

## Recent trends in atmospheric methyl bromide: analysis of post-Montreal Protocol variability

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**Abstract.** The atmospheric methyl bromide (CH<sub>3</sub>Br) burden has declined in recent years, in response to the phaseout of agricultural and structural fumigation consumption under the amendments to the Montreal Protocol. The timing and magnitude of this decrease represents an opportunity to examine our current understanding of atmospheric CH<sub>3</sub>Br and its budget, response to the phaseout, and response to interannual variability in biomass burning and global OH. In this study, simulations obtained from a time-dependent global model of atmospheric CH<sub>3</sub>Br emissions and uptake are compared to observations from the NOAA flask network. The model includes a detailed gridded ocean model coupled to a time-dependant atmospheric 2-box model. The phaseout of CH<sub>3</sub>Br production for agricultural uses began in 1998, concurrent with the pulse in biomass burning associated with the 1998 El Niño. The combined effects of three factors (biomass burning, global OH, and anthropogenic phaseout) appear to explain most of the observed atmospheric methyl bromide variability over the 1997–2008 period. The global budget remains imbalanced, with a large missing source indicated. The missing source does not exhibit a systematic decline during the phaseout period, and therefore, is not the result of significantly underestimating non-QPS agricultural CH<sub>3</sub>Br emissions. The model results suggest that the oceans should be less undersaturated than before the phaseout began.

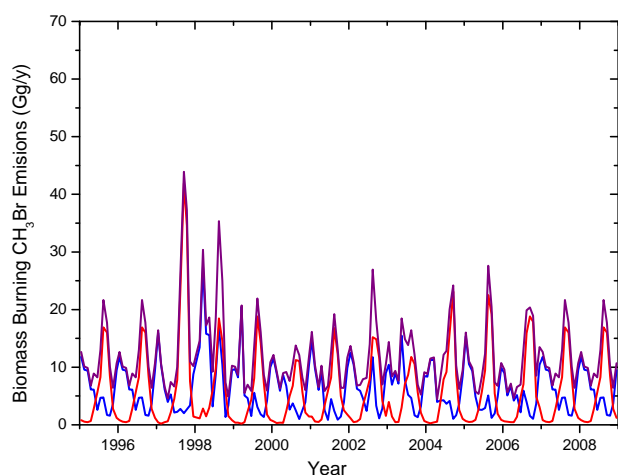
### 1 Introduction

CH<sub>3</sub>Br is a stratospheric ozone depleting substance that, unlike many other ozone-depleting compounds, has both natural and anthropogenic sources. The use of CH<sub>3</sub>Br as an agricultural fumigant has been reduced according to the amendments to the Montreal Protocol (UNEP, 1995), and phaseout began in 1998. Although many sources and sinks of CH<sub>3</sub>Br have been identified and quantified, the global budget of atmospheric CH<sub>3</sub>Br for the pre-phaseout atmosphere is not balanced (Montzka and Fraser et al., 2003). The best estimate of the annual global budget for 1996 had an imbalance of nearly 37 Gg between sources and sinks (Table 1). This imbalance is clearly a result of our incomplete knowledge, rather than a real difference between sources and sinks, because the atmosphere was not rapidly changing at that time (Yokouchi et al, 2002; Montzka et al., 2003). The imbalance may reflect uncertainty in both natural and anthropogenic components of the budget. Knowledge of the emissions from terrestrial plants and ecosystems is quite limited (Montzka and Fraser et al., 2003; Gan et al., 1998; Dimmer et al., 2001; Redecker et al., 2000; Rhew et al., 2001; Varner et al., 1999). Even the anthropogenic emissions of CH<sub>3</sub>Br from agricultural fumigation are not easily quantified, since soil uptake during fumigation can be significant, and may vary with soil conditions and application technique (MBTOC, 2006).

The decline in atmospheric CH<sub>3</sub>Br burden resulting from the phaseout of agricultural emissions presents an opportunity to test our understanding of global CH<sub>3</sub>Br cycling. Yokouchi et al. (2002) and Montzka et al. (2003) detected the atmospheric decline using measurements from flask air networks. Those authors, as well as Reeves (2003), noted that the initial decline during 1998–2002 was roughly twice



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**Fig. 1.** The trend in biomass burning emissions of  $\text{CH}_3\text{Br}$  for the southern hemisphere (red line), the northern hemisphere (blue line), and the globe (purple line). Prior to 1997 and after 2006, the biomass burning emissions are shown as the monthly averages of the 1997–2006 data excluding the highest and lowest values for a given month (van der Werf et al., 2005 and updates from <http://ess1.ess.uci.edu/~jranders/data/GFED2/>).

as large as expected. They suggested that the observations could be explained if the anthropogenic component of the total emissions was larger than previously thought. This assertion also required an atmospheric lifetime  $\geq 14\%$  longer than the best estimate of 0.7 yr based on the known  $\text{CH}_3\text{Br}$  sinks (reaction with OH, photolysis, uptake by the ocean, and uptake by soils) (Yvon-Lewis and Butler, 1997). In this study, we revisit the atmospheric decline during phase-out using a slightly longer data set, covering 1995–2008 (Montzka et al., 2003 – with updates from NOAA/GMD [urlftp://ftp.cmdl.noaa.gov/hats/methylhalides/ch3br/flasks/](http://ftp.cmdl.noaa.gov/hats/methylhalides/ch3br/flasks/)), and an updated, time-dependent global model of  $\text{CH}_3\text{Br}$  emissions and uptake.

