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Atmospheric variability of methyl chloride during the last 300 years from an Antarctic ice core and firn air

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[1] Measurements of methyl chloride (CH_3Cl) in Antarctic polar ice and firn air are used to describe the variability of atmospheric CH_3Cl during the past 300 years. Firn air results from South Pole and Siple Dome suggest that the atmospheric abundance of CH_3Cl increased by about 10% in the 50 years prior to 1990. Ice core measurements from Siple Dome provide evidence for a cyclic natural variability on the order of 10%, with a period of about 110 years in phase with the 20th century rise inferred from firn air. Thus, the CH_3Cl increase measured in firn air may largely be a result of natural processes, which may continue to affect the atmospheric CH_3Cl burden during the 21st century. *INDEX TERMS:* 0312 Atmospheric Composition and Structure: Air/sea constituent fluxes (3339, 4504); 0322 Atmospheric Composition and Structure: Constituent sources and sinks; 0365 Atmospheric Composition and Structure: Troposphere—composition and chemistry; 1610 Global Change: Atmosphere (0315, 0325). **Citation:** Aydin, M., E. S. Saltzman, W. J. De Bruyn, S. A. Montzka, J. H. Butler, and M. Battle (2004), Atmospheric variability of methyl chloride during the last 300 years from an Antarctic ice core and firn air, *Geophys. Res. Lett.*, *31,* L02109, doi:10.1029/2003GL018750.

1. Introduction

[2] Methyl chloride (CH_3Cl) is the most abundant halocarbon in the atmosphere with a global mixing ratio of about 550 pmol mol^{-1}. This gas accounts for more than 10% of the ozone-depleting halogen delivered to the stratosphere and its sources are primarily natural. Little is known about the variability or the climate sensitivity of atmospheric CH_3Cl, and there is little basis on which to predict future changes in its abundance. The best estimate for the lifetime of atmospheric CH_3Cl is 1.3 years and the current mixing ratio of CH_3Cl over Antarctica is about 530 pmol mol^{-1} [S. A. Montzka, NOAA/CMDL unpublished data, 2003], slightly lower than the global mean value. The current understanding of the atmospheric CH_3Cl budget is summarized in the recent review by *Montzka and Fraser* [2003] and references therein.

[3] In this study, we used CH_3Cl measurements in ice core and firn air samples from Antarctica to describe the variability of atmospheric CH_3Cl. The interstitial air in polar firn and ice contains a record of past atmospheric composition. The composition of firn air is altered relative to that of the overlying atmosphere primarily by diffusion, and to a lesser extent by gravitational settling and other processes. Below the firn-ice transition zone, the interstitial air is isolated and locked within the ice as bubbles. The firn column acts as a low-pass filter, smoothing variations in the atmospheric composition of a gas over decadal time scales comparable to the diffusive transport time through the firn [*Schwander et al.*, 1993; *Battle et al.*, 1996; *Trudinger et al.*, 1997].

[4] The ice core samples were obtained from the Siple Dome C core, drilled in December 1995 at Siple Dome, West Antarctica (81.65°S, 148.81°W) as part of the West Antarctic Ice Sheet Program (WAISCORES). Size of the ice core samples used for gas analysis ranged from 400–700 g. Air was extracted from the ice core samples using a dry extraction technique [*Etheridge et al.*, 1988; *Sowers and Jubenville*, 2000]. The samples yielded 20–40 ml STP of air, which was analyzed for trace gases with a gas chromatograph with quadrupole mass spectrometer detection at the University of California, Irvine. The details of the analytical and ice core extraction methods, and a discussion of how the precision of the ice core data are calculated based on calibration and blank uncertainties can be found in *Aydin et al.* [2002].

