

Active chlorine in the remote marine boundary layer: Modeling anomalous measurements of $\delta^{13}\text{C}$ in methane

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Abstract. Measurements of $\delta^{13}\text{C}$ in methane in the marine boundary layer (MBL) of the extratropical Southern Hemisphere imply a kinetic isotope fractionation much larger than would be expected if the hydroxyl radical were the only tropospheric methane sink. We use a simple chemical box model to show that the assumption of a MBL active chlorine (Cl^*) sink can explain these anomalous observations provided there is a seasonal cycle in the Cl^* sink with a summer-winter concentration difference $\sim 6 \cdot 10^3 \text{ cm}^{-3}$. The required summer maximum and yearly mean Cl^* concentrations are plausible, and imply a global Cl^* sink strength for methane of $< 5 \text{ Tg yr}^{-1}$. Choice of a Cl^* sink seasonal cycle linked to the nonsinusoidal dimethyl sulfide seasonal cycle gives the observed fractionation with a smaller yearly mean Cl^* concentration than equivalent sinusoidal Cl^* cycles.

1. Introduction

Methane (CH_4) is an important greenhouse gas and is responsible for a significant fraction of anthropogenic climate forcing [e.g., *Lelieveld et al.*, 1998]. It also plays an important role in atmospheric chemistry in the troposphere, where it is a major regulator of the hydroxyl radical (OH) and a source of hydrogen and carbon monoxide.

Atmospheric CH_4 contains mainly $^{12}\text{CH}_4$ with about 1% of $^{13}\text{CH}_4$, other isotopomers being insignificant. Measurement of the ^{13}C isotopic composition of CH_4 in the atmosphere can provide constraints on the global CH_4 budget because several CH_4 sources can be distinguished by characteristic ^{13}C signatures [e.g., *Stevens and Engelkemeir*, 1988]. For CH_4 , $^{13}\text{C}/^{12}\text{C}$ isotopic ratios are reported through the $\delta^{13}\text{C}$ ratio defined by

$$\delta^{13}\text{C} \equiv \frac{[^{13}\text{CH}_4]/[^{12}\text{CH}_4]}{R_0} - 1, \quad (1)$$

where $R_0 = (^{13}\text{C}/^{12}\text{C})_{\text{PDB}}$ has an accepted value of 0.0112372 for the isotope standard, peedee belemnite (PDB) [*Craig*, 1957]. Usually, $\delta^{13}\text{C}$ is scaled by a factor of 1000 and reported as per mill “‰.” For compactness we refer to the $\delta^{13}\text{C}$ of the carbon in CH_4 as “ $\delta^{13}\text{CH}_4$.” Note that $\delta^{13}\text{CH}_4$ is a very sensitive measure of changes in isotopic content.

The removal of $^{13}\text{CH}_4$ by OH is slightly slower than that of $^{12}\text{CH}_4$ (i.e., $k_{13} < k_{12}$ where k is the mass-

dependent collisional rate constant), an effect known as isotope fractionation. We take $(k_{13}/k_{12})_{\text{OH}} = 0.9946$ [*Cantrell et al.*, 1990] and define the “kinetic isotope effect” (KIE) as $\epsilon = (k_{13}/k_{12}) - 1$. Then $\epsilon_{\text{OH}} = -0.0054$ (or -5.4‰), the KIE for the $\text{CH}_4 + \text{OH}$ reaction. The molar mixing ratio (MR) is defined as moles of CH_4 per mole of dry air. If Δ_{MR} is the relative change in MR over a short time (say 1 year) and $\Delta\delta$ is the corresponding change in $\delta^{13}\text{CH}_4$ about the mean value δ_0 , then

$$\Delta\delta \approx \epsilon(1 + \delta_0)\Delta_{\text{MR}}. \quad (2)$$

Plotting $\Delta\delta$ versus Δ_{MR} gives the “(KIE) line” of slope $\epsilon(1 + \delta_0)$. Expression (2) strictly applies to a closed box, and if observations were available for such a closed box, the KIE ϵ could be derived from the measured slope of the KIE line [*Allan et al.*, 2001].

