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

U. Platt¹, W. Allan², and D. Lowe²

¹Institut für Umweltphysik, University of Heidelberg, INF 229, D-69120 Heidelberg

²NIWA, Private Bag 14-901, Kilbirnie, Wellington, New Zealand

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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}C compared with ^{12}C in atmospheric methane. This property can be used to estimate the likely minimum 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 Tg yr^{-1} , or about 3.3% of the total CH_4 sink. However, its impact on the methane stable carbon isotope budget is large and warrants further attention.

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 CH_4 reduces the rate of stratospheric ozone destruction. As the most abun-

dant 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 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 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 (O^1D) with water vapour. Thus its concentration peaks in the ETSH in December near the time of 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° . This is indeed observed as shown in Fig. 1 for methane mixing ratio measurements made at Baring Head, New Zealand (41°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

Correspondence to: U. Platt
(ulrich.platt@iup.uni-heidelberg.de)

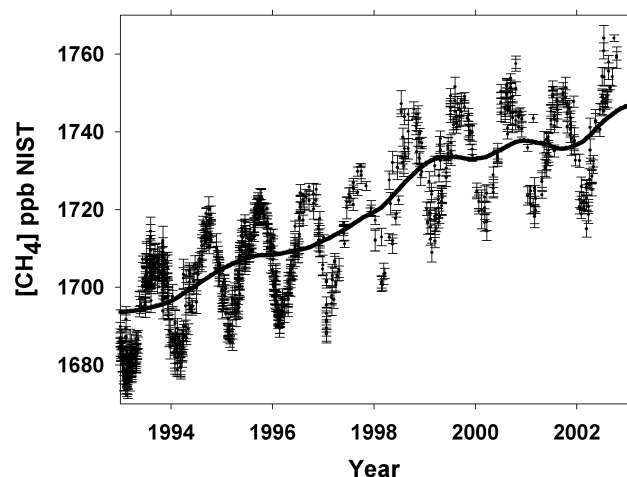


Fig. 1. Atmospheric methane mixing ratio at Baring Head New Zealand, 41°S . The symbols with error bars indicate individual air sample mixing ratios and the thick line represents the long-term growth rate of methane at the site.

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 “delta” notation where $\delta^{13}\text{C}$ 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 $\varepsilon = -3.9\text{‰}$ (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 Δc , respectively, and $\Delta\delta$ is the corresponding change in $\delta^{13}\text{C}(\text{CH}_4)$ about a mean value δ_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 $<0.1\text{‰}$ and to be 180° or 6 months out of phase with the methane mixing ratio signal. However, a time series of measurements of $\delta^{13}\text{C}(\text{CH}_4)$

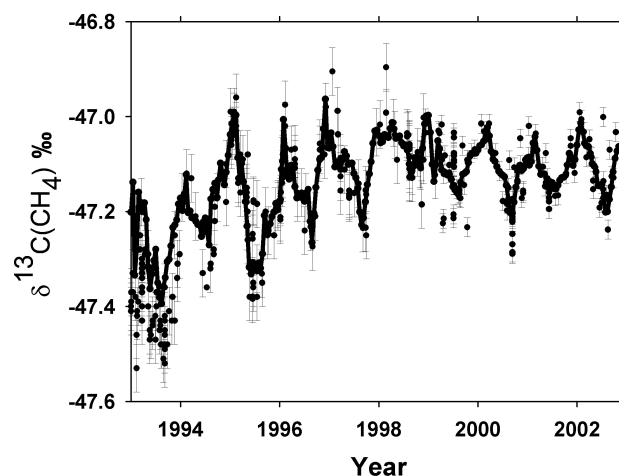


Fig. 2. Atmospheric $\delta^{13}\text{C}(\text{CH}_4)$ at Baring Head with the same symbol system as used in Fig. 1. The full line shows a fit to the data with minimal smoothing.

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 size of the minor axes of these ellipses is a function of “source effects”, in particular that the biomass burning source lengthens the minor axis and “broadens” the ellipse because of this source’s high ^{13}C enrichment and strong seasonal amplitude. The other major conclusion of their work is that the gradient 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. Recent work (Allan et al., submitted, 2004¹) shows that there is considerable interannual variation in the apparent KIE derived using this technique. At Baring Head, the

¹Allan, W., Lowe, D. C., Gomez, A. J., Struthers, H., and Brailsford, G. W.: Interannual variation of ^{13}C in tropospheric methane: Implications for a possible atomic chlorine sink in the marine boundary layer, *J. Geophys. Res.*, submitted, 2004.

values ranged from -17‰ in 1997 to -6‰ in 1999. At Scott Base (78°S), the magnitudes of the apparent KIE were similar, but the interannual variation was different in detail.

