2,000-year record of atmospheric methyl bromide from a South Pole ice core

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This study reports measurements of methyl bromide (CH\textsubscript{3}Br) in air bubbles from a South Pole ice core, with gas ages covering the past two millennia. The air was extracted by mechanical shredding of the core under vacuum and the evolved gases were analyzed by gas chromatography with high resolution mass spectrometry and isotope dilution. These samples had estimated mean gas ages ranging from 160 BCE to 1860 CE. The mean CH\textsubscript{3}Br mixing ratio in the ice core samples was 5.39 ± 0.06 ppt (i.e., n = 113). The CH\textsubscript{3}Br measurements from this core agree with those from a Siple Dome ice core for mean gas ages between 1671 and 1860 CE, where there is overlap between the cores. The data show no linear trend over the 2000 year period prior to industrialization. Together, Antarctic ice core and firm air measurements clearly demonstrate that the increase in atmospheric CH\textsubscript{3}Br during the twentieth century exceeds natural variability during the past 2000 years. There is evidence of centennial-scale variability in CH\textsubscript{3}Br on the order of ±10–20% that may indicate a natural climate sensitivity of the atmospheric levels of this ozone depleting substance. The analysis of CH\textsubscript{3}Br in additional Antarctic ice cores will be needed to confirm that the centennial-scale variability observed in this core represents a southern hemisphere atmospheric history.

1. Introduction

Methyl bromide, CH\textsubscript{3}Br, is present in the modern troposphere at a global mean mixing ratio of about 8 parts per trillion, and has an atmospheric lifetime of about 0.7 years [Montzka et al., 2003b]. CH\textsubscript{3}Br is of considerable environmental importance as an ozone depleting substance, contributing an estimated 50% of the stratospheric bromine burden [Pfeilsticker et al., 2000]. The principle anthropogenic use of CH\textsubscript{3}Br is as a fumigant for agricultural soils, and for durable goods, produce, and structures. In 1998, phase-out of CH\textsubscript{3}Br production began under the Montreal Protocol and its Amendments. Since that time, the atmospheric abundance of CH\textsubscript{3}Br has decreased by several parts per trillion [Yokouchi et al., 2002; Montzka et al., 2003a, 2003b].

The natural biogeochemical cycle of CH\textsubscript{3}Br is complex, with emissions from both oceanic and terrestrial ecosystems, and from biomass burning. Removal from the atmosphere occurs primarily via reaction with OH, uptake by the oceans and by soils. As noted in several reviews, there remains considerable uncertainty in the atmospheric budget of CH\textsubscript{3}Br [Clerbaux et al., 2006; Kurylo et al., 1999; Montzka et al., 2003a]. For example, a best estimate “bottom-up” inventory of the 1996 atmospheric CH\textsubscript{3}Br budget yielded total sources of 141 Gg, and total sinks of 173 Gg [Montzka et al., 2003a]. This imbalance reflects uncertainty in the magnitude of both natural sources and anthropogenic emissions. Terrestrial plant emissions probably represent the most uncertain term in the global budget, because relatively few plant species or biomes have been studied to date, and because of the challenges associated with differentiating between net and gross fluxes [Rhew et al., 2003; Varner et al., 2003; Redeker et al., 2004; White et al., 2005].

Several studies have used air trapped in polar firm and ice to determine preindustrial atmospheric levels of CH\textsubscript{3}Br and to reconstruct its atmospheric history. Antarctic firm air from South Pole, Siple Dome, and Law Dome yielded early twentieth century levels of roughly 5–6 ppt in reasonable agreement with the known pattern of CH\textsubscript{3}Br production and usage [Butler et al., 1999; Reeves, 2003; Trudinger et al., 2004]. To date, only one study of CH\textsubscript{3}Br from an Antarctic ice core has been published [Saltzman et al., 2004]. CH\textsubscript{3}Br in air extracted from bubbles in a Siple Dome ice core covering the years 1671–1942 CE yielded a mean level of 5–6 ppt, in good agreement with the content of basal firm air at South Pole.

