Methyl Bromide In Preindustrial Air: Measurements From an Antarctic Ice Core

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**Recommended Citation**

Methyl bromide in preindustrial air: Measurements from an Antarctic ice core


Received 17 September 2003; revised 2 December 2003; accepted 14 January 2004; published 2 March 2004.

1 This paper presents the first ice core measurements of methyl bromide (CH$_3$Br). Samples from a shallow Antarctic ice core (Siple Dome, West Antarctica), ranging in mean gas dates from 1671 to 1942, had a mean CH$_3$Br mixing ratio of 5.8 ppt. These results extend the existing historical record derived from air and Antarctic firn air to about 350 years before present. Model simulations illustrate that the ice core results are consistent with estimates of the impact of anthropogenic activity (fumigation, combustion, and biomass burning) on the atmospheric CH$_3$Br burden, given the large current uncertainties in the modern atmospheric CH$_3$Br budget. A preindustrial scenario assuming no fumigation, no combustion, and a 75% reduction in biomass-burning sources yields a Southern Hemisphere mean mixing ratio of 5.8 ppt, in good agreement with the ice core results. There is a significant imbalance between the known CH$_3$Br sources and sinks in the modern atmospheric CH$_3$Br budget. The ice core data do not sufficiently constrain the model to determine how much of the “unknown source” was present in the preindustrial budget. The results do indicate that most of the southern hemisphere component of this “unknown source” is not anthropogenic.

1. Introduction

Methyl bromide (CH$_3$Br) is a significant contributor to the stratospheric halogen burden and to stratospheric ozone depletion. As a result, industrial production of this compound has been phased out under the Amendments to the Montreal Protocol. CH$_3$Br is markedly different from many other regulated halogen compounds, such as CFC’s, in that it has a complex biogeochemical cycle, with natural sources and sinks in both terrestrial and oceanic environments. Our understanding of the biogeochemical cycle of CH$_3$Br has improved in recent years, as a result of numerous field, laboratory, and modeling studies. However, the sources and sinks are still not well characterized, and there remain significant uncertainties associated with the major terms in the global atmospheric budget [Montzka et al., 2003b]. These uncertainties limit our ability to predict the atmospheric impact of declining industrial production. For example, Yokouchi et al. [2002] and Montzka et al. [2003a] recently noted that the atmospheric CH$_3$Br decrease since 1998 is about two-fold larger than anticipated.

Instrumental records of atmospheric CH$_3$Br extend only as far back as the late 1970s [Khalil et al., 1993; Miller, 1998; Montzka et al., 2003a]. Firn air measurements at four locations in Antarctica extend the record to the mid-1900s, and a few samples from the basal firn air at South Pole extend the record further to about 1900 [Butler et al., 1999; Sturges et al., 2001]. The data suggest a 1 ppt (pmol mol$^{-1}$) increase in Southern Hemisphere CH$_3$Br over the first half of the twentieth century, followed by a 2 ppt increase during the latter half of the century. While Antarctic firn air appears to contain a paleoatmospheric archive, this is not the case in Greenland. Greenland firn air exhibits evidence of in situ production, with elevated CH$_3$Br levels near the base of the firm [Butler et al., 1999; Sturges et al., 2001], and evidence of photochemical production of CH$_3$Br in near-surface snow [Swanson et al., 2002]. The precursors and mechanisms of in situ production are not yet known.

In this paper, we present the first measurements of CH$_3$Br in preindustrial air extracted from an Antarctic ice core. The study of polar ice cores can potentially provide a strong constraint on preindustrial atmospheric levels, and, therefore, on the atmospheric impact of anthropogenic emissions. Ice core records can also provide longer-term

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0148-0227/04/2003JD004157
1. Ice Core Characteristics and Dating

The mean age of CH$_3$Br in individual ice core samples was estimated by applying the ice age/gas age difference to the ice age as determined from annual layer counting (R. B. Alley, personal communication, 2003). In the firn air model, the variation of diffusivity with depth was empirically tuned to obtain agreement between measured firn air profiles of CFC-12 [Etheridge et al., 1996; Tans et al., 1996] and the reconstructed atmospheric history of Walker et al. [2000]. The model was run using a mean annual snow accumulation rate of 100 kg m$^{-2}$ yr$^{-1}$ and a CH$_3$Br diffusivity in air of 9.7 × 10$^{-6}$ m$^2$ s$^{-1}$ [Wilke and Lee, 1955]. For CH$_3$Br, the mean ice age/gas age difference at Siple Dome is approximately 316 years, the mean gas age of firn at close-off is approximately 58 years, and the full width of the gas age distribution is about 25 years at half height.