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 $6 \cdot 10^3 \text{ atoms cm}^{-3}$. In addition there might be an “offset” level of Cl atoms always present that cannot be detected using the “isotope phase ellipse” technique. The interannual variation of the apparent KIE implies a similar variation in the amplitude of the Cl seasonal cycle in the marine boundary layer. The offset level of Cl atoms cannot be determined using this isotope technique, but we consider that the maximum observed amplitude of the Cl seasonal cycle provides a lower bound on the maximum Cl concentration in the ETSH marine boundary layer.

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.

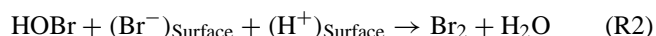
2 Reactive halogen species in the troposphere

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 CH_3Br , CHBr_3 or CHCl_3 .

(b) Oxidation of sea salt halogenides (Br^- or Cl^-) 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.

The most likely mechanism involves conversion of Br^- or Cl^- present in sea salt aerosol or sea salt deposits to Br_2 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 McConnell (1996):



Detailed, quantitative model calculations of the heterogeneous processes by Vogt et al. (1996) supported the early

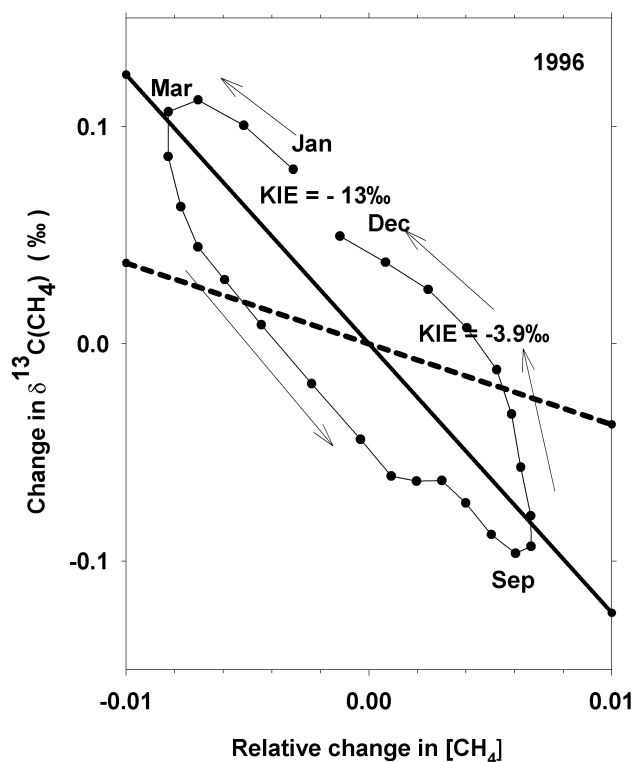


Fig. 3. Phase ellipse at Baring Head, New Zealand, for 1996 (see Allan et al., 2001a, for details). The apparent KIE is -13‰ (full line) compared with the KIE for OH of -3.9‰ (dashed line) measured in the laboratory by Saueressig et al. (2001). The time evolution of the ellipse is indicated by arrows.

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_2 or BrCl or from photochemical degradation of the ubiquitous CH_3Br (occurring at about 10 ppt in the entire troposphere) are most likely to react with ozone:

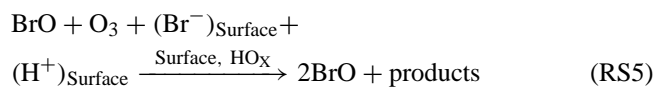


Alternatives to Reaction (3) include $\text{Br} + \text{HO}_2 \rightarrow \text{HBr} + \text{O}_2$ and $\text{Br} + \text{HCHO} \rightarrow \text{HBr} + \text{CHO}$, which, however, under clean air conditions contribute $<1\%$ to the loss of Br. Bromine monoxide radicals, in turn, are most likely to react with hydro-peroxy radicals:



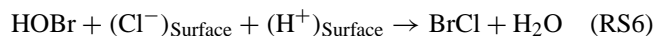
Here alternative reactions are the BrO self reaction, $\text{BrO} + \text{OH}$, $\text{BrO} + \text{DMS}$, or BrO photolysis. However all these reactions are of minor importance compared to Reaction (4). Moreover, they lead to Br_2 or (like BrO photolysis) to Br atoms, which are rapidly reconverted to BrO. Additional Br is then released from sea salt via R2 again followed by release of Br_2 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 O_3 with 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 HO_2 levels and thus make Reaction (4) inefficient.