## 2 Global model, budget and data sources

This study of the seasonal and interannual variations in atmospheric  $\text{CH}_3\text{Br}$  was carried out using a numerical model that simulates the major processes involved in the global biogeochemical cycle of  $\text{CH}_3\text{Br}$ , including oceanic production and consumption, soil uptake, terrestrial plant emissions, fumigation, gasoline combustion, biomass burning, biofuel emissions, atmospheric loss via reaction with OH and photolysis in the stratosphere. The model is described in detail by Saltzman et al. (2004). It consists of two well-mixed atmospheric boxes representing northern and southern hemispheres. Transport between the hemispheres is governed by an interhemispheric exchange time constant of 1 year. Surface fluxes of methyl bromide are seasonally and spatially

variable. For the oceans, monthly,  $1^\circ \times 1^\circ$ , average ocean parameters from the NOAA/GFDL Global Oceanographic Data Set Atlas (available at <http://dss.ucar.edu/datasets/ds279.0>) were used to characterize oceanic temperatures, salinities, mixed layer depths, and 10 m wind speeds. Oceanic  $\text{CH}_3\text{Br}$  production rates are specified based on the observed saturation state of the pre-phaseout ocean extrapolated on the basis of the saturation anomaly vs. SST relationship identified in King et al. (2002). Each surface ocean cell maintains a mass balance for  $\text{CH}_3\text{Br}$  and interacts independently with the atmosphere. Land surface sources and sinks are distributed using the International Satellite Land Surface Climatology Project (ISLSCP) (Meeson et al., 1995; Sellers et al., 1995) and Matthews (1983) databases as described in Saltzman et al. (2004).

The pre-phaseout source and sink fluxes incorporated here are shown in Table 1 and reflect a revision in the budget described by Montzka and Fraser (2003). The sinks and corresponding oceanic emission terms were adjusted for the revised tropospheric burden of 125 Gg (atmospheric burden 132 Gg) observed in 1996 (Montzka et al., 2003 with updates from NOAA/GMD [ftp://ftp.cmdl.noaa.gov/hats/methylhalides/ch3br/flasks/](http://ftp.cmdl.noaa.gov/hats/methylhalides/ch3br/flasks/)). Separate peatland and rice paddy emissions are not shown as the databases do not distinguish them from wetlands (Saltzman et al., 2004). Biofuel emissions were added, and seasonal variations in biomass burning were included. This budget is not balanced, and the missing source implied from this imbalance is discussed below. The details of the sources and sinks used in this model are described in Saltzman et al. (2004). Changes made since then are discussed below.

Monthly fire distributions for 1997–2006 were determined from satellite observations by van der Werf et al. (2006) with subsequent updates (<http://ess1.ess.uci.edu/~jranders/data/GFED2/>).  $\text{CH}_3\text{Br}$  emissions from these fires are scaled to the CO fluxes calculated for the fires using emissions factors from Andreae and Merlet (2001). The resulting annual average  $\text{CH}_3\text{Br}$  emissions from biomass burning for 1997–2006 range from 11 to 16  $\text{Gg yr}^{-1}$ . This range is lower than the previous best estimate of 20 Gg for biomass burning emissions in the Montzka and Fraser (2003) budget. There is an initial increase in biomass burning emission in 1998 with a subsequent decline in emissions through 2004 (Fig. 1, Table 2). For the model simulations prior to 1997 and after 2006, the biomass burning emissions used are the monthly averages of the 1997–2006 data excluding the highest and lowest values for a given month.

The pseudo first order loss rate constant for  $\text{CH}_3\text{Br}$  by reaction with OH was computed using the temperature-dependent rate constant from Sander et al. (2006) and the OH and temperature fields from Spivakovsky et al. (2000). The pseudo first order rate constants are averaged for each hemispheric troposphere for each month to generate a seasonal hemispheric OH sink for  $\text{CH}_3\text{Br}$ . Interannual variability in global OH is simulated (Fig. 2, Table 2) by scaling OH in the

**Table 1.** Global CH<sub>3</sub>Br budgets for 1996 and 2007. The 1996 budget is modified from Montzka and Fraser et al. (2003) and Clerbaux and Cunnold et al. (2007). The italicized numbers highlight budget terms that changed between 1996 and 2007. Superscripts indicate references.

Sources	Best Estimate (Gg/y)		
	Pre-Phaseout 1996	Pre-Phaseout 1996 (60% Ag) <sup>§</sup>	Recent 2007 (60% Ag) <sup>§</sup>
Ocean	42.0 <sup>*,1</sup>	42.0 <sup>*,1</sup>	42.0 <sup>**</sup>
Fumigation-Quarantine and Preshipment	12.3 <sup>2</sup>	12.3 <sup>2</sup>	13.82 <sup>3</sup>
Fumigation-Soils and Other	31.0 <sup>3</sup>	36.6 <sup>3</sup>	5.2 <sup>3</sup>
Gasoline	5.7 <sup>4</sup>	5.7 <sup>4</sup>	5.7 <sup>4</sup>
Biomass Burning	11.3 <sup>5,6</sup>	11.3 <sup>5,6</sup>	11.3 <sup>5,6</sup>
Biofuel	6.1 <sup>6,7</sup>	6.1 <sup>6,7</sup>	6.1 <sup>6,7</sup>
Wetlands	4.6 <sup>8</sup>	4.6 <sup>8</sup>	4.6 <sup>8</sup>
Salt marshes	14.6 <sup>9</sup>	14.6 <sup>9</sup>	14.6 <sup>9</sup>
Shrublands	1 <sup>10</sup>	1 <sup>10</sup>	1 <sup>10</sup>
Rapeseed	6.6 <sup>11</sup>	6.6 <sup>11</sup>	6.6 <sup>5</sup>
Fungus	1.7 <sup>12</sup>	1.7 <sup>12</sup>	1.7 <sup>12</sup>
Subtotal Sources	137	143	113
Sinks			
Ocean	-56 <sup>13,14</sup>	-56 <sup>13,14</sup>	-48.6 <sup>13,14</sup>
OH and hv	-77 <sup>14,15</sup>	-77 <sup>14,15</sup>	-63.6 <sup>14,15,16</sup>
Soils	-41 <sup>14,17</sup>	-41 <sup>14,17</sup>	-34.0 <sup>14,17</sup>
Plants	-	-	-
Subtotal Sinks	-174	-174	-146
Total (Sources+Sinks)	-37 <sup>***</sup>	-31 <sup>***</sup>	-32 <sup>***</sup>

<sup>§</sup> The 60% Ag refers to the change from 50% emission during fumigation to 60% emission (scenario 8).