The TM2 transport model results given by *Allan et al.* [2001] showed that CH_4 sources (particularly biomass burning) that are structured in space and time broaden the KIE line into a “phase ellipse”, different source scenarios giving different ellipse shapes. *Allan et al.* [2001] also showed that, for an OH sink acting alone in a variety of source scenarios, the modeled tilt of the phase ellipse in the extratropical Southern Hemisphere (ETSH) was a robust predictor of the -5.4‰ value of ϵ_{OH} assumed in the model. The ETSH can be taken as approximating a closed box in the sense that the major axis of a phase ellipse approximates the KIE line.

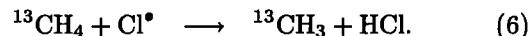
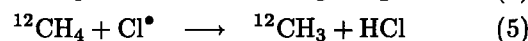
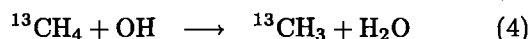
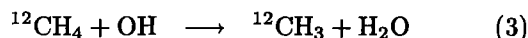
Thus, if OH were the only tropospheric sink for CH_4 , observations of $\delta^{13}\text{CH}_4$ in the ETSH could then be used to measure ϵ_{OH} . However, such observations over the period 1993–1996 imply an anomalously large value of ϵ , typically -13‰ rather than the expected -5.4‰ [*Lowe et al.*, 1999; *Allan et al.*, 2001]. *Lowe et al.* [1999] and *Allan et al.* [2001] suggested that this anomaly might be a result of competitive removal of CH_4 by active chlorine (Cl^*) in the ETSH marine boundary layer (MBL), since ϵ_{Cl} has been measured at -66‰ [*Saueressig et al.*, 1995; *Tyler et al.*, 2000].

Here we use a simple chemical box model of the ETSH MBL including CH_4 destruction by both OH and Cl^* to estimate the magnitude and form of the Cl^* sink required to explain the anomalous $\delta^{13}\text{CH}_4$ observations resulting in an increased phase ellipse tilt and a value of -13‰ for ϵ .

2. Model

The existence of Cl^* in the MBL has been a topic of recent observational and modeling work [e.g., *Singh and Kasting*, 1988; *Finlayson-Pitts*, 1993; *Gupta et al.*, 1996; *Singh et al.*, 1996; *Vogt et al.*, 1996; *Win-*

genter *et al.*, 1996, 1999]. Here we model the remote ETSH MBL as a closed box in which the CH_4 carbon isotopic components undergo the following reactions.



The rate constants for reactions (3) and (5) are taken as $k_{\text{OH}}^{12} = 2.45 \cdot 10^{-12} \exp(-1775/T)$ and $k_{\text{Cl}}^{12} = 1.10 \cdot 10^{-11} \exp(-1400/T)$ respectively [DeMore *et al.*, 1997], where T is temperature in K, and all rate constants are in units of $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. For (4) and (6), the corresponding rate constants are $k_{\text{OH}}^{13} = k_{\text{OH}}^{12}(1 + \epsilon_{\text{OH}})$ and $k_{\text{Cl}}^{13} = k_{\text{Cl}}^{12}(1 + \epsilon_{\text{Cl}})$, where we use $\epsilon_{\text{OH}} = -5.4\%$ and $\epsilon_{\text{Cl}} = -66\%$ (see section 1). We take $T = 287 \text{ K}$ as typical for the ETSH remote MBL at midlatitudes and assume an average MBL thickness of 1 km.

