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U. Platt, W. Allen, D. Lowe. Hemispheric average Cl atom concentration from  $^{13}\text{C}/^{12}\text{C}$  ratios in atmospheric methane. *Atmospheric Chemistry and Physics Discussions*, 2004, 4 (3), pp.2283-2300. hal-00301186

**HAL Id: hal-00301186**

**<https://hal.science/hal-00301186>**

Submitted on 18 Jun 2008

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concentration

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# Hemispheric average Cl atom concentration from $^{13}\text{C}/^{12}\text{C}$ ratios in atmospheric methane

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Received: 16 February 2004 – Accepted: 9 March 2004 – Published: 4 May 2004

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## Abstract

Methane is a significant atmospheric trace gas in the context of greenhouse warming and climate change. The dominant sink of atmospheric methane is the hydroxyl radical (OH). Recently, a mechanism for production of chlorine radicals (Cl) in the marine boundary layer (MBL) via bromine autocatalysis has been proposed. The importance of this mechanism in producing a methane sink is not clear at present because of the difficulty of in-situ direct measurement of Cl. However, the large kinetic isotope effect of Cl compared with OH produces a large fractionation of  $^{13}\text{C}$  compared with  $^{12}\text{C}$  in atmospheric methane. This property can be used to estimate the likely size of the methane sink attributable to MBL Cl. By taking account of the mixing of MBL air into the free troposphere, we estimate that the global methane sink due to reaction with Cl atoms in the MBL could be as large as  $19 \text{ Tg yr}^{-1}$ , or about 3.3% of the total  $\text{CH}_4$  sink.

## 1. Introduction

Atmospheric methane has more than doubled in the atmosphere over the last 150 years due to increases in agricultural and industrial sources (Etheridge et al., 1998). Because of its strong absorption in the infrared, methane plays an important role in the Earth's radiation balance and is responsible for a significant fraction of anthropogenic climate forcing (Crutzen, 1995). Methane also plays a significant role in the stratosphere where its oxidation releases water vapour, which modifies both, the radiative balance and stratospheric chemistry. In addition the reaction of Cl atoms with  $\text{CH}_4$  reduces the rate of stratospheric ozone destruction. As the most abundant hydrocarbon in the troposphere it is a major regulator of OH and source of tropospheric carbon monoxide and hydrogen. Over the last 15 years the growth rate of atmospheric methane has decreased from levels as high as 1% per year observed in the 1970s and 1980s to lower but highly variable values ranging from zero to 1% per year (Dlugokencky et al., 1998) The reasons for the change in growth rate are not understood but

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clearly represent a shift in the source-sink budget of atmospheric methane.

In the extra tropical southern hemisphere (ETSH), measurements of atmospheric mixing ratios of methane show smooth seasonal cycles having peak-to-peak amplitudes of about 40 ppb with maxima in September and minima in March. These are superimposed on a long-term trend (Dlugokencky et al., 1998; Prather et al., 2001)

The primary mechanism for the removal of methane from the atmosphere is due to hydrogen abstraction from the methane molecule by the OH radical to form water



OH is formed photochemically from the photolysis of ozone and subsequent reaction of the excited oxygen atoms ( $\text{O}^1\text{D}$ ) with water vapour. Thus its concentration peaks in the ETSH in December at minimum solar zenith angle. Hence if reaction (1) is the primary removal process for methane we would expect smooth seasonal cycles in the mixing ratio of methane following those of OH with a phase shift of  $90^\circ$ . This is indeed observed as shown in Fig. 1 for methane mixing ratio measurements made at Baring Head, New Zealand ( $41^\circ\text{S}$ ), where the peak-to-peak amplitude is about 35 ppb.

