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

Kristal R. Verhulst,¹ Murat Aydin,¹ and Eric S. Saltzman¹

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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.

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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, savannahs and grasslands [Yokouchi et al., 2002; Xiao et al., 2010]. Leaf litter CH₃Cl emissions arise from an abiotic chemical reac-

tion between Cl⁻ and methoxy groups in plant pectin and exhibit a strong positive temperature dependence [Hamilton et al., 2003; Derendorp et al., 2012]. Emissions of CH₃Cl from temperate and subtropical ecosystems have also been observed but comprise a relatively small fraction of the total budget [Varner et al., 1999; Rhew et al., 2000; Rhew, 2011]. On a global scale, the oceans are a relatively small net source in the atmospheric CH₃Cl budget. Warm oceans are generally supersaturated with respect to the atmosphere and act as a CH₃Cl source, while the polar oceans are undersaturated and act as a sink [Moore et al., 1996]. The major atmospheric loss pathway of CH₃Cl is oxidation by hydroxyl radical (OH). Other loss processes include microbial degradation in soils, loss to the oceans, and loss to the stratosphere [Yoshida et al., 2004]. The environmental factors controlling CH₃Cl emissions from various ecosystems remain poorly understood because there have been few field process studies.

[4] Measurements in firm air and shallow ice cores suggest that atmospheric CH₃Cl is preserved in the Antarctic ice archive [Butler et al., 1999; Aydin et al., 2004; Williams et al., 2007]. The data from these studies suggest atmospheric CH₃Cl levels increased by roughly 10% during the twentieth century, and climate-related variations of similar magnitude also occurred over the past millennium. There are limited CH₃Cl measurements from deep Antarctic ice cores (Dome Fuji and Siple Dome, Antarctica) showing some evidence of post-depositional CH₃Cl enrichment, particularly in ice with high dust content from the last glacial period and glacial/interglacial transition [Saito et al., 2007; Saltzman et al., 2009]. Saito et al. [2007] showed that elevated calcium levels (a proxy for dust) are a possible indicator of in situ production of CH₃Cl using ice core samples from the Dome Fuji ice core.

Additional supporting information may be found in the online version of this article.

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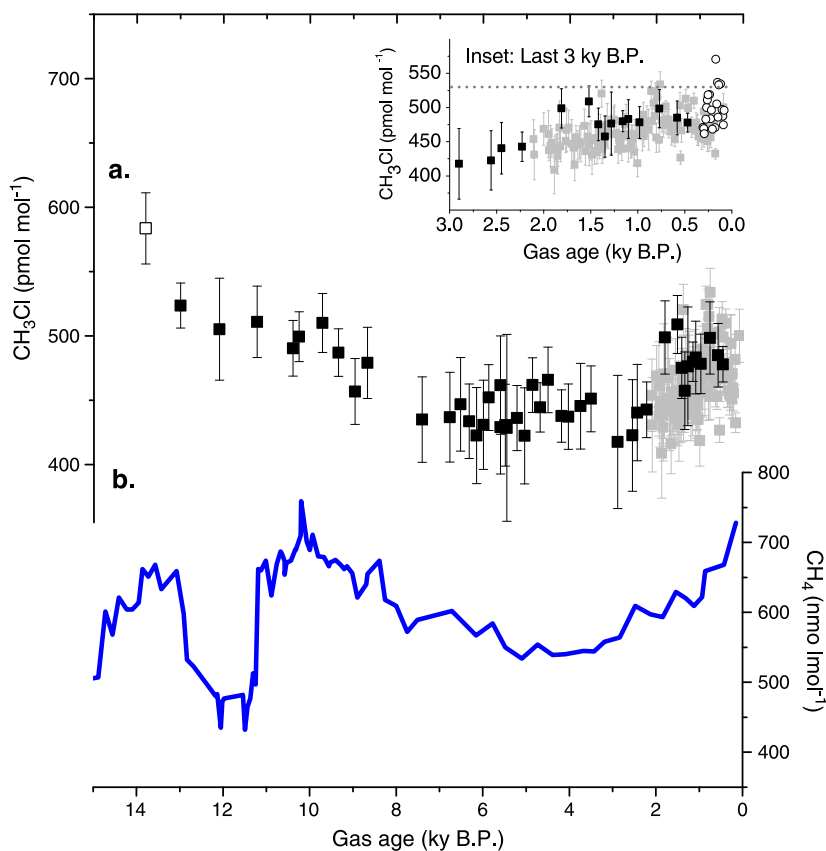


