

Interannual variation of ^{13}C in tropospheric methane: Implications for a possible atomic chlorine sink in the marine boundary layer

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[1] We present methane mixing ratio and $\delta^{13}\text{C}$ time series measured at Baring Head, New Zealand, and Scott Base, Antarctica, over the years 1991–2003. These data demonstrate that the apparent kinetic isotope effect (KIE) of the methane atmospheric sink (derived from the amplitudes of the mixing ratio and $\delta^{13}\text{C}$ seasonal cycles) is generally much larger than would be expected if the sink were the hydroxyl radical alone and has changed significantly during the observation period on a timescale of ~ 3 years. We show using a global transport model that this technique for deriving the KIE should be quite accurate for a single atmospheric sink and that the change with time is unlikely to arise from El Niño–Southern Oscillation transport effects. We infer that a sink in addition to hydroxyl is required. A strong candidate for this extra sink is atomic chlorine in the marine boundary layer (MBL). We derive the amplitude of the chlorine concentration seasonal cycle that would fully account for the apparent KIE. This amplitude ranges from $\sim 10^4$ atom cm^{-3} in 1994–1996 to about 3×10^3 atom cm^{-3} in 1998–2000. If the KIE is enhanced throughout the free troposphere, the seasonal mean concentrations of atomic chlorine required in the MBL would be about 3×10^4 atom cm^{-3} in 1994–1996 and $\sim 10^4$ atom cm^{-3} in 1998–2000.

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1. Introduction

[2] Methane (CH_4) is a significant species in the atmosphere, both from its effect on the Earth's radiation balance and from its role in atmospheric chemistry. Model estimates suggest that CH_4 accounts for $\sim 20\%$ of the incremental trace gas radiative forcing since preindustrial times [Myhre *et al.*, 1998]. CH_4 plays an important role in the regulation of stratospheric ozone levels and consumes $\sim 25\%$ of hydroxyl (OH^\bullet) radicals in the troposphere, thus becoming an in situ source of carbon monoxide (CO) and ozone (O_3) [Thompson, 1992].

[3] The mean mixing ratio of CH_4 in the atmosphere (abbreviated from now on as MR) has more than doubled over the last 150 years [Etheridge *et al.*, 1998]. Over the last 40 years the average atmospheric growth rate of CH_4 has been nearly 1% per year [e.g., Etheridge *et al.*, 1998]. However, the average growth rate has slowed over the last 20 years to

$<0.5\%$ per year and was approximately zero from 1999 through 2002 [Dlugokencky *et al.*, 1998, 2003]. These changes are at present not fully understood, a situation that is directly related to uncertainties in the size, spatial distribution, and trends of identified methane sources. Measuring the stable isotopic (^{13}C) composition of atmospheric CH_4 can reduce these uncertainties because several CH_4 source types can be distinguished by their characteristic isotope signatures [e.g., Bergamaschi *et al.*, 2001].

[4] Allan *et al.* [2001a] extended the utility of isotope measurements to assess indirectly the properties of CH_4 sinks in a limited region of the atmosphere, namely, the extratropical Southern Hemisphere (ETSH) (south of 23.5°S). For CH_4 the $^{13}\text{C}/^{12}\text{C}$ ratio is reported through the $\delta^{13}\text{C}$ ratio defined by

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

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], and $\delta^{13}\text{C}$ is scaled by a factor of 1000, being reported as per mil, “‰.” Allan *et al.* [2001a] showed that when the change in $\delta^{13}\text{C}(\text{CH}_4)$ is plotted versus the relative change in MR measured in the ETSH over a seasonal cycle, an ellipse-like figure (a “phase ellipse”) is obtained. Their modeling study demonstrated that the shape of the phase ellipse is modified by source effects but that the slope of the ellipse major axis appeared to be a robust measure of the kinetic isotope effect (KIE) ϵ of the oxidation process removing CH_4 from the ETSH lower troposphere. Here $\epsilon = (k_{13}/k_{12}) - 1$, where k_{13} and k_{12} are the rate constants for ^{13}C and ^{12}C removal, respectively, by the oxidation process. Note that from now on, ^{13}C and $\delta^{13}\text{C}$ should be taken as referring to the carbon in CH_4 .

[5] Allan *et al.* [2001a] modeled this using OH^\bullet as the sole oxidant and found that ϵ derived from the simulated phase ellipse major axis slope was consistent with the value of ϵ_{OH} supplied as input to the model. However, comparison with measurements in New Zealand and Antarctica showed that ϵ derived from observed ellipses was significantly larger in magnitude than expected for OH^\bullet oxidation alone (-3.9‰ [Saueressig *et al.*, 2001]), with a value of about -13‰ . We refer to this observed ϵ as ϵ_A , the “apparent KIE.” Allan *et al.* [2001b] used a simple chemical box model to demonstrate that a plausible seasonal cycle of chlorine radicals (Cl^\bullet) in the marine boundary layer (MBL) acting together with the expected OH^\bullet seasonal cycle could potentially account for the magnitude of ϵ_A .

[6] A mean of the data from the years 1993–1996 was used for the above comparison, as these years yielded phase ellipses with similar major axis slopes. However, a time series of measurements from 1991 to 2003 is now available, and it is apparent that there is considerable interannual variation in the structure of the phase ellipses over this period. In particular, the period 1997–2003 is significantly different from the period 1993–1996 considered in our earlier work. In the present paper, we describe the complete data set and give example phase ellipses at two observing sites in the ETSH. We employ two new methods, reduced major axis (RMA) regression and nonlinear least squares fitting of sinusoids, to derive ϵ_A for the years 1991–2003, including uncertainties in ϵ_A that could not be obtained in our earlier work. These uncertainties show that ϵ_A varies significantly on a timescale of ~ 3 years. We employ a new version of a general circulation model to show that the large and variable values of ϵ_A inferred from the data are not a result of El Niño–Southern Oscillation (ENSO) transport effects. This adds strong support to our earlier hypothesis that a CH_4 sink mechanism additional to OH^\bullet is required in the MBL and that this sink is probably Cl^\bullet . We then show that such a Cl^\bullet sink for CH_4 would also have to vary significantly on a timescale of ~ 3 years to account for the observed ϵ_A variation. We derive the Cl^\bullet concentrations in the MBL that would be required to produce this effect.