When OH removes methane, a Kinetic Isotope Effect (KIE) results in the slightly faster removal of the predominant (about 99%) stable isotopomer,  $^{12}\text{CH}_4$ , in preference to the heavier and less abundant (about 1%)  $^{13}\text{CH}_4$  isotopomer. The main reason for this effect is that the mass dependent rate constant for the reaction of OH with  $^{12}\text{CH}_4$  ( $k_{12}$ ) is slightly greater than the equivalent rate constant with  $^{13}\text{CH}_4$  ( $k_{13}$ ). The result is that the isotopic ratio  $^{13}\text{C}/^{12}\text{C}$  in the methane remaining in the atmosphere increases as methane is removed by reaction (1). This effect has been measured in the laboratory by Cantrell et al. (1990) ( $k_{13}/k_{12}=0.9946$ ) and most recently by Saueressig et al. (2001) ( $k_{13}/k_{12}=0.9961$ ). Measurements of the  $^{13}\text{C}/^{12}\text{C}$  isotopic ratio of a species like methane are usually reported with respect to a standard in a “delta” notation where

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$\delta^{13}\text{C}$  is defined as:

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

where  $R_0$  is an international standard with an accepted value of  $R_0 = {}^{13}\text{C}/{}^{12}\text{C} = 0.0112372$ .

If we define a KIE factor,  $\varepsilon = (k_{13}/k_{12}) - 1$ , then the Saueressig et al. (2001) result equates to  $\varepsilon = -3.9\%$  (parts per 1000 or per mille). If the average level and change in the molar mixing ratio in methane over a year are  $\bar{c}$  and  $\Delta c$ , respectively, and  $\Delta\delta$  is the corresponding change in  $\delta^{13}\text{C}(\text{CH}_4)$  about a mean value  $\delta_0$ , Allan et al. (2001a) show for a closed reaction system that

$$\Delta\delta = \varepsilon (1 + \delta_0) \frac{\Delta c}{\bar{c}} \quad (2)$$

Plotting  $\Delta\delta$  versus  $\Delta c/\bar{c}$  yields a “KIE line” of slope,  $\varepsilon(1 + \delta_0)$ .

Hence, making the assumption that the ETSH approximates a closed box remote from local sources of methane, we expect measurements of  $\delta^{13}\text{C}(\text{CH}_4)$  to show smooth cycles with a peak to peak amplitude of  $<0.1\%$  and to be  $180^\circ$  or 6 months out of phase with the methane mixing ratio signal. However, a time series of measurements of  $\delta^{13}\text{C}(\text{CH}_4)$  made in the ETSH at Baring Head (Fig. 2) shows highly irregular seasonal cycles with a peak to peak amplitude a factor of about 4 higher from 1993 to 1998 decreasing to a factor of about 2 thereafter. In addition the cycles have a different phase to that predicted on the basis of simple removal by OH outlined above. The long-term variation in the seasonal cycle amplitude of  $\delta^{13}\text{C}(\text{CH}_4)$  is currently under investigation. Allan et al. (2001a) show that smoothed data from Baring Head plotted using Eq. (2) result in ellipses (see e.g. Fig. 3) rather than the expected straight “KIE line” indicating that the  $\delta^{13}\text{C}(\text{CH}_4)$  and methane mixing ratio cycles cannot be exactly six months out of phase. They show that the minor axes of these ellipses are a function of “source effects” with a major conclusion of their work being that the gradient

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of the major axes of the ellipses is equivalent to the “apparent KIE” for the removal of methane from the atmosphere in the ETSH. The Baring Head results show that the apparent KIE is much larger than that expected from OH oxidation alone, for example the KIE derived for the 1996 ellipse shown in Fig. 3 is about  $-13\%$  compared with  $-3.9\%$  for the OH KIE. Note that Allan et al. (2001a) used the average ellipse for 1993–1996, but we show the 1996 ellipse here, to demonstrate that it is similar to the 1993–1996 average ellipse.

To explain the high apparent KIE for methane observed in the ETSH, Lowe et al. (1999) speculated that the removal process for methane might be enhanced by active chlorine in the marine boundary layer (MBL). Allan et al. (2001b) used a simple chemical box model to show that the anomalously high KIE could be explained by assuming the existence of a seasonal cycle in active chlorine (i.e. Cl atoms) in the marine boundary layer MBL of the ETSH with an amplitude (highest minus lowest Cl level) of about  $6 \cdot 10^3$  atoms  $\text{cm}^{-3}$ . In addition there might be an “offset” level of Cl atoms always present that cannot be detected using the “isotope phase ellipse” technique.