Figure 1. (a) Atmospheric history of CH_3Cl during the Holocene from the Taylor Dome (black squares, this study) and South Pole ice cores (gray squares) [Williams *et al.*, 2007]. All data are plotted with $\pm 1\sigma$ errors. The open square at 13.8 kyr B.P. is a Taylor Dome sample with calcium above $0.25 \mu\text{M}$ (see text). (inset) Comparison of Taylor Dome CH_3Cl measurements covering the last 3000 years (black squares, this study) with prior shallow ice core measurements from South Pole (filled grey squares) and Siple Dome C (open circles) [Williams *et al.*, 2007; Aydin *et al.*, 2004]. Dashed line represents modern-day mean level over Antarctica ($\sim 530 \text{ pmol mol}^{-1}$) [Aydin *et al.*, 2004]. (b) Atmospheric history of CH_4 from Taylor Dome [Brook *et al.*, 2000].

[5] Given our current understanding of the processes controlling atmospheric CH_3Cl today, we expect that CH_3Cl levels in the ancient atmosphere were sensitive to changes in tropical ecosystems and climate. A polar ice core based atmospheric history of CH_3Cl could provide a unique proxy signal that reflects changes in tropical conditions. Paleo-atmospheric CH_3Cl 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.

[6] In this study, we present measurements of CH_3Cl in air extracted from the Taylor Dome ice core. The data provide a record of CH_3Cl 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_3Cl variability over glacial/interglacial timescales. The CH_3Cl 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

[7] Taylor Dome is a 554 m ice core that was recovered in East Antarctica between 1991 and 1994 ($77^\circ 48'\text{S}$,

$158^\circ 43'\text{E}$ [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_3Cl 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).

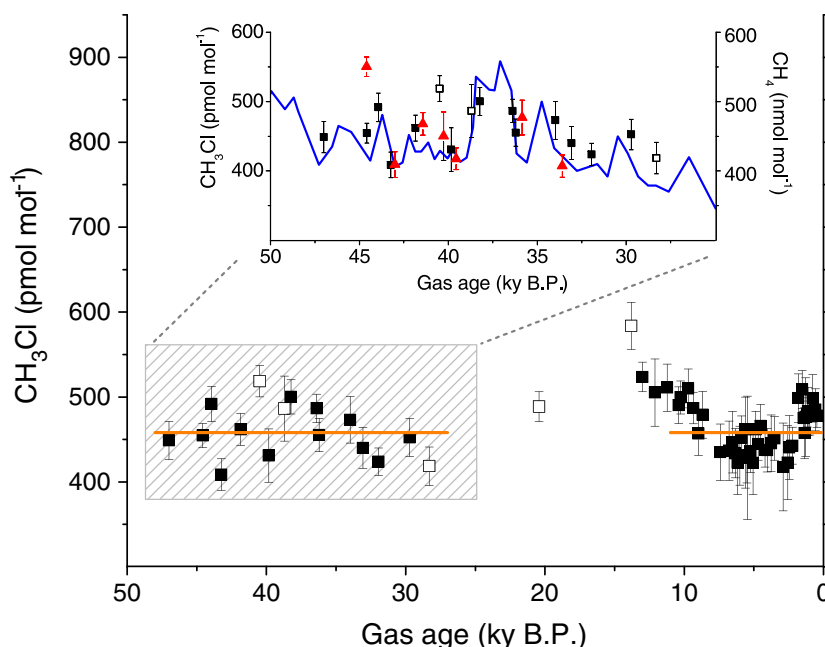


Figure 2. Methyl chloride measurements from the Taylor Dome ice core covering the last 50 kyr B.P. (black filled and open squares, left y axis). Orange lines represent the mean CH_3Cl level in samples from the last glacial period (50–30 kyr) and the Holocene (11–0 kyr). (inset) Enlarged view of the Taylor Dome CH_3Cl measurements from 50 to 25 kyr B.P., plotted with Siple Dome CH_3Cl 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 $\pm 1\sigma$ errors of the CH_3Cl measurements. Open squares indicate Taylor Dome samples with calcium at or above $0.25 \mu\text{M}$ (see text).