Reactions (3) to (6) are sufficient to describe the chemical system for our present purpose, as chemical feedbacks on OH and Cl^\bullet are assumed to be negligible. We take the OH and Cl^\bullet sinks to be specified drivers of the system, as their turnover times are very much shorter than that for CH_4 . Sink destruction of CH_4 is balanced by a constant input flux of $^{12}\text{CH}_4$ and $^{13}\text{CH}_4$ chosen to have a fixed $\delta^{13}\text{CH}_4$. The sinks have seasonal cycles, but no variation on a diurnal time scale. We use the Facsimile numerical integrator [Curtis and Sweetenham, 1988] to solve the system, running for 100 model years to ensure the solution for $\delta^{13}\text{CH}_4$ reaches a steady state [e.g., Tans, 1997].

The sink drivers are shown in Figure 1. The OH seasonal cycle is a sinusoid based on the OH concentrations given by Spivakovsky *et al.* [2000] in the vicinity of Baring Head, New Zealand (41° S). The Cl^\bullet seasonal cycle has a relatively sharp maximum in summer, lagging the OH maximum by about a month. The maximum (summer) and minimum (winter) $[\text{Cl}^\bullet]$ values can be chosen independently. We assume a typical winter minimum $[\text{Cl}^\bullet]$ to be 600 cm^{-3} , slightly less than the $[\text{Cl}^\bullet]$ of 720 cm^{-3} inferred in early spring at latitudes south of Tasmania, Australia [Wingenter *et al.*, 1999].

In the low NO_x ETSH atmosphere, sulfur species (e.g., SO_2 derived from dimethyl sulfide, DMS) lower

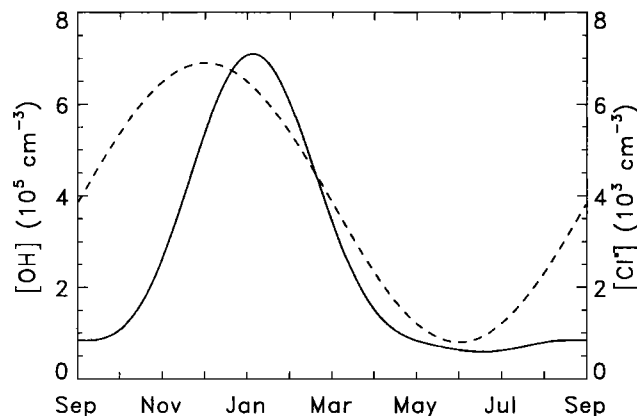


Figure 1. Seasonal cycles of the OH sink (dashed line) and the Cl^\bullet sink (full line).

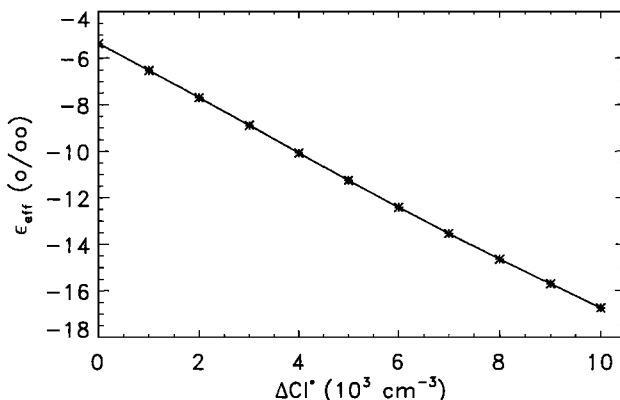


Figure 2. Effective isotopic fractionation ϵ_{eff} versus summer-winter difference in Cl^\bullet concentration ΔCl^\bullet .

the pH of sea-salt aerosol allowing acid-catalysed release of Cl^\bullet , as modeled by Vogt *et al.* [1996]. This result is supported by observation of a summer maximum in chloride deficits in marine aerosol that corresponds to the summer maximum in DMS-related sulfur species [Ayers *et al.*, 1999]. It is therefore plausible to assume that $[\text{Cl}^\bullet]$ is linearly related to DMS concentration. Based on this assumption, we generate the Cl^\bullet cycle in Figure 1 from 3 sinusoids with amplitudes and phases chosen so that their sum approximates the form of the DMS seasonal cycle measured at the Cape Grim Baseline Station in Tasmania [Gillett *et al.*, 1993].