In this work we present details of a halogen activation mechanism capable of providing the required concentration and seasonal cycle of chlorine to produce the observed isotope effects in methane. We estimate the size of this additional sink process compared to the removal of methane by OH.

## 2. Reactive halogen species in the troposphere

Several experimental (Spicer et al., 1998; Pszenny et al., 1993; Stutz et al., 2002) and theoretical (Fan and Jacob, 1992; Vogt et al., 1996; Lary et al., 1996; Keene et al., 1999) studies have shown that inorganic halogen species, in particular Cl and Br atoms, can be released in the lower (marine) atmosphere by two different mechanisms (for a summary see Platt and Hönninger, 2003; Sander et al., 2003):

(a) Photochemical degradation of organic halogen compounds like  $\text{CH}_3\text{Br}$ ,  $\text{CHBr}_3$  or

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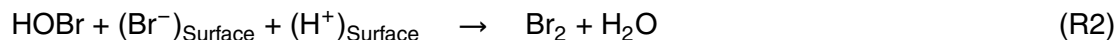
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CHCl<sub>3</sub>.

(b) Oxidation of sea salt halogenides (Br<sup>-</sup> or Cl<sup>-</sup>) in e.g. sea salt aerosol or sea salt deposits, where the release of inorganic halogen species from sea salt could proceed by different pathways.

5 The most likely mechanism involves conversion of Br<sup>-</sup> or Cl<sup>-</sup> present in sea salt aerosol or sea salt deposits to Br<sub>2</sub> or BrCl by strong oxidising agents. In particular HOBr is likely to be such an oxidant as originally suggested by Fan and Jacob (1992), Hausmann and Platt (1994), and Tang and McConnel (1996):



10 Detailed, quantitative model calculations of the heterogeneous processes by Vogt et al. (1996) supported the early suggestions, (see also Lary et al., 1996; Platt and Janssen, 1996; Platt and Lehrer, 1997).

Bromine atoms released to the atmosphere, by photolysis of Br<sub>2</sub> or BrCl or from photochemical degradation of the ubiquitous CH<sub>3</sub>Br (occurring at about 10 ppt in the entire troposphere) are most likely to react with ozone:

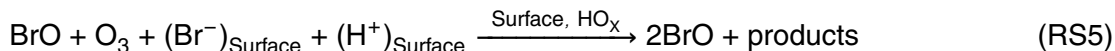


Alternatives to reaction (R3) include Br+HO<sub>2</sub>→HBr+O<sub>2</sub> and Br+HCHO→HBr+CHO, which, however, under clean air conditions contribute <1% to the loss of Br. Bromine monoxide radicals, in turn, are most likely to react with hydro-peroxy radicals:



Here alternative reactions are the BrO self reaction, BrO+OH, BrO+DMS, or BrO photolysis. However all these reactions are of minor importance compared to reaction (4). Moreover, they lead to Br<sub>2</sub> or (like BrO photolysis) to Br atoms, which are rapidly re-converted to BrO. Additional Br is then released from sea salt via (R2) again followed by release of Br<sub>2</sub> to the gas phase, and oxidation to BrO by reaction (3). In summary

the reaction sequence (R2)–(R4) is the most likely one and proceeds at typically small losses to provide the net reaction:



In addition, heterogeneous reactions of  $\text{O}_3$  with  $\text{Br}^-$  at surfaces can release reactive bromine (Oum et al., 1998a). Thus any (small) loss of Br in the above cycle could be replenished (Fan and Jacob, 1992; Tang and McConnel, 1996; Vogt et al., 1996). In fact, the above process summarised in reaction (RS5) effectively converts one gas phase BrO molecule into two by oxidising bromide at sea salt surfaces (e.g. aerosol). This process leads to an exponential growth of the BrO concentration in the atmosphere, which led to the term “Bromine Explosion” (Platt and Lehrer 1997; Wennberg, 1999). Note that the reaction sequences (5) and (8) (see below) are effectively “poisoned” by the presence of elevated amounts of NO (approx. 1 ppb), since these would suppress  $\text{HO}_2$  levels and thus make reaction (4) inefficient.