2. Ice Core Gas Extraction and Analysis

The air contained in 300–750 g ice core samples was extracted by mechanically shredding the ice in a stainless-steel chamber under vacuum at −48°C. The air evolved during this process (30–60 cc STP per sample) was cryogenically focused in a stainless-steel tube immersed in liquid He and analyzed using capillary gas chromatography with quadrupole mass spectrometry. CH$_3$Br was detected using electron impact ionization with selected ion monitoring of the parent ion (CH$_3$Br$^+$; m/e = 94). Details of the extraction, analysis, and standardization procedures are given by Aydin et al. [2002].

The analysis of each ice core sample consisted of three steps. Prior to shredding, 50 cc STP N$_2$ was added to the evacuated extraction chamber containing the solid ice core sample. After 25–30 minutes, the N$_2$ was cryogenically removed from the chamber and analyzed, as a “pre-shredding blank.” Next, the chamber was re-evacuated, the ice core sample was shredded, and the evolved air was collected and analyzed. Finally, the chamber containing the shredded ice core sample was re-evacuated, another 50 cc STP N$_2$ was added, and a “post-shredding blank” was obtained over the shredded ice (Figure 1). It is assumed that the ice core sample contains a blank similar to the N$_2$ blanks, so for each sample the mean of the two blanks was subtracted from the ice core sample signal. The uncertainties that resulted from this blank correction were mostly ±5% or lower. However, a few samples run early in the study had high blank levels and high variability between the “pre-” and “post-shredding” blanks, resulting in higher uncertainties of ±10–40%.

Standardization was based on high-pressure aluminum cylinders containing 10–20 nmol mol$^{-1}$ CH$_3$Br in N$_2$, prepared in our laboratory. These standards were diluted barometrically to 10–20 ppt with N$_2$ in humidified stainless-steel flasks and analyzed in the same manner as ice core samples. An informal intercalibration of our standards with NOAA/CMDL standards yielded agreement within ±3%.

2.3. Ice Core Results and Discussion

Twenty-three Siple Dome ice core samples ranging in depth from 55 to 85 m were analyzed for this study. The samples had CH$_3$Br mixing ratios ranging from 3.2 to 9.0 ppt, with a mean and standard error of 5.8 ± 0.3 ppt (Figure 2). Three samples at 73, 74, and 83 m depth had low CH$_3$Br mixing ratios in the 3 to 4 ppt range. These samples also had higher analytical uncertainty than most, resulting from large blank corrections. These samples were run early in the study when the pre- and post-shredding blanks were large. More thorough baking of the extraction chamber was carried out for later samples, resulting in lower blanks. One sample at about 65 m had a CH$_3$Br mixing ratio of nearly 8 ppt, considerably higher than the surrounding data points. This elevated sample is not supported by the adjacent samples, as might be expected for a real atmospheric excursion. The mixing of air in the firn causes significant overlap between the age ranges of adjacent samples. Single point excursions should be viewed with caution until confirmed by additional analyses. Two data points at 79

Figure 1. Selected ion-monitoring signal from GC/MS analysis of CH$_3$Br (m/e = 94) in a Siple Dome ice core sample (64.5 m; 750 g). (left) N$_2$ extraction chamber blank prior to sample extraction; (middle) 70 ml STP air extracted from the ice core sample; (right) N$_2$ extraction blank after extraction.

Records of natural variability and insight into the sensitivity of the CH$_3$Br cycle to climate change.

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and 80 m had mixing ratios around 9 ppt. Although these two points are in apparent agreement with each other, diffusion modeling suggests that they are unlikely to represent a real spike in atmospheric mixing ratios. A spike in atmospheric levels large enough to cause this excursion should cause adjacent samples above and below to be elevated as well. The elevated data points may result from contamination, either during storage or during extraction and analysis in the laboratory, but there is no independent evidence for contamination of these samples.

