A 2000 year atmospheric history of methyl chloride from a South Pole ice core: Evidence for climate-controlled variability

Margaret B. Williams,[1,2] Murat Aydin,[1] Cheryl Tatum,[1] and Eric S. Saltzman[1]

[1] Methyl chloride (CH_3Cl) is a naturally occurring ozone-depleting gas with a complex biogeochemical cycle involving tropical vegetation, soils, biomass burning and the oceans. This study presents CH_3Cl measurements in air extracted from a 300 m ice core from South Pole, Antarctica, covering the time period from 160 BC to 1860 AD. The data exhibit an increasing trend of 3 ppt (parts per trillion) over 100 years and higher frequency variations that appear to be climate-related. CH_3Cl levels were elevated from 900–1300 AD by about 50 ppt relative to the previous 1000 years, coincident with the warm Medieval Climate Anomaly (MCA). CH_3Cl levels decreased to a minimum during the Little Ice Age cooling (1650–1800 AD), before rising again to the modern atmospheric level of 550 ppt. These variations most likely reflect changes in tropical and subtropical conditions, and raise the possibility that a warmer future climate may result in higher tropospheric CH_3Cl levels. **Citation:** Williams, M. B., M. Aydin, C. Tatum, and E. S. Saltzman (2007), A 2000 year atmospheric history of methyl chloride from a South Pole ice core: Evidence for climate-controlled variability, *Geophys. Res. Lett.*, *34*, L07811, doi:10.1029/2006GL029142.

1. Introduction

[2] Methyl chloride (CH_3Cl) is the largest natural source of chlorine to the stratosphere and the most abundant halocarbon in the troposphere, with a global average mixing ratio of 550 ± 30 parts per trillion (ppt) [*Montzka et al.*, 2003]. Major sources of methyl chloride to the troposphere are biomass burning [*Lobert et al.*, 1999], oceanic emissions [*Khalil and Rasmussen*, 1999], direct emissions from vegetation [*Yokouchi et al.*, 2002] and indirect vegetative emissions from decaying leaf litter [*Hamilton et al.*, 2003; *Keppler et al.*, 2000]. The major sinks of atmospheric CH_3Cl are reaction with OH, microbial degradation in soils, and uptake by the oceans, giving an average atmospheric lifetime of 1.0–1.3 years [*Khalil and Rasmussen*, 1999; *Tokarczyk et al.*, 2003].

[3] CH_3Cl has been measured in Antarctic firn air (Siple Dome, South Pole, Law Dome, Dronning Maud Land) [*Aydin et al.*, 2004; *Butler et al.*, 1999; *Kaspers et al.*, 2004; *Trudinger et al.*, 2004]. These data suggest that CH_3Cl levels in the atmosphere increased by about 10% over the past century. This increase was initially interpreted as a result of anthropogenic emissions. Measurements of CH_3Cl in a shallow ice core from Siple Dome, Antarctica covering the past 300 years suggest that the twentieth century increase was part of a more complex, preexisting pattern of variability [*Aydin et al.*, 2004]. Limited measurements of CH3C1 in Deep ice from Dome Fuji, Antarctica [*Saito et al.*, 2007] imply that atmospheric levels were relatively constant throughout the Holocene. The firn air and ice measurements published to date suggest that the Antarctic ice archive contains a record of atmospheric CH_3Cl that is not severely overprinted by local effects or in situ production and loss.

[4] In this study we present CH_3Cl mixing ratios measured in air extracted from 112 samples from a shallow South Pole (SPRESSO) ice core drilled during the ITASE expedition (http://www2.umaine.edu/itase/index.html) (Figure 1). Details of sample collection, dating and analysis can be found in the auxiliary material[1]. The samples cover a 2000 year range in mean gas age from 160 BC to 1860 AD, greatly extending the atmospheric history for CH_3Cl. Methodology is similar to that described previously for trace gas measurements from the Siple Dome ice core [*Aydin et al.*, 2002, 2004; *Saltzman et al.*, 2004].