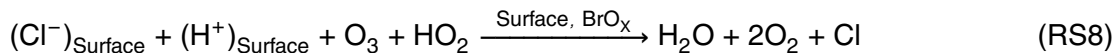
Once there is sufficient inorganic bromine present in the atmosphere it can catalyse oxidation of (sea salt)  $\text{Cl}^-$  to gas-phase Cl atoms:



The  $\text{H}^+$  required for reaction (6) and reaction (2), which appears (at least at temperatures above the freezing point) to occur at appreciable rates only at  $\text{pH} < 6.5$  (Fickert et al., 1999), could be supplied by strong acids, such as  $\text{H}_2\text{SO}_4$  and  $\text{HNO}_3$  originating from man made or natural sources (e.g. DMS oxidation). The BrCl formed in (R6) is readily photolysed:



leading to the overall reaction:



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In addition, gas-phase OH can release Cl<sub>2</sub> directly from sea salt surfaces (Oum et al., 1998b; Knipping et al., 2000; Laskin et al., 2003):



Molecular chlorine is then photolysed to Cl atoms.

For example  $1.8 \cdot 10^4$  Cl atoms  $\text{cm}^{-3}$  (in the MBL, see below) would require a net source of Cl atoms of about  $5 \cdot 10^4 \text{ cm}^{-3} \text{ s}^{-1}$ , since the main sink of Cl atoms is due to reaction with O<sub>3</sub>:



For ClO, the most likely loss process in the MBL is photolysis regenerating Cl atoms, so reaction of Cl atoms with CH<sub>4</sub> (R1) remains as the main net sink. Models and measurements show BrO around 1 ppt in the troposphere (with an effective BrOx lifetime of  $10^4$  s this level requires a net Br atom source of  $2.4 \cdot 10^3 \text{ cm}^{-3} \text{ s}^{-1}$ ). In other words each Br atom needs to undergo the reaction sequence R4+R6 once every  $\approx 300$  s. While the gas phase reaction (R4) is sufficiently fast in the MBL (mean time between two reactions  $\approx 1/([\text{HO}_2] \cdot k_4) \approx 100$  s), the rate of heterogeneous reaction (RS6) is more difficult to judge, but it is likely to be sufficiently fast in view of the fact that Cl<sup>-</sup>/Br<sup>-</sup> is about 600 in sea salt, while the required Cl atom source is only 10 times higher than the Br source.

In fact chloride and bromide deficits are usually observed in sea salt aerosol (e.g. Ayers et al., 1999). While chloride deficits could be explained by displacement of HCl by strong acids, this is not possible for bromide. Thus a bromide deficit is a good indicator of heterogeneous Br release.

### 3. Discussion and conclusions

Scientists of NOAA/CMDL have published several papers showing their “flying carpet” time series of atmospheric mixing ratio measurements. These data show non-uniform

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seasonal cycles in the data north of about 20° S. South of this latitude, which we define as the extra tropical southern hemisphere (ETSH), the cycles are much more sinusoidal in nature and the minima and maxima are phase shifted from the expected OH maxima and minima by about 3 months or 90°. This is precisely the behavior one would expect in a reactor used to study the behavior of the CH<sub>4</sub>+OH reaction with a seasonally varying OH level. It is clear that transport effects from the northern hemisphere and limited SH sources will still affect CH<sub>4</sub> data from Baring Head (at 41° S and well within the ETSH). However, because the data are collected during southerly wind trajectories (typical 4 day back calculated trajectories show air descending from 55° S), the shape of the seasonal cycle is dominated by the sink process. North of the ETSH boundary Allan et al. (2001a) have shown that the phase ellipse technique is difficult to use because of the impact of sources on the shape of the seasonal cycles. In the ETSH, NH sources (particularly biomass burning) can change the ellipse shape, but appear not to have a significant effect on the ellipse tilt, from which we deduce the enhanced KIE.

The high apparent KIE for CH<sub>4</sub> observed in the ETSH could be explained by a fraction of CH<sub>4</sub> being removed by reaction with chlorine atoms in the MBL as suggested by Lowe et al. (1999) and Allan et al. (2001a, b). The chlorine atom concentration in the MBL is required to have a seasonal cycle with an amplitude of about [Cl]<sub>max</sub>=6·10<sup>3</sup> atoms cm<sup>-3</sup> (Allan et al., 2001b) equivalent to a 24 h average of [Cl]<sub>av,tot</sub>=2.6·10<sup>3</sup> atoms cm<sup>-3</sup>. Any constant offset in [Cl] is not detectable by this method. Maxima in [Cl] should occur in summer, but with a phase shift relative to the OH annual cycle (Allan et al., 2001b).