An error-weighted linear regression of all the CH$_3$Br data against time yields a slope of $3 \times 10^{-3} \pm 0.003$ ppt yr$^{-1}$, indistinguishable from zero. We recalculated the linear regression omitting the 6 outliers identified above, and the deepest point, which is more than 50 years away from the neighboring data. An error-weighted linear regression of the remaining 16 points yields a statistically significant increasing trend of $0.005 \pm 0.001$ ppt yr$^{-1}$ for samples with mean CH$_3$Br dates ranging from 1717 to 1942 (Figure 3).

Antarctic firm air CH$_3$Br measurements from Siple Dome and South Pole are also shown in Figure 2. The deepest sample from the Siple Dome firn has a CO$_2$ date of 1948, based on a comparison of the measured CO$_2$ mixing ratio with the atmospheric history from the well-dated Law Dome ice core [Etheridge et al., 1996]. This sample has a CH$_3$Br mixing ratio of 6 ppt [Butler et al., 1999]. Similar results were obtained by Sturges et al. [2001] from firm air samples of similar age collected at Dome Concordia and Dronning Maud Land, Antarctica. In agreement with the firm data, the two shallowest ice core samples from this study have 6 ppt CH$_3$Br with mean CH$_3$Br dates corresponding to 1934 and 1942. The mixing ratio of CH$_3$Br is slightly lower at 5.1–5.3 ppt at the bottom of the South Pole firn where the CO$_2$ date is just over 1900 [Butler et al., 1999]. The firm data of Butler et al. [1999] and the trend we observed in the ice core data suggest that CH$_3$Br levels in the atmosphere may have been increasing slowly for about 200 years before the onset of rapid increase during the second half of the twentieth century. The average rate of increase in the ice core data is less than half of that reported by Butler et al. [1999] for the first half of the twentieth century based on the South Pole firn air data.

It should be noted that CH$_3$Br is unstable toward hydrolysis and chloride substitution in aqueous solution [Moelwyn-Hughes, 1938; Elliott and Rowland, 1995; King and Saltzman, 1997] and there is potential for similar chemistry in snow and ice. From these data, we cannot rule out the possibility that CH$_3$Br slowly degrades in firn and ice. Longer ice core records are needed to fully assess this issue.

3. Model Simulations of Preindustrial CH$_3$Br
3.1. Model Description

A numerical model was developed in order to provide a basis for comparison of the ice core results with our current understanding of the atmospheric CH$_3$Br budget. This model simulates the major processes involved in the global biogeochemical cycle of CH$_3$Br, including oceanic production and consumption, soil uptake, terrestrial plant emissions, fumigation, gasoline combustion, biomass burning, atmospheric loss via reaction with OH and photolysis in the stratosphere. The model is time-dependent and is run for several years to obtain “equilibrium” simulations for modern (1995–1998) and preindustrial conditions, assuming various emissions scenarios. In this model, the atmosphere is represented by well-mixed Northern and Southern Hemisphere tropospheric boxes, and transport between them is governed by an interhemispheric exchange.
The rate expression of chemical loss, and a uniform biological degradation was estimated assuming a rate constant of 0.029 yr$^{-1}$ [1997]. A minor additional loss from stratospheric photolysis [2000] with the rate constant from [2003]. This global uptake rate was recalculated on the basis of the adjustment in the atmospheric burden discussed above, giving 41.7 Gg yr$^{-1}$. We apportioned their global soil uptake rate constant between the Northern and Southern Hemispheres using the hemispheric distribution of biomes types given by [1983]. Soil uptake is parameterized in the model as a first-order loss rate constant specified for each hemisphere. Seasonality was modeled after [1995] by assigning “active” and “inactive” months to the various biomes.

The biomass-burning source for the modern atmosphere is based on the $\Delta$CH$_3$Br/$\Delta$CO$_2$ emissions ratios estimated by [1994] and [1996]. The seasonality and hemispheric distributions of biomass-burning emissions are as given by [1998]. The total emissions from fumigation of soils, durables, perishables, and structures and from gasoline combustion are 45.8 Gg yr$^{-1}$ [1999]. The hemispheric distribution and seasonality of these sources in the model is based on government and industry statistics, as given by [1998].

