

Bromoform as a source of stratospheric bromine

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Abstract. We have measured bromoform (CHBr_3) in the troposphere and lower stratosphere (sea level to 17 km) from balloons, aircraft and ground stations. The concentrations ranged from 2 to 20 ppt at sea level, and 0.1 to 1 ppt in the upper troposphere. Above the tropopause the concentrations declined sharply to less than 0.01 ppt above 14 km. CHBr_3 accounted for 3% of total measured organic bromine (Br_o) at the extratropical tropopause, and appeared to potentially contribute at least 9% of reactive bromine (Br_y) in stratospheric air of mean age less than 1 year. Inclusion of dibromomethane and the mixed bromochloromethanes increased these figures to about 10% of Br_o and 20% of Br_y , respectively. Observations of CHBr_3 in both Arctic and mid-latitude stratospheric air, and in air masses with mean ages of more than 1.5 years, suggests that the CHBr_3 in these locations originates predominantly from extratropical stratosphere-troposphere exchange.

Introduction

Reactive bromine (Br_y) is an important contributor to stratospheric ozone destruction [Ravishankara *et al.*, 1999]. Conventionally it has been considered that the halons and methyl bromide (CH_3Br) are the sole carriers of bromine to the stratosphere, although more recently the contributions from CH_2Br_2 and CH_2BrCl have been included in calculations of Br_y [Wamsley *et al.*, 1998]. There is, however, evidence of a possible discrepancy between Br_y estimated from individual halocarbons (the 'organic' method) and that modelled from measurements of BrO (the 'inorganic' method). Wamsley *et al.* [1998], for instance, estimated Br_y at 20–25 km (mean age of air of 5–6 yr from SF_6) in the 1994 Northern Hemispheric (NH) stratosphere to be 16 ± 2 ppt from the organic method. Using the inorganic method, taking BrO measurements made in the same year, they derived a mean Br_y in the oldest air parcels of 20 ppt; albeit with large error limits (+11, -9.8 ppt). More closely-constrained values of Br_y from BrO have subsequently been reported of 20 ± 2.5 ppt for the 1996/97 stratosphere [Harder *et al.*, 2000], with indications of lower values in the upper stratosphere (i.e. older air).

Ko *et al.* [1997] suggested that additional bromine in inorganic form might enter the stratosphere which would be 'missed' by the organic bromine method. Wamsley *et al.* [1998] pointed out that reactive organobromines not included in their scheme might also

contribute, and noted that bromoform (CHBr_3) was a potential candidate. Dvortsov *et al.* [1999] modelled the potential impact of CHBr_3 and concluded that as much as 2 ppt of stratospheric Br_y might originate from this source, partly from decomposition of CHBr_3 in the upper troposphere, and partly from injection of CHBr_3 itself in to the stratosphere.

CHBr_3 is the second most abundant 'reactive' organobromine gas (i.e. one with a tropospheric sink) in the background troposphere. CH_3Br is more abundant but has a longer lifetime ($\tau_{\text{atmos}} = 1.7$ yr, predominantly from reaction with OH [Kurylo *et al.*, 1999]) than CHBr_3 ($\tau_{\text{OH}} = 100$ days at 275 K, and $\tau_{\text{hm}} = 36$ days for globally and seasonally averaged J-values at 5 km [Kurylo *et al.*, 1999]). ClIBr_3 also carries three bromine atoms, and is therefore a potentially significant contributor to reactive bromine in the upper troposphere/lower stratosphere region. CHBr_3 is almost entirely of natural, biogenic origin. The dominant sources appear to be macrophytes and marine microalgae [Gschwend *et al.*, 1985; Sturges *et al.*, 1992]. There is also a small anthropogenic contribution from water chlorination [Gschwend *et al.*, 1985].

Here we present observations of CHBr_3 profiles in both the troposphere and stratosphere that clearly demonstrate penetration of CHBr_3 in to the stratosphere, in spite of its short tropospheric lifetime.

Measurements

Whole air samples were collected from the stratosphere using a balloon-borne cryosampler [Engel *et al.*, 1997] during flights from Aire sur l'Adour (ASLA), Southern France and Kiruna, Northern Sweden. Tropospheric whole air samples were collected from the UK Met Office C-130 Hercules during the 'ACSOE Azores' missions over the subtropical North Atlantic west of the Azores. Passivated stainless steel flasks were pressurised using metal bellows pumps. Further pumped whole air samples were collected using the 'CARIBIC' automated atmospheric research package [Brenninkmeijer *et al.*, 1999] on board a Boeing 767 ER operated between Germany and the Maldives (48°N and 5°N respectively) at a cruising altitude of approximately 10 km. In situ measurements were made at the Mace Head Atmospheric Research Station, Galway on the west coast of Ireland over a three week period in May 1997, comprising consecutive 45 min integrated concentrations.