2. Experimental Techniques and Results

[7] Analyses of ^{13}C in atmospheric CH_4 are made as described by Lowe *et al.* [2004]. Samples are collected approximately every 2 weeks at Scott Base (SB), Antarctica (78°S , 167°E), and at Baring Head (BH), New Zealand (41°S , 175°E). Methane in the air samples was converted to

CO_2 by combustion in a platinum furnace. Quantitative conversion during this process ensures that the carbon isotopic composition of the CO_2 is the same as that of the parent methane. Using a highly modified 6 inch Nuclide isotope ratio mass spectrometer (IRMS) [Lowe *et al.*, 1994], $\delta^{13}\text{C}$ measurements of methane in air samples collected from 1989 to 1994 were made. Subsequent measurements used a Finnigan MAT 252 IRMS. The $^{13}\text{C}/^{12}\text{C}$ ratios are measured against a laboratory standard, itself calibrated against Peedee belemnite using a quality-controlled protocol as described by Lowe *et al.* [2004]. The overall precision (1σ) of the $\delta^{13}\text{C}$ determinations in atmospheric CH_4 is estimated to be 0.1‰ (1989–1991), 0.05‰ (1991–1995), and 0.02‰ (1996–2003).

[8] MR measurements were made using HP5890 series II and HP6890 gas chromatographs with a flame ionization detector as described by Lowe *et al.* [2004]. MRs are referenced to CH_4 standard reference materials from the U.S. National Institute of Standards and Technology (NIST). These reference materials have been intercompared with reference gases defined on a scale from the U.S. NOAA/Climate Monitoring and Diagnostics Laboratory (CMDL) [e.g., Lang *et al.*, 1992], and our estimate of the ratio of the NOAA/CMDL scale to the NIST values is 0.986 ± 0.001 . The 1σ precision of these measurements is ~ 3 ppb, or $\sim 0.2\%$ of ambient MR.

[9] For the analyses in the present work we have detrended the MR and $\delta^{13}\text{C}$ data using the seasonal and trend decomposition (STL) procedure described in section 3 and accumulated them in monthly bins to minimize the effects of unavoidable gaps in the observational data. The results are shown in Figure 1 for BH (Figures 1a and 1c) and SB (Figures 1b and 1d). Seasonal cycles are clear at both sites, but there is more variation in the seasonal amplitude of $\delta^{13}\text{C}$ than of MR. At both BH and SB the MR mean value increases from 1675 to 1740 ppb during the period shown, and the $\delta^{13}\text{C}$ mean value at both sites is -47.14‰ over that period. Note that there are some missing $\delta^{13}\text{C}$ data at SB (Figure 1d) resulting from Antarctic logistical problems.

3. Phase Ellipses

[10] The observational phase ellipses presented by Allan *et al.* [2001a] were obtained by binning and averaging 4 years of data into 26 points per year and by using the STL procedure of Cleveland *et al.* [1990] to obtain detrended smoothed seasonal cycles for MR and $\delta^{13}\text{C}$. This process is not suitable for the present work as we are interested in changes from year to year. We therefore work directly with the monthly binned data in Figure 1.

[11] Figure 2 shows phase ellipses for the years 1996 and 1999 at BH and SB. We have chosen these years to illustrate ellipses with very different characteristics at BH and also to show how different the ellipses can be between BH and SB in the same year. Ellipses for individual years are much more irregular than the 4 year averaged and smoothed ellipses of Allan *et al.* [2001a]. Also shown in Figure 2 are straight lines fitted by RMA regression [Sokal and Rohlf, 1981] to the ellipse points, representing approximations to the ellipse major axes from the slopes of which ϵ_A can be estimated.

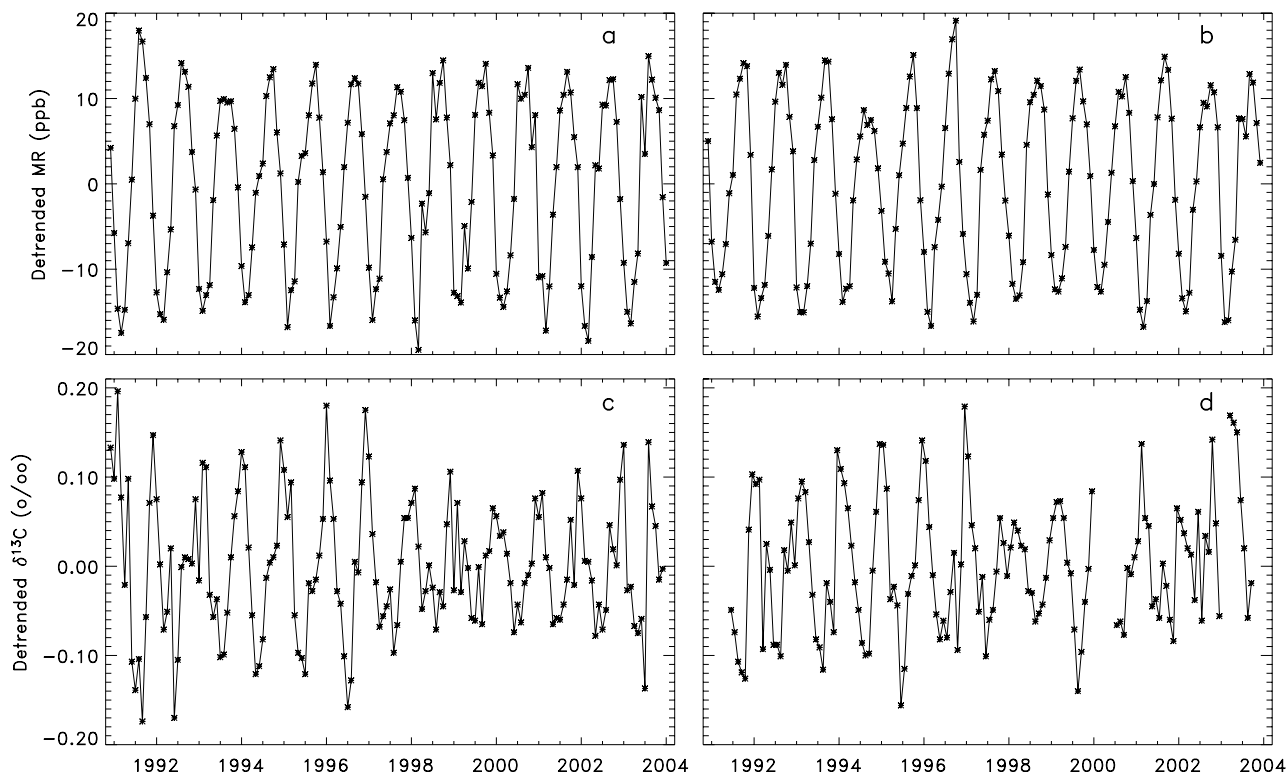


Figure 1. Detrended and monthly binned values of mixing ratio (MR) at (a) Baring Head and (b) Scott Base. (c and d) Corresponding values of $\delta^{13}\text{C}$.