The Antarctic ice and firm air results contrast markedly with results from Greenland. Firm air at both Summit and Tunu exhibit evidence of subsurface CH\textsubscript{3}Br production [Sturges et al., 2001; Swanson et al., 2002]. Elevated levels of CH\textsubscript{3}Br were also observed in GISP2 ice core samples from Summit, demonstrating that CH\textsubscript{3}Br-enriched firm air is incorporated into the ice [Aydin et al., 2007]. Interestingly,
CH$_3$Br in Summit ice does not appear to increase down core, suggesting that production of CH$_3$Br occurs prior to close-off.

[6] In this study, we report measurements of CH$_3$Br from a South Pole ice core, covering the past two millennia. Gas samples from the uppermost portion of this core overlap in time with the Siple Dome ice core measurements, and greatly extend the time span of preindustrial CH$_3$Br measurements. Together with firm air measurement, the two records provide a stronger basis for assessing the natural variability of CH$_3$Br and the magnitude of the anthropogenic impact.

2. Methods

2.1. Drilling Site and Ice Core Characteristics

[7] The South Pole ice core used in this study was drilled in 2002 as part of the International Trans-Antarctic Scientific Expedition project [ITASE, 1990]. The 10 cm diameter ice core was dry-drilled to a depth of 295 m. The core was located at 89.93°S, 144.39°W, at the South Pole Remote Earth Science and Seismic Observatory (SPRESSO). For this study, 112 samples were analyzed, at depth intervals of 1 m. The samples analyzed were longitudinal 1/2 core sections, approximately 15 cm in length, and ranging in mass from 400–600 g.

2.2. Ice Core Gas Dating

[8] The age of air in the ice core bubbles was estimated by determining the age of the enclosing ice, then applying an ice age/gas age difference. Ice ages for the SPRESSO core were based on visual layer counting to a depth of 208 m (D. Meese and T. Gow, personal communication), and linear extrapolation below that depth. The resulting age/depth curve suggests a mean ice accumulation rate of 8.3 cm/a (D. Meese and T. Gow, personal communication), and linear extrapolation below that depth. The resulting age/depth curve suggests a mean ice accumulation rate of 8.3 cm/a from 208 to 295 m (D. Meese and T. Gow, personal communication), and linear extrapolation below that depth. The resulting age/depth curve suggests a mean ice accumulation rate of 8.3 cm/a from 208 to 295 m (D. Meese and T. Gow, personal communication), and linear extrapolation below that depth.

2.3. Ice Core Gas Extraction

[11] A dry extraction technique was used to sample the air bubbles in the ice core samples [Aydin et al., 2007]. This was done by mechanically shedding the ice core sample across a stainless steel grater in a stainless steel vacuum chamber. Prior to use, the chamber was heated overnight to 120°C and repeatedly humidified and evacuated. Ice core samples were mechanically scraped to remove several mm of surface ice before being sealed in the chamber. The ice and chamber were repeatedly evacuated and flushed with clean N$_2$, then precooled to -50°C. The chamber was maintained at this temperature during extraction. After final pumping, the sample was shredded for approximately 15 min, and the evolved air was cryogenically condensed into a stainless steel tube immersed in liquid helium (4 K) for subsequent analysis. N$_2$ “blanks” were collected from the chamber before and after the sample was shredded, as discussed below.

2.4. Gas Analysis

[12] Ice core gas samples were analyzed by gas chromatography with high resolution mass spectrometric analysis and quantification was based on isotope-labeled internal standards [Aydin et al., 2007]. The analytical instrumentation and techniques are different from those used for our earlier ice core Siple Dome CH$_3$Br measurements [Saltzman et al., 2004], and have significantly reduced the analytical uncertainties. The ice core gas sample was allowed to flow through a stainless steel u-trap containing glass beads, immersed in liquid nitrogen. During this process, the non-condensable gases were expanded into an evacuated 300 cm$^3$ calibrated volume held at constant temperature. The sample size was determined by measuring the pressure increase in the calibrated volume. An aliquot of internal standard containing CD$_3$Br was added to the u-trap containing the ice core sample, using the same procedure. This gas standard typically consisted of 30 cm$^3$ of 80 ppt CD$_3$Br in humidified N$_2$. The combined sample and standard was thermally transferred into a He carrier stream into a liquid nitrogen-cooled 0.32 mm ID fused silica trap, and thermally injected onto the gas chromatographic column.

