

One-decade trend analysis of stratospheric BrO over Harestua (60° N) and Lauder (45° S) reveals a decline

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A trend analysis is performed of stratospheric BrO from ground-based UV-visible observations at Harestua (60° N, 11° E) and Lauder (45° S, 170° E) from 1995 through 2005. At both stations, a positive trend of about +2.5% per year is found for the 1995-2001 period, while a negative trend of about -1% per year is obtained between 2001 and 2005. Given a mean age of air of about 4 ± 1 years, the decline in stratospheric bromine since 2002 follows the decline of tropospheric organic bromine observed since the second half of 1998, as a result of the Montreal Protocol. These findings confirm that the impact of the Montreal Protocol restrictions on brominated substances have now reached the stratosphere. From our study, we have also derived a contribution of 6 ± 4 ppt of the brominated very short-lived substances and inorganic bromine tropospheric sources to the total bromine loading.

1. Introduction

Atmospheric bromine together with chlorine are known to be largely responsible for the depletion of stratospheric ozone. Although present in much smaller quantities than chlorine, stratospheric bromine significantly contributes to the global ozone loss (currently by about 25%), owing to its much higher ozone depletion potential relative to chlorine [e.g., *WMO*, 2007]. The main sources of bromine in the stratosphere are long-lived and very short-lived brominated organic compounds. Long-lived source gases can be of natural origin like methyl bromide (CH_3Br) or being man-made like CH_3Br again and halons. The delivery of inorganic bromine (Br_y) to the stratosphere by the long-lived sources has been estimated at ~ 17 pptv in 1998, with contributions from CH_3Br and halons of ~ 9.8 and ~ 7.0 pptv, respectively [*Dorf et al.*, 2006; *WMO*, 2007]. Long-term observations of CH_3Br at the surface have shown that this substance, after peaking in 1998, has declined by 1.3 pptv (14%) by mid-2004, as a result of the Montreal Protocol On Substances that Deplete the Ozone Layer [*Yokouchi et al.*, 2002; *Montzka et al.*, 2003; *Simmonds et al.*, 2004; *WMO*, 2007]. In case of the halons, they are still increasing, but at a slower rate [*WMO*, 2007]. Taken together, this has led to a decline in total organic bromine from long-lived species by 0.6 to 0.9 pptv (3 to 5%) during the 1998-2004 period [*WMO*, 2007]. In comparison, the very short-lived substances (VSLS) have mainly a natural (oceanic) origin. Their contribution to the total stratospheric bromine budget is smaller than that from long-lived source gases and is still subject to speculations (estimates range from 3 to 8 pptv [e.g., *Pfeilsticker et al.*, 2000; *Salawitch et al.*, 2005; *Sinnhuber et al.*, 2005; *Dorf*

et al., 2006; *Sioris et al.*, 2006; *Hendrick et al.*, 2007; *WMO*, 2007]. The exact role of the VSLs in ozone depletion is also not fully understood.

In the present paper, we report on the results of a trend analysis of long-term ground-based UV-visible observations of stratospheric bromine monoxide (BrO) at two NDACC (Network for the Detection of Atmospheric Composition Change) stations: Harestua, Southern Norway (60° N, 11° E) and Lauder, New Zealand (45° S, 170° E). BrO is the most abundant inorganic bromine species during daytime (BrO/Br_y is ~ 0.6 with $\text{Br}_y = \text{Br} + \text{BrO} + \text{BrONO}_2 + \text{HBr} + \text{HOBr} + \text{BrCl}$) and is therefore representative of the total inorganic bromine loading Br_y .

2. Methods

2.1. Ground-based UV-visible observations

The trend study is performed on stratospheric BrO vertical column densities (VCDs) retrieved by applying a profiling technique to ground-based zenith-sky UV-visible observations at Harestua and Lauder. The profiling algorithm is based on the Optimal Estimation Method [*Rodgers*, 2000] and is described in detail in *Hendrick et al.* [2007]. It should be noted that the forward model includes a stacked box photochemical model in order to reproduce the strong diurnal variation of BrO. The photochemical model also allows to convert the retrieved profiles (and corresponding VCDs) to any solar zenith angle (SZA) within the retrieval procedure. The period covered by the ground-based observations is January 1995-October 2005. While the UV-visible spectrometer at Lauder has been operating continuously during this period, the Harestua dataset presents gaps before 1998 (between May 1995 and November 1995 and between March 1996 and December 1997).

