



Long-term observations of stratospheric bromine reveal slow down in growth

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[1] The total stratospheric inorganic bromine burden (Br_y) was derived from balloon-borne bromine monoxide (BrO) observations performed with the LPMA/DOAS (Limb Profile Monitor of the Atmosphere/Differential Optical Absorption Spectroscopy) balloon payload in the last ten years. The measurements show that significantly more ozone-depleting bromine ($(4.1[\text{or } 4.3] \pm 2.5)$ ppt) reaches the stratosphere than the atmospheric transport of the major stratospheric bromine source gases, methyl bromide (CH_3Br) and all halons can account for. The major contributors to this discrepancy are varying amounts of bromine tied in inorganic gases, particulate matter and very short-lived substances (VSLs) of natural origin. Despite the significant contribution of stratospheric bromine from natural processes, international protocols introduced to limit the production of brominated gases have been effective by slowing down the overall growth of Br_y .

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1. Introduction

[2] Although bromine is much less abundant than chlorine in the atmosphere, it is known to deplete stratospheric ozone 45 to 69 times more efficiently on a per atom basis [Sinnhuber *et al.*, 2006]. Reactions involving bromine contribute about half of the seasonal polar ozone loss and about 45% of the long-term column loss at northern mid-latitudes [Sinnhuber *et al.*, 2006], with chlorine species being largely responsible for the remainder. The stratospheric budget of chlorine is well understood and, thanks to controls carried out for the long-lived source gases, we have confidence in future predictions of a decreasing stratospheric abundance. In contrast, there is currently great uncertainty in the present stratospheric bromine budget, how it has evolved over the past decade and how it will change in the future. In particular, there is great uncertainty on how naturally released organic species, their inorganic product

gases (PG) and bromine tied to aerosols, contribute to total stratospheric inorganic bromine burden (Br_y). These uncertainties limit our ability to understand past changes in stratospheric ozone and to predict its future evolution [Sinnhuber *et al.*, 2006; Salawitch *et al.*, 2005; Salawitch, 2006].

[3] From analyses of whole air samples of organic bromine compounds taken at the surface and in the upper troposphere and lowermost stratosphere, past studies indicate the following stratospheric sources of Br_y [Wamsley *et al.*, 1998; Pfeilsticker *et al.*, 2000; Montzka *et al.*, 2003; Butler *et al.*, 2006]:

[4] 1. Natural and man-made methyl bromide (CH_3Br), which has a sufficiently long lifetime (~ 0.7 yrs) so that a major fraction reaches the stratosphere [Montzka *et al.*, 2003; Saltzman *et al.*, 2004].

[5] 2. The man-made halons CBrClF_2 (H-1211), CBrF_3 (H-1301), $\text{CBrF}_2\text{CBrF}_2$ (H-2402) and CBr_2F_2 (H-1202), for which the industrial production started in the late 1950s. As a consequence of their continued use and long atmospheric lifetimes, their atmospheric mixing ratios have steadily been increasing [Montzka *et al.*, 2003] (see also auxiliary material¹).

[6] 3. A variety of very short-lived substances (VSLs), such as CHBr_3 , CH_2Br_2 , CH_2ClBr , $\text{C}_2\text{H}_5\text{Br}$, CHBrCl_2 and CHBr_2Cl , which are mostly of oceanic (i.e. natural) origin. In atmospheric air sampled close to biologically productive ocean waters, these species are found to reach some 10 ppt. Due to their short atmospheric lifetimes (< 0.5 yrs) and variable atmospheric transport, their contribution to stratospheric Br_y , and thus relevance for stratospheric ozone is still poorly understood [Sinnhuber *et al.*, 2006; Salawitch, 2006; Wamsley *et al.*, 1998; Pfeilsticker *et al.*, 2000; Butler *et al.*, 2006; Chuck *et al.*, 2005].

[7] In this paper we present estimates of stratospheric Br_y based on balloon-borne observations of BrO in the middle stratosphere over the past decade. We combine these results with surface trend data of the major stratospheric bromine source gases; methyl bromide (CH_3Br) and halons. By comparing the observed source gas changes in the lower atmosphere with Br_y , we determine the net contribution to Br_y from other short-lived species ($\text{Br}_y^{\text{VSLs}}$) and assess the trends in all bromine sources for the past decade. Figure 1 updates the observations of CH_3Br (1) and halons (2) through 2005. At the surface, the globally averaged mixing ratio of CH_3Br increased from pre-industrial levels of about (5.8 ± 0.3) ppt to a peak value of ~ 9.8 ppt in 1998. Owing to international regulations on its use as a fumigant values have been