Ratios of DMS summer maxima to winter minima are typically ~ 10 [Gillett *et al.*, 1993]. The Wingenter *et al.* [1999] ETSH $[\text{Cl}^\bullet]$ values were inferred in early spring at a time of unusually low DMS concentration, a factor of 2 to 3 lower than normal [Hainsworth *et al.*, 1998]. If these early spring $[\text{Cl}^\bullet]$ values were therefore comparable with typical winter values, then summer $[\text{Cl}^\bullet]$ could be a factor of 10 larger than the Wingenter *et al.* [1999] spring values. The summer ETSH MBL might then resemble more closely the “polluted” North Atlantic air mass of Wingenter *et al.* [1996] (with inferred $[\text{Cl}^\bullet]$ values of $3.3\text{--}6.5 \cdot 10^4 \text{ cm}^{-3}$) than the extremely clean air mass of Wingenter *et al.* [1999].

3. Results

We ran the model with a range of summer maximum Cl^\bullet concentrations. The CH_4 MR and $\delta^{13}\text{CH}_4$ seasonal cycles in the final year of each run were then used to determine the effective ϵ value (ϵ_{eff}) from the KIE line relationship (2) for the combined OH+ Cl^\bullet sink. Figure 2 shows the results, with ϵ_{eff} plotted versus summer-winter $[\text{Cl}^\bullet]$ change (ΔCl^\bullet). When ΔCl^\bullet is zero (summer maximum $[\text{Cl}^\bullet]$ is 600 cm^{-3}), ϵ_{eff} is -5.4% . As ΔCl^\bullet increases, the magnitude of ϵ_{eff} increases almost linearly. For $\epsilon_{\text{eff}} = -13\%$ (as inferred from observations at Baring Head and Scott Base, Antarctica), the value of ΔCl^\bullet is $6.5 \cdot 10^3 \text{ cm}^{-3}$. This ΔCl^\bullet was used to plot the Cl^\bullet seasonal cycle in Figure 1.

Figure 3a shows the CH_4 MR for the cases of OH alone and OH+ Cl^\bullet with $\Delta\text{Cl}^\bullet = 6.5 \cdot 10^3 \text{ cm}^{-3}$. The input CH_4 flux was chosen to give a mean MR of 1680 parts per billion (ppb) at steady state in each case, this being the observed mean at Baring Head in the period 1993–1996 [Allan *et al.*, 2001]. Including Cl^\bullet results