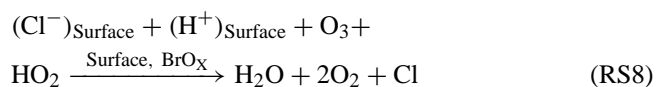
Once there is sufficient inorganic bromine present in the atmosphere it can catalyse oxidation of (sea salt) Cl^- to gas-phase Cl atoms:



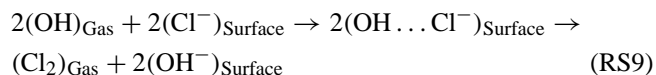
The H^+ required for Reaction (6) and Reaction (2), which appears (at least at temperatures above the freezing point) to occur at appreciable rates only at $\text{pH} < 6.5$ (Fickert et al., 1999), could be supplied by strong acids, such as H_2SO_4 and HNO_3 originating from man made or natural sources (e.g. DMS oxidation). The BrCl formed in R6 is readily photolysed:



leading to the overall reaction:



In addition, gas-phase OH can release Cl_2 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 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_3 :



For ClO, the most likely loss process in the MBL is photolysis regenerating Cl atoms, so reaction of Cl atoms with CH_4

(R1) remains as the main net sink. Thus, (R10) followed by photolysis of ClO constitutes a null cycle with respect to Cl atoms providing (at 20 ppb O_3) about 60% of the Cl atoms reacting with CH_4 , while about 40% would come from RS8 and RS9. 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) and (R6) once every ≈ 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^-/Br^- 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 seasonal cycles 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 $\text{CH}_4 + \text{OH}$ 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_4 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_4 observed in the ETSH could be explained by a fraction of CH_4 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 $[\text{Cl}]_{\text{max}} = 6 \cdot 10^3$ atoms cm^{-3} (Allan et al., 2001b) equivalent to a 24 h average of

$[\text{Cl}]_{\text{av,tot}}=2.6\cdot 10^3$ atoms cm^{-3} . Any constant offset in $[\text{Cl}]$ is not detectable by this method. Maxima in $[\text{Cl}]$ 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 $2.6\cdot 10^3$ cm^{-3} in a 1 km thick marine boundary layer could give the observed increase in KIE of the CH_4 in that boundary layer. However, CH_4 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 profiles of CH_4 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_4 . Therefore, Cl concentrations in the MBL must be sufficient to affect all the CH_4 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^{-3} . This is within the broad range of literature values derived from indirect measurements by e.g. relative rates of degradation of different hydrocarbons (also known as “hydrocarbon clock” observations), which give widely varying results ranging from 10^4 to 10^6 cm^{-3} in the MBL (Graedel and Keene, 1995), around or below 10^4 cm^{-3} in the global atmosphere (Singh et al., 1996), or $1.6\cdot 10^4$ cm^{-3} (taking $1/4$ of the noontime Cl concentration of $6.4\cdot 10^4$ cm^{-3} derived from Lagrangian experiments in the North Atlantic conducted by Wingenter et al., 1996). 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 Hönninger (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 ^{13}C -rich methane into the ETSH. Using model results (e.g., Rosenlof and Holton, 1993) on downward mass fluxes into the ETSH from the lower stratosphere, Allan

et al. (2001a) estimated that at most about 5% of ETSH methane might originate from stratospheric exchange. Breninkmeijer 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 ETSH, 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 confirmed 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).

Observation of the apparent KIE may be sensitive to the contribution of Cl atoms to CH_4 degradation averaged over a large fraction of our globe. The Allan et al. (2001b) model requires a CH_4 flux into the 1 km thick MBL of $9.4\cdot 10^{13}$ molecules $\text{m}^{-2} \text{s}^{-1}$ to replace the CH_4 destroyed by Cl. If we assume that this rate of CH_4 destruction occurs over the global ocean, and is scaled as above to the entire tropospheric column, then the global CH_4 sink magnitude required is of the order of 19Tg yr^{-1} . This represents 3.3% of the total CH_4 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).

Such a Cl sink for CH_4 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_4 , namely 26Tg yr^{-1} 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 $\delta^{13}\text{C}$ results in a requirement that the yield of CO from CH_4 oxidation be reduced from 0.8 to 0.7. This issue is at present unresolved.

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