Only 80° SZA afternoon BrO VCDs have been considered for this study. The reason is that morning measurements are systematically noisier, possibly due to instrumental instability at rising sun [Hendrick *et al.*, 2007]. A description of the instrumental set-up at Harestua and Lauder can be found in Hendrick *et al.* [2007] and Schofield *et al.* [2004], respectively. Measured zenith radiance spectra are analyzed using the DOAS (Differential Optical Absorption Spectroscopy) technique [Platt, 1994]. Similar DOAS settings are applied to both data sets. In brief, the spectral signatures of NO₂, O₃, O₄, OClO (Lauder does not fit OClO because there is no OClO at 45° S), and the Ring effect are taken into account. Retrievals of BrO at both stations rely in the same BrO cross sections [Wilmouth *et al.*, 1999]. The fitting windows are 345-359 nm and 342-357 nm for Harestua and Lauder, respectively. More details on the DOAS settings can be found in Theys *et al.* [2007] and Schofield *et al.* [2004]. The BrO differential slant column densities (DSCDs), which are the direct product of the DOAS analysis, are evaluated using daily reference spectra. The effective residual amount of BrO in the reference spectra is directly fitted by the profiling algorithm. The term 'effective' is used because the fitted quantity also includes the tropospheric contribution to the total BrO column [Hendrick *et al.*, 2004, 2007]. Therefore, the BrO DSCD provided to the profiling algorithm are only sensitive to the stratospheric BrO and this, combined with the use of a tropospheric BrO content close to zero in the a priori profiles, leads to retrieved vertical profiles representative of the stratosphere [Hendrick *et al.*, 2004], while the sensitivity to the troposphere is lost. It should be noted that performing the DOAS analysis with daily reference spectra allows

to minimize the impact of the possible long-term degradation of the instruments on the BrO DSCD time series, and therefore on the stratospheric BrO trend study.

2.2. Trend analysis

Stratospheric BrO shows a marked seasonality related to the NO₂ seasonal cycle, with a maximum in winter and a minimum in summer [e.g., *Sinnhuber et al.*, 2002]. Therefore, a model with a linear trend and seasonal components has to be used to fit the stratospheric BrO VCD time series. We have adopted a model described by polyharmonic functions of the form [*Bergamaschi et al.*, 2000]:

$$m(t) = A + B(t - t_0) + \sum_{n=1}^3 C_n \cos(n2\pi(t - t_0)) + \sum_{n=1}^3 D_n \sin(n2\pi(t - t_0)) \quad (1)$$

where $m(t)$ is the monthly BrO VCD at month t , t_0 is the first month of the period on which the trend model is applied (t and t_0 are expressed in fractional year), and A , B (linear trend), C_n , and D_n are the fit parameters.

The number of sine and cosine functions is optimized through minimization of fit residuals. Three sine and cosine functions were found to give the lowest fit residuals.

3. Results

Time series of monthly averaged stratospheric BrO VCDs at Harestua and Lauder are presented in Figure 1. At first glance, we see that BrO VCDs increase from 1995 to 2001, reach a maximum in 2001, and after that, decrease. The calculation of BrO VCD annual means also confirms this feature. Accordingly, the trend model has been applied

separately to the 1995-2001 and 2001-2005 periods. The values obtained for linear trend (parameter B) are summarized in Table 1. As can be seen, the trend values derived at both stations agree within their combined error bars: over Harestua, a positive trend of $+2.5 \pm 0.5\%/year$ and a negative trend of $-0.9 \pm 0.4\%/year$ are found for the 1995-2001 and 2001-2005 periods, respectively. These percentage values are calculated with respect to the start values in 1995 and 2001, respectively. Over Lauder, BrO increases by $+2.2 \pm 0.2\%/year$ from 1995 to 2001 and decreases by $-1.3 \pm 0.3\%/year$ from 2001 to 2005. It should be noted that sensitivity tests performed by adding cosine and sine functions with time dependent C_n and D_n fitting parameters to Equation 1 in order to take into account of a possibly non-constant stratospheric BrO interannual variability have shown no significant change (up to $0.2\%/year$) in the above trend values. The standard deviation σ_B of the trend is estimated as in *Weatherhead et al.* [1998] and *van der A et al.* [2006] using the standard deviation of the remainders (differences between the modeled and measured BrO VCD monthly means) and their autocorrelation coefficient:

$$\sigma_B = \frac{\sigma_N}{n^{3/2}} \sqrt{\frac{1+\phi}{1-\phi}} \quad (2)$$

where σ_N and ϕ are the standard deviation and the autocorrelation coefficient of the remainders, respectively, and n is the length of dataset in years.