[8] 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_3Cl 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 ($\text{CFC-12} > 1 \text{ pmol mol}^{-1}$), 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 $6 \pm 2.6\%$ (1σ) of the measured levels.

2.1. Excess Methyl Chloride

[9] We examined calcium as a proxy for dust following Saito *et al.* [2007], using major ion data from Mayewski *et al.* [1996]. There is no correlation between Ca^{2+} and CH_3Cl in the Taylor Dome samples, suggesting there is no in situ production of methyl chloride (see Figure S2). In Siple Dome ice, there is evidence of “excess CH_3Cl ” in samples with

Ca^{2+} above $0.25 \mu\text{M}$ [Saltzman *et al.*, 2009]. Five measurements from the Taylor Dome ice core have Ca^{2+} at or above this level and are highlighted in Figures 1, 3, and S2. Holocene methyl chloride measurements from Siple Dome are elevated and scattered relative to Taylor Dome, even in samples with Ca^{2+} below $0.25 \mu\text{M}$ (Figure S2). This suggests that other site-specific properties may influence the CH_3Cl signal in Antarctic ice cores [Saltzman *et al.*, 2009].

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_3Cl levels begin to decline, reaching a broad minimum during the mid-Holocene. The CH_3Cl minimum lasts from about 7.4 to 3.5 kyr B.P., with a mean level of $440 \pm 14 \text{ pmol mol}^{-1}$ (1σ SD, $n = 21$). At 3.5 kyr, CH_3Cl 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_3Cl measurements from Antarctic ice cores. The late Holocene CH_3Cl 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

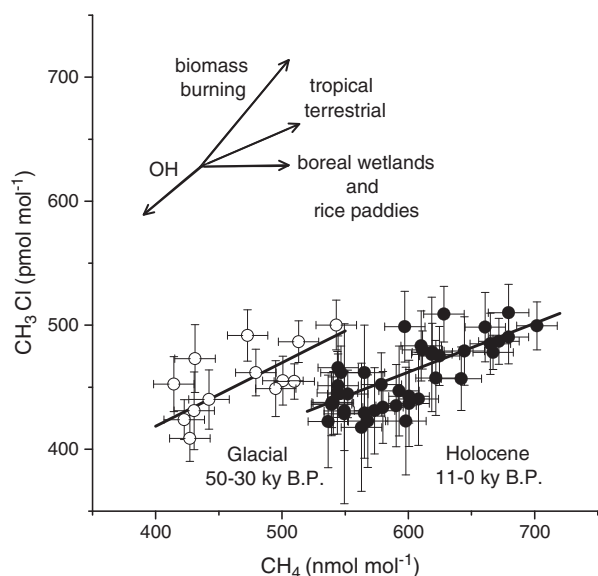


Figure 3. Taylor Dome CH_3Cl measurements from glacial (open circles) and Holocene (filled circles) samples plotted against CH_4 levels. CH_4 levels were determined at the CH_3Cl sample depths by linear interpolation of the Taylor Dome CH_4 record from Brook *et al.* [2000]. Three measurements around the Younger Dryas/Pre-Boreal are omitted. Black lines represent the slopes of Holocene and glacial samples. (inset) Lifetime-corrected $\text{CH}_3\text{Cl}/\text{CH}_4$ atmospheric response ratios calculated for various sources and sinks shared by the two trace gases using the preindustrial CH_4 and CH_3Cl lifetimes (see Table 2). The slope of the arrows reflects the change in the atmospheric $\text{CH}_3\text{Cl}/\text{CH}_4$ ratio that would result from an increase in various sources or sinks.

