THE DETERMINATION OF δ^{13}C IN ATMOSPHERIC METHANE IN THE SOUTHERN HEMISPHERE

D.C. LOWE, M.R. MANNING
National Institute of Water and Atmospheric Research (NIWA),
Wellington, New Zealand

Abstract. A technique to make measurements of δ^{13}C in atmospheric methane (δ^{13}CH$_4$) to a precision of 0.02‰ (1 sigma) is presented. Measurements of the mixing ratio and δ^{13}CH$_4$ from Baring Head, New Zealand and Scott Base, Antarctica are reviewed for the period 1989 to 1998. The data show persistent but irregular seasonal cycles in δ^{13}CH$_4$ ranging from 0.1 - 0.3‰ superimposed on an increasing secular trend of about 0.04‰.year^{-1}. In 1990/91 a 0.2‰ positive anomaly appeared in this trend. The causes of the anomaly remain unresolved but, during 1992 when it disappeared, the decrease in δ^{13}C was approximately coincident with a decrease in growth rate consistent with a decrease in biomass burning sources, which are relatively enriched in ^{13}CH$_4$. δ^{13}CH$_4$ data are also reported from large clean air samples collected every 2.5° to 5° of latitude on four voyages across the Pacific between New Zealand and the West Coast of the USA in 1996 and 1997. These data show that the inter-hemispheric gradient for δ^{13}CH$_4$ was highly dependent on season, and varied from less than 0.1‰ in June 1996 to more than 0.5‰ in November 1996 with an estimated annual mean of 0.2–0.3‰.

1.   INTRODUCTION

Atmospheric methane mixing ratios have increased rapidly over the last 200 years due to an excess of sources over sinks [1, 2]. Methane is released to the atmosphere by many kinds of anaerobic sources e.g. ruminant animals, rice paddies and wetlands, leakage and venting of natural gas and biomass burning, especially in the tropics [3, 4]. The major sink for atmospheric methane is oxidation by hydroxyl, OH, radicals and the current loss rate by this process, which depends strongly on OH mixing rates and the reaction rate constant with methane, is estimated at 400–600 Tg year^{-1} [4]. Soils are believed to be a minor sink for atmospheric methane and may account for a further 5–58 Tg year^{-1} [5].

Extensive mixing ratio measurements made over several years at a number of sites in the northern and southern hemispheres have been used to develop a consistent picture of the global methane budget using atmospheric chemistry and transport models [4, 6, 7]. In addition measurements of variations in the isotopic composition of atmospheric methane have provided additional constraints on the budget because several of the sources can be distinguished by characteristic ^{14}C, ^{13}C and ^{2}H signatures [8–12]. For example, methane produced by methanogenesis under anaerobic conditions is depleted in ^{13}C [13] whereas methane released from biomass burning is relatively enriched in ^{13}C, retaining values close to that of the parent carbon in the fuel [14, 15]