The current best estimate for global plant emissions is about 24 Gg yr$^{-1}$ [2003]. The global rapeseed emissions estimated by [1998] are distributed between the two hemispheres in proportion to the distribution of cultivated land cover from [1983]. The global salt marsh emissions from [2000] are distributed between the hemispheres according to the salt marsh distribution in the International Satellite Land Surface Climatology Project (ISLSCP) [1995; Sellers et al., 1995]. The global shrubland emissions from [2001] are distributed between the hemispheres according to the shrubland distribution of [1983]. The global wetland emissions from [1999a] are distributed between the hemispheres according to the wetland distribution in the ISLSCP. The active season

### Table 1. Various Parameters Specified in the Model for Both Modern and Preindustrial Simulations

<table>
<thead>
<tr>
<th></th>
<th>Southern Hemisphere</th>
<th>Northern Hemisphere</th>
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<tbody>
<tr>
<td><strong>Atmospheric Loss Rate Constants, yr$^{-1}$</strong></td>
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<tr>
<td>OH</td>
<td>0.51</td>
<td>0.60</td>
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<tr>
<td>Soils</td>
<td>0.18</td>
<td>0.44</td>
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<tr>
<td>Stratospheric photolysis</td>
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<td>0.03</td>
</tr>
<tr>
<td>Interhemispheric exchange</td>
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<td>1.00</td>
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<tr>
<td><strong>Oceanic Loss Rate Constants, yr$^{-1}$</strong></td>
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<td></td>
</tr>
<tr>
<td>CH$_3$Br production rate, pm d$^{-1}$</td>
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<td>0.29</td>
</tr>
<tr>
<td>Water column loss rate constant, d$^{-1}$</td>
<td>0.18</td>
<td>0.25</td>
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*Atmospheric terms are based on Montzka et al. [2003], and ocean terms are based on Yvon-Lewis and Butler [1997], with modifications as described in text.
from 240 days in each hemisphere. The global fungus emissions for these terrestrial sources is assumed to be the warmest model simulation of atmospheric CH$_3$Br using Figure 4. The unknown source is adjusted in order to balance the global budget, and to agree with atmospheric observations in both hemispheres in terms of mean levels and seasonality [Cicerone et al., 1988; Wingenter et al., 1998; Montzka et al., 2003a]. Note the marked difference in seasonality between the two hemispheres. The Northern Hemisphere has a seasonal amplitude greater than 1 ppt, with the late summertime minimum and late wintertime maximum expected for a gas whose dominant sink is reaction with OH. The Southern Hemisphere has a much smaller seasonal amplitude. At least in part, this behavior reflects the importance of the oceans in the Southern Hemisphere budget. The Southern Hemisphere oceans vary seasonally from a large net sink during winter to a small net source during summer, offsetting the influence of atmospheric OH. The hemispheric mean annual net fluxes of CH$_3$Br into and out of the atmosphere are shown in Table 2.

Figure 4. Model simulation of atmospheric CH$_3$Br using the “modern” and case 2 “preindustrial” scenarios. For each simulation, the upper and lower solid lines are results for the Northern and Southern Hemispheres, respectively. The dashed lines are the global average results for each simulation.

for these terrestrial sources is assumed to be the warmest 240 days in each hemisphere. The global fungus emissions from Lee-Taylor and Holland [2000] are distributed between the hemispheres according to the tropical forest distribution of Matthews [1983], and the active season for this emission is assumed to be 365 days.

[20] Peatlands and rice paddies [Redeker et al., 2000; Dimmer et al., 2001] are not included as independent sources in this model. These land cover types are classified as wetlands in the ISLSCP land cover databases. When a suitable land cover database is available, reclassifying some of the wetlands as peatlands and rice paddies will result in a small reduction in “known” global emissions.

[21] The model is integrated using an explicit, variable time step, Runge-Kutta algorithm [Bogacki and Shampine, 1989]. The model is integrated for several years, until it reaches an annual steady state.

[22] There is a significant imbalance in the “best estimate” CH$_3$Br budget [Montzka et al., 2003b], with atmospheric losses exceeding the known sources by 37.6 Gg yr$^{-1}$ after adjusting to the 128 Gg atmospheric burden and removing peatland and rice paddy emissions. The magnitude of the unknown source(s) was adjusted in the model to achieve agreement with the mean 1995–1998 tropospheric hemispheric mixing ratios of 10.5 (NH) and 8.2 (SH) ppt and their seasonalities [Montzka et al., 2003a]. This required additional emissions of 18.3 and 19.3 Gg yr$^{-1}$ in the Northern and Southern Hemispheres, respectively. In each hemisphere, the seasonality of this unknown source was adjusted to match the seasonality of the monthly mean mixing ratios. It is likely that at least some of the imbalance between sources and sinks is attributable to emissions from terrestrial plants. To date, only limited emissions surveys from terrestrial plants and ecosystems have been carried out [Gan et al., 1998; Redeker et al., 2000; Rhew et al., 2000, 2001; Varner et al., 1999a; Dimmer et al., 2001; Yokouchi et al., 2002]. The imbalance could also result from underestimating anthropogenic emissions, but this explanation cannot account for the imbalance in the Southern Hemisphere, as demonstrated below using model results.