<sup>1</sup>King et al. (2002), <sup>2</sup>Buffin (2004), <sup>3</sup>MBTOC (2006), <sup>4</sup>Thomas et al. (1997), <sup>5</sup>van der Werf et al. (2006)

<sup>6</sup>Andreae and Merlet (2001), <sup>7</sup>Yevich and Logan (2003), <sup>8</sup>Varner et al. (1999), <sup>9</sup>Rhew et al. (2000)

<sup>10</sup>Rhew et al. (2001), <sup>11</sup>Gan et al. (1998), <sup>12</sup>Lee-Taylor and Holland (2000), <sup>13</sup>Yvon-Lewis and Butler (2002)

<sup>14</sup>Saltzman et al. (2004), <sup>15</sup>Spivakovsky et al. (2000), <sup>16</sup>Prinn et al. (2005), <sup>17</sup>Shorter et al. (1995)

\*Net ocean flux=-14.0 Gg/y

\*\*Net ocean flux=-6.6 Gg/y

\*\*\* Assumed to be a natural missing source

model to the variations inferred by Prinn et al. (2005) through 2003 from the ALE-GAGE network measurements of methyl chloroform. According to those estimates, global OH decreased by approximately 13% during 1997/1998 compared to other years, though such large changes are not consistent with observations of other trace gases during this period, such as CH<sub>4</sub> (Lelieveld et al., 2006). After 2003, the model retains the 2003 OH levels and seasonality.

Previous modeling studies do not include emissions from combustion of biofuels. However, they were included in the most recent budget estimate (Clerbaux and Cunnold, 2007). While some of these emissions can be accounted for through the satellite fire database described for the biomass burning emission distributions, the emissions associated with burning of biofuels inside houses and structures cannot be observed from satellites. Emissions from biofuels, minus the outdoor burning that would be a part of the biomass burning

calculations, equal approximately 6.1 Gg yr<sup>-1</sup> and are primarily in the northern hemisphere (Andreae and Merlet, 2001; Yevich and Logan, 2003). The biofuel emissions were determined for each country with a 20% increase for developing countries to bring the emissions to a value appropriate for 1995 according to Yevich and Logan (2003) and those emissions were then sorted into their respective hemispheres resulting in emissions of 5.2 Gg yr<sup>-1</sup> CH<sub>3</sub>Br in the northern hemisphere (NH) and 0.9 Gg yr<sup>-1</sup> in the southern hemisphere (SH). Yevich and Logan (2003) caution that their biofuel emission estimates could have an uncertainty of ±50%. This uncertainty directly applies to the CH<sub>3</sub>Br emissions from biofuels, as we used emission factors from Andreae and Merlet (2001) to convert the Yevich and Logan (2003) biofuel emissions to CH<sub>3</sub>Br emissions.

**Table 2.** Annual global biomass burning emissions, consumption for non-QPS fumigation, and the pseudo first order rate constant for reaction with OH.

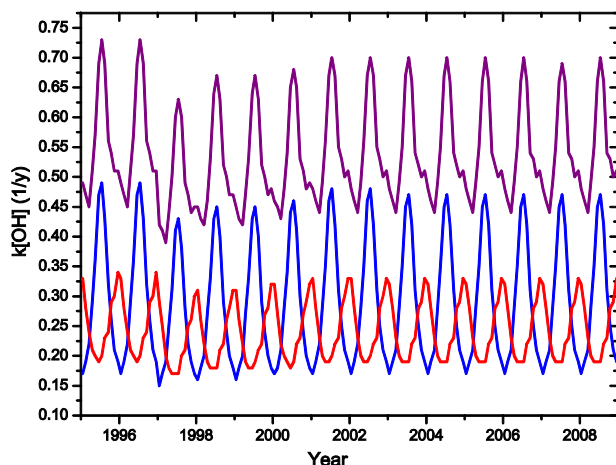
Year	Biomass Burning <sup>1</sup> (Gg)	Non-QPS Fumigation <sup>2</sup> (Gg)	K[OH] <sup>3,4</sup> (yr <sup>-1</sup> )
1995	11.3	61.0	0.56
1996	11.3	61.0	0.56
1997	15.9	61.0	0.49
1998	17.0	58.2	0.52
1999	11.2	47.4	0.52
2000	9.7	40.8	0.53
2001	10.5	34.3	0.55
2002	12.0	25.6	0.55
2003	11.4	21.4	0.54
2004	11.6	26.1	0.54
2005	11.8	16.7	0.54
2006	11.2	13.8	0.54
2007	11.3	8.7	0.54
2008	11.3	8.7	0.54

<sup>1</sup>van der Werf et al. (2006)

<sup>2</sup>MBTOC (2006) in years after 1997; assumed constant at 61 Gg/yr from 1995–1997

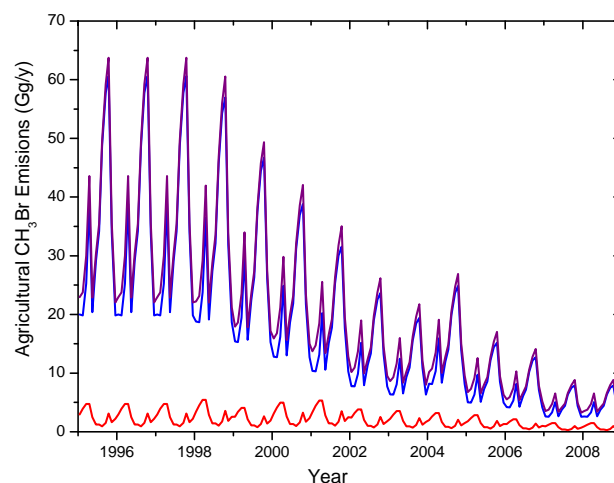
<sup>3</sup>Spivakovsky et al. (2000)

<sup>4</sup>Prinn et al. (2005)



**Fig. 2.** The trend in the pseudo first order loss rate constant for loss of CH<sub>3</sub>Br to reaction with OH for the southern hemisphere (red line), the northern hemisphere (blue line), and the globe (purple line). For model years 1997–2003, OH is scaled by the interannual variations given by Prinn et al. (2005). For the remainder of the simulation, the 2003 OH scaling factor was used.