The whole air samples from the balloon flights and the CARIBIC package were analysed with a gas chromatograph – tri-sector mass spectrometer combination (Micromass VG Autospec GC-MS) operating in single ion mode, with a DB5 or DB-VRX capillary column for chromatographic separation. Three high-pressure air standards in passivated aluminium tanks, all collected at Niwot Ridge, Colorado (3200 m), were also analysed in the same way. The in-situ measurements at Mace Head and the

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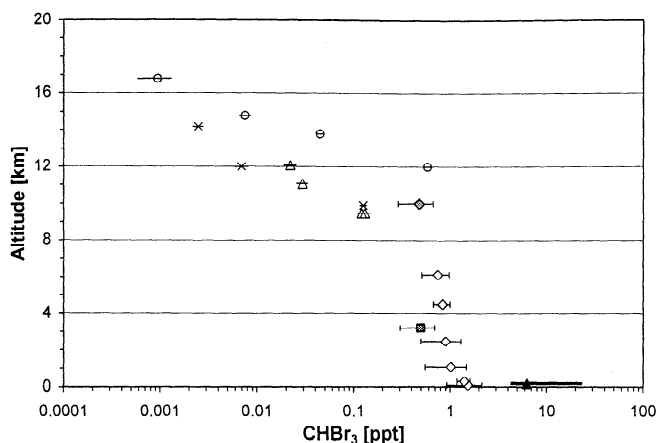


Figure 1. Summary of CHBr_3 measurements from balloons (open circles = ASLA, October 1994; crosses = Kiruna, February 1997; open triangles = Kiruna, February 1999), aircraft (shaded diamond = CARIBIC flights, March – August 1998/99; open diamonds = AC SOE Azores campaign, September 1997), and ground stations (shaded square = Niwot Ridge, Colodaro; black triangle = Mace Head, Ireland, May 1997). The thick shaded bar represents a range of measured concentrations, the thin bars with end caps are 1-sigma standard deviations of the mean from several samples, and the thin uncapped bars are 1-sigma total propagated analytical precision values from replicate analyses of single samples.

whole air samples from the C-130 were analysed with a gas chromatograph – quadrupole mass spectrometer combination (Hewlett-Packard 6890-5973) operating in selective ion mode, and fitted with a DB-VRX column.

Experimental details including calibration procedures are given elsewhere (Fraser *et al.*, 1999; Carpenter *et al.*, 1999). The detection limit of the tri-sector GC-MS for CHBr_3 was <0.001 ppt in 500 ml of air. SF_6 was measured using the tri-sector GC-MS, and also by GC - electron capture detection (GC-ECD) for flights BI31 and BI34. SF_6 concentrations were normalised to the scale of Maiss and Levin [1994]. N_2O was measured by GC-ECD.

Results

Figure 1 shows the combined measurements of CHBr_3 in the troposphere and stratosphere. Note the use of a logarithmic scale due to the wide variation in measured concentrations. The highest values were found at the coastal site in close proximity to macrophyte beds, a supposed major source of atmospheric CHBr_3 . Lower values were found away from coastlines over the subtropical North Atlantic. The tropospheric profiles there (mean of four separate flights in September 1997, binned into six altitude levels from a total of 38 samples) showed generally declining concentrations with height, although with a high level of variability. This profile is similar to that reported from the tropical Pacific (NASA 1996 PEM Tropics Campaign [Schauffler *et al.*, 1999]), which showed values declining from approximately 1.5 ppt at the surface to about 0.5 ppt at 7 km, and about 0.3 ppt at 11 km. We measured a mean of 1.4 ppt near the ocean surface, declining to 0.7 ppt at 6 km. Also shown in Figure 1 is the mean of three samples from the Colorado Mountains. These samples contained similar levels of bromoform as in the Azores profiles, despite the greater distance from marine sources at this location.

The mean CHBr_3 concentration from three flights of the CARIBIC sampler (June and August 1998 and March 1999) in the upper troposphere/tropopause region was 0.5 ± 0.2 ppt (33 samples), with a tendency to higher values nearer the tropics. These values can be compared with the NASA 1996 STRAT campaign [Schauffler *et al.*, 1998; Schauffler *et al.*, 1999]. At northern mid-latitudes they report CHBr_3 at the tropopause ranging from below their detection limit (~ 0.05 ppt) to a maximum of ~ 0.7 ppt. They found concentrations to generally be higher in winter than in summer, which may reflect differences in convective activity or a longer photolytic lifetime in winter. We did not, however, observe any significant differences between the spring and summer CARIBIC flights.

