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Methyl chloride variability in the Taylor Dome ice core during the Holocene

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[1] Methyl chloride (CH3Cl) is a naturally occurring, ozone-depleting trace gas and one of the most abundant chlorinated compounds in the atmosphere. CH3Cl was measured in air from the Taylor Dome ice core in East Antarctica to reconstruct an atmospheric record for the Holocene (11–0 kyr B.P.) and part of the last glacial period (50–30 kyr B.P.). CH3Cl variability throughout the Holocene is strikingly similar to that of atmospheric methane (CH4), with higher levels in the early and late Holocene, and a well-defined minimum during mid-Holocene. The sources and sinks of atmospheric CH3Cl and CH4 are located primarily in the tropics, and variations in their atmospheric levels likely reflect changes in tropical conditions. CH3Cl also appears to correlate with atmospheric CH4 during the last glacial period (50–30 kyr B.P.), although the temporal resolution of sampling is limited. The Taylor Dome data provide information about the range of natural variability of atmospheric CH3Cl and place a new constraint on the causes of past CH4 variability.


1. Introduction

[2] Methyl chloride is the most abundant naturally occurring halocarbon gas in the atmosphere, with a global mean level of 550 ± 30 pmol mol−1 and an atmospheric lifetime of about 1 year. Currently, CH3Cl comprises about 16% of the stratospheric chlorine burden. Future stratospheric ozone projections generally assume constant atmospheric CH3Cl because there is little basis on which to predict future changes [Montzka and Reimann, 2010].

[3] Atmospheric measurements, field and laboratory flux studies, and atmospheric models estimate global CH3Cl emissions to be approximately 4.1 to 4.4 Tg yr−1 [Montzka and Reimann, 2010; Xiao et al., 2010]. The largest sources and sinks are located primarily in the tropics, based on latitudinal patterns in atmospheric CH3Cl abundance [Yoshida et al., 2004; Xiao et al., 2010]. Terrestrial emissions are the dominant CH3Cl sources and include direct biogenic emissions from vascular plants, abiotic release from leaf litter, and biomass burning of tropical forests, savannas and grasslands [Yokouchi et al., 2002; Xiao et al., 2010]. Leaf litter CH3Cl emissions arise from an abiotic chemical reac-
Given our current understanding of the processes controlling atmospheric CH$_3$Cl today, we expect that CH$_3$Cl levels in the ancient atmosphere were sensitive to changes in tropical ecosystems and climate. A polar ice core based atmospheric history of CH$_3$Cl could provide a unique proxy signal that reflects changes in tropical conditions. Paleo-atmospheric CH$_3$Cl levels might also reflect changes in atmospheric reactivity (i.e., global OH), and the interpretation of such a record requires disentangling the competing effects of changes in sources and sinks.

In this study, we present measurements of CH$_3$Cl in air extracted from the Taylor Dome ice core. The data provide a record of CH$_3$Cl covering the Holocene (11–0 thousand years before 1950, kyr B.P.), with more limited coverage of the last glacial period between 50–30 kyr B.P. The Taylor Dome record provides new information about the range of natural CH$_3$Cl variability over glacial/interglacial timescales. The CH$_3$Cl data from Taylor Dome also exhibit a relationship to atmospheric CH$_4$, which has not been previously observed.

2. Ice Core Sampling, Analysis, and Dating

Taylor Dome is a 554 m ice core that was recovered in East Antarctica between 1991 and 1994 (77°48’S, 158°43’E [Steig et al., 2000]. Air was extracted from bubbles in ice core samples by mechanical shredding at −50°C under vacuum in an evacuated stainless steel chamber. The extracted air was collected in a stainless steel tube cooled with liquid helium (4K). Sample air was analyzed by gas chromatography with high-resolution mass spectrometry using an internal isotope-labeled gas standard calibrated against ppm-level primary gas standards. The apparatus and procedures used to extract and analyze gases from the ice core samples were similar to those used in earlier studies [Saltzman et al., 2004; Aydin et al., 2007; Saltzman et al., 2009]. A correction of approximately −1% was applied to the measured CH$_3$Cl mixing ratios to account for gravitational enrichment in firn air, based on a bubble lock-in depth of 66 m and a mean annual surface air temperature of −42.5°C [Craig et al., 1988]. Gas ages for the Holocene samples used in this study are based on stratigraphic correlation of the CO$_2$ record from Taylor Dome ice core to the European Project for Ice Coring in Antarctica (EPICA) Dome C and Dronning Maud Land ice cores [Monnin et al., 2004]. Gas ages for the last glacial and transition samples are based on correlation of CO$_2$ and CH$_4$ records from Taylor Dome to the Greenland Ice Sheet Project 2 ice core [Brook et al., 2000; Ahn and Brook, 2008] (see Table S1 in the supporting information).
Figure 2. Methyl chloride measurements from the Taylor Dome ice core covering the last 50 kyr B.P. (black filled and open squares, left y axis). Orange lines represent the mean CH$_3$Cl level in samples from the last glacial period (50–30 kyr) and the Holocene (11–0 kyr). (inset) Enlarged view of the Taylor Dome CH$_3$Cl measurements from 50 to 25 kyr B.P., plotted with Siple Dome CH$_3$Cl measurements (red triangles) and atmospheric CH$_4$ levels from Taylor Dome (blue line, right y axis) [Saltzman et al., 2009; Brook et al., 2000]. Error bars in both panels represent ±1σ errors of the CH$_3$Cl measurements. Open squares indicate Taylor Dome samples with calcium at or above 0.25 μM (see text).