The total industrially-derived emissions from fumigation of soils, durables, perishables, and structures was 43.3 Gg yr<sup>-1</sup> (~25% of total emissions including the missing source) in 1996 (Table 1). For this study, it is assumed that consumption equal use and stockpiling is not considered. The hemispheric distribution, seasonality, and annual



**Fig. 3.** The trend in non-QPS agricultural emissions of CH<sub>3</sub>Br, assuming 50% of consumption is emitted, from 1995 through 2008 for the southern hemisphere (red line), the northern hemisphere (blue line), and the globe (purple line).

trend of the non-quarantine and preshipment (non-QPS) fumigation source are based on government and industry statistics on consumption (MBTOC, 2006) (Fig. 3, Table 2) with agricultural soil emissions maintained at 2005 values after that time. The quarantine and preshipment (QPS) emissions remained constant at 12.3 Gg yr<sup>-1</sup> from 1995 through 1998 (Buffin, 2004). The trend in QPS emissions from 1999 through 2005 is based on the QPS trends reported in MBTOC (2006). These data suggest an increase in QPS emissions in 2005 that reflected the increased use to meet new guidelines for regulating wood products in international trade (IPPC, 2002; Federal Register, 2004). The elevated 2005 values were maintained for the remainder of the simulation time (e.g. 2007, Table 1).

### 3 Results and discussion

#### 3.1 Model initialization and scenarios

The model is initialized by running it for several years with the 1996 CH<sub>3</sub>Br budget and Spivakovsky et al. (2000) OH levels, until a repeatable annual cycle in atmospheric CH<sub>3</sub>Br is obtained. As noted earlier, there is a significant imbalance in the “best estimate” CH<sub>3</sub>Br budget (Table 1), with atmospheric losses exceeding the known sources by ~37 Gg yr<sup>-1</sup> after adjusting to the 125 Gg tropospheric burden. With the inter tropical convergence zone (ITCZ) located at the equator, the magnitude and seasonality of the unknown source(s) were adjusted in the model by trial and error to achieve agreement with the mean 1995–1998 tropospheric hemispheric mixing ratios (NH=10.2 ppt, SH=8.0 ppt) and seasonalities (Montzka et al., 2003) (Fig. 4a). This resulted in annually

**Table 3.** Model scenarios used in this study. If not explicitly stated, sources and sinks are maintained as in the 1996 model year.

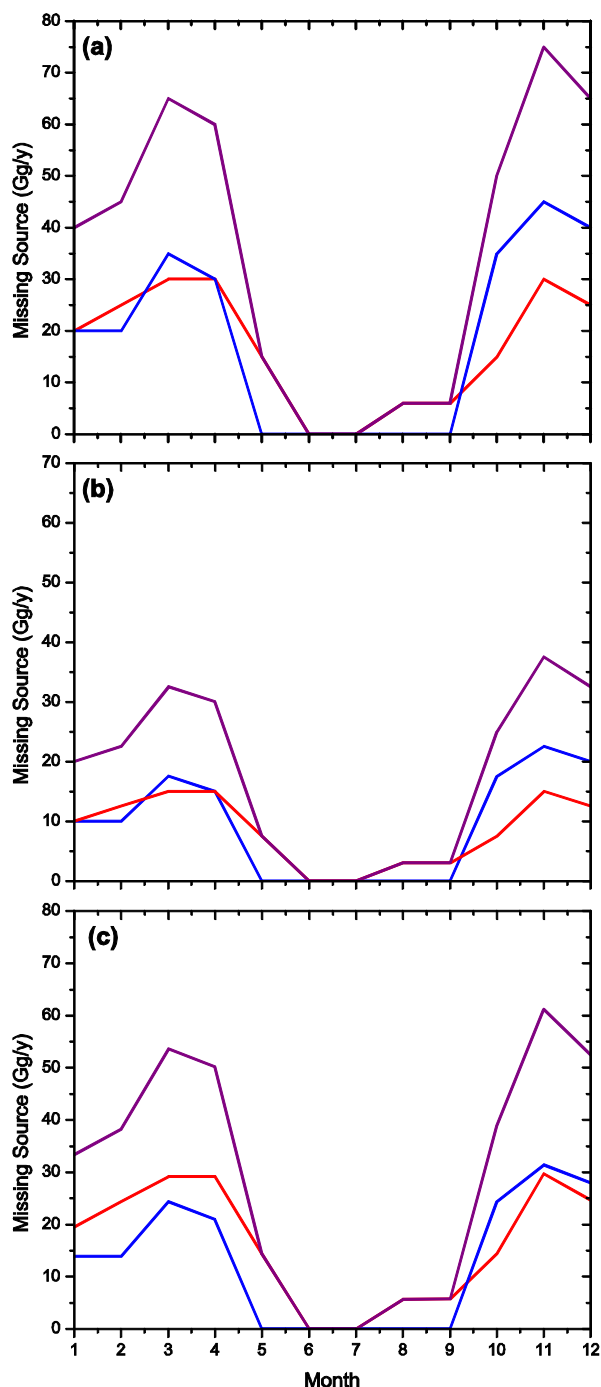
Scenarios to examine interannual variations in sources/sinks:	
1	Interannual variability in biomass burning only
2	Interannual variability in OH only. After 2004, no interannual variations are included.
3	Interannual variability in non-QPS anthropogenic emissions only due to phaseout.
4	Interannual variability in biomass burning, OH and non-QPS anthropogenic emissions.
Scenarios to examine missing source and atmospheric lifetime:	
5	Missing source term treated as agricultural emissions and allowed to decrease with phaseout. Interannual variability in biomass burning, OH and non-QPS anthropogenic emissions included.
6	Missing source reduced by 50%, and atmospheric lifetime of CH <sub>3</sub> Br increased to 0.84 yr. Remaining missing source adjusted to match the observed pre-phaseout seasonality and treated as agricultural. Interannual variability in biomass burning, OH and non-QPS anthropogenic emissions included.
7	Missing source reduced by 50%, and atmospheric lifetime of CH <sub>3</sub> Br increased to 0.84 yr. Remaining missing source adjusted to match the observed pre-phaseout seasonality and treated as natural with no interannual variability. Interannual variability in biomass burning, OH and non-QPS anthropogenic emissions included.
8	Agricultural emissions increased to 60%, and atmospheric lifetime kept as it was in scenarios 1–5. Missing source reduced by the amount of the agricultural increase. Interannual variability in biomass burning, OH and non-QPS anthropogenic emissions included.

averaged emissions for the unknown source of  $\sim 19 \text{ Gg yr}^{-1}$  in the northern hemisphere and  $\sim 17 \text{ Gg yr}^{-1}$  in the southern hemisphere. This approach is the same as that used in Saltzman et al. (2004), with only slightly different emissions being derived for this unknown source.