introduces uncertainty into the comparison of individual samples. Nonetheless, the Taylor Dome CH_3Cl measurements from the last 2 kyr have a mean level of 483.6 ± 14 (1σ SD) and agree well with South Pole data where sample ages overlap. The average rate of increase in Taylor Dome samples between 3.5 and 0.5 kyr B.P. is roughly $30 \text{ pmol mol}^{-1}/1000$ years, identical to the trend observed in the South Pole ice core from 2.2 to 0.2 kyr B.P. [Williams *et al.*, 2007] (see Figure 1 (inset)). The South Pole and Siple Dome C results also agree where the two cores overlap [Williams *et al.*, 2007]. The mean CH_3Cl level measured in Holocene samples from Taylor Dome is also similar to the Holocene mean measured in the Dome Fuji ice core (Figure S3) [Saito *et al.*, 2007]. The agreement between the new Taylor Dome data and prior South Pole measurements supports the idea that atmospheric CH_3Cl remains intact in the bubbles trapped in Antarctic ice cores and that these ice core measurements represent an atmospheric history of CH_3Cl .

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 $0.25 \mu\text{M}$, as discussed earlier (see section 2 and Figure S2, supporting information). Taylor Dome data are similar to glacial CH_3Cl 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 $456 \pm 27 \text{ pmol mol}^{-1}$ (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 CH_3Cl levels in glacial ice samples compared to the Holocene in the Dome Fuji ice core. The CH_3Cl enhancement was likely related to elevated impurity (dust) levels in the Dome Fuji ice core. The mean CH_3Cl level measured in glacial Taylor Dome samples is significantly lower than the glacial Dome Fuji measurements, even after the measurements were corrected for excess CH_3Cl production (Figure S3). This suggests that the in situ CH_3Cl 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 CH_4 (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 CH_3Cl 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, CH_3Cl and CH_4 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 CH_3Cl levels during periods with elevated CH_4 levels (Figure 2 (inset)). Between 50 and 30 kyr B.P., CH_4 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 $\text{CH}_3\text{Cl}/\text{CH}_4$ covariance is particularly notable within interstadial 8, around 38 kyr B.P.

[15] The relationship between CH_3Cl and CH_4 is shown in a regression plot (Figure 3, Table 1). To construct this plot, we linearly interpolated the Taylor Dome CH_4 data at the CH_3Cl depths. Regression fits are based on a weighted linear least squares regression with errors in both variables [Reed, 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 CH_4 . Interestingly, CH_3Cl levels show no change during the YD, based on a single CH_3Cl 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 CH_3Cl and CH_4 Correlations in the Taylor Dome Ice Core (see Figure 3)^a

Time Period (kyr B.P.)	Slope $\pm 2^*\text{s.e.}$	r	n
50–30	0.46 ± 0.25	0.66	13
11–0	0.39 ± 0.10	0.75	41
11–6	0.62 ± 0.11	0.96	12
3–0.5	1.13 ± 0.68	0.67	13

^aUnits for the slope are $\text{pmol mol}^{-1} \text{CH}_3\text{Cl}/\text{nmol mol}^{-1} \text{CH}_4$.

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

Source	CH ₄ Emissions Tg y ⁻¹	CH ₃ Cl Emissions Tg y ⁻¹	Emission Ratio Tg CH ₃ Cl/ Tg CH ₄	Atmospheric Response Ratio pmol mol ⁻¹ CH ₃ Cl/ nmol mol ⁻¹ CH ₄
Boreal wetland	43.3	0.011	2.44 × 10 ⁻⁴	0.01
Rice paddies	28.6	0.05	1.75 × 10 ⁻³	0.08
Tropical wetland	151.3	0.037	2.44 × 10 ⁻⁴	0.01
Tropical vegetation	–	2.2	–	–
Tropical terrestrial	151.3	2.237	1.48 × 10 ⁻²	0.51 ± 0.1
Pyrogenic	23.5	0.917	3.9 × 10 ⁻²	1.43 ± 0.3

^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.