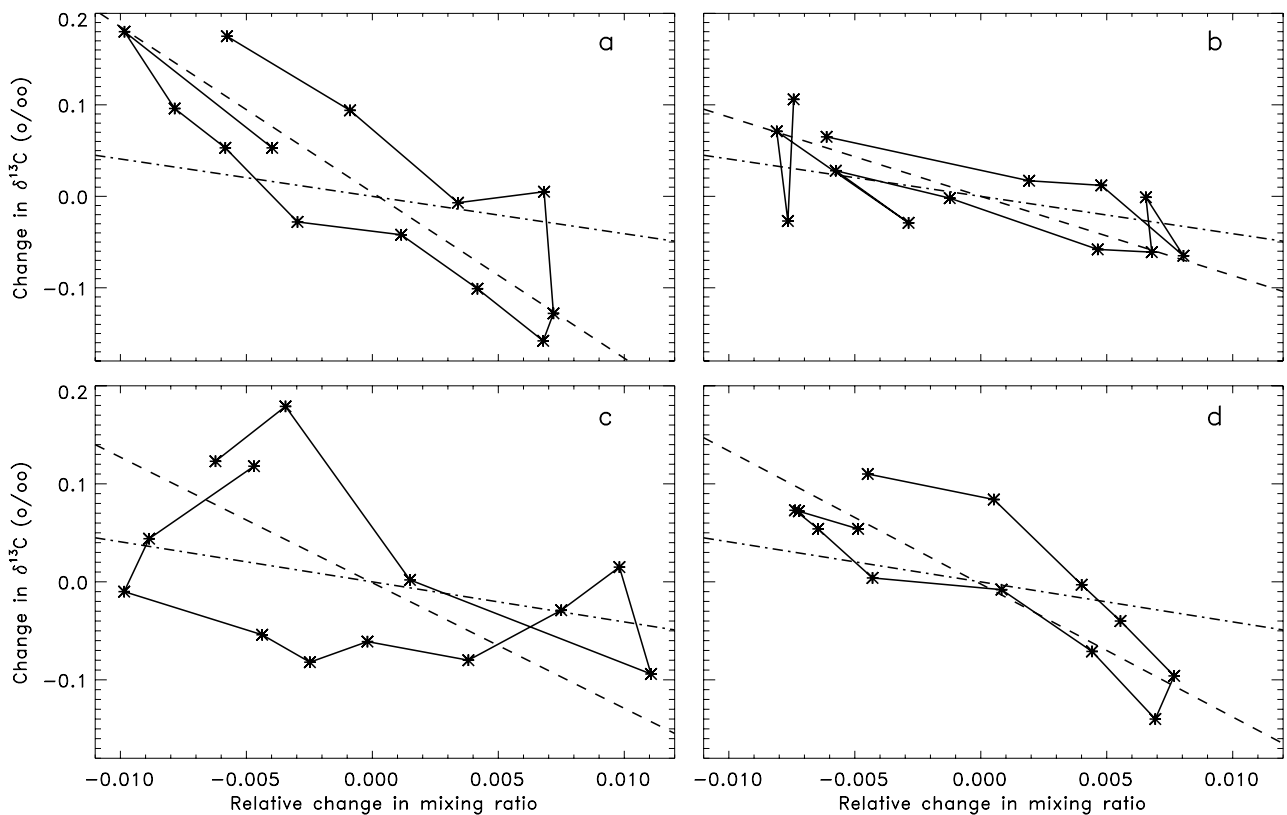


Figure 2. Phase “ellipses” at Baring Head for (a) 1996 and (b) 1999, using the monthly values in Figure 1. (c and d) Corresponding phase ellipses at Scott Base. The dashed lines are fitted by reduced major axis regression to the ellipse points. The dash-dotted lines correspond to $\epsilon_{\text{OH}} = -3.9\%$.

[12] The most recent laboratory measurement [Saueressig *et al.*, 2001] of ϵ_{OH} is $-3.9 \pm 0.4\%$. If we take this as the most likely value for the atmosphere and assume that OH^\bullet is the only atmospheric sink for CH_4 , then we would expect the ellipses to provide an apparent KIE of the same magnitude. Comparisons with the KIE lines for $\epsilon_{\text{OH}} = -3.9\%$ (also in Figure 2) show that the RMA regression lines generally have significantly larger slopes than the ϵ_{OH} lines. For 1996 and 1999 at BH, ϵ_A values derived from the RMA lines are $-19.0 \pm 3.1\%$ and $-9.1 \pm 2.0\%$, while for 1996 and 1999 at SB, ϵ_A values are $-13.4 \pm 3.6\%$ and $-14.2 \pm 2.3\%$. Other years have similar values, with comparable interannual variability.

4. KIE Time Variation

[13] The phase ellipse approach is excellent to obtain a visual “feel” for the tilt and shape of ellipses and how these vary with time. However, the irregular “ellipses” in Figure 2 contain variability related to short-term local transport effects as well as the underlying seasonal sink variation. RMA regression includes all variability, and the assumption that the resulting fitted line represents the major axis of the underlying sink-driven ellipse is likely to overestimate the major axis slope and hence the magnitude of the derived KIE. An alternative method that minimizes the effect of short-term transport variability is the fitting of sinusoidal seasonal cycles to the separate detrended time series for MR and $\delta^{13}\text{C}$. The underlying model is that the atmospheric sink has a sinusoidal seasonal cycle. This is reasonable, as the OH^\bullet fields of Spivakovsky *et al.* [2000] have an ETSH spatially averaged value that is well represented by a sinusoidal function [see also Allan *et al.*, 2001b]. If the ETSH were an isolated box containing a steady CH_4 source of fixed isotope ratio, such a sink would produce a sinusoidal seasonal cycle in MR, and an approximately sinusoidal $\delta^{13}\text{C}$ seasonal cycle in antiphase with it, giving KIE lines like those shown in Figure 2. We fit the sinusoids to the data points using the Marquardt nonlinear least squares gradient expansion algorithm [Bevington and Robinson, 1992]. The period is fixed at 1 year, and the fitting process allows both the amplitude and phase of the sinusoid to be determined. Uncertainties in the amplitude and phase correspond to the square roots of the diagonal terms in the error matrix.