In this work we provide a brief review of ^{13}C measurements made in atmospheric methane at various sites in the Pacific. These include Baring Head, New Zealand, 41°S, Scott Base, Antarctica, 78°S and measurements made from air samples collected on board of container ships crossing the Pacific between New Zealand and the US west coast (see Figure 1). The data are used to determine the inter-hemispheric gradient of δ^{13}C in atmospheric methane and its seasonal variations and to provide a better understanding of methane transport into the extra-tropical Southern Hemisphere. In addition a primary purpose of this work is to provide a comprehensive description of the techniques used to make the measurements.
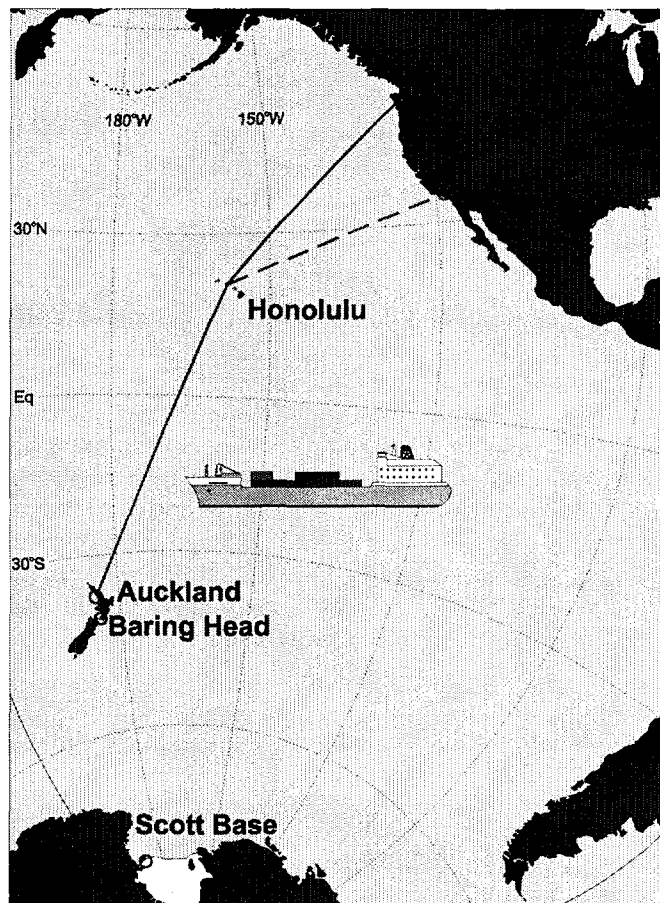
Figure 1: Location of the ground sites and typical container ship voyage tracks used to collect large clean air samples for $\delta^{13}CH_4$ analysis.

2. EXPERIMENTAL

The $^{13}CH_4$ measurements are made using dry whole air samples collected at Baring Head, Scott Base and aboard Blue Star Line (now part of P&O Nedlloyd) container ships, the "Melbourne Star" and the "Argentina Star" which make frequent voyages between New Zealand and the West Coast of the United States. A typical voyage track, ("Melbourne Star" in June 1996) is shown in Figure 1 as well as the positions of the Baring Head and Scott Base sites. Sampling techniques at the two sites and on the ships have been described by *Lowe et al.* [16, 17]

Mixing ratio determinations of the methane in the air samples are made using gas chromatography with flame ionisation detection and all results are reported as ppb (nmole.mole^{-1}), in dry air. The primary standard reference materials are prepared by the US National Institute of Standards and Technology (NIST) and laboratory working standards are calibrated against these. Full details of the gas chromatography used have been reported by *Lowe et al.* [17]

To determine $^{13}C/^{12}C$ ratios in methane from the large air samples, we use a gas source isotope ratio mass spectrometer (IRMS). However, the methane must first be quantitatively extracted from the air samples and converted to CO_2. This is done on a vacuum conversion line using a modification of a "flow through" procedure developed by *Lowe et al.* [18] and inspired by the early work of *Stevens and Krout* [19]. Briefly the air sample is stripped of remaining water, CO_2, N_2O, and NMHC by passage at 1 liter.min^{-1} (controlled by an

integrating mass flow controller) through a series of cryogenic traps held at liquid nitrogen temperature. In addition CO is removed from the stream by passage through a 350 g bed of Schütze reagent where the active reagent is iodine pentoxide on a silica gel support. Subsequently, methane in the air sample is combusted at $790°C$ in a furnace containing 100 g of 1% platinum catalyst supported on 3 mm alumina pellets. The resulting CO_2, which retains the $^{13}C/^{12}C$ and $^{14}C/^{12}C$ ratios from the methane in the air samples, and water from the combustion are collected in cryogenic traps immediately after the furnace. The water is removed at $-80°C$ in alcohol dry ice traps by triple vacuum distilling the CO_2 from the cryogenic traps into small pyrex bottles or flame sealed pyrex tubes. This CO_2 is analyzed for ^{13}C by IRMS and the same gas may be used for ^{14}C determinations by conversion into graphite targets for accelerator mass spectrometry [18].

$^{13}C/^{12}C$ ratio measurements of the CO_2 derived from the methane are made at NIWA using a Finnigan MAT (Bremen, Germany) 252 IRMS running in dual inlet mode. The sample inlet side of the IRMS has been modified by inserting a 500 µl cold finger stainless steel volume at the head of the sample capillary with the inlet isolated by a pneumatically actuated gold seated dual valve (Finnigan MAT, Bremen). This allows the direct introduction of 10–80 µl CO_2 samples from volumes of either 0.5 or 2.5 ml into the IRMS ion source. With this inlet system m/z = 44 signals are typically 4 volts (collector resistance 3×10^8 Ω) for the atmospheric methane samples and the internal precision of individual $\delta^{13}C$ determinations (10 changeovers between sample and working reference) is typically 0.01‰.