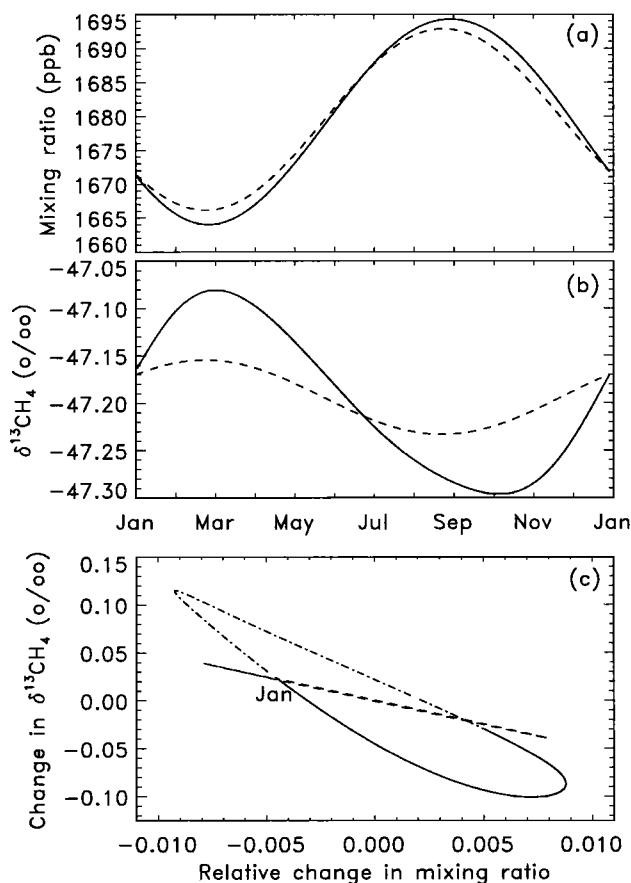


Figure 3. (a) Methane mixing ratio and (b) $\delta^{13}\text{CH}_4$ for OH alone (dashed lines) and OH+Cl* (full lines), where the OH and Cl* cycles in Figure 1 are used. (c) The corresponding phase diagrams for OH alone (dashed line) and OH+Cl* (dashed-dotted line for the first 6 months; full line for the second 6 months with January marked). This figure should be compared with the Baring Head data in Figure 8 of Allan *et al.* [2001], which have been omitted here for clarity.

in a relatively small increase in the MR seasonal amplitude. Figure 3b shows $\delta^{13}\text{CH}_4$ for OH alone, and for OH+Cl* with $\Delta\text{Cl}^* = 6.5 \cdot 10^3 \text{ cm}^{-3}$. The input value of $\delta^{13}\text{CH}_4$ was chosen to give a mean $\delta^{13}\text{CH}_4$ value in the box of -47.20‰ at steady state in each case, this being the observed Baring Head mean for 1993–1996. Inclusion of seasonally varying Cl* results in a very large increase in the $\delta^{13}\text{CH}_4$ seasonal amplitude, and a distinctly asymmetric shape for the $\delta^{13}\text{CH}_4$ seasonal cycle. When we used an aseasonal [Cl*] of $6.5 \times 10^3 \text{ cm}^{-3}$ in the model, the inferred KIE did not change from the OH value of -5.4‰ . This illustrates the sensitivity of $\delta^{13}\text{CH}_4$ to changes in the sink structure.

In Figure 3c we plot the change in $\delta^{13}\text{CH}_4$ versus the relative change in MR, derived from Figures 3a and 3b. This gives the “phase diagram” discussed by Allan *et al.* [2001]. For OH alone MR and $\delta^{13}\text{CH}_4$ are in antiphase, giving a phase diagram that is essentially a straight line, the KIE line defined by (2) consistent with $\epsilon_{\text{OH}} = -5.4\text{‰}$. When Cl* is included, a phase shift occurs between MR and $\delta^{13}\text{CH}_4$, resulting in a distorted ellipse-like shape, the major axis slope of this “ellipse” being consistent with $\epsilon_{\text{eff}} = -13\text{‰}$.

The format of Figure 3 is chosen for easy comparison with the Baring Head observations in Figure 8 of Allan *et al.* [2001]. The most important feature of the comparison is that the amplitude of the observed $\delta^{13}\text{CH}_4$ cycle is similar to that of the modeled $\delta^{13}\text{CH}_4$ cycle including OH and Cl*, giving the increased tilt of the phase ellipse described earlier. Phase differences between observed and modeled $\delta^{13}\text{CH}_4$ cycles are a source effect, as discussed by Allan *et al.* [2001].

4. Discussion

If we interpret the anomalous tilt of the observed phase ellipse in the ETSH [Allan *et al.*, 2001] as indicating the existence of an atmospheric sink in addition to OH and if we take this sink to be Cl* in the MBL, then the results in section 3 can give us important information on the properties of this assumed Cl* sink. The summer maximum [Cl*] of $7.1 \cdot 10^3 \text{ cm}^{-3}$ and the resulting seasonal mean [Cl*] of $2.6 \cdot 10^3 \text{ cm}^{-3}$ are plausible and consistent with model values quoted by Vogt *et al.* [1996] and Singh *et al.* [1996]. This approach to estimating the seasonal mean [Cl*] requires that ΔCl^* be much larger than the winter minimum [Cl*]. This should be valid in the ETSH, but is almost certainly invalid in the tropics because of smaller seasonal effects. The ETSH therefore appears to be the ideal region in which to estimate “natural” [Cl*] using this method.