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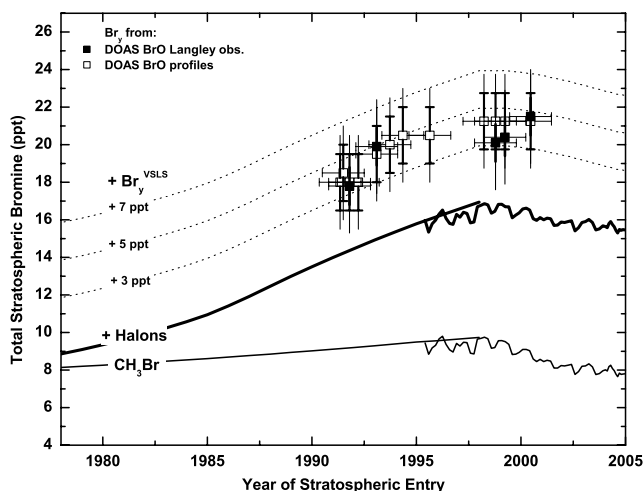


Figure 1. Measured trends for bromine (ppt) in the near-surface troposphere (lines) and stratosphere (squares). Global tropospheric bromine from methyl bromide as measured in ambient air and firn air (thin solid line - no correction has been made for tropospheric loss of CH_3Br) Butler *et al.* [1999] till 1998 and Montzka *et al.* [2003] past 1995; global tropospheric bromine from the sum of methyl bromide plus halons as measured in ambient air, archived air and firn air (thick solid line) Butler *et al.* [1999] and Fraser *et al.* [1999] till 1998 and Montzka *et al.* [2003] past 1995; and, bromine from CH_3Br and halons plus bromine from VLSL organic bromine compounds near the tropopause or transport of bromine bearing inorganic gases or bromine containing aerosols [Murphy and Thompson, 2000] across the tropopause ($\text{Br}_y^{\text{VLSL}}$) [Salawitch *et al.*, 2005; Pfeilsticker *et al.*, 2000], assuming total contributions of 3, 5, or 7 ppt of these species to Br_y (thin dotted lines). Total inorganic bromine derived from stratospheric measurements of BrO and photochemical modeling that accounts for BrO/ Br_y partitioning from slopes of Langley BrO observations above balloon float altitude (filled squares) and lowermost stratospheric BrO measurements (open squares). Bold/faint error bars correspond to the precision/accuracy of the estimates, respectively. The years indicated on the abscissa are sampling times for tropospheric data. For stratospheric data, the date corresponds to the time when the air was last in the troposphere, i.e. sampling date minus estimated mean time in stratosphere. Preindustrial levels of CH_3Br were (5.8 ± 0.3) ppt [Saltzman *et al.*, 2004] in the southern hemisphere and 0 ppt for the halons [Reeves *et al.*, 2005].

decreasing since then, reaching ~ 7.8 ppt by late 2004. For the halons major contributions to stratospheric Br_y are H-1211 (presently ~ 4.2 ppt) and H-1301 (presently ~ 2.6 ppt) as measured in regularly collected flask samples (update of Montzka *et al.* [2003]). Since H-2402 has been measured only periodically in these samples, a constant 0.95 ppt of Br from H-2402 has been added from 1995 to 2005 based upon results of Fraser *et al.* [1999], Montzka *et al.* [2003] and trends projected in World Meteorological Organization [2003]. Neglecting H-1202, the total contribution of the halons to Br_y reached about 7.75 ppt by late 2004.

[8] The contribution of VLSL (3) to Br_y has not been well established. Furthermore, bromine that originates from

sea-salt aerosols and from the destruction of the bromo-organics in the troposphere may also reach the stratosphere [Salawitch *et al.*, 2005; Fitzenberger *et al.*, 2000]. Quantification of the contribution of all VLSL species to stratospheric Br_y in a ‘bottom up’ approach remains difficult, mainly because of variable surface emissions, uncertainties of the atmospheric lifetime and transport timescales of the brominated species to the stratospheric entry level, i.e. the tropical and subtropical upper troposphere and lowermost stratosphere (15 to 20 km).