The significance of a trend can be tested by computing the ratio between the trend and its standard deviation [*Santer et al.*, 2000; *van der A et al.*, 2006]:

$$t_B = |B/\sigma_B| \quad (3)$$

A commonly applied decision rule for trend detection is that a trend B is real with a 95% confidence level when $t_B > 2$ [Weatherhead *et al.*, 1998; van der A *et al.*, 2006]. t_B values are presented in Table 1. We see that at both stations, t_B is greater than 2 for both 1995-2001 and 2001-2005 periods. Therefore, the trend values can be considered as significant with a 95% confidence level.

4. Discussion

In order to check whether the observed trends in stratospheric bromine over Harestua and Lauder follow the trend in bromine long-lived source gases, we have compared the variation of stratospheric inorganic bromine burden Br_y derived from the retrieved BrO profiles to the variation in bromine long-lived source gases. As in Theys *et al.* [2007], the BrO to Br_y conversion is performed using the Br_y/BrO ratio calculated by the stacked box photochemical model PSCBOX included in the profiling algorithm and daily initialized with SLIMCAT 3D chemical transport model output [Chipperfield, 2006; Feng *et al.*, 2007]. In contrast to the estimations of Br_y made from balloon observations [Dorf *et al.*, 2006], the BrO volume mixing ratio (vmr) around 30 km (altitude where organic bromine species are not present anymore) cannot be used here because of the low sensitivity to BrO and low vertical resolution of the retrieved BrO profiles at this altitude [Hendrick *et al.*, 2007]. Therefore, the BrO vmr at the maximum of the sensitivity to BrO (around 21 km, see Hendrick *et al.* [2007]) has been used. At this altitude, bromine is mostly in its inorganic forms. However, a small correction to account for the partitioning between the organic and inorganic bromine species total contents is applied based on the SLIMCAT model. The uncertainty in the inferred Br_y depends mainly on the uncertainties in the

BrO measurement and on the modeled Br_y/BrO ratio. To a large extent, the uncertainty in the BrO measurement is dominated by the 10% uncertainty in the BrO cross sections. Sensitivity tests have been performed using the PSCBOX model to determine the main parameters affecting the Br_y/BrO ratio at 21 km of altitude. Using the JPL 2006 chemistry, these were found to be the termolecular reaction $\text{BrO} + \text{NO}_2 + \text{M}$ (the uncertainty in the reaction rate has an impact of 11% on BrO), the NO_2 concentration (impact of 5%), and the BrONO_2 photolysis (impact of 8%). When added in quadrature, this gives a total error on the inferred Br_y of 18%, which is similar to that of *Sioris et al.* [2006].

The comparison between the trends in stratospheric Br_y vmr annual means at Harestua and Lauder and bromine long-lived source gases is shown in Figure 2. Since the abscissa corresponds to the sampling time of tropospheric data, stratospheric data have been adjusted to the time when the measured air masses were last in the troposphere, i.e. the measurement date minus the mean age of air in the stratosphere. The mean age of stratospheric air over both stations is estimated using the correlation between the volume mixing ratio of the tracer N_2O and the mean age of air [*Engel et al.*, 2002]. The N_2O mixing ratio profiles for the 1995-2005 period are taken from the SLIMCAT model. In order to estimate a mean age of air representative of the effective altitude region probed by the ground-based UV-visible instrument at 21 km, the calculated mean age of air vertical profile in this altitude region has been weighted by the stratospheric BrO column averaging kernels. A mean age of air of 4.2 ± 1.0 years and 3.9 ± 1.0 years is found at 21 km at Harestua and Lauder, respectively. The uncertainty in the age of air is estimated using the variability of the SLIMCAT N_2O profiles and the uncertainty in the N_2O and

mean age of air correlation method. Figure 2 shows that, given the uncertainty in the mean age of air, the trends in stratospheric Br_y follow the change in bromine long-lived source gases. This is an indication that the decline of stratospheric bromine observed over both stations since the end of 2001 is largely related to the corresponding decline in the surface mixing ratio of CH_3Br observed since the second half of 1998, and resulting from the restrictions on the use of ozone-depleting brominated substances imposed by the Montreal Protocol [Montzka *et al.*, 2003; WMO, 2007].