3.2. Model Results and Discussion

[23] The model described above was used to carry out simulations of atmospheric CH$_3$Br using a “modern” scenario and four “preindustrial” scenarios. The modern case utilizes the best estimate parameterizations for all sources and sinks including the additional unknown source (Figure 4). The unknown source is adjusted in order to balance the global budget, and to agree with atmospheric observations in both hemispheres in terms of mean levels and seasonality [Cicerone et al., 1988; Wingenter et al., 1998; Montzka et al., 2003a]. Note the marked difference in seasonality between the two hemispheres. The Northern Hemisphere has a seasonal amplitude greater than 1 ppt, with the late summertime minimum and late wintertime maximum expected for a gas whose dominant sink is reaction with OH. The Southern Hemisphere has a much smaller seasonal amplitude. At least in part, this behavior reflects the importance of the oceans in the Southern Hemisphere budget. The Southern Hemisphere oceans vary seasonally from a large net sink during winter to a small net source during summer, offsetting the influence of atmospheric OH. The hemispheric mean annual net fluxes of CH$_3$Br into and out of the atmosphere are shown in Table 2.

[24] A “preindustrial” scenario (case 1) was constructed starting from the modern budget and setting the fumigation and gasoline combustion sources to zero. The unknown source needed to balance the modern CH$_3$Br budget is included in this scenario. This scenario yields a preindustrial southern hemisphere CH$_3$Br level of 6.6 ppt, slightly higher than the ice core measurements. Eliminating the current best estimate of anthropogenic emissions is insufficient to explain the preindustrial ice core levels, assuming that all of the unknown source was present in preindustrial times. This result suggests that either these components of the budget underestimate the anthropogenic input while overpredicting natural sources or that some of the natural sources have changed over the past century.

[25] A second preindustrial scenario (case 2) was constructed by (1) eliminating the anthropogenic sources as in case 1 and (2) decreasing global biomass-burning emissions to 25% of their modern value, from 20 to 5 Gg yr$^{-1}$. As above, the unknown source is included in this scenario. This simulation yields a preindustrial southern hemisphere CH$_3$Br level of 5.9 ppt, in close agreement to the ice core measurements. Today, the majority of biomass burning is carried out in the tropics to clear forested land for agricultural use. It seems likely that this burning source would have been significantly lower during preindustrial times. However, to our knowledge, there is no objective basis for estimating preindustrial biomass-burning rates.

[26] A third preindustrial scenario (case 3) was run to illustrate the uncertainty associated with the imbalance in the CH$_3$Br budget. In this case, fumigation and combustion sources in the CH$_3$Br budget are set to zero as in case 1. In addition, we assume that all of the unknown emissions in the Northern Hemisphere, 18.3 Gg yr$^{-1}$, are anthropogenic and remove them from the budget. An additional 1.3 Gg yr$^{-1}$ of
the unidentified emissions in the Southern Hemisphere are also designated as anthropogenic, on the basis of the estimate that 7% of the global anthropogenic emissions are believed to occur in the Southern Hemisphere. This simulation results in a Southern Hemisphere CH$_3$Br level of 5.9 ppt, which is also consistent with the ice core results. This result demonstrates that the ice core data do not a priori preclude a significantly larger anthropogenic contribution to the modern CH$_3$Br budget than assumed in the best estimate budget of Montzka et al. [2003b]. However, this scenario requires that biomass-burning emissions remain constant, and that the remaining 18.0 Gg yr$^{-1}$ flux of unidentified sources occurs only within the Southern Hemisphere.

[27] A fourth preindustrial scenario (case 4) was run to illustrate the sensitivity of southern hemisphere atmospheric CH$_3$Br mixing ratios to the unknown source in that hemisphere. In this case the emissions are the same as in case 3, but we also remove the remaining 18.0 Gg yr$^{-1}$ unknown source from the budget. This scenario gives a Southern Hemisphere CH$_3$Br level of 4.5 ppt, which is below the ice core results. This result demonstrates that there must have been an unidentified southern hemisphere source of CH$_3$Br to the preindustrial atmosphere. This result is consistent with the model results of Reeves [2003] based on the firn air data.