[5] The firn air samples were obtained during three different Antarctic field expeditions: to South Pole in 1995 (SPO-95), to South Pole in 2001 (SPO-01), and to Siple Dome in 1996 (SDM-96) [*Butler et al.*, 1999], using established methods [*Schwander et al.*, 1993; *Bender et al.*, 1994; *Battle et al.*, 1996; *Butler et al.*, 1999]. Measurements of CH_3Cl in the SPO-95 and SDM-96 firn samples were published previously by *Butler et al.* [1999], but are updated here to account for revised and updated calibration scales. SPO-01 firn air was collected from two boreholes drilled to the firn-ice transition at 89.98°S, 118.73°W and 89.98°S, 118.93°W. Glass and steel flasks were filled and analyzed using GC-MS techniques at NOAA-CMDL. Standardization of measurements at the UCI and NOAA/CMDL laboratories is based on high-pressure gas cylinders prepared and maintained independently. An intercalibration effort in 2002 yielded agreement to within ±3% and no adjustments were made to measurements from either laboratory for this study.

2. Methods

[6] We used a 1-dimensional forward model of a firn air column to simulate how a specified atmospheric history of CH_3Cl is incorporated into the air in firn or ice [*Schwander et al.*, 1988]. The model simulates gas phase diffusion and gravitational separation based on specified depth profiles of

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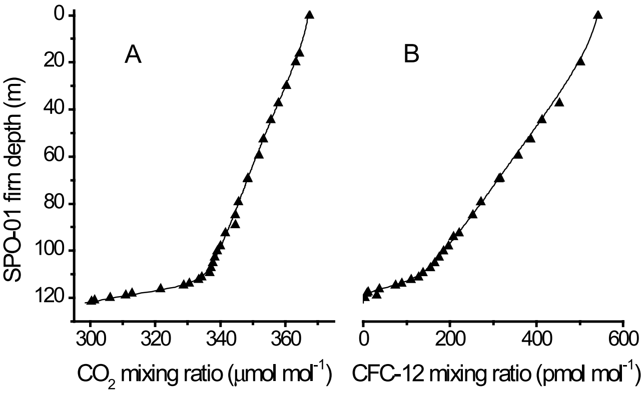

Figure 1. (a) Firn air measurements of CO_2 (solid triangles) from SPO-01 compared with model simulations (solid line). (b) Firn air measurements of CFC-12 from SPO-01 (solid triangles) compared with model simulations (solid line).

diffusivity for a constant accumulation rate. The distribution of open porosity with depth was obtained using measured density profiles and a density-open porosity relationship. Open porosity is assumed to vanish at the deepest sampling depth for each firn hole. For Siple Dome, the model runs were initiated with an accumulation rate of 100 kg m^{-2} y^{-1} (60 kg m^{-2} y^{-1} for South Pole) and a mean annual temperature of $-25°C$ ($-50°C$ for South Pole). Molecular diffusion coefficients for CO_2, CFC-12, and CH_3Cl in air for annual-mean temperature and pressure were calculated as 1.3×10^{-5}, 0.8×10^{-5}, and 1.1×10^{-5} m^2 s^{-1} for Siple Dome, and 1.4×10^{-5}, 0.8×10^{-5}, and 1.2×10^{-5} m^2 s^{-1} for South Pole [*Wilke and Lee*, 1955].

[7] The model was initiated using a CO_2 atmospheric history for the last 170 years determined from Law Dome ice core measurements [*Etheridge et al.*, 1996] and NOAA/CMDL flask data through 2001 [*Tans et al.*, 2001]. The relationship between open porosity and diffusivity in the model was "tuned" to obtain agreement with the CO_2 firn air measurements at each location (Figure 1a). The tuning process is a trial and error procedure, in which the non-linear relationship between diffusivity and depth is manually adjusted to achieve agreement between the model results and the firn data. Following the CO_2 simulation, we tested the robustness of the derived diffusivity-depth relationship by simulating a CFC-12 depth profile with the atmospheric history of *Walker et al.* [2000], and observed good agreement with the data (Figure 1b). Based on the successful reproduction of firn profiles for CO_2 and CFC-12, we suggest that the "tuned" model simulates realistic firn profiles given a known atmospheric history, regardless of any possible inaccuracies in the prescribed diffusion and the accumulation rate. In the following sections, the firn model is used to explore the atmospheric evolution of CH_3Cl and to develop atmospheric histories that are consistent with the observations in firn and ice core air.

