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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. Introduction

Methyl chloride (CH\textsubscript{3}Cl) is the most abundant halocarbon in the atmosphere with a global mixing ratio of about 550 pmol mol\textsuperscript{-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\textsubscript{3}Cl, and there is little basis on which to predict future changes in its abundance. The best estimate for the lifetime of atmospheric CH\textsubscript{3}Cl is 1.3 years and the current mixing ratio of CH\textsubscript{3}Cl over Antarctica is about 530 pmol mol\textsuperscript{-1} [S. A. Montzka, NOAA/CMDL unpublished data, 2003], slightly lower than the global mean value. The current understanding of atmospheric CH\textsubscript{3}Cl budget is summarized in the recent review by Montzka and Fraser [2003] and references therein.

2. Methods

We used a 1-dimensional forward model of a firn air column to simulate how a specified atmospheric history of CH\textsubscript{3}Cl 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
diffusion and the accumulation rate. In the following sections, the firn model is used to explore the atmospheric evolution of CH$_3$Cl and to develop atmospheric histories that are consistent with the observations in firn and ice core air.

3. The Firn Air Record

An atmospheric history for CH$_3$Cl was constructed based on the SPO-01 data, assuming that; (1) the atmospheric mixing ratio of CH$_3$Cl increased monotonically from an unknown, constant value; (2) the atmospheric mixing ratio of CH$_3$Cl 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).

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$_3$Cl 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$_3$Cl 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$_3$Cl currently in the atmosphere is anthropogenic, in agreement with the conclusion of Butler et al. [1999].

In the most recent review of the atmospheric CH$_3$Cl 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 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).

Figure 2. Atmospheric histories for CH$_3$Cl derived from firn air and ice core data: “firn air only” history developed to fit the SPO-01 CH$_3$Cl 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.
unlikely that anthropogenic emissions are responsible for the increase implied by the “firm air only” history. Increased biomass burning might explain the increase; this would require biomass burning emissions to nearly double over this period. Alternatively, the “firm 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$_3$Cl.

4. The Ice Core Record

[11] A longer atmospheric history of CH$_3$Cl can be constructed from measurements of CH$_3$Cl 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$_3$Cl measurements could be closely reproduced by the model, using a sine function of the general form $A \sin \left(2\pi t / P + \alpha \right) + C$ 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 ($\alpha$) 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$_3$Cl 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$_3$Cl budget. Given the apparent dominance of tropical plants as a CH$_3$Cl 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$_3$Cl 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 firm air data. For the period between 1940 and 1990, this atmospheric history is similar to the “firm 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 “firm air only” simulations and generally display good agreement with the firm observations (Figures 3a, 3b, and 3c). The ability of the “sinusoidal” history to simulate the firm air data demonstrates that the evolution of atmospheric CH\textsubscript{3}Cl 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\textsubscript{3}Cl levels in the modern atmosphere. It also argues against a large anthropogenic effect on the atmospheric lifetime of CH\textsubscript{3}Cl, 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\textsubscript{3}Cl would remain constant at the current global average mixing ratio of 550 pmol mol\(^{-1}\) [e.g., Montzka and Fraser, 2003]. If CH\textsubscript{3}Cl in the atmosphere continues to oscillate as suggested in the past by the “sinusoidal” history, the CH\textsubscript{3}Cl 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\textsubscript{3}Cl 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\textsubscript{3}Cl variability.

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References


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