[16] The slope of the Holocene and last glacial data are identical within their respective uncertainties, suggesting that the processes controlling atmospheric variability of these trace gases may not have been dramatically different under glacial and interglacial conditions (Figure 3). During the transition between the last glacial (50–30 kyr B.P.) and interglacial (11–0 kyr B.P.) periods, the mean CH₄ level increased by about 180 nmol mol⁻¹ [Brook *et al.*, 2000], while the mean CH₃Cl level did not change. The shift from glacial to interglacial conditions likely affected the global budgets of these two gases differently.

3.4. Lifetime-Weighted Atmospheric Response Ratios

[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:

$$\frac{\partial \text{CH}_3\text{Cl}}{\partial \text{CH}_4} \left(\frac{\text{pmol/mol}}{\text{nmol/mol}} \right) = \frac{E_{\text{CH}_3\text{Cl}}}{E_{\text{CH}_4}} \frac{\tau_{\text{CH}_4}}{\tau_{\text{CH}_3\text{Cl}}} \frac{16}{50.5} \times 10^3 \quad (1)$$

where $E_{\text{CH}_3\text{Cl}}$ and E_{CH_4} are the emissions of methyl chloride and methane, respectively, from a particular source (Tg y⁻¹), $\tau_{\text{CH}_3\text{Cl}}$ and τ_{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 3. Parameters Used in the CH₃Cl Box Model^a

Parameter	Symbol	Value	Reference
Mass of atmosphere (mol)	M	1.42 × 10 ²⁰	
Mean mixed layer depth (m)	z	75	
Surface area of the ocean (m ²)	A	361 × 10 ¹²	
Mean air-sea exchange coefficient (m y ⁻¹)	K _w	1.5 × 10 ³	
Henry's law constant (m ³ atm mol ⁻¹)	H	8.78 × 10 ⁻³	Moore <i>et al.</i> [1995]
Mean diffusivity through thermocline (m ² y ⁻¹)	D _z	5.4 × 10 ³	
In situ degradation rate (y ⁻¹)	k _d	25.55	Tokarczyk <i>et al.</i> [2003]
Mean "eddy degradation" rate (m y ⁻¹)	K _{ed} = (D _z k _d) ^{0.5}	371.4	
Ocean production rate (mol CH ₃ Cl y ⁻¹)	P _o	7.68 × 10 ¹⁰	see text

^aValues are from Butler [1994] unless otherwise noted.

Table 4. Methyl Chloride Global Budget Terms Estimated for the Modern Atmosphere Using the CH₃Cl Box Model

Emissions	Gg yr ⁻¹	Lifetime (y)
Vegetation and biomass burning	2596	
Ocean	500	
Anthropogenic	344 ^a	
Total source	3440	
Losses		
OH		1.3
Ocean		3.8
Soil		16.4
Stratosphere		35
Total lifetime		1.16

^aAnthropogenic CH₃Cl sources are estimated at 10% of the modern budget, based on prior firm air and shallow ice core studies [Butler *et al.*, 1999; Aydin *et al.*, 2004].

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

$$\frac{dM_a}{dt} = S_{\text{terr}} + F_{\text{oa}} - F_l = 0 \quad (2)$$

$$\frac{dM_o}{dt} = P_o - F_{\text{oa}} - F_d - F_{\text{ed}} = 0 \quad (3)$$

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_{terr} is the sum

of terrestrial sources, including biomass burning and vegetative emissions, F_{oa} is the net exchange across the air/sea interface, and F_l 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_{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:

$$\frac{dM_a}{dt} = S_{\text{terr}} + \frac{K_w A}{H} (p_w - p_a) - (k_{\text{OH}} + k_{\text{soil}} + k_{\text{strat}}) p_a M \quad (4)$$

$$\frac{dM_o}{dt} = P_o - \frac{K_w A}{H} (p_w - p_a) - k_d M_o - \frac{K_{\text{ed}}}{z} M_o \quad (5)$$