Simulations were run to examine the sensitivity of the location of the “missing source” to the position of the model ITCZ. Moving the ITCZ in the model northward from the equator to 5N shifts the missing source almost entirely to the southern hemisphere. This is a consequence of shifting a significant fraction ( $\sim 20\%$ ) of the OH sink in the NH to the SH. In the 5N ITCZ case, it is not possible to simulate the observed amplitude of NH seasonal variations in CH<sub>3</sub>Br because there is no missing source with which to adjust NH seasonality. Further studies of this type should be carried out using 3-D transport models that are capable of more realistic simulation of interhemispheric mixing.

This model reproduces pre-phaseout atmospheric observed seasonal variations quite well, considering the crude seasonal parameterizations for the terrestrial sources and soil sink, and the fact that interhemispheric exchange is based on mean hemispheric levels. While the lack of atmospheric dynamics in this model precludes investigation of the spatial distribution of the missing source, the model can be used to examine the nature of the missing source through interannual variations in sources and sinks and the impact of a change in lifetime on the seasonal variations and interannual trends.

Eight model scenarios are discussed here (Table 3). The first four cases are used to examine the impact of interannual variations in selected sources and sinks. The calculated hemispheric missing source strengths and seasonalities were fixed for the duration of Scenarios 1–4. Scenarios 5–8 are used to examine the nature of the missing source and the possibility of a longer atmospheric lifetime for CH<sub>3</sub>Br. The model is also used to investigate the impact of the atmospheric variability on the saturation state of the ocean.



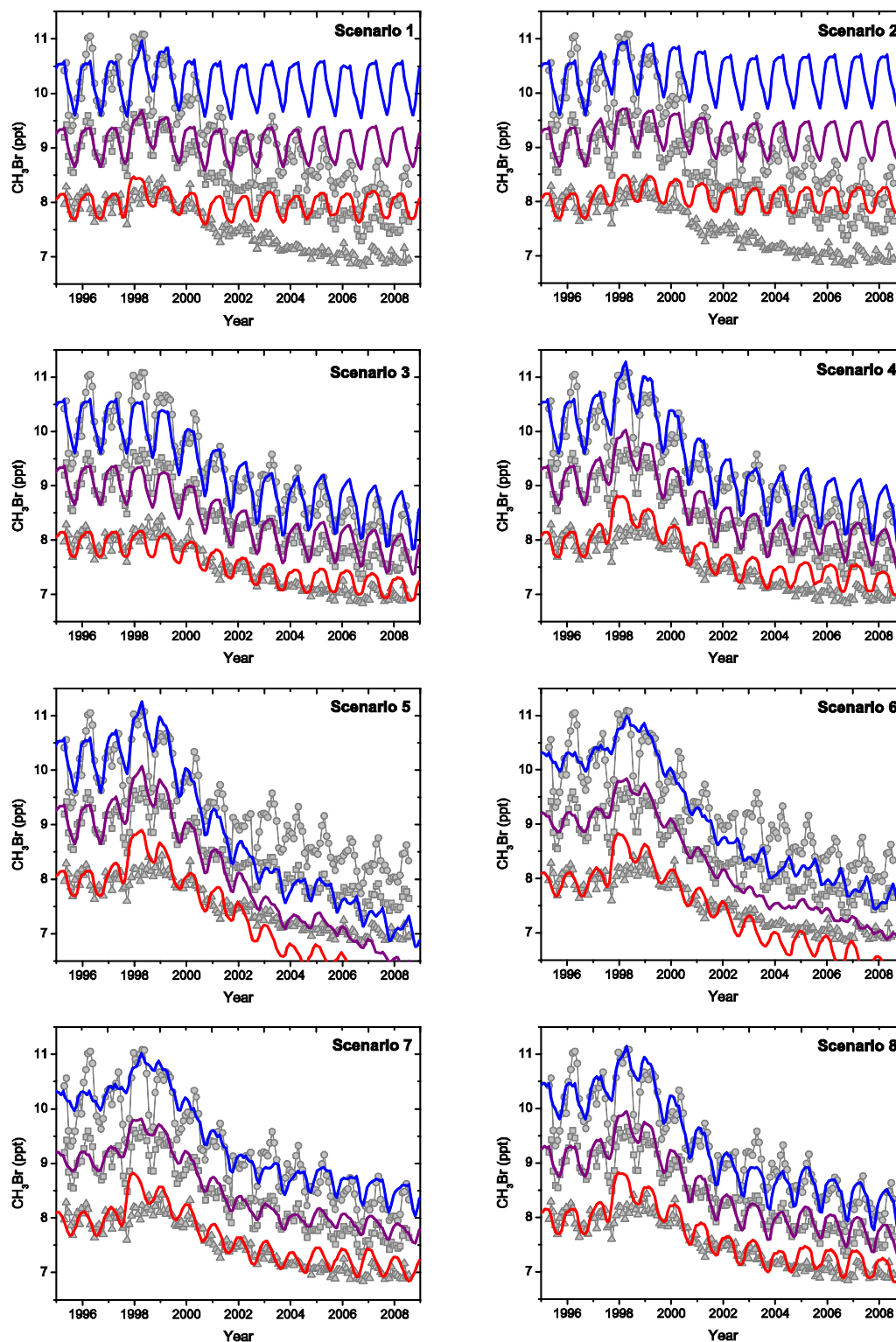
**Fig. 4.** Seasonal cycle in the missing source for the southern hemisphere (red line), the northern hemisphere (blue line) and the globe (purple line) for (a) scenarios 1–4, (b) scenario 7 and (c) scenario 8.