[13] Chromatographic separation was carried out on a DB-1 column, thermally programmed from -50 to 120°C. CH$_3$Br and CD$_3$Br were monitored at m/z 93.94 and 96.96, respectively, using an Autospec dual focusing mass spectrometer (Waters, Bedford MA) in electron impact ionization mode. The instrument was tuned to a resolution (m/∆m at 5% peak height) of approximately 6000. At this resolution, the mass deficit of bromine causes the CH$_3$Br peaks to be completely separated from isobaric hydrocarbons. To provide a “lock mass” for mass calibration of the instrument, deuterated dodecane was bled continuously into the ion source.

2.5. Standardization

[14] The calibration of CH$_3$Br in this study was ultimately based on primary gas standards containing 10 ppb CH$_3$Br.
These are prepared in our laboratory in high pressure aluminum cylinders by volumetric addition of pure CH$_3$Br to a gravimetrically determined amount of N$_2$. The ppb-level standards are diluted into humidified, electropolished canisters to generate ppt-level working standards. The CD$_3$Br internal standards are prepared in the same manner. The isotope-labeled standards are regularly calibrated against freshly prepared unlabeled working standards. Several cylinders in our laboratory with unlabeled CH$_3$Br standards are periodically monitored and the calibration scale used in this laboratory is periodically intercompared with standards used by NOAA GMD.

2.6. Extraction Blanks

A critical aspect of the analysis is the estimation of the procedural “blank” associated with contact between the gas sample and 1) the stainless steel surfaces of the extraction chamber, 2) the ice core and snow surfaces, and 3) the tubing and valves used to handle the gas sample during the extraction and analysis. Pre- and post-extraction blanks were obtained by adding a volume of clean N$_2$, roughly equivalent to the air content of the sample, to the chamber containing the ice core sample. The N$_2$ is collected and analyzed in the same manner as the air extracted from the ice core sample. The average of pre- and post-extraction blanks is assumed to apply to the ice core sample. The magnitude of the blanks appears to be related to how recently the extraction chamber was baked out prior to use, and to the rigor of the chamber bake-out procedures. The ratio of signal to blank for these samples ranged from 7 to 70.

2.7. Uncertainty Analysis

The total uncertainty in an ice core CH$_3$Br analysis is estimated by propagating the individual uncertainties derived from the precision of the calibration runs and the variability of the ice core N$_2$ blanks. For the measurements reported in this study, the mean overall relative uncertainty (reported as 1σ) was 15 ± 7%, calculated as the square root of the sum of the squares of the calibration and N$_2$ blank uncertainties. The magnitude of the uncertainty is highly dependent on the ice core sample size.

No correction was made for possible loss of analyte to the chamber or ice/snow surfaces during extraction. Experiments were carried out in which air and gas standards with known CH$_3$Br mixing ratios (8–40 ppt) were added to the chamber with no ice, intact ice core sample, and shredded ice core sample, then extracted and analyzed. No loss of CH$_3$Br was detectable in these experiments, within the uncertainty of the analysis.

2.8. Quality Control Criteria

Samples with CFC-12 levels greater than 5 ppt or CH$_3$Br blanks greater than 20% of the ice core signal were eliminated from the data set. These criteria eliminated 10 measurements. The cut-off limit of 5 ppt is roughly twice the CFC-12 detection limit for the smallest samples. Most of the samples rejected on the basis of CFC-12 were from the shallowest section of the core (<133 m). This likely reflects the existence of a small amount of open porosity near the close-off depth, which closes during storage, trapping modern air.