Our estimates of the stratospheric Br_y are similar at both stations, with maximum values around 2001 of 23.9 ± 4.3 ppt at Harestua and 23.1 ± 4.2 ppt at Lauder. Figure 2 shows that a good agreement between stratospheric Br_y and bromine sources can only be obtained if an additional contribution from VSLs and inorganic tropospheric bromine sources of about 6 ± 4 ppt is assumed. This contribution is consistent with most published estimates [e.g., Pfeilsticker *et al.*, 2000; Salawitch *et al.*, 2005; Sinnhuber *et al.*, 2005; Dorf *et al.*, 2006; Sioris *et al.*, 2006; Hendrick *et al.*, 2007; WMO, 2007].

5. Conclusions

As already reported in Dorf *et al.* [2006], our findings further confirm that the impact of the Montreal Protocol restrictions on brominated substances have now reached the stratosphere. The total stratospheric inorganic bromine content inferred from BrO column measurements in both hemispheres since 1995 is found to have reached a maximum in 2001 and, since then, decreases at a rate of $-1\%/year$. This evolution closely matches the changes in source gas emissions measured at the surface, which strongly suggests that the observed stratospheric changes are largely driven by changes in tropospheric

sources. At this stage and given the large uncertainties on the potential feedback from climate change on the emissions of brominated source gases [e.g., *Salawitch*, 2006], one can only speculate about the definitive nature or not of the currently observed decline in stratospheric bromine. This calls for continued long-term monitoring of the atmospheric bromine content.

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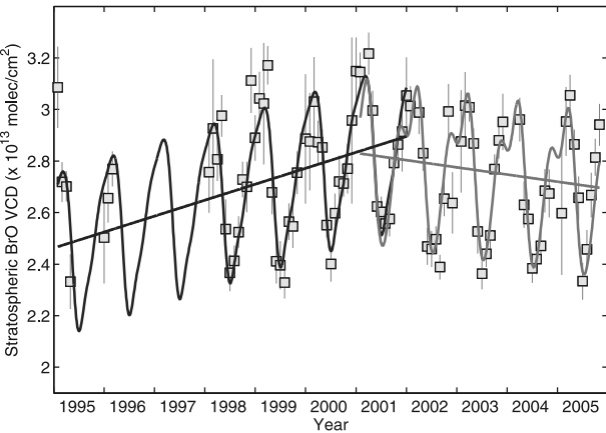
Figure 1. Times series of monthly averaged ground-based UV-visible BrO vertical column densities (VCDs) at Harestua (60°N, upper plot) and Lauder (45°S, lower plot). The grey error bars correspond to the standard error of the monthly mean. The black and grey thick solid lines represent the trend analyses (BrO VCDs modeled using Equation 1) for the 1995-2001 and 2001-2005 periods, respectively. The thick straight lines correspond to the linear trend for both periods.

Figure 2. Trends in stratospheric Br_y vmr annual means at Harestua and Lauder (filled and open squares, respectively) and bromine long-lived source gases ($\text{CH}_3\text{Br} + \text{halons}$; black solid lines). The smooth black solid line prior to 1995 is based on a combination of Antarctic firn air reconstructions and ambient air measurements from a number of studies, adjusted to represent mean global abundances, and updated here with mean ambient air measurements (non-smoothed black solid line post-1995) from NOAA global monitoring stations (adapted from *Dorf et al.* [2006]; see also *WMO* [2007]). The dashed line correspond to the sum of CH_3Br plus halons plus an assumed 6 ppt contribution from VSLs and inorganic tropospheric bromine sources (this curve has been constructed from Figure 1 of *Dorf et al.* [2006] assuming a contribution of 6 ppt from VSLs). The abscissa is the sampling time of tropospheric data. For stratospheric Br_y , the date corresponds to the time when the air entered into the stratosphere, i.e. the measurement date minus the mean age of air in the stratosphere. The vertical and horizontal error bars correspond to the uncertainties in the Br_y estimates and in the mean age of air, respectively.

Table 1. Results of BrO trend analyses in Harestua and Lauder. The trend values (B) and their standard deviation (σ_B) appear in 10^{12} molec/cm²/year (lines 1-2) and in %/year (lines 4-5). t_B (line 3) is the ratio between B and σ_B (see Equation 3).

	Harestua		Lauder	
	1995-2001	2001-2005	1995-2001	2001-2005
Trend B	+0.62	-0.27	+0.52	-0.36
σ_B	0.13	0.12	0.06	0.08
t_B	4.8	2.3	9.0	4.5
Trend B	+2.5	-0.9	+2.2	-1.3
σ_B	0.5	0.4	0.2	0.3

Harestua (60°N, 11°E)



Lauder (45°S, 170°E)