We use the standard notation:

$$\delta^{13}C = (R_s/R_r - 1) \times 1000 \text{ [in ‰]}$$

to calculate $^{13}C/^{12}C$ ratios as parts per mille (‰), where R_s and R_r are the $^{13}C/^{12}C$ ratios of the unknown sample and a working reference gas respectively. The working reference is dry CO_2 stored in a 25 liter glass flask at 1.1 bar and is metered as required via 3 mm OD stainless steel lines and Nupro high vacuum valves into the variable volume bellows on the reference side of the MAT 252. The reference CO_2 was made from combusted, purified, land fill methane and mixed with CO_2 derived from marine carbonates to produce a $\delta^{13}C \approx -47‰$, which is in the middle of the range expected for atmospheric methane samples. Two working references denoted CH4WR1 and CH4WR2 were prepared in this fashion. These isotopically "light" CO_2 working reference gases are compared with CO_2 evolved every 6–12 months from NBS-19 carbonate supplied by the International Atomic Energy Agency (IAEA), Vienna, Austria [20]. This provides the link to the V-PDB scale widely used in the literature and all measurements reported here are as ‰ deviations from V-PDB. CH4WR1 and CH4WR2 were first determined at $\delta^{13}C = -47.07 \pm 0.01‰$ and $-47.02 \pm 0.01‰$ V-PDB respectively versus NBS-19 in January 1995 and repeated comparisons since then show that any drift in these values is less than 0.005‰ in more than 4 years. As a control, the two light working reference gases are compared against each other on the MAT 252 IRMS at the start of each day that $\delta^{13}C$ in methane analyses are made. In this work, we will refer to the $\delta^{13}C$ of the carbon in methane as "$\delta^{13}CH_4$", noting that this is for ease of nomenclature only.

An additional assurance of calibration is provided by a light barium carbonate reference material supplied by the IAEA in Vienna, IAEA-CO-9, also known as NZCH [18, 20]. The published stable isotope values for this material are $\delta^{13}C = -47.119 \pm 0.149‰$ and $\delta^{18}O = -15.282 \pm 0.093‰$. CO_2 from this material is evolved and compared with NBS19 and the working references, CH4WR1 and CH4WR2, as described above. Quality assurance is also provided by the routine measurement of $\delta^{13}CH_4$ in methane mixtures in synthetic air and ambient methane in dry air samples collected at Baring Head, New Zealand and stored or "archived" in stainless steel tanks as described by Lowe et al. [16]. These controls provide

confidence in the sample preparation and analysis techniques and the $\delta^{13}CH_4$ data reported here and a series of tests are shown in the regression line in figure 2. The overall precision of the technique, 1 sigma, as determined by $\delta^{13}CH_4$ analyses of sets of duplicate air samples collected at Baring Head, is 0.02‰. Inter-calibration has also routinely been carried out with other laboratories making $\delta^{13}CH_4$ measurements in air. For example, a set of 15 air samples exchanged between Paul Quay, University of Washington, Seattle and NIWA and analysed for $\delta^{13}CH_4$ by both labs showed a mean difference of 0.01±0.05‰ [16]. A similar inter-calibration exercise is currently in progress with the Geosciences Department, University of California, Irvine and a set of 16 samples exchanged between the two labs from early 1995 to mid 1998 shows a mean analysis difference for $\delta^{13}CH_4$ of 0.01±0.06‰.