2.1. Excess Methyl Chloride

[9] Methyl chloride analysis requires 400–600 g of high-quality ice, without fractures, and clean sampling, extraction, and analytical procedures. The aim of this study was to measure CH$_3$Cl in Taylor Dome ice core samples with equally spaced gas ages throughout the length of the core. However, ice samples of sufficient size/quality were limited for the last glacial period. As a result, the sample age distribution was heavily biased towards the Holocene. We analyzed 41 Taylor Dome ice core samples at 250–300 year intervals over the last 11 kyr B.P. and four additional samples from 15–11 kyr B.P. There were sampling gaps around 8 and 4 kyr B.P. due to lack of ice availability. In total, 94 ice core samples were analyzed. Data from only 62 samples were of sufficient quality for use in this study. Two samples were below the age-depth scale, and the remainder were considered poor quality due to (1) drill fluid contamination (n-butyl acetate), (2) modern air contamination (CFC-12 >1 pmol mol$^{-1}$), and (3) contamination of the extraction vessels [Aydin et al., 2007, 2010] (see Figure S1). Methyl chloride levels in the samples ranged from 412 to 588 pmol mol$^{-1}$. The average analytical uncertainty was 6 ± 2.6% (1σ) of the measured levels.

3. Results

3.1. Holocene and Pre-Boreal Period (15–0 kyr B.P.)

[10] Methyl chloride variability during the Holocene ranges from about 418 to 515 pmol mol$^{-1}$ (Figure 1a). Three measurements around the Younger Dryas/Pre-Boreal (YD/PB, about 13–11 kyr B.P.) range from 509 to 527 pmol mol$^{-1}$ and show little difference from Early Holocene mixing ratios. After 10 kyr B.P., CH$_3$Cl levels begin to decline, reaching a broad minimum during the mid-Holocene. The CH$_3$Cl minimum lasts from about 7.4 to 3.5 kyr B.P., with a mean level of 440 ± 14 pmol mol$^{-1}$ (1σ SD, n = 21). At 3.5 kyr, CH$_3$Cl levels begin to increase and reach 480 pmol mol$^{-1}$ at 0.5 kyr B.P.

[11] The Taylor Dome results from the Holocene can be validated by comparison to existing CH$_3$Cl measurements from Antarctic ice cores. The late Holocene CH$_3$Cl measurements overlap with prior measurements from the Siple Dome and South Pole shallow ice cores (see Figure 1 (inset)) [Aydin et al., 2004; Williams et al., 2007]. The Taylor Dome and South Pole time scales are independent, which
3.2. Last Glacial Period (50–20 kyr B.P.)

[12] High-quality methyl chloride data were obtained in 17 samples with gas ages ranging from 50 to 20 kyr B.P. (Figure 2). Four of these samples exhibit elevated calcium levels, above 0.25 μM, as discussed earlier (see section 2 and Figure S2, supporting information). Taylor Dome data are similar to glacial CH3Cl levels measured in the Siple Dome ice core (Figure 2). The mean of methyl chloride measurements from the last glacial period (50–30 kyr B.P.) is 456 ± 27 pmol mol⁻¹ (1σ SD, n = 13). Methyl chloride levels measured in glacial ice samples are not statistically different from the interglacial levels (t = 2.67, p = 0.01, two-tailed Student’s t test). Saito et al. [2007] found significantly higher CH3Cl levels in glacial ice samples compared to the Holocene in the Dome Fuji ice core. The CH3Cl enhancement was likely related to elevated impurity (dust) levels in the Dome Fuji ice core. The mean CH3Cl level measured in glacial Taylor Dome samples is significantly lower than the glacial Dome Fuji measurements, even after the measurements were corrected for excess CH3Cl production (Figure S3). This suggests that the in situ CH3Cl enhancement in Dome Fuji ice is likely larger than previously estimated [Saito et al., 2007].