[14] The modeling results of Allan *et al.* [2001a] showed that for any individual CH_4 source the “phase ellipse” in the ETSH is always a straight line with slope determined by the KIE of the single atmospheric sink assumed in the model. When sources with different seasonal cycle amplitudes and distinct ^{13}C compositions are combined in the model, the size of the minor axis of the ellipse changes, broadening or narrowing the ellipse. This is equivalent to shifting the phase of the $\delta^{13}\text{C}$ sinusoid relative to the MR sinusoid. In no case was there any significant change in the slope of the major axis from which the atmospheric sink KIE is derived. Thus we suggest that changes in the amplitudes of the $\delta^{13}\text{C}$ and MR seasonal sinusoids relate dominantly to sink effects and changes in the relative phase between these sinusoids relate dominantly to source effects.

[15] Therefore the apparent KIE ϵ_A can be obtained from the amplitudes of the seasonal cycles fitted to the MR and $\delta^{13}\text{C}$ time series [Allan *et al.*, 2001a]:

$$\epsilon_A \approx \Delta\delta / [(1 + \delta_0)\Delta\text{MR}/\text{MR}_0], \quad (2)$$

where δ_0 is the mean $\delta^{13}\text{C}$ for the year, ΔMR is the amplitude of the MR seasonal cycle sinusoid, MR_0 is the mean MR for the year, and $\Delta\delta$ is the amplitude of the $\delta^{13}\text{C}$ seasonal cycle sinusoid. An uncertainty estimate for ϵ_A can then be calculated from the uncertainties in the amplitudes of the two sinusoidal fits by adding the relative uncertainties of the individual amplitudes to give a relative uncertainty for the quotient in (2). Figure 3 shows such fits for the 1996 and 1999 years at BH using the detrended data. The amplitudes of the fitted MR cycles are similar for the 2 years, but the amplitudes of the $\delta^{13}\text{C}$ cycles are very different. Using (2), the values of ϵ_A at BH for 1996 and 1999 are $-17.4 \pm 2.9\%$ and $-6.1 \pm 2.8\%$, respectively. Note that as expected, the magnitudes of the ϵ_A values obtained from nonlinear least squares fitting are somewhat smaller than those obtained from RMA regression, with similar and overlapping uncertainties.

[16] Figure 4a shows ϵ_A derived at BH for the years 1991–2003, and Figure 4b shows ϵ_A derived at SB for late 1991–2002. Values have been plotted at the midpoints of the years for which 1 January was the starting point (as in Figure 3). Some years at SB are affected by missing data. For 1991 and 2002 we have shifted the starting point of the fit to make use of the available data and have plotted the value at the appropriate midpoint of the shifted year. Insufficient data were available at SB in 2003 to derive a useful value. There is interannual variation at both BH and SB, but the variation is different at each site. The uncertainty bars for successive years often overlap, but if the values are considered over an interval of ~ 3 years, there is a significant change with time. For example, the period 1994–1996 has an apparent KIE of about -15% , and the period 1998–2000 has an apparent KIE of about -7% , with well-separated uncertainty bars.

5. Model Simulations

5.1. Global Modeling

[17] A limitation of the Allan *et al.* [2001a] analysis is that the TM2 model used only 1987 wind fields, so that the effect of interannual transport variation on the phase ellipse major axis slope could not be obtained. To investigate this and other source and transport effects in detail, we are currently developing a modification of the unified model (UM) [Cullen and Davies, 1991], a general circulation model used for weather forecasting and climate prediction in the United Kingdom. This modification includes the surface emission, atmospheric transport, and in situ destruction of CH_4 . The dynamical model used is the version 4.5, atmosphere-only, configuration of the UM with a horizontal resolution of 2.5° (latitude), 3.75° (longitude), and 19 vertical levels [Pole *et al.*, 2000]. Two methane isotopic species ($^{12}\text{CH}_4$ and $^{13}\text{CH}_4$) are transported by the dynamical model and are chemically destroyed via reaction with an OH^\bullet climatology based on Houweling *et al.* [1998]. We intend to include a seasonally varying chlorine sink in the