### 3.2 Interannual Variability in biomass burning, atmospheric OH, and anthropogenic $\text{CH}_3\text{Br}$ emissions

The first scenario examines the impact of interannual variability in biomass burning  $\text{CH}_3\text{Br}$  emissions on the atmospheric  $\text{CH}_3\text{Br}$  burden (Table 3, Fig. 5). During the 1997–1998 period, the emissions from biomass burning increased by  $3.0 \text{ Gg y}^{-1}$  (NH) and  $5.6 \text{ Gg y}^{-1}$  (SH) over the mean values used for the pre-phaseout conditions (Fig. 1, Table 2). This case yields an increase in the annually averaged atmospheric  $\text{CH}_3\text{Br}$  of 0.27 ppt (NH) and 0.26 ppt (SH) over the mid-1997 to mid-1998 period that is consistent with the observations. The effect of increased biomass burning was much larger (on a relative basis) in the southern hemisphere, both because the increase in emissions was larger than in the northern hemisphere, and because biomass burning is a larger fraction of the total emissions in the southern hemisphere. Given the mean lifetime of about 0.7 years, roughly one third of the emissions in each hemisphere are transported to the other hemisphere. As noted by Saltzman et al. (2004) the approach of using hemispherically averaged atmospheric boxes may underestimate the interhemispheric mixing of low latitude sources, like biomass burning. Hemispheric averaging also undoubtedly slightly overestimates the atmospheric lifetime of low latitude emissions which are released in the region of highest OH and atmospheric reactivity.

The second scenario examines the effect of interannual variability in global OH (Table 3, Fig. 5). Model OH levels are fixed at the Spivakovsky et al. (2000) values from 1995–1996. For model years 1997–2003, OH loss is scaled by the interannual variations given by Prinn et al. (2005) (Fig. 2, Table 2). For the remainder of the simulation, the 2004 OH scaling factor was used. The decline in OH concentrations during 1998 results in a noticeable increase in the atmospheric burden of  $\text{CH}_3\text{Br}$ . The subsequent increase in OH back to pre-1998 values results in a decrease and subsequent leveling off of the atmospheric  $\text{CH}_3\text{Br}$ .

The third scenario examines the effect of anthropogenic phaseout (Table 3, Fig. 5). The phaseout imposed by the Montreal Protocol and its amendments resulted in a nearly 86% reduction in emissions from regulated non-QPS agricultural fumigation applications from the 1996 budget to 2007. Critical Use Exemptions (CUEs) in non-QPS applications have allowed the emissions to decrease at a slower rate than originally specified by the amendments to Montreal Protocol (Fig. 3, Table 2). For this model case, biomass burning was fixed at the 1996 values for the entire run, and OH loss was maintained at the 1995–1996 values. The model results show that the decline in anthropogenic emissions results in a significant decline in atmospheric  $\text{CH}_3\text{Br}$  levels from 1996 to 2007. The phaseout alone appears to account for most of the overall change in atmospheric burden from 1996 to 2007. However, this scenario does not accurately capture the initial increase in  $\text{CH}_3\text{Br}$  in 1997/1998, and it does not result in low enough atmospheric values in 2007.



**Fig. 5.** Modeled and measured trends in atmospheric  $\text{CH}_3\text{Br}$  concentrations for 1995–2008. In all plots, the data points for Southern Hemisphere ( $\Delta$ ), the Northern Hemisphere ( $\circ$ ), and the globe ( $\square$ ) are observations from NOAA/GMD (<ftp://ftp.cmdl.noaa.gov/hats/methylhalides/ch3br/flasks/>). Model results are shown for the southern hemisphere (red line), the northern hemisphere (blue line), and the globe (purple line) for the scenarios described in Table 3.

The fourth scenario examines the combined effect of interannual variability in biomass burning, OH, and anthropogenic phaseout (Table 3, Fig. 5). This case does a good job of simulating northern hemisphere variability, capturing both the 1998 increase and subsequent decline of CH<sub>3</sub>Br. In the southern hemisphere, the simulation overestimates the initial increase in CH<sub>3</sub>Br during late 1997 and early 1998. After the peak, southern hemispheric levels in the model run decreased rapidly, bringing the simulation back into agreement with the atmospheric measurements for several years. From 2004 through 2007, the model shows a leveling off of southern hemisphere CH<sub>3</sub>Br levels, while the atmospheric measurements show a continued decline until 2007. The overestimates in the SH in 1997/8 and after 2004 could both be a result of the distributions of biomass burning near the equator and the location of the ITCZ in the model calculation.

One of the limitations of this study is the inability to evaluate other biogeochemical impacts of the 1998 El Niño or other natural variations on other CH<sub>3</sub>Br sources and sinks. In particular, the droughts associated with the El Niño could have significantly affected both terrestrial emissions and the soil sink. Widespread changes in carbon cycling occurred as a result of the 1998 El Niño, as evidenced by the subsequent increase in atmospheric CO<sub>2</sub>. Increased CO<sub>2</sub> at that time was caused, at least in part, by a decrease in vegetative growth and an increase in soil respiration (Cramer et al., 2001; Nemani et al., 2003; Erbrecht and Lucht, 2006). However, there is insufficient information at present with which to assess how such changes affected CH<sub>3</sub>Br cycling.

The results discussed above suggest that the initial phaseout began right after elevated background CH<sub>3</sub>Br mixing ratios were observed as a result of the combined increase in biomass burning associated with the 1998 El Niño (van der Werf et al., 2004) and the decrease in OH associated with the increased biomass burning emissions. This caused the initial decrease in CH<sub>3</sub>Br associated with the phaseout to appear larger than expected from the change in agricultural emissions. By accounting here for these non-anthropogenic influences, having additional years of data to analyze during which such perturbations were diminished, and incorporating a revised calibration for the NOAA CH<sub>3</sub>Br data a more robust accounting of industrially-derived CH<sub>3</sub>Br in the atmosphere is possible. This analysis is consistent with a ratio of anthropogenic to total emissions of ~25%, or fairly close to the updated estimate of 30 (20–40)% in Clerbaux and Cunnold (2007).

### 3.3 The “Missing CH<sub>3</sub>Br Source” and atmospheric CH<sub>3</sub>Br lifetime

The model results discussed above demonstrate that the major features of the recent variability in atmospheric CH<sub>3</sub>Br can be reasonably well simulated by simultaneously imposing interannual variability in biomass burning, global OH, and anthropogenic emissions on the 1996 best-estimate

global budget including an unknown seasonally varying natural source that exhibits no interannual variability (Fig. 5). However, there are still biases in the model results.