3.3. Relationship to Methane

[13] Methyl chloride variability during the Holocene is strikingly similar to that of atmospheric CH4 (Figure 1b). Both records exhibit a saddleback pattern with relative maxima in the early and late Holocene and a well-defined, contemporaneous minimum during the mid-Holocene. Methane levels decrease by roughly 20% from the early to mid-Holocene (from about 700 to 550 nmol mol⁻¹), while CH3Cl levels decrease by about 10–15% over the same period (from about 490–500 pmol mol⁻¹ in the early Holocene to 440 pmol mol⁻¹ in the mid-Holocene). After 3.5 kyr, CH3Cl and CH4 rise by 11% and 19%, respectively, reaching their peak preindustrial levels (Figure 1).

[14] Measurements from the last glacial period show evidence of a similar relationship, with higher CH3Cl levels during periods with elevated CH4 levels (Figure 2 (inset)). Between 50 and 30 kyr B.P., CH4 exhibits a baseline level between 400 and 450 nmol mol⁻¹, with positive excursions associated with interstadial warming events [Chappellaz et al., 1993a; Brook et al., 2000]. The CH3Cl/CH4 covariance is particularly notable within interstadial 8, around 38 kyr B.P.

[15] The relationship between CH3Cl and CH4 is shown in a regression plot (Figure 3, Table 1). To construct this plot, we linearly interpolated the Taylor Dome CH4 data at the CH3Cl depths. Regression fits are based on a weighted linear least squares regression with errors in both variables [Reed et al., 2010]. Eight measurements were excluded from the regression analyses: three from the YD/PB transition and five with the highest calcium levels (Figure S2). The YD is marked by a rapid drop in atmospheric CH4. Interestingly, CH3Cl levels show no change during the YD, based on a single CH3Cl measurement around 12.1 kyr B.P. (Figure 1). Samples from the YD/PB period were excluded from the regression analyses due to the limited availability of samples.

**Table 1. Regression Statistics for CH3Cl and CH4 Correlations in the Taylor Dome Ice Core (see Figure 3)**

<table>
<thead>
<tr>
<th>Time Period (kyr B.P.)</th>
<th>Slope ± 2σ s.e.</th>
<th>r</th>
<th>n</th>
</tr>
</thead>
<tbody>
<tr>
<td>50–30</td>
<td>0.46 ± 0.25</td>
<td>0.66</td>
<td>13</td>
</tr>
<tr>
<td>11–0</td>
<td>0.39 ± 0.10</td>
<td>0.75</td>
<td>41</td>
</tr>
<tr>
<td>11–6</td>
<td>0.62 ± 0.11</td>
<td>0.96</td>
<td>12</td>
</tr>
<tr>
<td>3–0.5</td>
<td>1.13 ± 0.68</td>
<td>0.67</td>
<td>13</td>
</tr>
</tbody>
</table>

*Units for the slope are pmol mol⁻¹ CH3Cl/nmol mol⁻¹ CH4.
The mean CH₃Cl level did not change. The shift from increased by about 180 nmol mol⁻¹ [17] We can estimate how changes in various sources influence the CH₃Cl/CH₄ ratio in the atmosphere by computing a lifetime-weighted atmospheric response ratio:

\[
\frac{\partial CH_3Cl}{\partial CH_4} (\text{pmol/mol CH}_4 \text{ nmol/mol}) = \frac{E_{CH_3Cl}}{E_{CH_4}} \frac{t_{CH_3Cl}}{t_{CH_4}} \frac{16}{50.5} \times 10^3 \tag{1}
\]

where \(E_{CH_3Cl}\) and \(E_{CH_4}\) are the emissions of methyl chloride and methane, respectively, from a particular source (Tg y⁻¹), \(t_{CH_3Cl}\) and \(t_{CH_4}\) are the preindustrial atmospheric lifetimes of the two gases (0.75 year for CH₃Cl and 6.9 years for CH₄), and 16/50.5 is the ratio of the molecular weights.

[18] Lifetime-weighted atmospheric response ratios were calculated for various sources using information about the modern and preindustrial methane and methyl chloride budgets (Table 2). The CH₃Cl/CH₄ emissions ratio for tropical terrestrial sources was calculated using the sum of emissions from tropical wetlands and tropical vegetation [Bergamaschi et al., 2007; Xiao et al., 2010]. Based on these estimates, the lifetime-weighted atmospheric response ratio is 0.51 ± 0.1 pmol mol⁻¹ CH₃Cl/nmol mol⁻¹ CH₄ for tropical terrestrial emissions and 1.43 ± 0.3 pmol mol⁻¹ CH₃Cl/nmol mol⁻¹ CH₄ for pyrogenic emissions. The uncertainty estimates are based on the range and magnitude of CH₃Cl emissions from tropical plants and pyrogenic sources, respectively [Xiao et al., 2010]. The calculations of tropical terrestrial CH₃Cl and CH₄ emissions are described in the supporting information. Atmospheric OH is the major loss pathway for both CH₄ and CH₃Cl. Therefore, a change in atmospheric OH results in a similar fractional change in steady state atmospheric CH₃Cl and CH₄ levels and an atmospheric response ratio near unity (Figure 3 (inset)).