Measurements from the balloon flights shown in Figure 1 displayed rapidly declining concentrations with height. Since a height scale has been used there are evident differences in profiles between the wintertime Arctic flights and the autumn mid-latitude flight. The higher tropopause height of the latter is discerned by a CHBr_3 concentration at 12 km similar to that observed in upper tropospheric air, whereas in the former CHBr_3 levels were significantly lower even at 9–10 km. Samples were collected at altitudes of up to 32 km, but no CHBr_3 was detected above 17 km. The NASA STRAT campaigns [Schauffler *et al.*, 1998; Schauffler *et al.*, 1999] showed only occasional evidence of CHBr_3 (at their detection limit) at stratospheric altitudes up to 20 km, again with more occurrences of detectable values in winter, and more at mid-latitudes than in the tropics.

Other brominated species in addition to CHBr_3 were also measured in the stratosphere in this work, including CH_3Br , CH_2Br_2 , mixed bromochloromethanes, and four halon gases. These data have been binned according to N_2O concentration, and the means and standard deviations given in Table 1. For comparison the results for two other reactive gases, chloroform (CHCl_3) and methyl iodide (CH_3I), are also shown. The latter are both useful additional tracers of recent transport of tropospheric air in to the stratosphere. CH_3I is also of interest due to the high catalytic reactivity of iodine with ozone in the stratosphere [Solomon *et al.*, 1994]. No detectable levels of CH_2ClI or $\text{C}_2\text{H}_5\text{I}$ could be discerned in the stratospheric samples, although they were consistently observed at the surface [Carpenter *et al.*, 1999].

The mean age of air was determined from measured SF_6 values using the quadratic global mean surface SF_6 time series of Geller *et al.* [1997] corrected for non-linearity according to Volk *et al.* [1997]. Since SF_6 was referenced to surface concentrations, there is no implicit correction for any lag time between SF_6 mixing ratios at the surface and the tropical tropopause (such as estimated by Volk *et al.* [1997]). As a result, at and below the tropopause the influence of NH tropospheric air resulted in apparent negative mean ages. The mean ages are, therefore, all likely to be lower limits relative to the tropical tropopause.

Discussion

That CHBr_3 was detectable in air masses with mean ages of greater than 1.5 years is seemingly incompatible with its short photolytic lifetime. It is unlikely that it could have entered the stratosphere through tropical upwelling and survived transport to mid- or even Arctic latitudes. Reported measurements of CHBr_3 near the tropical tropopause [Schauffler *et al.*, 1998; Schauffler *et al.*, 1999] confirm that very little CHBr_3 reaches the stratosphere in this region, although Br₂ released by photolysis of CHBr_3 in

Table 1. Summary of mean age of air and concentrations of organobromines, chloroform, and methyl iodide binned into N₂O concentration ranges for flights BI27, BI31, and BI34. Figures in parentheses are 1-sigma standard deviations.

N ₂ O (ppb)	Mean age of air (yr)	CHBr ₃ (ppt)	CH ₃ Br (ppt)	CH ₂ BrCl (ppt)	CHBr ₂ Cl (ppt)	CHBrCl ₂ (ppt)	CH ₂ Br ₂ (ppt)	H1301 (ppt)	H1211 (ppt)
>310	-1.0 (0.7)	0.22 (0.25)	10.7 (1.9)	0.11 (0.11)	0.05 (0.06)	0.07 (0.13)	0.47 (0.45)	2.0 (0.1)	3.9 (0.2)
310-290	0.7 (0.6)	0.01 (0.01)	6.1 (2.9)	0.04 (0.02)	0.01 (0.01)	0.02 (0.02)	0.18 (0.12)	1.9 (0.1)	3.1 (0.0)
<290	1.5 (0.8)	0.01 (0.01)	6.3 (1.9)	0.02 (0.02)	0.01 (0.01)	0.01 (0.01)	0.09 (0.11)	1.6 (0.1)	2.0 (0.2)