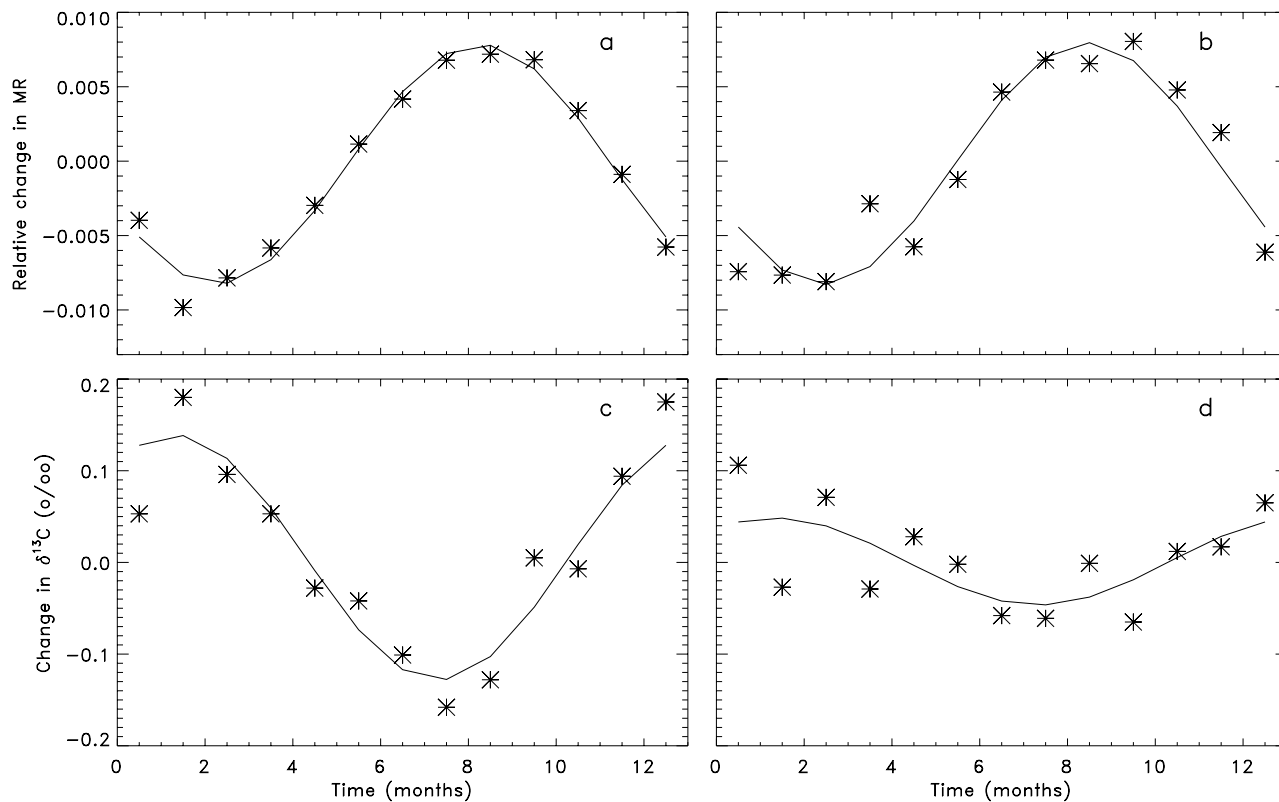


Figure 3. Monthly binned MR values at Baring Head for (a) 1996 and (b) 1999. (c and d) Corresponding $\delta^{13}\text{C}$ values. The full curves are sinusoids fitted by nonlinear least squares.

MBL to investigate the detailed effect of this; however, model development and testing will not reach this stage for some time.

[18] For initial model tests we included surface CH_4 sources and the OH^\bullet sink from the International Geosphere-Biosphere Program Global Atmospheric Methane Synthesis scenario (GAMEs) (S. Houweling, personal communication, 2001), taking $\epsilon_{\text{OH}} = -3.9\%$. The CH_4 sources (biomass burning, rice cultivation, termites, bogs, swamps, coal, oil, gas, animals, and landfills) are specified at each horizontal grid point of the model, as is a soil sink. The biomass burning, rice, bog, and swamp sources and the soil sink vary on a monthly basis, with the same annual cycle of sources being repeated each year of the model integration. The other sources are constant. The total annual CH_4 source is 580 Tg per year. The constant $\delta^{13}\text{C}$ values for the sources are assigned as specified in the GAMEs scenario, with a weighted mean source $\delta^{13}\text{C}(\text{CH}_4)$ of -51.5% .

[19] The model was initialized using a zonally uniform CH_4 field whose latitudinal variation was empirically fitted to data from the NOAA/Climate Monitoring and Diagnostics Laboratory network (available at <ftp://ftp.cmdl.noaa.gov/ccg/ch4/>). The details of the empirical fit are not important as the initialization is intended only to speed up the model's convergence to its final steady state. The $\delta^{13}\text{C}(\text{CH}_4)$ value was initially set to -47% throughout the model domain, this value being close to the current atmospheric average.

[20] We drove the UM with the composite 4 year El Niño and La Niña sea surface temperature (SST) cycle developed by Spencer *et al.* [2004]. Spencer and Slingo [2003]

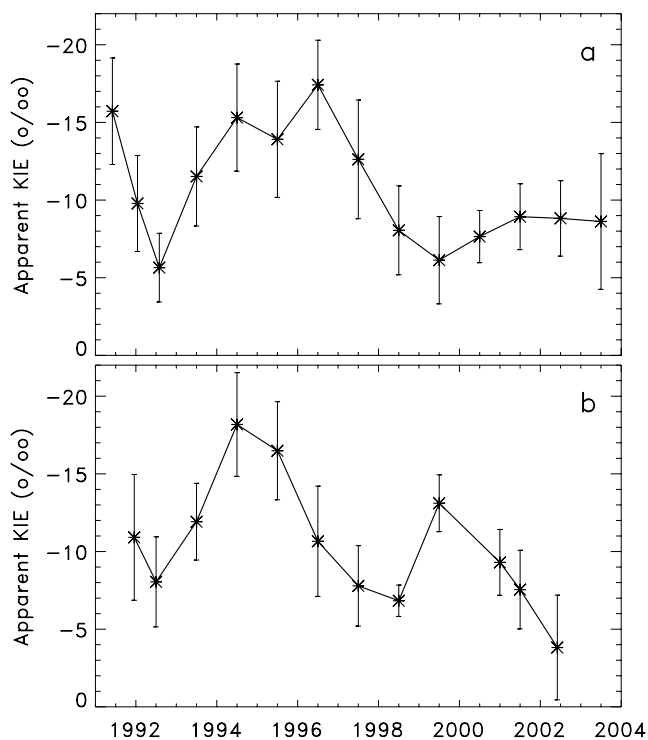


Figure 4. (a) Apparent kinetic isotope effect (KIE) inferred at Baring Head, plotted at the midpoints of the appropriate years. (b) Corresponding values at Scott Base. The uncertainty bars are calculated from the uncertainties of the fitted sinusoid amplitudes (see Figure 3).

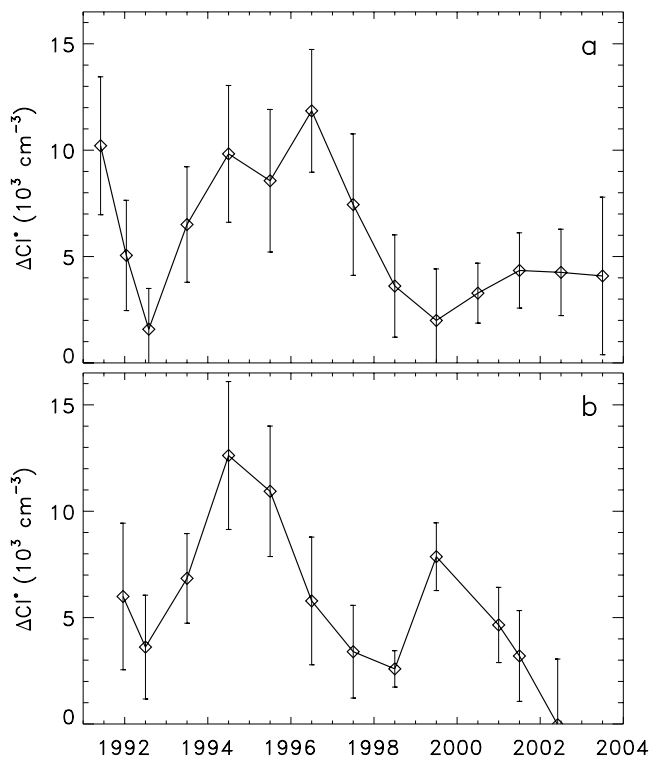


Figure 5. (a) Inferred seasonal cycle amplitude ΔCl^\bullet in Cl^\bullet concentration at Baring Head, plotted at the midpoints of the appropriate years. (b) Corresponding values at Scott Base. The uncertainties are derived via function (3) from the KIE uncertainties in Figure 4. Note that the zero 2002 value at Scott Base has large uncertainty.