[19] The slopes of the CH₃Cl versus CH₄ correlations for the Holocene and last glacial period are similar to the atmospheric response ratio from tropical terrestrial emissions (Figure 3). This is not surprising given that the major CH₃Cl sources are tropical. The slope of the CH₃Cl versus CH₄ regression is not compatible with changes due to biomass burning or boreal sources alone but could reflect the weighted sum of changes in multiple sources or in atmospheric OH. In contrast, the mean atmospheric CH₄ level increased between the glacial and interglacial periods without a corresponding increase in CH₃Cl levels. This points to a change in boreal sources as the primary cause for this shift. It is unlikely that rice paddy emissions play a major role, as they did not become significant until the late Holocene and are a relatively small part of the preindustrial CH₄ budget [Zhou, 2011]. Samples from the YD/PB transition were excluded from the regression analyses due to limited sample availability. The negative CH₄ excursion observed during the YD is not apparent in the CH₃Cl record (Figure 1). This could reflect changes in extratropical CH₄ sources during

### Table 2. Source Strengths, Emissions Ratios, and Lifetime-Corrected Atmospheric Response Ratios Calculated for Methyl Chloride and Methane (Figure 3 (inset))

<table>
<thead>
<tr>
<th>Source</th>
<th>CH₄ Emissions (Tg y⁻¹)</th>
<th>CH₃Cl Emissions (Tg y⁻¹)</th>
<th>Emission Ratio Tg CH₃Cl/Tg CH₄</th>
<th>Atmospheric Response Ratio pmol mol⁻¹ CH₃Cl/nmol mol⁻¹ CH₄</th>
</tr>
</thead>
<tbody>
<tr>
<td>Boreal wetland</td>
<td>43.3</td>
<td>0.011</td>
<td>(2.44 \times 10^{-4})</td>
<td>0.01</td>
</tr>
<tr>
<td>Rice paddies</td>
<td>28.6</td>
<td>0.05</td>
<td>(1.75 \times 10^{-5})</td>
<td>0.08</td>
</tr>
<tr>
<td>Tropical wetland</td>
<td>151.3</td>
<td>0.037</td>
<td>(2.44 \times 10^{-4})</td>
<td>0.01</td>
</tr>
<tr>
<td>Tropical vegetation</td>
<td>–</td>
<td>2.2</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>Tropical terrestrial</td>
<td>151.3</td>
<td>2.237</td>
<td>(1.48 \times 10^{-2})</td>
<td>0.51 ± 0.1</td>
</tr>
<tr>
<td>Pyrogenic</td>
<td>23.5</td>
<td>0.917</td>
<td>(3.9 \times 10^{-3})</td>
<td>1.43 ± 0.3</td>
</tr>
</tbody>
</table>

*aWe assumed a preindustrial atmospheric lifetime of 6.9 years for CH₄ and 0.75 year for CH₃Cl. Emissions estimates are described in the supporting information. Tropical terrestrial emissions are the sum of emissions from tropical wetlands plus tropical vegetation.

### Table 3. Parameters Used in the CH₃Cl Box Model

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Symbol</th>
<th>Value</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mass of atmosphere (mol)</td>
<td>M</td>
<td>(1.42 \times 10^{20})</td>
<td></td>
</tr>
<tr>
<td>Mean mixed layer depth (m)</td>
<td>z</td>
<td>75</td>
<td></td>
</tr>
<tr>
<td>Surface area of the ocean (m²)</td>
<td>A</td>
<td>(361 \times 10^{12})</td>
<td></td>
</tr>
<tr>
<td>Mean air-sea exchange coefficient (m y⁻¹)</td>
<td>Kₐ</td>
<td>(1.5 \times 10^{11})</td>
<td></td>
</tr>
<tr>
<td>Henry’s law constant (m³ atm mol⁻¹)</td>
<td>H</td>
<td>(8.78 \times 10^{-3})</td>
<td>Moore et al. [1995]</td>
</tr>
<tr>
<td>Mean diffusivity through thermocline (m²y⁻¹)</td>
<td>Dₚ</td>
<td>(5.4 \times 10^{3})</td>
<td></td>
</tr>
<tr>
<td>Mean &quot;eddy degradation&quot; rate (y⁻¹)</td>
<td>kₑ</td>
<td>25.55</td>
<td>Tokarczyk et al. [2003]</td>
</tr>
<tr>
<td>Ocean production rate (mol CH₃Cl y⁻¹)</td>
<td>Pₒ</td>
<td>(7.68 \times 10^{10})</td>
<td>see text</td>
</tr>
</tbody>
</table>

*aValues are from Butler [1994] unless otherwise noted.*
the YD that are not linked to CH3Cl. Future studies should investigate the relationship between atmospheric CH4 and CH3Cl during the YD/PB period.