[28] In these simulations, the atmospheric burden of CH$_3$Br does not respond linearly to a change in anthropogenic emissions. For example, in the case 2 and case 3 preindustrial budgets, the total net emissions into the atmosphere are about 71 and 67 Gg yr$^{-1}$. The modern budget contains an additional 61–64 Gg yr$^{-1}$. Therefore one might expect the atmospheric CH$_3$Br burden to have nearly doubled (increase by a factor of 1.9) between preindustrial and modern times. The model response to addition of the anthropogenic sources was an increase of only 3.5 ppt, or a factor of about 1.6. The “missing” anthropogenic CH$_3$Br, about 20 Gg, was taken up by the oceans. For the preindustrial scenarios, the oceans ranged from a small net sink (case 1) to a large net source (cases 2–4). The increasing atmospheric burden caused by anthropogenic emissions caused the oceans to become a large net sink for atmospheric CH$_3$Br. This coupling between the oceans and atmosphere has the effect of stabilizing the atmosphere against increases caused by terrestrial or anthropogenic emissions, as described by Butler [1994].

[29] In these scenarios we have not addressed the possibility of preindustrial/industrial changes in atmospheric CH$_3$Br lifetime resulting from changes in atmospheric OH. Although there is little consensus as to the magnitude (or even the sign) of such changes, model calculations suggest that tropospheric OH has changed by less than 20% during the industrial era. Wang and Jacob [1998] argued that the effect of such changes on the atmospheric lifetimes of most gases is negligible. In their model, decreasing global mean OH during the past century was offset by increasing OH levels in the warmer lower troposphere, where most oxidation of CH$_3$Br occurs. This effect is further reduced because OH is only responsible for roughly half of the total atmospheric loss of CH$_3$Br, i.e., a change of 10% in the partial lifetime of CH$_3$Br with respect to OH, would cause a change of about 6% in the total lifetime of CH$_3$Br or in its atmospheric levels.

### 4. Implications

[30] Together, the ice core and firn air measurements and the model simulations provide a reasonably consistent picture of how anthropogenic activities have modified the atmospheric CH$_3$Br burden during the past century. Over that time, the global atmospheric burden appears to have increased by 3.5 ppt, or roughly 50% of the preindustrial level. The major uncertainty in the modern atmospheric budget of CH$_3$Br remains the fact that the known sinks exceed the known sources. It is important to determine whether the unidentified CH$_3$Br sources are anthropogenic or natural. We can state conclusively that not all of the unidentified emissions can be treated as anthropogenic. If all of the 37.6 Gg yr$^{-1}$ of unknown emissions in the modern budget were treated as anthropogenic, the preindustrial scenario would give a Southern Hemisphere atmospheric level of about 4.5 ppt (Table 2), well below the ice core measurements.

[31] The model simulations show that the ice core data alone is insufficient to determine whether the unidentified
source was present in the preindustrial northern hemispheric budget or not. The model does clearly show that a large unidentified source is needed in the preindustrial Southern Hemisphere. The limitations on our ability to constrain the preindustrial atmospheric CH$_3$Br budget stem largely from the fact that ice core data are available for the Southern Hemisphere only, and the lack of an objective basis on which to assign preindustrial biomass-burning emissions.

[32] The analysis presented here implicitly assumes that the natural components of the budget remained constant. This assumption may not necessarily be justified. It is also possible that human activities, particularly land use practices, may alter emissions from terrestrial vegetation in ways that are not accounted for in the budget. It seems likely that variations in climatic conditions would have a marked impact on plant emissions, soil uptake, and oceanic production. Longer ice core records including periods of major climate change may reveal the impact of climate variability on the CH$_3$Br budget.

[33] Acknowledgments. We wish to thank Jim Butler, Steve Montzka, Rob Rhew, Ryszard Tokarczyk, Mark Battle, Michael Bender, and Michael Prather for helpful discussions. We also wish to thank Ken Taylor, Mark Twickler, and the staff of the WAISCORES project and NICL. This research was supported by the Office of Polar Programs and the Chemical Oceanography Programs at the National Science Foundation.

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