The cause of the imbalance between sources and sinks is one of the most puzzling aspects of the global CH<sub>3</sub>Br budget. This imbalance has persisted for more than a decade in all global budgets, despite continued research on both sources and sinks. It is generally suspected that the missing source is related to emissions from terrestrial vegetation. The modeling results of Warwick et al. (2006) suggest that the missing source could be from a combination of tropical and subtropical plants and biomass burning. To date, only limited emissions surveys from terrestrial plants and ecosystems have been carried out, and it can be argued that the seasonality of these sources is not well documented (Montzka and Fraser et al., 2003; Gan et al., 1998; Dimmer et al., 2001; Redecker et al., 2000; Rhew et al., 2001; Varner et al., 1999).

In model scenarios 5–8, the magnitude and nature of the missing source is examined beginning with the thesis of Yokouchi et al. (2002) and Montzka et al. (2003). After they detected the rapid decline in atmospheric CH<sub>3</sub>Br from 1998 to 2002, they suggested that the rapid decline could indicate that the anthropogenic component of the budget was larger than previously thought. This required either an upward revision of the anthropogenic emissions (as part or all of the missing source) or an upward revision of the atmospheric lifetime to  $\geq 0.8$  yr (Montzka et al., 2003) from the current best estimate of 0.7 yr (Yvon-Lewis and Butler, 1997).

Model scenario 5 examines this possibility by augmenting non-QPS anthropogenic emissions to account entirely for the missing source (Table 3, Fig. 5). The missing source along with its seasonality is added to the agricultural emissions in each hemisphere. No additional missing source is included. This results in a larger decline in absolute emissions during the phase-out of anthropogenic methyl bromide. The biomass burning trend, OH trend, and phaseout rate are maintained as in scenario 4. Including the missing source in the non-QPS anthropogenic emissions results in a model-predicted decline during phaseout more rapid than observed, and lower concentrations than observed at the end of the record (Fig. 5e). This result suggests it is not likely that the missing source can be accounted for entirely by an underestimation of the mean release fraction of industrial CH<sub>3</sub>Br in non-QPS fumigation applications. For the missing source to be entirely anthropogenic, and for the model to reproduce the atmospheric trend, this source must consist of QPS emissions which are not subject to the phaseout. It is unlikely that QPS emissions were underestimated by nearly 100%.

Model scenario 6 examines the effect of increasing the lifetime of CH<sub>3</sub>Br to reduce the “missing source” to half of the amount required to balance the 1996 budget (18.5 Gg yr<sup>-1</sup>) (Table 3, Fig. 5). This is done by reducing both the missing source and the soil uptake in each hemisphere relative to the best estimate 1996 budget. This results in an increase in the atmospheric lifetime to 0.84 yr (~13%



increase over the best estimate). With the longer lifetime, the model also underestimates the seasonal amplitude of atmospheric CH<sub>3</sub>Br, particularly in the northern hemisphere. Increasing the atmospheric lifetime still further to account for the entire missing source would lead to an even larger discrepancy in terms of the amplitude of the seasonal cycle. The phaseout of anthropogenic emissions results in an underestimate of atmospheric CH<sub>3</sub>Br levels after 2002 due to the loss of the remaining missing source, as it was included as an anthropogenic non-QPS emission in this scenario.

Scenario 7 assumes that the reduced global missing source described in scenario 6 is natural and does not decline with the anthropogenic phaseout (Table 3, Fig. 5). The lifetime is kept at 0.84 yr as in scenario 6. The seasonality of this missing source was optimized to try to achieve the pre-phaseout observed seasonal amplitude in the CH<sub>3</sub>Br burden (Fig. 4b). Other conditions are as in scenario 6. The model results exhibit fairly good agreement with the observations. However, as in scenario 4, the model overpredicts the atmospheric values after 2004 slightly. As in scenario 6, seasonal amplitudes pre-phaseout and post 2004 are underestimated. The longer atmospheric lifetime makes it impossible for the model to achieve the seasonal amplitude observed in the NH. Achieving the observed amplitude requires imposing a negative missing source at certain times of the year. That would effectively shorten the atmospheric lifetime back to the original value.

While the interannual variations in OH introduced in case 2 have an effect on the atmospheric CH<sub>3</sub>Br lifetime, this effect is very small and is largest for 1997/1998 with an approximately 0.04 yr (<6%) increase in the lifetime for those two years (Fig. 5). After 1998, the CH<sub>3</sub>Br lifetime in the model gradually returns to the initial 0.75 yr value. An increase in the lifetime large enough to account for only half of the missing source results in a seasonal amplitude that is smaller than observed pre-phaseout (Fig. 5f and g). The missing source is not likely the result of overestimated sinks.

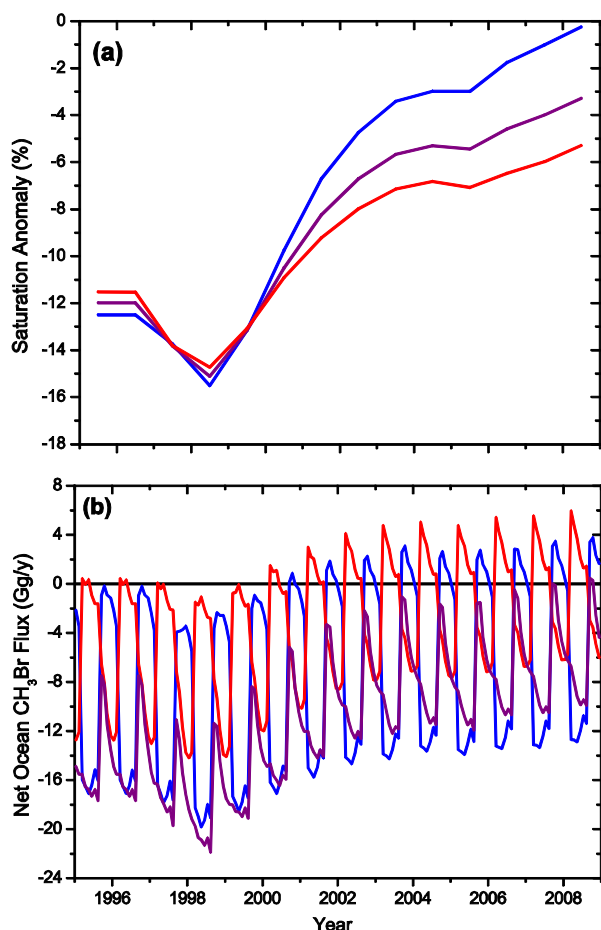
Scenario 8 involves increasing the escape rate of agricultural CH<sub>3</sub>Br to 60% of the amount applied rather than the 50% assumed in scenarios 1–4 (Table 3, Fig. 5). This increases the anthropogenic to total emission fraction to ~28% which is closer to the estimate of 30 (20–40)% given by Clerbaux and Cunnold (2007). The lifetime is the same as in scenarios 1–5 (~0.75 yr). The missing source in each hemisphere is reduced by the amount that the agricultural emission increased and seasonality was adjusted to match the 1995–1998 tropospheric mixing ratios (NH=10.2 ppt, SH=8.0 ppt) and seasonalities (Montzka et al., 2003) (Fig. 4c). This revised pre-phaseout budget is given in Table 1 as the 1996 (60% Ag) budget. The prescribed interannual variations in biomass burning emissions, reaction with OH, and anthropogenic emissions are the same as in scenario 4. By maintaining the original lifetime, the seasonal amplitude of the atmospheric CH<sub>3</sub>Br is closer to the observed seasonality for the entire simulation. The 1997