4. Modeling

[20] Simple steady state global box models of CH3Cl and CH4 were used to explore the sensitivity of Holocene CH3Cl levels to changes in emissions and atmospheric lifetime. In the modern atmosphere, the CH3Cl interhemispheric gradient is negligible. Pole-to-equator gradients are only about 5% because most of the sources and sinks are located in the tropics [Yoshida et al., 2004]. Currently, there is no information about paleo-interhemispheric CH3Cl gradients. Future studies utilizing both Greenland and Antarctic ice cores could provide such information and allow more sophisticated model treatments. By comparing ice core data and model simulations, we make the implicit assumption that latitudinal CH3Cl gradients did not change.

4.1. Methyl Chloride Box Model

[21] A box model is used to compute the global steady state atmospheric abundance of methyl chloride based on prescribed, time-varying emissions histories. The atmosphere is coupled to the global ocean, also represented by a single box, where the net oceanic flux of CH3Cl varies as a function of the atmospheric level. Since CH3Cl is both produced and consumed in the ocean, the oceanic CH3Cl flux will oppose changes in the atmospheric mixing ratio, resulting in a negative feedback or “buffering” effect on atmospheric CH3Cl levels caused by changes in other sources or sinks [Butler, 1994; Yvon and Butler, 1996]. This model was first developed by Butler [1994] for methyl bromide, and we use the same notation here. The mass balance equations for the coupled ocean-atmosphere CH3Cl model are

\[ \frac{dM_a}{dt} = S_{\text{terr}} + F_{\text{oa}} - F_T = 0 \]  
\[ \frac{dM_o}{dt} = P_o - F_{\text{oa}} - F_d - F_{\text{ed}} = 0 \]  

where \( M_a \) and \( M_o \) are the burden of CH3Cl in the atmosphere and surface ocean (mol). All other terms in equations (2) and (3) are fluxes (mol y\(^{-1}\)). In equation (2), \( S_{\text{terr}} \) is the sum of terrestrial sources, including biomass burning and vegetative emissions, \( F_{\text{oa}} \) is the net exchange across the air/sea interface, and \( F_T \) is the atmospheric loss of CH3Cl due to OH, stratosphere, and soils. In equation (3), \( P_o \) is the oceanic production of CH3Cl, \( F_d \) is the aquatic degradation rate of CH3Cl, and \( F_{\text{ed}} \) is the loss rate from downward vertical mixing and chemical or biological degradation through the thermocline.

[22] The mass balance equations for the coupled ocean-atmosphere model are parameterized as follows:

\[ \frac{dM_a}{dt} = S_{\text{terr}} + \frac{K_{\text{oa}} A}{H} (p_w - p_a) - (k_{\text{OH}} + k_{\text{soil}} + k_{\text{strat}}) p_a M \]  
\[ \frac{dM_o}{dt} = P_o - \frac{K_{\text{oa}} A}{H} (p_w - p_a) - k_{\text{soil}} M_o - \frac{K_{\text{ed}}}{z} M_o \]

where \( K_w \) is the mean air-sea exchange coefficient, \( A \) is the surface area of the ocean, \( H \) is the Henry’s law constant [Moore et al., 1995], \( p_w \) is the partial pressure of CH3Cl in the water (atm), \( p_a \) is the partial pressure of CH3Cl in the atmosphere at sea level (atm), \( k_{\text{OH}}, k_{\text{soil}}, \) and \( k_{\text{strat}} \) are the first-order loss rate constants for reaction with OH, soil degradation, and loss to the stratosphere, \( M \) is the total mass of the atmosphere, \( k_d \) is the pseudo-first-order loss constant for aquatic degradation in the surface layer, \( K_{\text{ed}} \) is the downward removal of CH3Cl from the surface ocean by mixing, and \( z \) is the thickness of the surface layer [Butler, 1994]. Equations (4) and (5) are solved simultaneously using the parameter values listed in Table 3.

[23] Source and sink strengths used to estimate the modern atmospheric CH3Cl level in the model are consistent with current estimates (Table 4) [Xiao et al., 2010]. Terrestrial vegetative and biomass-burning emissions are treated as a single-budget term in the box model. The global oceanic production rate \( P_o \) of 7.68 \times 10^{10} \text{ mol CH}_3\text{Cl y}^{-1} \) was tuned to give a net ocean flux of 500 Gg y\(^{-1}\) using the source and sink strengths listed in Table 4. This oceanic production rate gives an oceanic CH3Cl concentration of 81 pM and a partial atmospheric CH3Cl lifetime with respect to the oceans of 3.8 y, consistent with current estimates [Moore et al., 1996; Tokarczyk et al., 2003]. We use a partial atmospheric CH3Cl lifetime with respect to soil uptake based on Yoshida et al. [2004].