compared the UM's atmospheric response to a composite of five El Niño and five La Niña events with National Centers for Environmental Prediction/National Center for Atmospheric Research reanalysis data. The UM was forced by observed SSTs and sea ice data taken from the Global Sea Ice and SST data set. Anomalies in sea level pressure, precipitation, 200 hPa velocity potential, and 200 hPa asymmetric stream function averaged over the five composites were compared for December, January, and February and March, April, and May. Good agreement was found between the model and reanalysis fields in the tropics. Some discrepancies in the model's extratropical response were associated with the limited vertical resolution of the 19 level version of the model. Future work will include testing the transport characteristics of a 30 level version of the model.

[21] Using the 19 level version, we ran the model for 25 composite ENSO cycles (100 years). At this point the model had been in steady state for a considerable time as measured by constant global mean CH_4 MR and $\delta^{13}\text{C}$. From the results we inferred the tropospheric CH_4 lifetime against OH loss to be 9.6 years, with a whole atmospheric lifetime of 8.5 years. Both are consistent with Intergovernmental Panel on Climate Change estimates [Prather *et al.*, 2001].

[22] We applied the sinusoidal least squares fitting approach described in section 4 to the MR and $\delta^{13}\text{C}$ model output for each of the 4 years of the 25th ENSO cycle and obtained the following estimates of the apparent KIE ϵ_A : year 1 (El Niño), $-4.2 \pm 0.4\%$; year 2 (El Niño), $-4.4 \pm$

0.4% ; year 3 (La Niña), $-3.9 \pm 0.4\%$; and year 4 (La Niña), $-3.8 \pm 0.3\%$. There is no significant difference between these estimates, and the overall weighted mean is $-4.03 \pm 0.18\%$, a good estimate of the input KIE $\epsilon_{\text{OH}} = -3.9\%$. These results show that (1) the KIE for a single atmospheric sink can be derived using the MR/ $\delta^{13}\text{C}$ technique from a completely different transport model to TM2 and (2) changing transport effects during the composite ENSO cycle do not significantly affect the derived KIE. We are therefore confident that the measured variations of the apparent KIE shown in Figure 4 do not arise from spurious variations in the apparent KIE for the OH $^\bullet$ sink and so most likely relate to a CH_4 sink mechanism additional to OH $^\bullet$.

5.2. Local Box Modeling

[23] Allan *et al.* [2001b] applied a simple local box model to examine oxidation of $^{12}\text{CH}_4$ and $^{13}\text{CH}_4$ in the MBL. Seasonally varying OH [Spivakovsky *et al.*, 2000] and Cl^\bullet sinks were specified as drivers of the system, with the form of the Cl^\bullet seasonal cycle in the MBL based on the dimethylsulfide (DMS) seasonal cycle but with a variable seasonal trough-to-peak amplitude ΔCl^\bullet in the concentration of Cl^\bullet . They presented a plot showing how ϵ_A increased in magnitude from the chosen OH value of -5.4% to larger values as ΔCl^\bullet increased. They showed that the addition of a fixed (aseasonal) Cl^\bullet sink in the MBL with a Cl^\bullet concentration of the order of 10^3 – 10^4 atom cm^{-3} had only a small effect on the amplitude of the MR seasonal cycle and no effect on the $\delta^{13}\text{C}$ seasonal cycle. However, they also showed that a Cl^\bullet sink with $\Delta\text{Cl}^\bullet \sim 7 \times 10^3$ atom cm^{-3} in tandem with a Spivakovsky *et al.* [2000] OH $^\bullet$ cycle (with $\epsilon_{\text{OH}} = -5.4\%$) could account for an observed $\epsilon_A \sim -13\%$. Note that the Cl^\bullet concentrations quoted are averages over day-night cycles. Because the production of Cl^\bullet is a photochemical process, peak daytime values of Cl^\bullet would be more than twice as large as the quoted values.

[24] We modified the box model of Allan *et al.* [2001b] to use the more recently published value $\epsilon_{\text{OH}} = -3.9\%$ rather than the value -5.4% used by them. The resulting relationship between ΔCl^\bullet and ϵ_A is given by the following cubic function (in units of 10^3 atom cm^{-3}) fitted by least squares to the model output:

$$\Delta\text{Cl}^\bullet = -3.74945 - 1.05066\epsilon_A - 0.0237175\epsilon_A^2 - 8.499289 \times 10^{-4}\epsilon_A^3 \pm 0.05. \quad (3)$$

This is valid in the ϵ_A range -3.9 to -21.3% and assumes that the Cl^\bullet sink has the seasonal shape described by Allan *et al.* [2001b], with an extended minimum between June and October and a sharp maximum peaking in January. The change in ϵ_{OH} from -5.4 to -3.9% results in an increase of $\sim 10^3$ atom cm^{-3} in the ΔCl^\bullet required to reach a given value of ϵ_A . Therefore the results are relatively insensitive to the value of ϵ_{OH} used. Figure 5 shows the inferred ΔCl^\bullet for BH and SB derived using (3) and the values of ϵ_A in Figure 4. The error bars were obtained by passing the extreme values of the ϵ_A error bars in Figure 4 through function (3).

6. Discussion

[25] Figure 4a shows that over the period 1991–2003 at Baring Head, apparent KIE values for CH_4 derived from the

MR/ $\delta^{13}\text{C}$ technique vary considerably with time and are always larger in magnitude than expected from OH oxidation. Although uncertainty ranges tend to overlap from year to year, when considered in periods of ~ 3 years, there appears to be a significant variation of the KIE magnitude with time. For example, the period 1994–1996 has an apparent KIE of about -15% , while the period 1998–2000 has an apparent KIE of about -7% . The results for Scott Base in Figure 4b are broadly similar but differ in detail (noting that the small apparent KIE in 2002 at SB has large uncertainty).