2. Methodology

[9] An alternative ‘top down’ approach is used here to derive total stratospheric Br_y and its trend during the last 10 years (Figure 1 and auxiliary material). This method monitors bromine monoxide (BrO), which is the major daytime stratospheric bromine species, using high precision balloon-borne UV/visible solar occultation spectroscopy. The spectra are collected on-board the azimuth-controlled LPMA/DOAS (Limb Profile Monitor of the Atmosphere/Differential Optical Absorption Spectroscopy) balloon payload. The BrO retrieval is performed by the DOAS method [Platt and Stutz, 2006] in the wavelength range from 346 nm to 360 nm as recommended by Aliwell *et al.* [2002] and discussed in detail by Ferlemann *et al.* [1998, 2000], Harder *et al.* [1998, 2000] and Dorf *et al.* [2006]. Measurements are performed in the low and mid-stratosphere, where all bromine from the organic source gases (1–3), their product gases and aerosols, is released into inorganic bromine. The method applies a photochemical correction for the actual BrO/ Br_y ratio using results from the 3-D off-line CTM SLIMCAT [Chipperfield, 1999], which comprises a detailed treatment of stratospheric photochemistry (see auxiliary material). Output was saved at 00:00 UT every 2 days, interpolated to the location of the balloon flights. A 1-D column model was then used to reconstruct the diurnal cycle for comparison with the observations. The SLIMCAT and 1-D model version are the same as in Dorf *et al.* [2006]. Two methods are used to determine total stratospheric Br_y ; the profile inversion and the Langley plot (see auxiliary material for details). 1. The profile inversion compares measured and photochemically modeled BrO slant column densities (BrO-SCDs) directly [e.g., Harder *et al.*, 2000] and includes an optimal estimation profile inversion technique [Rodgers, 2000]. Throughout the study, the total measurement error is propagated through the profile inversion algorithm and the BrO absorption cross section error is subsequently added by Gaussian error propagation. For 12 balloon flights performed since 1996, which covered a wide range of geophysical conditions, reasonably good agreement of the observed and modeled profiles is found [see Harder *et al.*, 2000; Dorf *et al.*, 2006]. 2. The Langley method is used to infer BrO mixing ratios above balloon float altitude. The method relies on the measurements of the BrO absorption as a function of total air mass (Air-SCD) at balloon float altitude (29 to 33 km). Details on the method and an error estimate are described by Dorf *et al.* [2006] and Ferlemann *et al.* [1998]. In practice, the method is found to work well for 5 out of the 13 balloon flights performed to date. The results are presented in Table 1. Stratospheric Br_y is calculated from inferred BrO mixing ratios and modeled

Table 1. Contribution of VLSL to Stratospheric Br_y Derived From DOAS BrO^a

	Leon 1996	Kiruna 1999	Aire sur l'Adour 2003	Kiruna 2004	Teresina 2005
Br _y from BrO, ppt	17.8	19.9	20.1	20.4	21.5
Age, years	5	6	5	5	5
CH ₃ Br, ppt	9.2	9.3	9.6	9.5	8.8
Halons, ppt	5.2	5.8	7.2	7.2	7.5
Br _y ^{VLSL} , ppt	3.4	4.7	3.3	3.7	5.2

^aThe 1- σ precision of Br_y estimated using the Langley method is on average 0.7 ppt. The total error is 2.5 ppt, which represents the precision as well as uncertainties in the BrO cross section ($\pm 8\%$) and the photochemical correction used to convert BrO to Br_y ($\pm 8\%$). Estimates of the bromine content of CH₃Br and halons are obtained from *Montzka et al.* [2003], assuming no tropospheric loss of CH₃Br.

BrO/Br_y partitioning weighted with the relative BrO concentration in each atmospheric layer. In fact, the photochemical modeling indicates that the BrO abundance above 30 km during daytime is largely dominated (>90%) by the photolysis of BrO and the reaction of Br with O₃.

[10] Consequently, uncertainties in the Br_y assessment can come from errors in the BrO measurement itself with the largest contribution coming from the uncertainty in the BrO absorption cross section (8%). Other errors include the UV-A actinic fluxes, estimated to be 4% [*Bösch et al.*, 2001], the measured ozone concentration, estimated to be 2%, and the reaction rate coefficient for reaction of Br with O₃, estimated to be 6% at 273 K (JPL-2002). Gaussian addition of all error sources then results in a Br_y error of 2.5 ppt (12%).

[11] Furthermore, the air mass age is determined by tracer measurements of N₂O and by using the correlation between N₂O and mean age as given by *Engel et al.* [2002]. N₂O is measured simultaneously using the LPMA FT-IR spectrometer for direct sun observation during balloon ascent of the LPMA/DOAS payload (see also auxiliary material). The profile retrieval from the LPMA spectra is performed using a least squares fitting method that generates N₂O vertical mixing ratio profiles [e.g., *Payan et al.*, 1998]. In this study the N₂O air mass age is used to determine the year of stratospheric entry of a probed air mass as indicated in Figure 1. The accuracy of 10% of the LPMA measurements and the correlation between N₂O and mean age result in a ± 1 year uncertainty for the age of air.