4.2. Methane Box Model

[24] The CH4 box model is also coupled to a CH4 box model to explore the relationship between atmospheric CH3Cl and CH4 and to quantify changes in the atmospheric lifetimes of the two trace gases. The CH4 box model is used to compute the steady state atmospheric CH4 burden using the following equation:

\[ M_{\text{CH}_4} = \frac{S}{k_{\text{OH}} + k_{\text{soil}} + k_{\text{strat}}} \]

where \( M_{\text{CH}_4} \) is the atmospheric CH4 burden (mol), \( S \) is the total CH4 source, and \( k_{\text{OH}}, k_{\text{soil}}, \) and \( k_{\text{strat}} \) are the first-order loss rate constants for reaction with OH, soil loss, and the stratosphere, and soil uptake. Oceanic CH4 emissions are relatively small and are assumed to be constant.

[25] Methane is also a major sink for OH and, as a result, the OH lifetime of methane is a related to the atmospheric...
Figure 4. (left column) Model Scenario 1: Base Case results using variable CH₄ emissions, OH-methane feedback, and fixed terrestrial CH₃Cl emissions. (middle column) Model Scenario 2: OH-only results using fixed CH₄ emissions, fixed terrestrial CH₃Cl emissions, and variable OH lifetimes for CH₄ and CH₃Cl. (right column) Model Scenario 3: Fixed emissions ratio results using prescribed terrestrial CH₄ emissions, OH-methane feedback, and a fixed CH₃Cl/CH₄ ratio for tropical terrestrial emissions (solid lines) and biomass-burning emissions (dashed lines). (from top to bottom rows) Modeled atmospheric CH₄ (magenta line) and Taylor Dome and EPICA Dome C ice core data (filled and open blue squares) [Brook et al., 2000; Flückiger et al., 2002], partial atmospheric lifetimes with respect to OH for CH₄ (left y axis) and CH₃Cl (right y axis), prescribed total CH₄ emissions, terrestrial and oceanic CH₃Cl emissions, and modeled atmospheric CH₃Cl (red line) and ice core data from Taylor Dome (black squares) and South Pole (open squares) [Williams et al., 2007].
methane burden. The following expression is used to calculate changes in atmospheric CH4 lifetime taking into account the methane feedback on atmospheric OH:

\[ k_{\text{OH-CH}_4}^* = \left(1 - \frac{\partial \ln \text{OH}}{\partial \ln \text{CH}_4} R \right) k_{\text{OH-CH}_4} \]  

(7)

where

\[ R = \frac{M_{\text{CH}_4}^* - M_{\text{CH}_4}^*}{M_{\text{CH}_4}} \]  

(8)

and \( \partial \ln \text{OH}/\partial \ln \text{CH}_4 \) is the magnitude of the CH4 feedback on atmospheric OH, \( k_{\text{OH-CH}_4}^* \) is the present-day first-order loss rate constant for reaction of CH4 with OH, and \( M_{\text{CH}_4}^* \) is the modern atmospheric CH4 burden. We use \( k_{\text{OH-CH}_4}^* = (1/9.6) \) yr\(^{-1} \) and \( M_{\text{CH}_4}^* = 251 \) Tmol CH4 (equivalent to 1774 nmol mol\(^{-1}\)) as conditions for the modern atmosphere [DeMan et al., 2007]. The magnitude of the CH4 feedback on OH is taken as \( \partial \ln \text{OH}/\partial \ln \text{CH}_4 = -0.32 \), based on Ehhalt et al. [2001]. The steady state CH4 burden and atmospheric OH lifetime are calculated by solving the equations (6)–(8) iteratively using the Matlab fsolve function.

[26] To couple the CH2Cl and CH4 box models, the OH lifetime of CH2Cl is scaled to the OH lifetime of CH4:

\[ k_{\text{OH-CH}_2\text{Cl}}^* = \left( \frac{1.3}{9.6} \right) k_{\text{OH-CH}_4}^* \]  

(9)

where \( k_{\text{OH-CH}_2\text{Cl}}^* \) and \( k_{\text{OH-CH}_4}^* \) are the first-order loss rate constants for loss of CH2Cl and CH4, and 1.3 and 9.6 are the modern OH lifetimes of CH2Cl and CH4, respectively.

4.3. Model Scenarios and Results

[27] Three model scenarios were examined using various assumptions about atmospheric lifetimes and the relationship between methyl chloride and methane emissions. In each case, emissions are specified at 0.5 kyr intervals from 11 to 0.5 kyr and the oceanic CH3Cl production rate is held constant at the modern value. The simulation results are summarized in Figure 4.