[26] If we interpret the apparent KIE values in terms of a possible Cl^\bullet sink in the MBL, Figure 5 shows the ΔCl^\bullet that sink would require in terms of our simple box model of the MBL. In Figure 5a the inferred ΔCl^\bullet at BH has a maximum of $\sim 10^4$ atom cm^{-3} in the period 1996–1998 and minima of $(\pm 2) \times 10^3$ atom cm^{-3} in 1992 and 1999. These latter values are indistinguishable from zero given the size of the uncertainty. Again, although adjacent yearly values have uncertainties that overlap, the periods 1994–1996 and 1998–2000 appear to have distinctly different values of ΔCl^\bullet .

[27] We have no way of estimating the seasonal mean value of Cl^\bullet , as our technique is sensitive only to ΔCl^\bullet . To the extent that the seasonal maximum is roughly twice the seasonal mean, Allan *et al.* [2001b] suggested that half the maximum value of ΔCl^\bullet could give a rough indication of the seasonal mean of Cl^\bullet . If so, the BH 1996–1998 maximum would give a Cl^\bullet seasonal mean concentration of about 5×10^3 atom cm^{-3} . The largest inferred ΔCl^\bullet at SB in Figure 5b is similar to that at BH, but the smallest reliable value (excluding 2002, which has a zero value with large uncertainty) is about 3×10^3 atom cm^{-3} , giving a seasonal mean of about 1.5×10^3 atom cm^{-3} . Because free tropospheric measurements suggest that the observed enrichment of ^{13}C in CH_4 may spread throughout the troposphere, it is possible that the Cl^\bullet mean concentration in the MBL could be significantly larger than the values suggested above. This was discussed by Platt *et al.* [2004]. They estimated that for the enrichment of ^{13}C in CH_4 to be spread uniformly through the free troposphere, an increase by a factor of ~ 6 in the Cl^\bullet mean concentration in the MBL would be required. This implies that the BH seasonal mean for 1996–1998 might actually be equivalent to about 3×10^4 Cl^\bullet atom cm^{-3} in the MBL. Although this value is relatively large, it is within the range of values quoted in the literature [e.g., Graedel and Keene, 1995]. Using tetrachloroethylene as an indicator, the global approach of Singh *et al.* [1996] inferred Cl^\bullet concentrations in the MBL to be < 0.5 – 1.5×10^4 atom cm^{-3} . Note also that we infer seasonal mean values of $\sim 10^4$ Cl^\bullet atom cm^{-3} in the period 1998–2000 using the troposphere factor of 6 above. The reason for the apparent variation of MBL Cl^\bullet concentrations on a timescale of ~ 3 years is at present unknown. We intend to investigate these ideas in detail using the unified model described in section 5.1.

[28] The values of ΔCl^\bullet discussed above were derived under the assumption [Allan *et al.*, 2001b] that the seasonal cycle of Cl^\bullet was closely related to the form and phasing of the DMS seasonal cycle measured at Cape Grim, Tasmania [e.g., Ayers *et al.*, 1995]. This follows from the possibility that oxidation products of DMS in the MBL could acidify

sea-salt droplets and allow the acid-catalyzed release of Cl^\bullet [e.g., Vogt *et al.*, 1996]. This process is quite likely to occur over regions of the Southern Ocean [e.g., Ayers *et al.*, 1999]. However, acids other than H_2SO_4 may be important in other regions, for example, HNO_3 and carboxylic acids in the vicinity of Amsterdam Island in the southern Indian Ocean [Moody *et al.*, 1991]. The exact form of the seasonal cycle of Cl^\bullet at middle to high latitudes is therefore uncertain. However, the evolution of Cl^\bullet in the MBL is a photochemical process, so a seasonal cycle of significant amplitude at middle to high latitudes seems likely, whatever the acidifying mechanism. Allan *et al.* [2001b] showed that the ΔCl^\bullet inferred from $\delta^{13}\text{C}$ measurements was relatively insensitive to the exact form and phasing of the Cl^\bullet seasonal cycle, although for given ΔCl^\bullet a cycle related to that of DMS somewhat reduced the Cl^\bullet seasonal mean concentration compared with a sinusoidal cycle.

7. Conclusions

[29] We have presented CH_4 mixing ratio and $\delta^{13}\text{C}$ data measured at Baring Head and Scott Base over the years 1991–2003. From these, seasonal phase and amplitude relationships can be derived, and hence the “apparent kinetic isotope effect (KIE)” of the CH_4 atmospheric sink can be obtained. Derived time series of this apparent KIE suggest considerable variability and greater magnitude than can be accounted for by OH^\bullet as a lone sink. The uncertainties in our results are such that the changes appear to be significant over periods of ~ 3 years. In 1994–1996 the apparent KIE was about -15% , and in 1998–2000 it was about -7% . We have shown using a global transport model that the technique we use to derive the apparent KIE should be quite accurate and that the KIE variation with time is unlikely to arise from ENSO transport effects. We infer that an atmospheric sink in addition to OH^\bullet is required.

[30] Assuming that this extra sink is Cl^\bullet in the MBL, we have derived the amplitude of the Cl^\bullet concentration seasonal cycle that would be required to give the observed effect in an isolated MBL. This amplitude ranges from 10^4 atom cm^{-3} in 1994–1996 to about 3×10^3 atom cm^{-3} in 1998–2000. If the measured enrichment of ^{13}C in CH_4 extends throughout the free troposphere, the seasonal mean concentrations of Cl^\bullet required in the MBL would be about 3×10^4 Cl^\bullet atom cm^{-3} in 1994–1996 and $\sim 10^4$ Cl^\bullet atom cm^{-3} in 1998–2000.

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References

- Allan, W., M. R. Manning, K. R. Lassey, D. C. Lowe, and A. J. Gomez (2001a), Modeling the variation of $\delta^{13}\text{C}$ in atmospheric methane: Phase ellipses and the kinetic isotope effect, *Global Biogeochem. Cycles*, *15*, 467–481.
- Allan, W., D. C. Lowe, and J. M. Cainey (2001b), Active chlorine in the remote marine boundary layer: Modeling anomalous measurements of $\delta^{13}\text{C}$ in methane, *Geophys. Res. Lett.*, *28*, 3239–3242.