We suggest that heterogeneous oxidation of chloride catalysed by bromine supplies the required levels of Cl atoms. The model results in Allan et al. (2001b) showed that a mean Cl concentration of 2.6·10<sup>3</sup> cm<sup>-3</sup> in a 1 km thick marine boundary layer could give the observed increase in KIE of the CH<sub>4</sub> in that boundary layer. However, CH<sub>4</sub> from the boundary layer is relatively quickly mixed into the free troposphere. Our measurements should relate to the free troposphere, as strongly suggested by (1) the observed

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profiles of CH<sub>4</sub> mixing ratio and its carbon isotopic composition being largely constant with altitude (Lowe et al., 1991; Mak et al., 2000); and (2) the fact that the tropospheric mixing time within each hemisphere (weeks) is short compared to seasonal change and the lifetime of CH<sub>4</sub>. Therefore, Cl concentrations in the MBL must be sufficient to affect all the CH<sub>4</sub> contained in the free troposphere up to a mean tropopause height of about 13 km. The integrated column density of the mean troposphere is 6.9 times that of a 1 km column starting at sea level, and 4.7 times that of an equivalent 1.5 km column. The MBL is not a completely contained region, and significant Cl concentrations may exist at heights greater than 1 km, say up to 1.5 km. The required increase in mean Cl within a 1 to 1.5 km MBL will be by a factor of 4.7 to 6.9 to affect the entire tropospheric column. The required range of Cl concentrations in the MBL would therefore be  $1.2 \cdot 10^4$  to  $1.8 \cdot 10^4$  cm<sup>-3</sup>. Within the MBL, these concentrations would result in an effective KIE of -33 to -41‰. However, these values are not directly observable. Note that there are indications that relevant levels (1–2 ppt) of reactive bromine (i.e. BrO) are found in the free troposphere (McElroy et al., 1999; Friess et al., 1999; van Roozendaal et al., 2002). In addition Fitzenberger et al. (2000) reported the first direct profile measurements of BrO in the free troposphere by balloon borne differential optical absorption spectroscopy yielding mixing ratios of 0.6–2.0 ppt. As noted by Platt and Hönniger (2003), these levels of reactive Br could also liberate Cl atoms from sea salt aerosol throughout the troposphere.

It is possible that stratosphere-troposphere exchange could introduce <sup>13</sup>C-rich methane into the ETS. Using model results (e.g. Rosenlof and Holton, 1993) on downward mass fluxes into the ETS from the lower stratosphere, Allan et al. (2001a) estimated that at most about 5% of ETS methane might originate from stratospheric exchange. Brenninkmeijer et al. (1995) measured a fractionation factor of 0.988 for methane in the SH lower stratosphere, the excess over the OH fractionation factor being attributed to stratospheric removal of methane by chlorine atoms. Assuming uniform mixing in the ETS, Allan et al. (2001a) estimated that stratospheric exchange can account for at most -0.5‰ of the KIE inferred at Baring Head. This result was con-

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5 firmed by the 2-D modelling studies of McCarthy et al. (2001) and Wang et al. (2002). The effect is thus minor compared to the discrepancy observed between the calculated annual average KIE at Baring Head and laboratory measurements of the effect for the methane OH reaction. However, we have determined that there is an as yet unexplained inter-annual variability in the calculated apparent KIE with values ranging from 13 to 6‰ over the 10-year period 1990 to 1999 (Lowe et al., 2000).