[28] Scenario 1 (Base Case) examines the magnitude of changes in atmospheric CH3Cl caused solely by the methane-OH feedback associated with the Holocene variations in atmospheric CH4. For this model run, CH4 emissions are specified to achieve agreement with data from the Taylor Dome and EPICA Dome C ice cores [Brook et al., 2000; Flückiger et al., 2002]. The CH4 burden is calculated using equations (6)–(8), and equation (9) is used to scale the atmospheric OH lifetime of CH3Cl. Terrestrial and biomass-burning CH3Cl emissions are fixed at 3.2 Tg yr\(^{-1}\). The result from the base case scenario shows that the mid-Holocene increase in OH resulting from the CH4 decrease alone accounts for about a 3% reduction in the atmospheric CH3Cl abundance (Figure 4).

[29] Scenario 2 (OH-only) examines the question of whether the mid-Holocene minimum in both CH4 and CH3Cl could be caused by changes in atmospheric lifetimes alone. In this scenario, we impose fixed CH3Cl and CH4 emissions throughout the Holocene, with the exception of oceanic CH3Cl emissions, which are based on a fixed oceanic production rate. The methane feedback on OH is turned off (\( \partial \ln \text{OH}/\partial \ln \text{CH}_4 = 0 \)). The OH lifetime of CH4 is specified in order to match the Holocene ice core CH4 data, and equation (9) is used to scale the atmospheric OH lifetime of CH3Cl. This simulation shows that a 26% decrease in CH4 lifetime from the early Holocene to the mid-Holocene minimum is required to match the ice core observations. Interestingly, a change in CH3Cl lifetime of this magnitude also provides a good fit to the ice core observations (Figure 4).

[30] Scenario 3 (Fixed CH3Cl/CH4 Emissions Ratio) is where tropical terrestrial CH3Cl and CH4 emissions are coupled throughout the Holocene using a constant emission ratio. We estimate this ratio to be 2.237 Tg CH3Cl/151.3 Tg CH4 (see Table 2 and supporting information). Total CH4 emissions are adjusted as in the Base Case scenario. The CH4 burden is calculated using equations (6)–(8), and equation (9) is used to scale the atmospheric OH lifetime of CH3Cl. Ocean buffering causes the net oceanic CH3Cl flux during the mid-Holocene to increase by about 200 Gg yr\(^{-1}\) relative to the modern value. Scenario 3 yields reasonable agreement with the ice core CH3Cl data (Figure 4), suggesting that changes in tropical terrestrial emissions (excluding pyrogenic emissions) are a viable explanation for the CH3Cl and CH4 trends. We also explored the possibility of changing pyrogenic emissions as a cause for the CH4 and CH3Cl trends. Methane emissions were adjusted as described above, and a fixed biomass-burning emissions ratio (0.917 Tg CH3Cl/23.5 Tg CH4, Table 2) was used to calculate pyrogenic CH3Cl emissions. In our model, biomass burning constitutes a larger fraction of the CH3Cl budget compared to its fractional contribution in the CH4 budget. This explains why eliminating the entire pyrogenic source is insufficient to match the atmospheric CH4 minimum but slightly overestimates the CH3Cl decline during the mid-Holocene (Figure 4). It appears unlikely that the entire CH3Cl decline was due to a decrease in pyrogenic emissions alone, however, because a very large fraction of the total pyrogenic emissions must be removed in order to match the ice core observations.

5. Discussion

[31] The most notable aspect of the atmospheric CH3Cl budget is the extent to which it is dominated by tropical sources. Current estimates suggest that 60–90% of the total CH3Cl emissions are from tropical regions, with the largest contributions from terrestrial plants and decaying leaf litter [Yoshida et al., 2004; Montzka and Reimann, 2010; Xiao et al., 2010]. Photochemical losses due to OH are also located primarily within the tropics. Thus, it is highly likely that variations in tropical conditions are responsible for the observed variations in atmospheric methyl chloride.

