masses probed by the balloons on 8 June and 17 June 2005 were above area

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with potentially different VSLS sources on the ground (e.g., the Atlantic Ocean). A contribution of VSLS changing with time (and location) is in contradiction with the assumption made to calculate the potential maximum PG injection (page 13005, lines 20-27). Could the authors clarify this?

On page 13005, line 22, we write that 'we can calculate a potential maximum PG injection for a locally balanced bromine-budget'. We know that the real world very likely looks different and shows high variability, but this is the best we can currently do. That is the motivation for asking for more comprehensive studies in the future, which include dynamical analysis of the transport of air masses, as well as SG and PG measurements, from the ground to the lower stratosphere (page 13005, lines 25 to 27.

Technical comments:

Page 13003, line 1: a blank is missing between 8217;BrO8217; and 8217;indicates8217;.

done

Page 13007, line 16: 8217;Boesch, H., ... 8217; instead of 8217;Boesch H, ...8217;.

done

Page 13007, line 17: 8217;Pepin, I., Pukite ...8217; instead of 8217;Pepin, I. Pukite ...8217;.

done

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Page 13009, lines 6-11: The title of the Laube et al. reference is not correct. According to the ACPD web site, the right one is 8217;Contribution of very short-lived organic sub- stances to stratospheric chlorine and bromine in the tropics : a case study8217;. The list of authors is also not correct: Dorf and Pfeilsticker should be removed and K. Grunow added.

done

Page 13009, line 24: 8217;Sturges, W. T8217;: a dot is missing after the T.

done

Page 13010, line 13: 8217;tropospheric8217; instead of 8217;trophospheric8217;.

done

Page 13010, line 24: 8217;Wamsley, P. R., Elkins, J. W., Fahey, D. W., ...8217; instead of 8217;Wamsley, P. R. and Elkins, J. W. and Fahey, D. W., ...8217;.

done

Interactive comment on Atmos. Chem. Phys. Discuss., 8, 12999, 2008.