10 Observation of the apparent KIE may be sensitive to the contribution of Cl atoms to CH<sub>4</sub> degradation averaged over a large fraction of our globe. The Allan et al. (2001b) model requires a CH<sub>4</sub> flux into the 1 km thick MBL of  $9.4 \cdot 10^{13}$  molecules m<sup>-2</sup> s<sup>-1</sup> to replace the CH<sub>4</sub> destroyed by Cl. If we assume that this rate of CH<sub>4</sub> destruction occurs over the global ocean, and is scaled as above to the entire tropospheric column, then the global CH<sub>4</sub> sink magnitude required is of the order of 19 Tgyr<sup>-1</sup>. This represents 3.3% of the total CH<sub>4</sub> sink quoted by Bergamaschi et al. (2001). Due to the property that our technique is only sensitive to variations in Cl levels, this figure is a lower limit to the true contribution of Cl to the total methane sink (which is still dominated by the OH reaction).

15 Such a Cl sink for CH<sub>4</sub> may have observable effects on the global budget of CO. It would produce 3.3% of the CO that is generated by the OH reaction with CH<sub>4</sub>, namely 26 Tgyr<sup>-1</sup> CO, or 0.9% of the total CO source (using the results of Bergamaschi et al., 2001). As discussed by Manning et al. (1997) and Bergamaschi et al. (2000), the effect of this on δ<sup>13</sup>C results in a requirement that the yield of CO from CH<sub>4</sub> oxidation be reduced from 0.8 to 0.7. This issue is at present unresolved.

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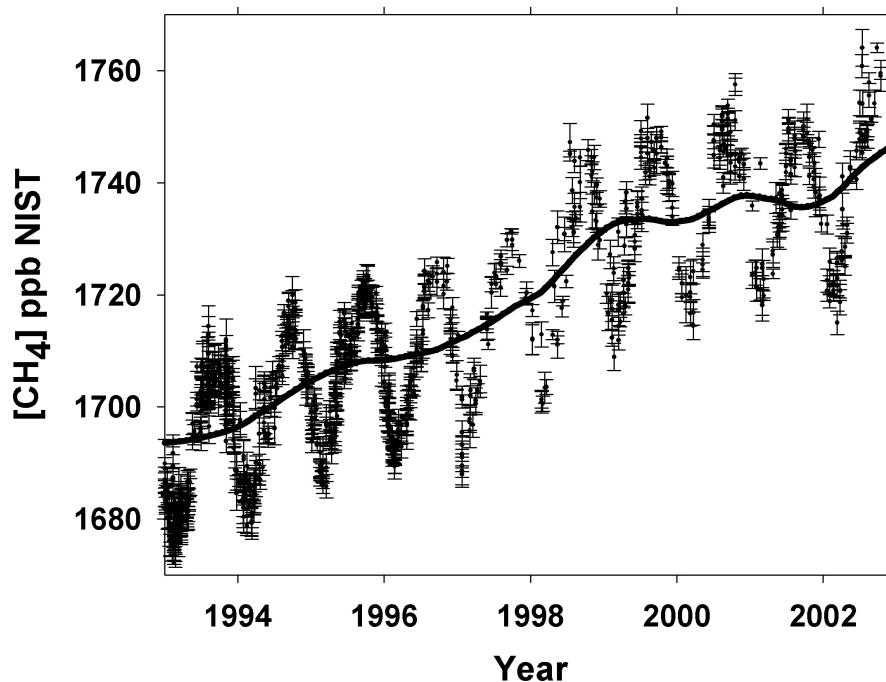
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**Fig. 1.** Atmospheric methane mixing ratio at Baring Head New Zealand, 41° S. The symbols with error bars indicate individual air sample mixing ratios and the thick line represents the long-term growth rate of methane at the site.