[32] Like CH3Cl, atmospheric CH4 has large tropical terrestrial sources. The most important natural source of atmospheric CH4 is anaerobic decomposition of organic material in wetlands. Together, tropical emissions from wetlands and biomass burning comprise roughly 30% of the sources in the modern CH4 budget [Bergamaschi et al., 2007] and likely accounted for greater than 60% of the sources during late preindustrial Holocene [Chappellaz et al., 1993b]. The causes of atmospheric CH4 variability over both centennial and millennial timescales have been extensively
Changes in tropical hydrology could also impact the tropical sources of CH₃Cl. As demonstrated in model Scenario 3, both the Holocene CH₃Cl and CH₄ ice core data can be reasonably simulated by reducing tropical terrestrial emissions by roughly 15% from the early to mid-Holocene. Assuming that the CH₃Cl/CH₄ ratio of tropical terrestrial emissions remained constant, emissions decreased by about 0.5 Tg CH₃Cl y⁻¹ and 33 Tg CH₄ y⁻¹ from the early to mid-Holocene. It is unlikely that the entire CH₃Cl minimum was driven by a decrease in biomass-burning emissions alone. Biomass burning constitutes only about 23% of the modern CH₃Cl budget, with the majority of these emissions occurring in the tropics [Xiao et al., 2010]. Most of the pyrogenic CH₄ emissions would have to be removed during the mid-Holocene in order to match the ice core results. Subtropical, temperate, and non-terrestrial CH₃Cl sources alone are also too small to explain the observed trend. However, it is possible that the CH₃Cl trend was driven by simultaneous changes in several smaller sources, such as biomass burning, oceans, and extratropical emissions. The CH₃Cl data argue against changes in boreal emissions or the introduction of rice agriculture as primary drivers of CH₄ variability during the Holocene [Ruddiman, 2003; Sapart et al., 2012], because CH₃Cl emissions from these sources are negligible [Lee-Taylor and Redeker, 2005].

[34] Atmospheric OH is the major loss pathway for both CH₃Cl and CH₄. Variations in atmospheric OH could explain the observed Holocene trends of both trace gases. The result from model Scenario 2 shows that a 26% decrease in the atmospheric lifetimes of CH₄ and CH₃Cl can be fit by the ice core data. This is significantly larger than the change in OH expected from the methane-OH feedback alone (model Scenario 1). It is also larger than the change in OH predicted in paleoatmospheric simulations involving full photochemistry and other climate feedbacks (ozone, water vapor, nonmethane hydrocarbons) [Martinerie et al., 1995; Valdes et al., 2005; Levine et al., 2011]. However, there are no observations that directly constrain paleo-OH, so this cannot be eliminated as a cause for the CH₃Cl and CH₄ trends.

[35] There is intriguing evidence in the glacial Taylor Dome data that CH₃Cl and CH₄ may be correlated during interstadial events (Figures 2–3). The glacial regression slope is similar to the atmospheric response ratio for tropical terrestrial emissions. Thus, it is possible that the emissions of both CH₃Cl and CH₄ were also influenced by low-latitude climatic and/or environmental changes during interstadial events [Chappellaz et al., 1993a], rather than solely due to changes in the northern latitude (boreal) sources [Dällenbach et al., 2000]. A high-resolution glacial methyl chloride record across several interstadial events is needed to confirm this relationship.

[36] Measurements from Taylor Dome show that the mean CH₃Cl level did not change between the last glacial (50–30 kyr B.P.) and interglacial (11–0 kyr B.P.) periods. Although CH₃Cl data are lacking for the last glacial maximum, the data suggest that the change in mean CH₄ level between the last glacial and interglacial period was not shared by CH₃Cl. This implies that most of the methane rise between the last glacial and interglacial period may have been due to increasing boreal emissions. This supports earlier suggestions, which attribute most of the CH₄ rise during the last glacial-interglacial transition to the expansion of high-latitude, boreal wetlands following the retreat of Northern Hemisphere ice sheets [Chappellaz et al., 1993b].

6. Conclusions

[37] The Taylor Dome results show that significant natural variations in atmospheric CH₃Cl occurred during the Holocene and last glacial period. Methyl chloride variability during the Holocene is strikingly similar to that of atmospheric methane, suggesting a common control on the natural variability of both trace gases. Both CH₃Cl and CH₄ have significant tropical terrestrial sources and share a major sink in OH. The underlying ecological and physiological factors controlling terrestrial vegetative emissions of CH₃Cl are not well understood. There are also no direct observations to constrain past changes in atmospheric OH. This limits the extent to which we can interpret ice core CH₃Cl as a measure of past environmental change. However, ice core CH₃Cl measurements provide a uniquely tropical signal that is archived along with other well-dated proxy signals in the polar ice core record.

[38] During preindustrial times, CH₃Cl was likely the major precursor of stratospheric chlorine. The ice core data suggest that natural CH₃Cl variability was on the order of 15–20% during the preindustrial Holocene. This is small compared to the fourfold increase in equivalent effective stratospheric chlorine that occurred during the twentieth century due to the anthropogenic emissions of CFCs and other chlorinated compounds [Montzka and Reimann, 2010]. Future changes in atmospheric CH₃Cl will likely be influenced by both climate and land use changes, particularly in tropical regions, as well as changes in the reactivity of the atmosphere induced by human activities. As a result, the Holocene observations may represent a lower limit to the range of CH₃Cl variability that could be expected in the future.

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