N ₂ O (ppb)	H1202 (ppt)	H2402 (ppt)	CHCl ₃ (ppt)	CH ₃ I (ppt)	Total Br _o (ppt)	Halons (%)	CH ₃ Br (%)	CHBr ₃ (%)	Others (%)
>310	0.04 (0.01)	0.39 (0.06)	4.0 (2.5)	0.041 (0.069)	19.2	34	56	3	6
310-290	0.03 (0.01)	0.30 (0.02)	1.3 (0.5)	0.001 (0.003)	12.1	46	50	<1	4
<290	0.02 (0.00)	0.24 (0.02)	0.7 (0.1)	0.000 (-)	10.8	39	58	<1	2

the upper troposphere might do so. The CHBr₃ we observed in the NH stratosphere is more likely to have originated from NH extratropical stratosphere-troposphere exchange. The rapid reduction in concentration with height is then a result both of photolytic loss and of progressive dilution of recently-introduced tropospheric air with older stratospheric air. The importance of recent stratosphere-troposphere exchange is highlighted by the steep profiles seen at Arctic latitudes in winter. It is interesting to speculate on whether this CHBr₃ may even have partly originated from Arctic or sub-Arctic latitudes. Certainly the lack of photolysis in the Arctic winter would favour this, and Arctic tropospheric CHBr₃ concentrations are known to be much higher in the winter than in summer [Cicerone *et al.*, 1988].

The sum of available organic bromine (Br_o) from the measured source gases is shown in Table 1 referenced to 1994 (halon measurements were only used from the 1994 flight in this calculation due to their increasing emissions with time). At the tropopause Br_o amounted to 19 ppt. Of this total, CH₃Br was the largest single contributor at all altitudes. CHBr₃ contributed a mean of 3% in the tropopause region. CHBr₃ and the 'other' short lived organobromine gases together contributed 10% of Br_o in the same region. Between the tropopause and the next N₂O level, Br_o dropped by 7.1 ppt, equivalent to the production of about 6.5 ppt of Br_y after allowance for the halon time trend [Fraser *et al.*, 1999]. Of this, CH₃Br contributed 65% of the Br_y evolved, CHBr₃ 9%, CH₂Br₂ 8%, the halons 15%, and the other organobromines 3%.

The proportionate importance of the short-lived species may, in fact, have been underestimated if some of the Br_y generated from these compounds in the upper troposphere also enters the stratosphere. This is particularly true of CHBr₃ which has the highest tropospheric loss rate of all the organobromines reported here [Kurylo *et al.*, 1999]. The CHBr₃ levels observed in upper troposphere/tropopause altitudes from the balloon and aircraft flights might be considered more representative of stratospheric entry level concentrations (i.e. up to 0.8 ppt CHBr₃, or 2.4 ppt Br_y). In this case direct injection of CHBr₃ would account for more than 10% of present estimates of total stratospheric Br_y.

Similarly the low measured concentrations of stratospheric CH₃I do not rule out the possibility that higher levels of reactive iodine, possibly released from CH₃I in the upper troposphere, might be present in the stratosphere.

Conclusions

The low detection limits obtained with the tri-sector mass spectrometer are sufficient to convincingly measure CHBr₃ in the lower stratosphere. The bromine from this source will be converted to Br_y and will be available for ozone loss cycles involving BrO. Because of the short lifetime of CHBr₃ compared to other bromine source gases, such as the halons and methyl bromide, it will be proportionately most significant as a source of Br_y in the region close to the tropopause.

The observations of measurable CHBr₃ in the lower stratosphere at both mid- and Arctic latitudes suggests that extratropical tropopause exchange may be significant in determining local levels of Br_y in the upper troposphere/lower stratosphere region. Other short-lived species with ozone depleting potentials, such as CH₃I, may also be able to enter the stratosphere in this way. The short-lived species may, in turn, be useful indicators of localised stratosphere-troposphere exchange.

Finally we might speculate on the implications in a warming world. The contribution of CHBr₃ in particular may be subject to a range of feedback effects. Changes in production rates of the marine biogenic sources are to be expected, whilst tropospheric loss processes (photolysis, OH, and wet deposition of Br_y) are also likely to be affected.

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References

- Brenninkmeijer, C.A.M., *et al.*, CARIBIC - Civil aircraft for global measurement of trace gases and aerosols in the tropopause region, *J. Atmos. Ocean. Technol.*, 16, 1373-1383, 1999.
- Carpenter, L.J., W.T. Sturges, S.A. Penkett, P.S. Liss, B. Alicke, K. Hebestreit, and U. Platt, Observations of short-lived alkyl iodides and bromides at Mace Head, Ireland: links to biogenic sources and halogen oxide production, *J. Geophys. Res.*, 104, 1679-1689, 1999.
- Cicerone, R.J., L.E. Heidt, and W.H. Pollock, Measurements of atmospheric methyl bromide and bromoform, *J. Geophys. Res.*, 93, 3745-3749, 1988.