3. Results and Discussion

[12] Figure 1 compares the tropospheric trends of the organic bromine compounds, CH₃Br and halons, with the total stratospheric inorganic bromine derived from DOAS observations (see caption for details). The following is found:

[13] First, from the early 1990s until the early 2000s, stratospheric Br_y increased from about (17.8 ± 2.5) ppt to (21.5 ± 2.5) ppt, but in recent years this increase appears to be slowing, consistent with restrictions on the use of CH₃Br as a fumigant. Although these restrictions also apply to halons, atmospheric mixing ratios of the man-made and longer-lived halon gases (primarily H-1211 and H-1301) continue to increase slowly in the background atmosphere.

[14] Second, in order to explain the difference between the sum of CH₃Br plus halons and our estimated stratospheric Br_y, brominated VLSL, PGs and possibly bromine tied to aerosols must also contribute. Our measurements indicate that these bromine-bearing species contribute

$(4.1[4.3] \pm 2.5)$ ppt (or presently around 20%), derived from the Langley method [profile inversion], to stratospheric Br_y on a global average, assuming that CH₃Br mixing ratios at stratospheric entry level are close to surface levels. This is supported by whole air measurements which show only small vertical gradients of CH₃Br across the troposphere. Our estimate for additional stratospheric bromine sources is in good agreement with other studies [*Pfeilsticker et al.*, 2000; *Sinnhuber et al.*, 2002; *Schofield et al.*, 2004; *Sinnhuber et al.*, 2005] and puts further constraints on the value of Br_y^{VLSL}. Much larger vertical gradients are found for the brominated VLSL (primarily CH₂Br₂ and CHBr₃) with small (i.e., sub ppt) but quantifiable amounts occurring at stratospheric entry level, thus suggesting efficient destruction of the VLSL and concurrent release of Br atoms in the troposphere [*Wamsley et al.*, 1998; *Pfeilsticker et al.*, 2000]. Furthermore, particle analysis has indicated some bromine tied to aerosols, but in amounts yet to be quantified [*Murphy and Thompson*, 2000]. The balloon soundings presented here reveal BrO mixing ratios typically in the range of 0 to 2 ppt at the tropopause, with a rapid increase above, which can only be explained by the fast release of additional bromine from short-lived bromine sources (see auxiliary material Figure S2).

4. Conclusion and Summary

[15] Arguably, the amount to which brominated VLSL, PGs and aerosols contribute to stratospheric Br_y may vary according to location and season. Relevant factors are the emission strength, location, lifetime of the individual VLSL, efficiency of atmospheric transport and potential losses of inorganic bromine on the way to the stratosphere [*Butler et al.*, 2006]. Our mid-stratospheric BrO measurements reveal the effective contribution of the brominated species (1–3) to Br_y. They also indicate that the contribution of the additional bromine has no strong latitudinal gradient and has not changed significantly during the last 10 years (see Table 1). Thus, our measurements show that stratospheric Br_y closely follows the tropospheric change that results primarily from changes in anthropogenic emissions of CH₃Br and the halons with an offset due to naturally released CH₃Br, the VLSL and bromine tied in aerosols and inorganic gases. Reasonably assuming that the latter contribution $((4.1[4.3] \pm 2.5)$ ppt) has not changed since pre-industrial times and adding CH₃Br found in pre-industrial air of polar ice $((5.8 \pm 0.3)$ ppt) [*Saltzman et al.*, 2004], the measurements reveal a natural Br_y burden of (9.9 ± 2.5) ppt for the pre-industrial stratosphere. Accordingly, the anthropogenic emissions of CH₃Br and the halons contributed (11.6 ± 2.5) ppt to Br_y in

5-year-old air analysed in the mid-stratosphere in 2005 (see Table 1). Our study also reveals that the increase in Br_y is slowing down, indicating that international restrictions on the use of the ozone-depleting brominated substances are now reaching the stratosphere. However, the threat of thinning the stratospheric ozone layer by bromine may not be over, since in a warmer climate the oceanic emission of VSLS will possibly become accelerated [e.g., Quack et al., 2004; Salawitch, 2006]. A sea-surface temperature increase [e.g., Levitus et al., 2005] and a concurrent increase of this additional source of Br_y is an important new aspect of atmospheric bromine, since it potentially links climate change occurring at the surface with the abundance of stratospheric ozone.

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