3. The Firn Air Record

[8] An atmospheric history for CH_3Cl was constructed based on the SPO-01 data, assuming that; (1) the atmospheric mixing ratio of CH_3Cl increased monotonically from an unknown, constant value; (2) the atmospheric mixing ratio of CH_3Cl leveled off at the present day Antarctic mixing ratio of 530 pmol mol^{-1}; and (3) the changes in the atmosphere occurred in a smooth, continuous manner (Figure 2). The timing and the amplitude of the increase during the mid-1900's, the rate of this increase, and the timing of the rollover to modern values were varied manually to better simulate the SPO-01 firn measurements (Figure 3a). We considered only the SPO-01 data because, they are of higher quality than SPO-95, and SDM-96 data do not reach as far back in time. The resulting atmospheric history is hereafter referred to as the "firn air only" history (Figure 2).

[9] Model simulations for the SPO-95 firn using the "firn air only" history slightly underestimate the measurements (Figure 3b), but the agreement is good between the simulated and observed mixing ratios for SDM-96 (Figure 3c), suggesting that the history is in reasonably good agreement with all firn data. In the "firn air only" history, the atmospheric abundance of CH_3Cl increases from about 470 pmol mol^{-1} in the 1940s to nearly 530 pmol mol^{-1} in the early 1990's. The steepest change is observed between 1955 and 1985 when CH_3Cl increases 50 pmol mol^{-1} in 30 years (Figure 2). If one presumes that any change that occurred during the 20th century is due to human activities, this record implies that roughly 10% of the CH_3Cl currently in the atmosphere is anthropogenic, in agreement with the conclusion of *Butler et al.* [1999].

[10] In the most recent review of the atmospheric CH_3Cl budget [*Montzka and Fraser*, 2003], the sinks (4005 Gg y^{-1}) exceed the known sources (2956 Gg y^{-1}), and the anthropogenic emissions total only 165 Gg y^{-1}, or roughly 4% of the total budget. About 60% of the anthropogenic emissions is attributed to coal combustion [*McCulloch et al.*, 1999; *Keene et al.*, 1999]. Considering the temporal pattern of emissions from coal combustion [*Keeling*, 1994], it is

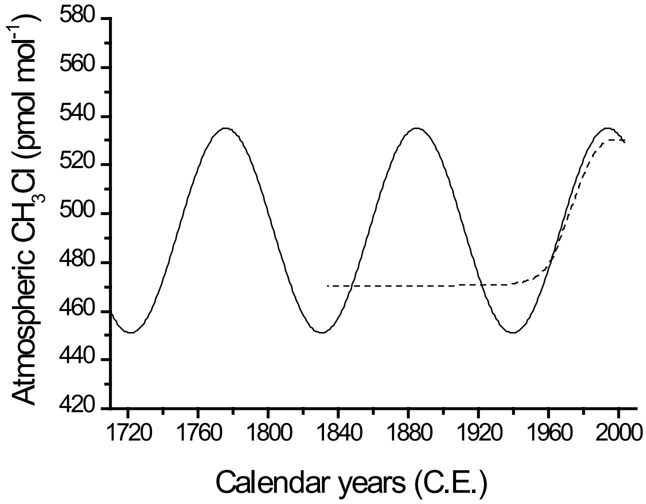

Figure 2. Atmospheric histories for CH_3Cl derived from firn air and ice core data: "firn air only" history developed to fit the SPO-01 CH_3Cl data (dashed line) and "sinusoidal" history (solid line). The "firn air only" history extends back 170 years but it is very loosely constrained by the firn data for the period before 1900 C.E. The "sinusoidal" history does not represent a fit but rather a close approximation to the amplitude and period observed in the ice core data.