3. Results and Discussion

CH$_3$Br measurements from the South Pole ice core samples are shown as a function of mean gas age in Figure 1. Of the 116 samples, three outliers were identified as lying outside ±2σ from the overall mean. These outliers most likely reflect artifacts, such as undetected cracks in the ice or contamination during storage and handling. There was no objective reason to discard these points based on our quality control criteria of elevated CFC-12 or analytical blanks. The remaining data gave a mean of 5.48 ± 0.076 ppt (1σ). These outliers most likely reflect artifacts, such as undetected cracks in the ice or contamination during storage and handling. There was no objective reason to discard these points based on our quality control criteria of elevated CFC-12 or analytical blanks. The remaining data gave a mean of 5.39 ± 0.06 ppt (1σ, n = 113). For most of the data points, there is overlap between the CH$_3$Br levels in adjacent samples, within the measurement uncertainty. This is expected, given the broad age distribution at South Pole, and the close spacing of the samples in terms of mean age.

There is no linear trend with age in the CH$_3$Br data set. A linear regression of the CH$_3$Br measurements weighted by analytical uncertainty against mean gas age yields a slope of 0.008 ± 0.007 ppt per 100 years which is not statistically different from zero. One robust conclusion from this result is that there is no evidence in the data for
The lack of linear trend in CH$_3$Br is notably different from that of CH$_3$Cl. CH$_3$Br is much more susceptible than CH$_3$Cl to biological uptake rates. The lack of trend in CH$_3$Br also argues against the CH$_3$Cl trend being due to changes in atmospheric OH or biomass burning.

Figure 2 shows the variations in CH$_3$Br and CH$_3$Cl, along with the multiproxy Northern Hemisphere climate record of Moberg et al. [2005]. Both trace gas records exhibit minima centered around the years 500, 800, and 1700 CE. These records suggest that the cool period of the Little Ice Age (~1400–1800 AD) was associated with lower levels of atmospheric methyl halides relative to the Late Holocene means for these gases. The behavior of the two gases is strikingly different around the warm period known as the Medieval Climate Anomaly (~800–1200 AD). CH$_3$Cl exhibits a strong and sustained maximum, apparently lagging the onset of warming record by about 75 years. At the CH$_3$Cl maximum (1180 AD), CH$_3$Br has a strong minimum. By about 1220 AD, the two reverse, with CH$_3$Br reaching its maximum of 7.2 ppt for the preindustrial record before decreasing into the Little Ice Age. Because these two gas records were measured on the same ice core, their dating relative to each other is quite precise, limited largely by the width of the gas age distributions. There are larger uncertainties associated with the relative dating of the ice core data and the multiproxy climate record, which have unrelated chronologies.

The fact that CH$_3$Br exhibits greater short-term variability than CH$_3$Cl (on a relative basis), is likely due in part to differences in analytical precision. The mixing ratio of CH$_3$Cl in this ice core is approximately 80-fold larger than that of CH$_3$Br. However, the CH$_3$Br deviations are consistently larger than those of CH$_3$Cl even where numerous measurements confirm extreme values, such as during the Little Ice Age minimum. The different patterns of variability of the two gases are surprising, given that they share most of the major budget terms in their biogeochemical cycles. As in the case of the long term trend discussed above, these differences seem to rule out simple explanations for the variability such as changes in atmospheric OH levels or biomass burning.

Figure 3 is a compilation of the data from this study and previously published measurements of CH$_3$Br from South Pole and Siple Dome ice cores and firn air archives, and from Law Dome firn air [Butler et al., 1999; Saltzman et al., 2004; Trudinger et al., 2004]. There is some temporal overlap between the mean gas ages of the uppermost
Siple Dome, West Antarctica

Conclusions

measurements on a Siple Dome ice core

Comparison of South Pole (SPRESSO) ice core

Figure 3. Comparison of South Pole (SPRESSO) ice core

CH3Br measurements and previously published data from

Siple Dome, West Antarctica [Saltzman et al., 2004].