2. Results

[5] The range of CH_3Cl mixing ratios for the SPRESSO dataset is 408–533 ppt, and the mean is 463 ± 24 ppt (1σ, n = 112). The mean analytical uncertainty of the ice core measurements is 13 ± 4 ppt, or about 3%. Air trapped in a South Pole ice core sample represents a mixture of ages encompassing several decades, because of the diffusion of air in the firn column prior to lock-in [*Battle et al.*, 1996; *Butler et al.*, 1999]. For this study, the ice core was sampled at roughly 1 meter intervals, corresponding to 12–15 years in mean gas age. Thus, air extracted from adjacent samples should have significant age overlap. In a few instances the differences in CH_3Cl mixing ratio between adjacent samples exceed the analytical uncertainty, suggesting that these samples may have been contaminated or altered by in situ production/loss. These include the three lowest and two highest mixing ratios measured at 950, 1400, 1775, 550 and 1850 AD (Figures 1 and 2). While there is no objective reason to discard these data, they would require extreme and rapid changes in atmospheric composition that are not realistic.

[6] Between 1700 and 1860 AD, the South Pole (SPRESSO) record overlaps with previous measurements on a shallow Siple Dome (SDMC) ice core [*Aydin et al.*, 2004]. The two records were measured in the same labora-

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[1]Department of Earth System Science, Croul Hall, University of California, Irvine, California, USA.

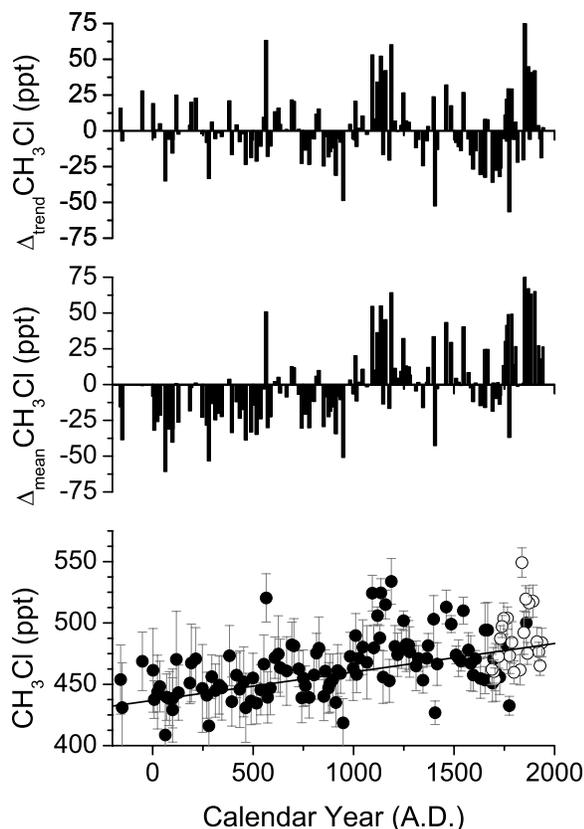[2]Now at Atmospheric Chemistry and Dynamics Branch, NASA-Ames Research Center, Moffett Field, California, USA.

Figure 1. CH_3Cl mixing ratios (parts per trillion, ppt) in air extracted from Antarctic ice cores, plotted against gas age in calendar years AD. Lower–South Pole (SPRESSO) ice core (solid circles; this study;), Siple Dome, West Antarctica (SDMC) ice core (open circles) [*Aydin et al.*, 2004] The linear regression line through the combined dataset has a slope of 0.027 ppt/yr and an intercept of 442 ppt. Middle-CH_3Cl anomaly ($\Delta_{mean}CH_3Cl$) calculated as a deviation from the mean ice core CH_3Cl values. Upper-CH_3Cl anomaly ($\Delta_{trend}CH_3Cl$) calculated as a deviation from the linear regression of the ice core data.

tory, with the same calibration scale. There is good agreement between the two data sets during the period of overlap (4 data points with mean gas ages within 4 years differ by 3% or less). For the remainder of this paper we discuss the combined data set from the two ice cores.

[7] The ice core CH_3Cl measurements exhibit a positive trend over the past 2000 years, with a linear regression slope of 3 ppt/100 years (Figure 1, lower). This trend could be either a secular increasing trend, reflecting environmental variability on time scales longer than this record, or a slow in situ loss of CH_3Cl due to chemical reactions occurring in the ice. Determining the cause of this trend will require longer CH_3Cl records recovered from multiple sites. We have recently obtained preliminary data from a deep ice core at Siple Dome, West Antarctica (unpublished data) covering a time scale of tens of thousands of years. These data do not exhibit a monotonic decrease with depth, suggesting that downcore chemical loss is not the cause of the linear trend.