- Dvortsov, V.L., M.A. Geller, S. Solomon, S.M. Schauffler, E.L. Atlas, and D.R. Blake, Rethinking reactive halogen budgets in the mid-latitude lower stratosphere, *Geophys. Res. Lett.*, **26**, 1699-1702, 1999.
- Engel, A., U. Schmidt, and R.A. Stachnik, Partitioning between chlorine reservoir species deduced from observations in the arctic winter stratosphere, *J. Atmos. Chem.*, **27**, 107-126, 1997.
- Fraser, P.J., D.E. Oram, C.E. Reeves, and S.A. Penkett, Southern Hemispheric halon trends (1978-1998) and global halon emissions, *J. Geophys. Res.*, **104**, 15985-15999, 1999.
- Geller, L.S., J.W. Elkins, J.M. Lobert, A.D. Clarke, D.F. Hurst, J.H. Butler, and R.C. Myers, Tropospheric SF₆: Observed latitudinal distribution and trends, derived emissions and interhemispheric exchange time, *Geophys. Res. Lett.*, **24**, 675-678, 1997.
- Gschwend, P.M., J.K. MacFarlane, and K.A. Newman, Volatile halogenated organic compounds released to seawater from temperate marine macroalgae, *Science*, **227**, 1033-1035, 1985.
- Harder, H., H. Bosch, C. Camy-Peyret, M.P. Chipperfield, R. Fitzenberger, S. Payan, D. Perner, U. Platt, B.-M. Sinnhuber, and K. Pfeilsticker, Comparison of measured and modeled stratospheric BrO: Implications for the total amount of stratospheric bromine, *J. Geophys. Res.*, in press, 2000.
- Ko, M.K.W., N.D. Sze, C.J. Scott, and D.K. Weisenstein, On the relation between stratospheric chlorine/bromine loading and short-lived tropospheric source gases, *J. Geophys. Res.*, **102**, 25507-25517, 1997.
- Kurylo, M.J., J.M. Rodriguez, M.O. Andrea, E.L. Atlas, D.R. Blake, J.H. Butler, S. Lal, D.J. Lary, P.M. Midgley, S.A. Montzka, P.C. Novelli, C.E. Reeves, P.G. Simmonds, L.P. Steele, W.T. Sturges, R.F. Weiss, and Y. Yokouchi, Chapter 2: Short-lived ozone-related compounds, in *Scientific Assessment of Ozone Depletion, 1998*, edited by C.A. Ennis, pp. 2.1-2.56, World Meteorological Organization, Geneva, 1999.
- Maiss, M. and I. Levin, Global increase of SF₆ observed in the atmosphere, *Geophys. Res. Lett.*, **21**, 569-572, 1994.
- Ravishankara, A.R., T.G. Shepherd, M.P. Chipperfield, P.H. Haynes, S.R. Kawa, T. Peter, R.A. Plumb, R.W. Portmann, W.J. Randel, D.W. Waugh, and D.R. Worsnop, Chapter 7: Lower stratospheric processes, in *Scientific Assessment of Ozone Depletion: 1998*, edited by C.A. Ennis, pp. 7.1-7.76, World Meteorological Organisation, Geneva, 1999.
- Schauffler, S.M., E.L. Atlas, F. Flocke, R.A. Lueb, V. Stroud, and W. Travnicek, Measurements of bromine containing organic compounds at the tropical tropopause, *Geophys. Res. Lett.*, **25**, 317-320, 1998.
- Schauffler, S.M., E.L. Atlas, D.R. Blake, F. Flocke, R.A. Lueb, J.M. Lee-Taylor, V. Stroud, and W. Travnicek, Distributions of brominated organic compounds in the troposphere and lower stratosphere, *J. Geophys. Res.*, **104**, 21513-21535, 1999.
- Solomon, S., R.R. Garcia, and A.R. Ravishankara, On the role of iodine in ozone depletion, *J. Geophys. Res.*, **99**, 20491-20499, 1994.
- Sturges, W.T., G.F. Cota, and P.T. Buckley, Bromoform emission from Arctic ice algae, *Nature*, **358**, 660-662, 1992.
- Volk, C.M., J.W. Elkins, D.W. Fahey, G.S. Dutton, J.M. Gilligan, M. Loewenstein, J.R. Podolske, K.R. Chan, and M.R. Gunson, Evaluation of source gas lifetimes from stratospheric observations, *J. Geophys. Res.*, **102**, 25543-25564, 1997.
- Wamsley, P.R., et al., Distribution of halon-1211 in the upper troposphere and lower stratosphere and the 1994 total bromine budget, *J. Geophys. Res.*, **103**, 1513-1526, 1998.

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