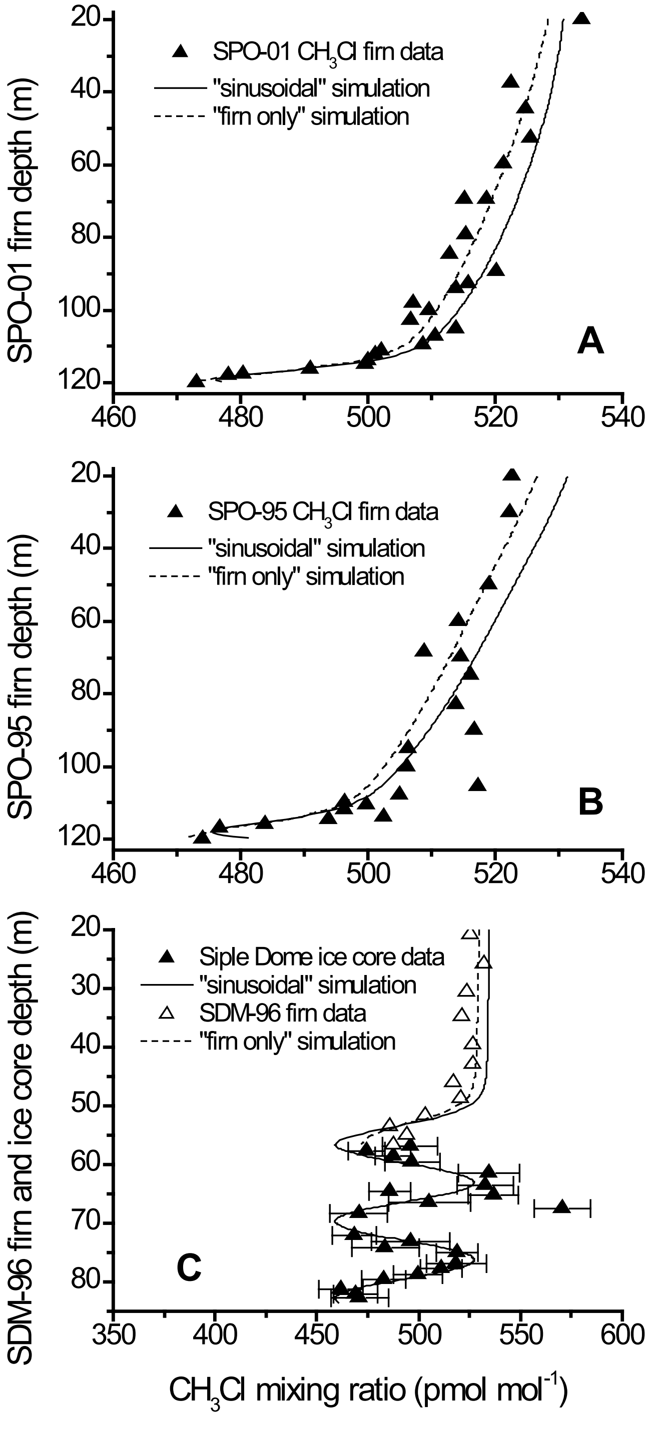

Figure 3. Depth profiles of CH_3Cl ice core data and firn air measurements, compared with model simulations based on the "firn only" and "sinusoidal" atmospheric histories shown in Figure 2: (a) South Pole (SPO-01), (b) South Pole (SPO-95), and (c) Siple Dome (ice cores, and SDM-96); the error bars represent the uncertainty in the ice core data. Results from the top 20 m of the firn are omitted because they are subject to seasonal variability. Note that the general trends in all firn data are correctly simulated with the "sinusoidal" history.

unlikely that anthropogenic emissions are responsible for the increase implied by the "firn air only" history. Increased biomass burning might explain the increase; this would require biomass burning emissions to nearly double over this period. Alternatively, the "firn air only" history may point to: (1) an as yet unidentified anthropogenic source; (2) indirect effects of human activities on natural sources and sinks, for example those caused by changes in land use patterns and agricultural practices; or (3) natural variability in the flux of CH_3Cl.