[8] Centennial scale variations are superimposed on the long-term trend. This is evident when the data are plotted as

a deviation from the trend, referred to as $\Delta_{trend}CH_3Cl$ (Figure 2, upper). A striking feature in $\Delta_{trend}CH_3Cl$ is the increase around 950 AD, to a maximum of +60 ppt near 1200 AD. $\Delta_{trend}CH_3Cl$ remained elevated until about 1300 AD, at which point it began to decline to its minimum of about −35 ppt in 1690 AD. Atmospheric CH_3Cl remained low for the period 1500–1750. Beginning in the mid 18th century, $\Delta_{trend}CH_3Cl$ increased again, reaching values of +40 ppt in the early 20th century, comparable to those around 1200 AD. Similar features are apparent when the data are plotted as a deviation from the mean CH_3Cl mixing ratio of the entire record (Figure 1, middle).

[9] The variability in $\Delta_{trend}CH_3Cl$ during the past two millennia has strong similarities to the historical climate record, as evidenced from various climate proxies. This is illustrated by comparison to the multi-proxy temperature reconstruction of *Moberg et al.* [2005] (Figure 2, lower). The maximum in $\Delta_{trend}CH_3Cl$ around 950–1250 AD coincides with the Medieval Climate Anomaly or MCA [*Stine*, 1994], a period of high global mean temperatures as evidenced by elevated borehole temperatures and retreating alpine glaciers in both hemispheres [*Broecker*, 2001; *Dahl-Jensen et al.*, 1998; *Grove and Switsur*, 1994]. The $\Delta_{trend}CH_3Cl$ minimum in the 16th, 17th and early 18th centuries is contemporaneous with the Little Ice Age (LIA), a period of unusually cold climate recorded by numerous climate proxies [*Bradley and Jones*, 1992; *Grove*, 1988]. By contrast, Antarctic temperature variations inferred from the δO^{18} of ice, do not exhibit strong climate variations in phase with the MCA and LIA [*Masson et al.*,
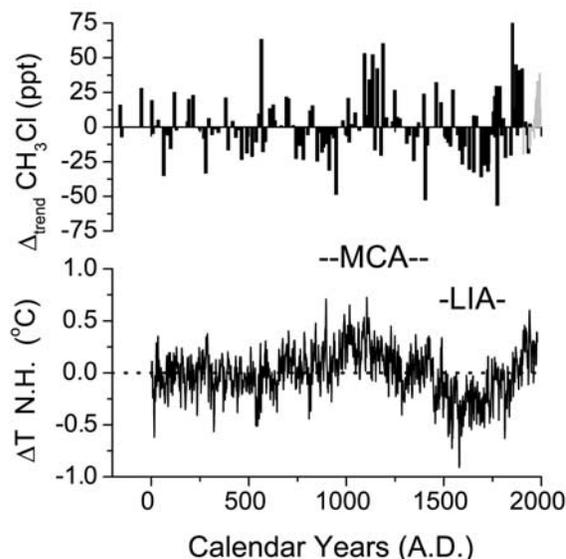

Figure 2. Comparison of CH_3Cl anomaly ($\Delta_{trend}CH_3Cl$) with the multi-proxy northern hemisphere temperature reconstruction of *Moberg et al.* [2005]. Lower-Northern hemisphere temperature is plotted as a deviation from the mean of the 2000 year record. Upper-Black bars are $\Delta_{trend}CH_3Cl$ for the combined ice core datasets from Siple Dome (SDMC) and South Pole (SPRESSO) covering the period 160 BC–1940 AD. Gray bars are $\Delta_{trend}CH_3Cl$ for the combined firn air datasets of *Aydin et al.* [2004], *Butler et al.* [1999], and *Trudinger et al.* [2004], covering the period 1930–1997 AD.

2000]. Hence, it appears that the ice core record of CH_3Cl is a global atmospheric signal, rather than an artifact related to variability in local Antarctic temperatures or snow accumulation at South Pole. There appears to be a time lag on the order of 100 years between the peaks of the MCA and LIA and those of the CH_3Cl record. While these offsets may be real, reflecting the time constants of terrestrial or oceanic climate responses, they may also reflect uncertainty in the time averaging and dating of these records.