Southern hemispheric concentrations are elevated compared to observations, as in scenario 4. The predicted concentrations from 2002–2007 are in better agreement with the observations than in any other scenario. The budget for 2007 from this scenario is shown in Table 1 as 2007 (60% Ag), and the anthropogenic to total emission fraction decreased to ~13%.

### 3.4 Ocean saturation state

In this study, oceanic CH<sub>3</sub>Br production (magnitude, geographic distribution, and seasonality) was calculated for 1996 conditions. This oceanic production was held constant for the duration of all model runs, as were the kinetic parameters affecting oceanic CH<sub>3</sub>Br cycling (wind speeds, mixed layer depths, surface ocean temperature, and biological degradation rate constants). Although oceanic production was held constant, the saturation state of the oceans with respect to the overlying atmosphere varies in the model runs as a function of the atmospheric CH<sub>3</sub>Br levels, and the internal cycling of CH<sub>3</sub>Br within the oceans. Figure 6a shows the time series of oceanic CH<sub>3</sub>Br saturation state calculated in scenario 8. The decrease in the calculated saturation anomaly for 1997 and 1998 results from the increase in atmospheric burden caused by increased biomass burning emissions and decreased OH concentrations in the model. The saturation state of the oceans increased substantially during the phaseout period in the model, shifting from a saturation anomaly (deviation from equilibrium) of –11.7% in 1996 to –6.0% in 2007 (Fig. 6a). The saturation anomaly decreased slightly during 2005 due to the increase in modeled atmospheric CH<sub>3</sub>Br concentrations resulting from increased QPS emissions, most notably in the southern hemisphere. Before phaseout, the northern hemisphere was more undersaturated than the southern hemisphere. This reversed during the first year of phaseout in the model, likely as a result of the much greater decline in emissions from the northern hemisphere.

The model results indicate that the oceans in both hemispheres, should now be closer to equilibrium than before the phaseout began. In fact, the model results indicate that the net flux is now positive (from sea to air) in the summer in each hemisphere. The global average net flux in 2007 is predicted to be –6.6 Gg yr<sup>–1</sup>, less than half the pre-phaseout global average of –14.0 Gg yr<sup>–1</sup> (Fig. 6b). Most of the published saturation anomaly measurements for CH<sub>3</sub>Br in the open ocean were conducted during pre-phaseout conditions (King et al., 2002), and there are insufficient data from the phaseout period for comparison. Saturation anomaly measurements across the major ocean basins during different seasons should be carried out to test this prediction and validate current models of oceanic cycling.



**Fig. 6.** From scenario 8, model predicted (a) annual average saturation anomaly (difference from equilibrium) of CH<sub>3</sub>Br in the ocean and (b) net ocean fluxes for the southern hemisphere (red line), the northern hemisphere (blue line), and the globe (purple line).

#### 4 Conclusions

The observed decrease in atmospheric CH<sub>3</sub>Br resulting from the Montreal Protocol places new constraints on the global CH<sub>3</sub>Br budget. This study suggests that a portion ( $\sim 7$  Gg yr<sup>-1</sup> or about 20%) of the CH<sub>3</sub>Br missing source is likely the result of underestimated anthropogenic fumigation emissions. The remainder ( $\sim 31$  Gg yr<sup>-1</sup> or about 80%) is not likely due to underestimation of the agricultural emissions and is not likely to be the result of overestimated sinks (underestimated lifetime). Increasing agricultural sources beyond a 60% escape rate does not yield an improved agreement with the observed atmospheric rate of decline even when the lifetime is increased (Fig. 5, scenario 5 and 6). The best estimate lifetime (0.7–0.8 years) and larger missing source are necessary to maintain the large observed seasonal amplitude both before the phaseout and after 2002. Assuming constant production of CH<sub>3</sub>Br in the oceans, the de-

creasing atmospheric levels imply a substantial increase in the saturation state of the oceans. The resulting change in air/sea flux represents an additional 7.4 Gg in net flux to the atmosphere from the ocean in 2007, relative to pre-phaseout conditions.

We conclude from this study that the behavior of the atmospheric CH<sub>3</sub>Br burden over the phaseout period is reasonably consistent with our current understanding of the global budget which includes a substantial unidentified source. Interannual variations in the atmospheric burden are sensitive not only to the anthropogenic phaseout but also to variations in biomass burning emissions and OH radical concentrations. The anthropogenic contribution to the global budget, approximately 28% of total emissions in the best case scenario, is consistent with the latest assessment (Clerbaux and Cunnold, 2007). The lifetime of 0.7–0.8 yr is also consistent with the best estimate (Yvon-Lewis and Butler, 1997). There remains a significant imbalance in the global budget, which is likely due to unknown or underestimated natural sources that exhibit little interannual variability, as shown by the model. Additional field and modeling studies are needed in order to better constrain the CH<sub>3</sub>Br source from terrestrial ecosystems, particularly in the tropics. The detailed nature of the ocean model coupled to the simple atmospheric model along with the results from this study also highlight the need for new measurements of oceanic CH<sub>3</sub>Br saturation anomalies, to provide a comparison of pre-phaseout and current conditions to validate current models of oceanic cycling.

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