4. The Ice Core Record

[11] A longer atmospheric history of CH_3Cl can be constructed from measurements of CH_3Cl in air bubbles from the Siple Dome ice core. Data from 22 ice core samples ranging in depth from 57 to 83 m have a mean of 499 ± 28 pmol mol^{-1} (1σ) and a range of 462 to 571 pmol mol^{-1} (Figure 3c). A striking feature of the data is the oscillatory behavior with two distinct cycles. The amplitude of the variability is approximately 30 pmol mol^{-1}, or about 6% of the mean ice core mixing ratio. The cycles in the ice core CH_3Cl measurements could be closely reproduced by the model, using a sine function of the general form $A sin\{2\pi(t - \alpha)/P\} + C$ as an atmospheric history, where t is time in years, and the amplitude (A), the period (P), the vertical shift (C), and the phase shift (α) are equal to 42, 110, 493, and -17 (Figure 2). Initially, we determined how the diffusive filtering altered the composition of firn air at Siple Dome from the SDM-96 simulations. Then, we applied this filter to the "sinusoidal" history to calculate the mixing ratio of CH_3Cl in each ice core sample, assuming that the physical properties of the firn and the accumulation rate remained constant over the time period the ice core samples were formed. The visual stratigraphy [R. B. Alley, unpublished data, 2003] and density data suggest that the accumulation rate was constant approximately at 100 kg m^{-2} y^{-1} over our sampling range at the Siple Dome ice core site.

[12] In the "sinusoidal" history, two full oscillations occur between 1720 and 1940 C.E., with a period of 110 years and an amplitude of 42 pmol mol^{-1} (Figure 2). The underlying cause of these cycles is not clear, but they predate significant industrial activity. This apparently natural variability may reflect climate-driven changes in the CH_3Cl budget. Given the apparent dominance of tropical plants as a CH_3Cl source [*Yokouchi et al.*, 2002], one can speculate that such variability may arise from changes in tropical flora as a response to changes in climatological conditions. It may also point to changes in the atmospheric lifetime of CH_3Cl. Oxidation of CH_3Cl with OH radicals, most of which occurs in the tropics, accounts for approximately 80% of the total sinks [*Khalil and Rasmussen*, 1999].

[13] Strong centennial-scale climatic oscillations during the late Holocene have been observed in Greenland ice cores [*Appenzeller et al.*, 1998; *Meeker and Mayewski*, 2002]. These variations appear to reflect large-scale atmospheric circulation changes associated with the North Atlantic Oscillation. Hundred year periodicities are also apparent in other climate proxy records during the last thousand years [*Overpeck et al.*, 1997; *Mann et al.*, 1998; *Briffa et al.*, 2001]. *Gleissberg* [1966] suggested that variability in solar activity may provide the forcing for

climate change on such time scales, but as yet there is no direct evidence for this mechanism.

[14] The "sinusoidal" history was extended through the 20th century to examine the implications of such cyclic behavior on the interpretation of firn air data. For the period between 1940 and 1990, this atmospheric history is similar to the "firn air only" history (Figure 2). Consequently, model simulations based on the "sinusoidal" history for the SPO-01, SPO-95, and SDM-96 closely follow the "firn air only" simulations and generally display good agreement with the firn observations (Figures 3a, 3b, and 3c). The ability of the "sinusoidal" history to simulate the firn air data demonstrates that the evolution of atmospheric CH_3Cl over Antarctica during the 20th century is consistent with preindustrial variability, without invoking anthropogenic contributions to its atmospheric budget. This surprising result, though only correlative, argues against a significant industrial or agricultural contribution to CH_3Cl levels in the modern atmosphere. It also argues against a large anthropogenic effect on the atmospheric lifetime of CH_3Cl, via perturbations to global, or at least to tropical, OH levels.

5. Summary

[15] This study underscores the importance of assessing the natural variability in atmospheric trace gases as part of the effort to understand their biogeochemical cycles and to make an assessment of the potential for future change. For example, the halocarbon scenarios used in stratospheric ozone assessments have assumed that, in the absence of anthropogenic perturbation, CH_3Cl would remain constant at the current global average mixing ratio of 550 pmol mol^{-1} [e.g., *Montzka and Fraser*, 2003]. If CH_3Cl in the atmosphere continues to oscillate as suggested in the past by the "sinusoidal" history, the CH_3Cl burden may decrease by up to 10% over the next half century. Here, we demonstrate that it may be possible to develop long-term paleo records for CH_3Cl from the polar ice core archives, which would reveal atmospheric variability over a wider range of climatic conditions. Clearly, the challenge ahead is to verify the current ice core record with data from multiple sites, to extend the historical record over longer periods of time, and to seek an understanding of the underlying mechanisms that can drive atmospheric CH_3Cl variability.

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