[10] The youngest sample in the combined SDMC and SPRESSO ice core datasets is at 1942 AD. Antarctic firn air measurements extend the CH_3Cl record to cover the last 100 years. Combining the ice core data with firn air measurements from South Pole, Siple Dome, and Law Dome (Figure 2, upper, gray bars), demonstrates a post-LIA increase in $\Delta_{trend}CH_3Cl$ with a complex pattern. From the late 17th century to the 20th century, $\Delta_{trend}CH_3Cl$ exhibits three distinct maxima, suggesting variability with a period of roughly 110 years [*Aydin et al.*, 2004]. This variability suggests that industrialization was not the major factor responsible for changes in the CH_3Cl budget during this period. This is consistent with current best emissions estimates indicating that anthropogenic (coal burning, incineration, rice agriculture) sources of CH_3Cl are roughly 4% of the total budget, or about 20 ppt of the current atmospheric burden [*Montzka et al.*, 2003]. The magnitude of $\Delta_{trend}CH_3Cl$ during the last 60 years is comparable to that during the MCA, when presumably anthropogenic sources represented a smaller percentage of the budget. At least some of the post-LIA increase in CH_3Cl levels may be associated with the general warming trend during this period [*Mann and Jones*, 2003], but the complexity of the CH_3Cl record suggests that it was not the only cause.

3. Discussion

[11] The ice core record shows a nearly 20% change in atmospheric CH_3Cl levels between the MCA maximum and LIA minimum. Today, more than 90% of the CH_3Cl sources and the majority of CH_3Cl sinks lie between 30°N and 30°S [*Khalil and Rasmussen*, 1999; *Yoshida et al.*, 2004]. Therefore, it is likely that climate-controlled variability in CH_3Cl reflects changes in tropical and subtropical conditions and the geographic extent of these biomes. The magnitude of the total atmospheric budget of CH_3Cl is reasonably well constrained to be about 4000 Gg/yr, based on the OH, soil, and ocean sinks. For many years, the inventory of known CH_3Cl sources accounted for only about 75% of the total budget [*Montzka et al.*, 2003]. Recent work suggests that emission from dead or living tropical vegetation may be sufficient to account for the apparent budget imbalance [*Yokouchi et al.*, 2002]. [*Hamilton et al.*, 2003] Climate-driven changes in any one or more of the major CH_3Cl sink or source terms can easily explain the observed variability in the ice core record of CH_3Cl. In reality, the terms in the global CH_3Cl budget are potentially all linked to climate variability and thus, do not vary in isolation from each other.

[12] Terrestrial CH_3Cl sources are likely to be sensitive to variations in the hydrological cycle associated with climate change. Proxy records show that tropical and subtropical regions experienced significant, but regionally diverse changes in precipitation associated with MCA and LIA

[*Cobb et al.*, 2003; *Fleitmann et al.*, 2003; *Hassan*, 1981; *Hodell et al.*, 1995; *Johnson et al.*, 2002; *Jones et al.*, 2006; *Rodbell et al.*, 1999; *Thompson et al.*, 2005; *Verschuren et al.*, 2000; *Wang et al.*, 2005]. These changes were associated with migration of the Intertropical Convergence Zone, changes in ENSO patterns, and changes in the strength of the Asian and Indian Ocean monsoons.

[13] Greenhouse experiments by *Yokouchi et al.* [2002] indicate large emission rates of CH_3Cl from certain tropical tree and fern species. Extrapolated emission rates from three species in the family Dipterocarpaceae in Southeast Asia alone are large enough to account for 23% of the total CH_3Cl sink strength (assuming 4005 Tg/yr total sinks [*Montzka et al.*, 2003]) suggesting that modest changes in emissions from tropical plants could produce variability of the magnitude observed in the ice core CH_3Cl record.

[14] Abiotic methylation of pectin in senescent or dead plant material has also been suggested as a major CH_3Cl source [*Hamilton et al.*, 2003]. This source would be highly sensitive to plant speciation, as well as soil moisture, with enhanced CH_3Cl production during dry conditions. Limited laboratory studies of CH_3Cl production via abiotic methylation show a positive temperature-dependence [*Hamilton et al.*, 2003] large enough to potentially account for the range of variability in the ice core CH_3Cl record. However, to date, such experiments have been carried out only with a few temperate plant species.