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_{OH} , k_{soil} , and k_{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_{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 7.68×10^{10} mol CH₃Cl 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 CH₃Cl 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:

$$M_{\text{CH}_4} = \frac{S}{k_{\text{OH}} + k_{\text{soil}} + k_{\text{strat}}} \quad (6)$$

where M_{CH_4} is the atmospheric CH₄ burden (mol), S is the total CH₄ source, and k_{OH} , k_{soil} , and k_{strat} are the first-order loss rate constants for reaction with OH, loss to 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 related to the atmospheric

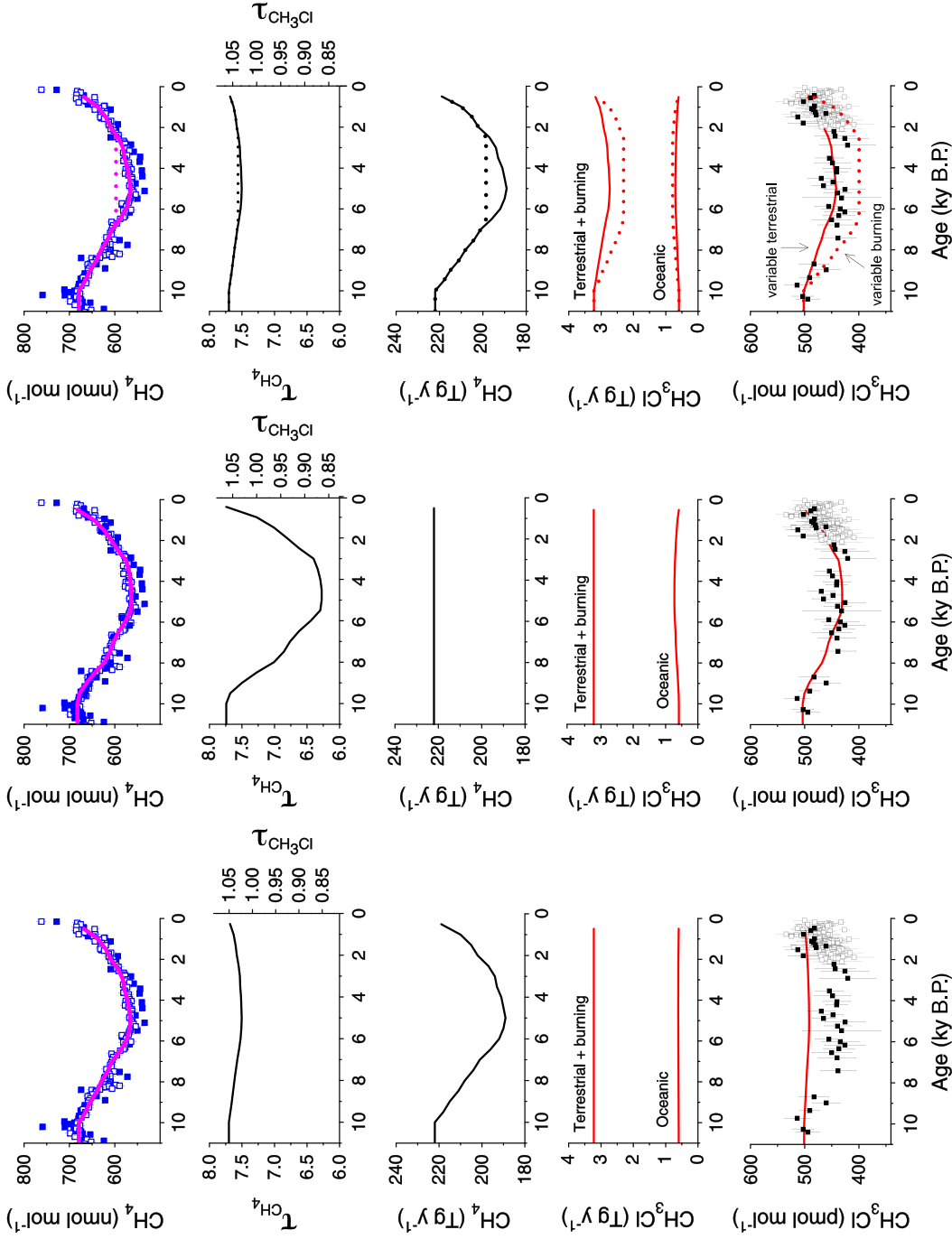


Figure 4. (left column) Model Scenario 1: Base Case results using variable CH_4 emissions, OH-methane feedback, and fixed terrestrial CH_3Cl emissions. (middle column) Model Scenario 2: OH-only results using fixed CH_4 emissions, fixed terrestrial CH_3Cl emissions, and variable OH lifetimes for CH_4 and CH_3Cl . (right column) Model Scenario 3: Fixed emissions ratio results using prescribed terrestrial CH_4 emissions, OH-methane feedback, and a fixed $\text{CH}_3\text{Cl}/\text{CH}_4$ ratio for tropical terrestrial emissions (solid lines) and biomass-burning emissions (dashed lines). (from top to bottom rows) Modeled atmospheric CH_4 (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 CH_4 (left y axis) and CH_3Cl (right y axis), prescribed total CH_4 emissions, terrestrial and oceanic CH_3Cl emissions, and modeled atmospheric CH_3Cl (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:

$$k_{\text{OH}+\text{CH}_4} = \frac{k_{\text{OH}+\text{CH}_4}^*}{\left(1 - \frac{\partial \ln \text{OH}}{\partial \ln \text{CH}_4} R\right)} \quad (7)$$

where

$$R = \frac{M_{\text{CH}_4} - M_{\text{CH}_4}^*}{M_{\text{CH}_4}^*} \quad (8)$$