If we assume the above inferred [Cl*] mean value to be valid for the MBL over the global ocean (noting that ΔCl^* will vary widely), then the total Cl* sink strength for CH₄ in the MBL would be about 3.1 Tg yr^{-1} . If $\sim 90\%$ of tropospheric Cl* is in the MBL [Singh *et al.*, 1996], then the total tropospheric Cl* sink strength for CH₄ (not including “anthropogenic” Cl*) would be about 3.5 Tg yr^{-1} , a minor CH₄ sink compared with the dominant OH sink.

The sink strengths above are fairly insensitive to the form of the Cl* seasonal cycle. For a sinusoidal Cl* cycle lagging the OH cycle by a month, the required summer maximum and yearly mean values of [Cl*] are $6.5 \cdot 10^3 \text{ cm}^{-3}$ and $3.6 \cdot 10^3 \text{ cm}^{-3}$ respectively. For a sinusoidal Cl* cycle in phase with the OH cycle, the corresponding values are $6.3 \cdot 10^3 \text{ cm}^{-3}$ and $3.5 \cdot 10^3 \text{ cm}^{-3}$. The global MBL sink strength in these cases would be about 4.3 Tg yr^{-1} . The DMS-linked cycle therefore requires a smaller yearly mean [Cl*] to give the same ϵ_{eff} . If we assume $\epsilon_{\text{OH}} = -3.9\text{‰}$ [Saueressig *et al.*, 1999], the summer maximum and yearly mean values of [Cl*] required in the MBL for the DMS-linked cycle increase to $8.0 \cdot 10^3 \text{ cm}^{-3}$ and $2.8 \cdot 10^3 \text{ cm}^{-3}$ respectively. Although our assumed direct linkage between the MBL Cl* cycle and the DMS cycle is speculative at present, it is clear that the primary requirement to reproduce the observed ϵ_{eff} is a Cl* seasonal cycle in the ETSH with $\Delta\text{Cl}^* \sim 6 \cdot 10^3 \text{ cm}^{-3}$; the exact form of this cycle is secondary.

5. Conclusions

Measurements of $\delta^{13}\text{CH}_4$ in the ETSH MBL imply a kinetic isotope fractionation of CH₄ much larger than expected if the tropospheric OH sink alone were involved. We have shown that the assumption of a MBL Cl* sink in addition to OH can explain these anomalous

observations provided there is an ETSH seasonal cycle in the Cl^\bullet sink with a summer-winter concentration difference $\sim 6 \cdot 10^3 \text{ cm}^{-3}$. The required summer maximum and yearly mean Cl^\bullet concentrations are plausible ($\sim 7 \cdot 10^3 \text{ cm}^{-3}$ and $3 \cdot 10^3 \text{ cm}^{-3}$ respectively) and imply a "natural" global Cl^\bullet sink strength for CH_4 of $< 5 \text{ Tg yr}^{-1}$ if the mean value applies over the global ocean.

Our plausible choice of a Cl^\bullet sink seasonal cycle linked to the dimethyl sulfide seasonal cycle gives the observed effective carbon isotopic fractionation with a smaller yearly mean Cl^\bullet concentration than equivalent sinusoidal Cl^\bullet cycles. Use of the phase diagram approach can potentially provide further information on the Cl^\bullet seasonal cycle from observations of $\delta^{13}\text{CH}_4$. However, more detailed chemical modeling and ETSH measurements of Cl^\bullet are required to elucidate the likely Cl^\bullet seasonal cycle structure in the ETSH.

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