- Ayers, G. P., S. T. Bentley, J. P. Ivey, and B. W. Forgan (1995), Dimethylsulfide in marine air at Cape Grim, 41°S , *J. Geophys. Res.*, *100*, 21,013–21,021.
- Ayers, G. P., R. W. Gillett, J. M. Caaney, and A. L. Dick (1999), Chloride and bromide loss from sea-salt particles in Southern Ocean air, *J. Atmos. Chem.*, *33*, 299–319.
- Bergamaschi, P., D. C. Lowe, M. R. Manning, R. Moss, T. Bromley, and T. S. Clarkson (2001), Transects of atmospheric CO , CH_4 , and their isotopic composition across the Pacific: Shipboard measurements and validation of inverse models, *J. Geophys. Res.*, *106*, 7993–8011.
- Bevington, P. R., and D. K. Robinson (1992), *Data Reduction and Error Analysis for the Physical Sciences*, McGraw-Hill, New York.
- Cleveland, R. B., W. S. Cleveland, J. E. McRae, and I. Terpenning (1990), STL: A seasonal-trend decomposition procedure based on loess, *J. Off. Stat.*, *6*, 3–73.
- Craig, H. (1957), Isotopic standards for carbon and oxygen and correction factors for mass spectrometric analysis of carbon dioxide, *Geochim. Cosmochim. Acta*, *12*, 133–149.
- Cullen, M. J. P., and T. Davies (1991), Conservative split-explicit integration scheme with fourth-order horizontal advection, *Q. J. R. Meteorol. Soc.*, *117*, 993–1002.
- Dlugokencky, E. J., K. A. Masarie, P. M. Lang, and P. P. Tans (1998), Continuing decline in the growth rate of the atmospheric methane burden, *Nature*, *393*, 447–450.
- Dlugokencky, E. J., S. Houweling, L. Bruhwiler, K. A. Masarie, P. M. Lang, J. B. Miller, and P. P. Tans (2003), Atmospheric methane levels off: Temporary pause or a new steady-state?, *Geophys. Res. Lett.*, *30*(19), 1992, doi:10.1029/2003GL018126.
- Etheridge, D. M., L. P. Steele, R. J. Francey, and R. L. Langenfelds (1998), Atmospheric methane between 1000 A.D. and present: Evidence of anthropogenic emissions and climatic variability, *J. Geophys. Res.*, *103*, 15,979–15,993.
- Graedel, T. E., and W. C. Keene (1995), Tropospheric budget of reactive chlorine, *Global Biogeochem. Cycles*, *9*, 74–77.
- Houweling, S., F. Dentener, and J. Lelieveld (1998), The impact of non-methane hydrocarbon compounds on tropospheric chemistry, *J. Geophys. Res.*, *103*, 10,673–10,696.
- Lang, P. M., L. P. Steele, L. S. Waterman, R. C. Martin, K. A. Masarie, and E. J. Dlugokencky (1992), Atmospheric methane data for the period 1983–1990 from shipboard flask sampling, *NOAA Tech. Memo., ERL CMDL-4*, NOAA, Boulder, Colo.
- Lowe, D. C., C. A. M. Brenninkmeijer, G. W. Brailsford, K. R. Lassey, A. J. Gomez, and E. G. Nisbet (1994), Concentration and ^{13}C records of atmospheric methane in New Zealand and Antarctica: Evidence for changes in methane sources, *J. Geophys. Res.*, *99*, 16,913–16,925.
- Lowe, D. C., K. Koshy, T. Bromley, W. Allan, H. Struthers, F. Mani, and M. Maata (2004), Seasonal cycles of mixing ratio and ^{13}C in atmospheric methane at Suva, Fiji, *J. Geophys. Res.*, *109*, D23308, doi:10.1029/2004JD005166.
- Moody, J. L., A. A. P. Pszenny, A. Gaudry, W. C. Keene, J. N. Galloway, and G. Polian (1991), Precipitation composition and its variability in the southern Indian Ocean: Amsterdam Island, 1980–1987, *J. Geophys. Res.*, *96*, 20,769–20,786.
- Myhre, J., E. J. Highwood, K. P. Shine, and F. Stordal (1998), New estimates of radiative forcing due to well-mixed greenhouse gases, *Geophys. Res. Lett.*, *25*, 2715–2718.
- Platt, U., W. Allan, and D. C. Lowe (2004), Hemispheric average Cl concentrations from $^{13}\text{C}/^{12}\text{C}$ ratios in atmospheric methane, *Atmos. Chem. Phys.*, *4*, 2393–2399.
- Pole, V. D., M. L. Gallani, P. R. Rowntree, and R. A. Stratton (2000), The impact of new physical parameterizations in the Hadley Centre climate model: HadAM3, *Clim. Dyn.*, *16*, 123–146.
- Prather, M., et al. (2001), Atmospheric chemistry and greenhouse gases, in *Climate Change 2001: The Scientific Basis—Contribution of Working Group I to the Third Assessment Report of the Intergovernmental Panel on Climate Change*, edited by J. Y. Houghton et al., pp. 241–287, Cambridge Univ. Press, New York.
- Saueressig, G., J. N. Crowley, P. Bergamaschi, C. Brühl, C. A. M. Brenninkmeijer, and H. Fischer (2001), Carbon 13 and D kinetic isotope effects in the reactions of CH_4 with $\text{O}(^1\text{D})$ and OH: New laboratory measurements and their implications for the isotopic composition of stratospheric methane, *J. Geophys. Res.*, *106*, 23,127–23,138.
- Singh, H. B., A. N. Thakur, Y. E. Chen, and M. Kanakidou (1996), Tetrachloroethylene as an indicator of low Cl atom concentrations in the troposphere, *Geophys. Res. Lett.*, *23*, 1529–1532.
- Sokal, R. R., and F. J. Rohlf (1981), *Biometry*, W. H. Freeman, New York.
- Spencer, H., and J. M. Slingo (2003), The simulation of peak and delayed ENSO teleconnections, *J. Clim.*, *16*, 1757–1774.
- Spencer, H., J. M. Slingo, and M. K. Davey (2004), Seasonal predictability of ENSO teleconnections: The role of the remote ocean response, *Clim. Dyn.*, *22*, doi:10.1007/s00382-004-0393-1.
- Spivakovsky, C. M., et al. (2000), Three-dimensional climatological distribution of tropospheric OH: Update and evaluation, *J. Geophys. Res.*, *105*, 8931–8980.
- Thompson, A. M. (1992), The oxidizing capacity of the Earth's atmosphere: Probable past and future changes, *Science*, *256*, 1157–1165.
- Vogt, R., P. J. Crutzen, and R. Sander (1996), A mechanism for halogen release from sea-salt aerosol in the remote marine boundary layer, *Nature*, *383*, 327–330.

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