and $\partial \ln \text{OH} / \partial \ln \text{CH}_4$ is the magnitude of the CH₄ feedback on atmospheric OH, $k_{\text{OH}+\text{CH}_4}^*$ 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 $k_{\text{OH}+\text{CH}_4}^* = (1/9.6) \text{ y}^{-1}$ and $M_{\text{CH}_4}^* = 251 \text{ Tmol CH}_4$ (equivalent to $1774 \text{ nmol mol}^{-1}$) as conditions for the modern atmosphere [Denman *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 lifetime are calculated by solving the equations (6)–(8) iteratively using the Matlab fsolve function.

[26] To couple the CH₃Cl and CH₄ box models, the OH lifetime of CH₃Cl is scaled to the OH lifetime of CH₄:

$$k_{\text{OH}+\text{CH}_3\text{Cl}} = \left(\frac{1.3}{9.6}\right) k_{\text{OH}+\text{CH}_4} \quad (9)$$

where $k_{\text{OH}+\text{CH}_3\text{Cl}}$ and $k_{\text{OH}+\text{CH}_4}$ are the first-order loss rate constants for loss of CH₃Cl and CH₄, and 1.3 and 9.6 are the modern OH lifetimes of CH₃Cl 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 y^{-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 $2.237 \text{ Tg CH}_3\text{Cl}/151.3 \text{ Tg CH}_4$ (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 y^{-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 ($0.917 \text{ Tg CH}_3\text{Cl}/23.5 \text{ Tg CH}_4$, 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

debated [Dällenbach *et al.*, 2000; Ruddiman, 2003; Valdes *et al.*, 2005; Levine *et al.*, 2011; Sapart *et al.*, 2012]; however, changes in tropical emissions are generally thought to be the primary driver of CH₄ variations during the preindustrial Holocene [Chappellaz *et al.*, 1997; Flückiger *et al.*, 2002; Harder *et al.*, 2007]. Changes CH₄ production from tropical wetlands during the Holocene have been attributed to orbitally driven variations in tropical hydrology [Singarayer *et al.*, 2011; Burns, 2011; Dykoski *et al.*, 2005; Wang *et al.*, 2007].

[33] 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 CH₃Cl 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 is required to fit 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 paleo-proxies 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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