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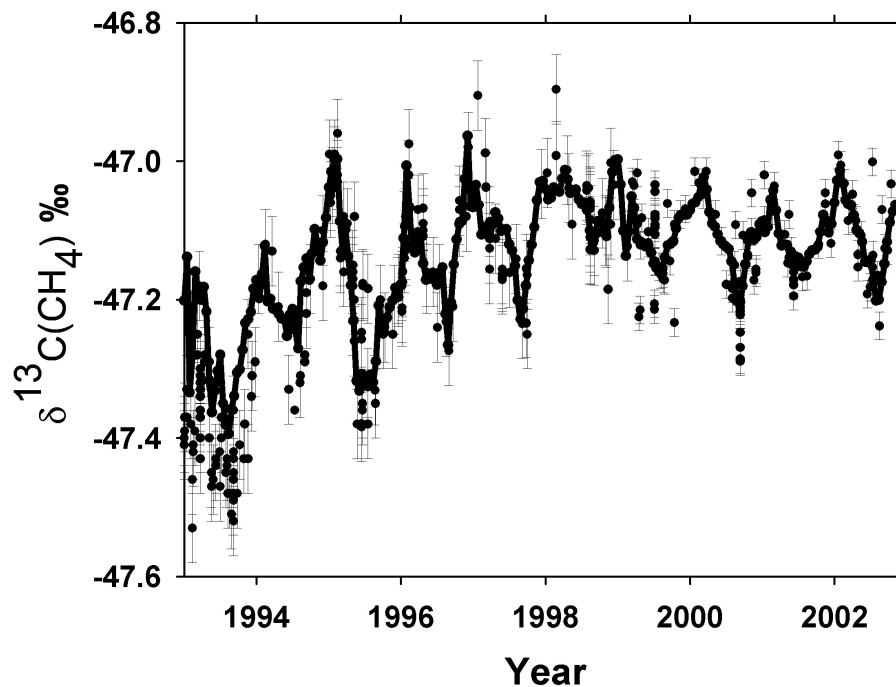
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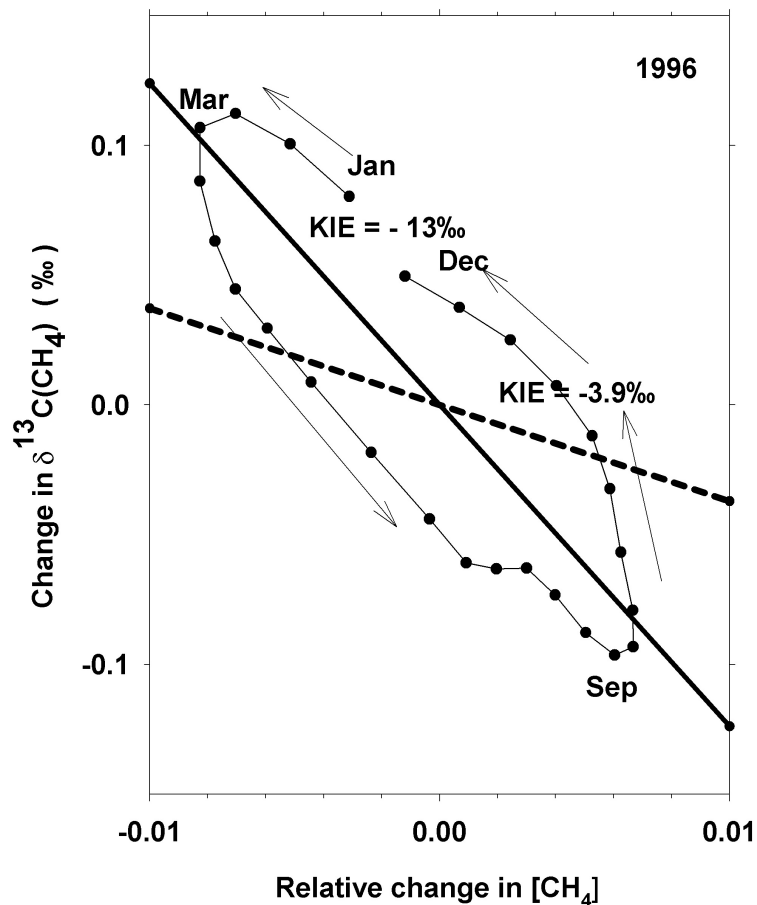
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**Fig. 2.** Atmospheric  $\delta^{13}\text{C}(\text{CH}_4)$  at Baring Head with the same symbol system as used in Fig. 1. The full line shows a fit to the data with minimal smoothing.

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**Fig. 3.** Phase ellipse at Baring Head, New Zealand, for 1996 (see Allan et al., 2001a, for details). The apparent KIE is  $-13\text{‰}$  (full line) compared with the KIE for OH of  $-3.9\text{‰}$  (dashed line) measured in the laboratory by Saueressig et al. (2001). The time evolution of the ellipse is indicated by arrows.

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