[15] It has been speculated that biomass burning rates declined during the past 1000 years, possibly as a result of a transition from warmer and drier conditions during the MCA to cooler and wetter conditions during the LIA [*Ferretti et al.*, 2005; *Savarino and Legrand*, 1998; *Swetnam*, 1993; *Verschuren et al.*, 2000]. *Ferretti et al.* [2005] inferred a 40% decline in burning emissions from 1000–1700 AD on the basis of $\delta^{13}CH_4$ and CO measurements in Antarctic ice. Such a decline is roughly consistent with the magnitude of the CH_3Cl decline from 1200–1700 AD, assuming the CH_3Cl budget at 1200 AD was similar to today. Prior to 1200 AD, the two records are not consistent. *Ferretti et al.* [2005] estimate relatively steady, high levels of burning prior to the MCA, while $\Delta_{trend}CH_3Cl$ was relatively low.

[16] Climate-driven changes in the ocean source of CH_3Cl may also have occurred during the late Holocene. There is evidence from high resolution sediment cores in both the Atlantic and Pacific oceans for elevated low latitude sea surface temperatures and salinity during the MCA, followed by cooling and freshening during the LIA [*Keigwin*, 1996; *Lund and Curry*, 2006; *Newton et al.*, 2006]. In the modern ocean, there is a strong positive correlation between sea surface temperature and CH_3Cl saturation state [*Moore et al.*, 1996]. This correlation is likely governed by the geographic extent of marine organisms responsible for production of methyl bromide (CH_3Br) and methyl iodide (CH_3I), which are chemically converted in seawater to CH_3Cl. One can speculate that climate change during the MCA and LIA resulted in expansion and contraction of the subtropical and tropical waters in which most CH_3Cl production occurs. Changes in circulation and nutrient distributions may also have led to more complex changes in oceanic biota but there is little basis on which to assess their possible impact on CH_3Cl emissions.

[17] Atmospheric OH is the major sink of atmospheric CH_3Cl. The temperature-dependence of the OH-initiated oxidation of CH_3Cl (2% per °C) is not large enough to account for the magnitude of CH_3Cl variability during MCA and LIA. Global OH levels and variability during the late Holocene have not been established, and cannot be ruled out as a cause for the observed CH_3Cl changes. Atmospheric OH is almost certainly sensitive to climate-driven changes in a number of factors, including hydrocarbon emissions from terrestrial ecosystems and NO_x production from lightning and soils.

4. Implications

[18] Although the underlying cause is not known, ice core CH_3Cl variability over the last two millennia suggests a positive relationship between atmospheric CH_3Cl and global mean temperature that has not been observed before. The validity of this relationship should be confirmed by analyzing multiple ice cores, and by extending the record to earlier periods of more dramatic climate change. Taking the correlation at face value implies that atmospheric CH_3Cl levels may rise due to future greenhouse-driven warming. The ice core measurements suggest a CH_3Cl climate response of about 90 ppt CH_3Cl/degree C, based on the observed change in $\Delta_{trend}CH_3Cl$ between the MCA maximum and LIA minimum and the *Moberg et al.* [2005] temperature reconstruction. Assuming a 3°C projected global temperature rise by the year 2100 [*Intergovernmental Panel on Climate Change*, 2001], a linear CH_3Cl temperature response results in a 270 ppt increase in atmospheric CH_3Cl. Such an increase in CH_3Cl would offset some of the projected decline in stratospheric chlorine under the Montreal Protocol and its amendments, slowing the recovery of stratospheric ozone. Of course, future changes in climate and atmospheric CH_3Cl will occur in the context of many other anthropogenically-driven environmental changes that were not present in the past. In particular, land use changes in the tropics and subtropics may alter the patterns of vegetative and biomass burning emissions. A full characterization of the trends and potential climate sensitivity of each component in the CH_3Cl budget is needed in order to carry out realistic projections of future stratospheric chlorine loading and its relationship to climate change. The results of this study highlight the importance of determining atmospheric histories for a wide range of trace gases, including other naturally-occurring ozone-depleting gases such as CH_3Br and shorter-lived polyhalogenated compounds.

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M. Aydin, E. S. Saltzman, and C. Tatum, Department of Earth System Science, Croul Hall, University of California, Irvine, Irvine, CA 92697, USA.

M. B. Williams, Atmospheric Chemistry and Dynamics Branch, MS 245-5, NASA-Ames Research Center, Moffett Field, CA 94035, USA. (mbwilliams@arc.nasa.gov)