SPRESSO samples and those of the earlier published

measurements on a Siple Dome ice core [Saltzman et al.,

2004]. For mean gas ages between 1671 and 1860 AD, the

SPRESSO and Siple Dome ice cores are in reasonable

agreement, with mean CH3Br levels from the two cores of

5.46 ± 0.83 and 5.61 ± 1.60 ppt, respectively. The scatter in

the SPRESSO data set is clearly smaller than that in the

older Siple Dome data. This probably reflects a combination

of improved analytical instrumentation and procedures, and

perhaps differences in ice core quality.

4. Conclusions

[25] The CH3Br measurements on this South Pole ice
core are generally consistent with Siple Dome ice core
measurements, and with firm air measurements from South
Pole and other Antarctic sites, lending support to the idea
that the Antarctic ice core archive preserves a record of
paleoatmospheric CH3Br. The South Pole CH3Br record
shows no evidence of a trend over the past 2,000 years and
exhibits less variability than the much shorter Siple Dome
ice core record. This is due in part to improved analytical
precision resulting from the use of more sensitive analytical
instruments, isotope dilution, and improved sample
processing techniques. The South Pole results suggest that
centennial-scale variations in atmospheric CH3Br over the
past two millennia, excluding the past century, was on the
order of ±10-20% (Figure 2). The centennial-scale variability
in the South Pole record is not likely to be due entirely to
analytical uncertainty, and both CH3Br and CH3Cl appear to
exhibit climate-related variability. We do not consider it yet
proven that the relatively small variations in either CH3Br or
CH3Cl represent atmospheric signals. This will require
measurements on additional ice cores covering the same
time period, and demonstration of a consistent temporal
pattern of variability.

[26] These ice core results establish a millennial time-
scale baseline for comparison with the variations in atmo-
spheric CH3Br during the past century. It is clear that man’s
influence on the atmospheric CH3Br burden during the last
century far exceeded natural variability during the past two
millennia. The difference in CH3Br levels in the modern
atmosphere and those prior to industrialization are generally
consistent with current best estimates for the anthropogenic
contribution to the atmospheric CH3Br budget. However,
there remains a significant imbalance in our inventories of
CH3Br sources and sinks. Balancing the modern CH3Br
budget using the best estimates for all the known sources and
sinks requires invoking a “missing source”, which is
thought to be related to emissions from terrestrial ecosys-
tems and which is roughly comparable in the northern and
southern hemispheres [Saltzman et al., 2004]. The “missing
source”, or at least the southern hemispheric portion of it, is
needed in order to maintain preindustrial mean levels of
5.5 ppt, assuming that the other natural budget terms remain
unchanged [Butler et al., 1999; Reeves, 2003; Saltzman et
al., 2004].

[27] There are several surprising aspects to this study.
First is the simple fact that there appears to be an ice core
record of atmospheric CH3Br at all, given the extremely low
mixing ratio of this gas and its susceptibility to nucleophilic
substitution reactions and hydrolysis. Second, atmospheric
CH3Br levels varied over a rather narrow range over the
past two thousand years during a period in which human
population and land use underwent major changes. Although
historical and proxy climate records show detectable cen-
tennial scale climate variability over this period, climate was
rather stable by comparison with glacial and earlier Holo-
cene variability. The modest variability in the CH3Br ice
core record likely indicate that the major terms in the CH3Br
budget (oceanic production and consumption, terrestrial
emissions, biomass burning, atmospheric OH, and soil
uptake) remained relatively constant over this period. Or,
it may indicate that the various CH3Br sources and sinks
varied in such a way that their changes offset one another,
leading to an apparently stable atmospheric CH3Br level.
Finally, differences in behavior between CH3Br and CH3Cl
in this ice core are unexpected, and highlight the need for a
better understanding of their biogeochemical budgets. Future
measurements covering a wider range of climatic conditions
may provide some insight into the extent of atmospheric
variability, and mechanisms controlling it.

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