3.   RESULTS AND DISCUSSION

Time series for CH_4 mixing ratio and $\delta^{13}CH_4$ are shown in Figure 2 for Baring Head and Scott Base. Both series show considerable secular and seasonal variability. The seasonal variations in mixing ratio are attributed to variations in the strength of the OH sink. OH is a maximum in summer when its production by UV photolysis of water and ozone is greatest and methane mixing ratios at both Baring Head and Scott Base both show corresponding minima in February March. The secular growth rate caused by the imbalance of sources and sinks is quite variable from 1989 to 1998 with a maximum growth rate of 16 ppb/year observed in 1991 and a minimum of close to zero in 1993. $\delta^{13}CH_4$ data at both sites also shows a variable seasonal cycle with an amplitude of 0.1–0.3‰ superimposed on a rather variable increasing secular trend of about 0.04‰ ·year^{-1}. This cycle is approximately six months out of phase with the corresponding methane mixing ratio cycle. In 1990/91 a large positive anomaly of about 0.2‰ was observed in $\delta^{13}CH_4$ at both Baring Head and Scott Base. The causes of the anomaly remain unresolved but, during 1992 when it disappeared, the decrease in $\delta^{13}C$ was approximately coincident with a decrease in growth rate. This is consistent with a decrease in biomass burning sources which are relatively enriched in $^{13}CH_4$ [21].

Methane mixing ratio measurements for air samples collected on four container ship voyages are plotted as a function of sine of latitude in Figure 3. The voyages took place in June and November 1996 ("Melbourne Star") and February and September 1997 ("Argentina Star"). Time coincident data from Suva, Fiji, 17°S, Baring Head, New Zealand, 41°S, Scott Base, Antarctica, 78°S, and data from a C130 flight in the troposphere between Christchurch, New Zealand, 43°S, and McMurdo Sound, Antarctica, 78°S in February 1997 are also plotted in Figure 3. All data sets show relatively uniform mixing ratios between 78°S and about 30°S indicative of a well mixed extra-tropical southern hemisphere. However, north of 15°S, a typical position for the South Pacific Convergence Zone (SPCZ) at 170°W [22] (see Figure 1), mixing ratio data from the voyages showed quite different trends.

For example, the voyages in November 1996 and February 1997 showed a steady increase from about 1710 to 1740 ppb between 10°S and 10°N, the position of the Inter Tropical Convergence Zone (ITCZ). Here there was an abrupt transition to much higher and more variable values ranging from 1740 to 1840 ppb indicative of the extra-tropical northern hemisphere. Higher methane mixing ratios are expected north of the ITCZ because most methane sources are in the Northern Hemisphere. For the June 1996 voyage, however, a local minimum of 1710 ppb occurred at the position of the SPCZ, 10°S, followed by a rapid rise to 1740 ppb by 5°S. Thereafter the mixing ratio was fairly uniform up to the ITCZ located at about 10°N. Thus on the voyage route in June 1996, a well defined SPCZ and ITCZ led to a confined region of well mixed air in the equatorial Pacific showing methane mixing ratios midway between the extra tropical southern and northern hemispheres.

The $\delta^{13}CH_4$ data for the four container ship voyages are also shown in Figure 3 with equivalent data from the other sites and the aircraft flight described above. In the June 1996 voyage from Auckland to Seattle, we measured a relatively uniform decrease in $\delta^{13}C$ from $-47.15‰$ at $35°S$ to a minimum value of $-47.35‰$ at the equator. However, there was a sharp increase in $\delta^{13}CH_4$ to $-47.15‰$ at $10°S$, which anti-correlated with a minimum in methane concentration and coincided with the position of the SPCZ. In the Northern Hemisphere, $\delta^{13}CH_4$ decreased gradually to about $-47.30‰$ at $20°N$. No abrupt change was observed at the ITCZ, located at about $10°N$, and the observed average gradient in $\delta^{13}CH_4$ between the hemispheres was relatively small, less than $0.1‰$. In November 1996, however, a large gradient between the hemispheres was measured in $\delta^{13}CH_4$ with relatively small variations ranging from about -47.00 to $-47.10‰$ up to about $5°N$ followed by a rapid drop to about $-47.50‰$ at about $30°N$. In February 1997 $\delta^{13}CH_4$ showed a virtually monotonic decrease from about $-47.05‰$ at $78°S$ to $-47.35‰$ at $30°N$ with most values falling midway between the June and November 1996 data. The September 1997 voyage, however, featured a broad but pronounced maximum in $\delta^{13}CH_4$ at about $10°S$ with minimum values in the mid-latitudes of both hemispheres.
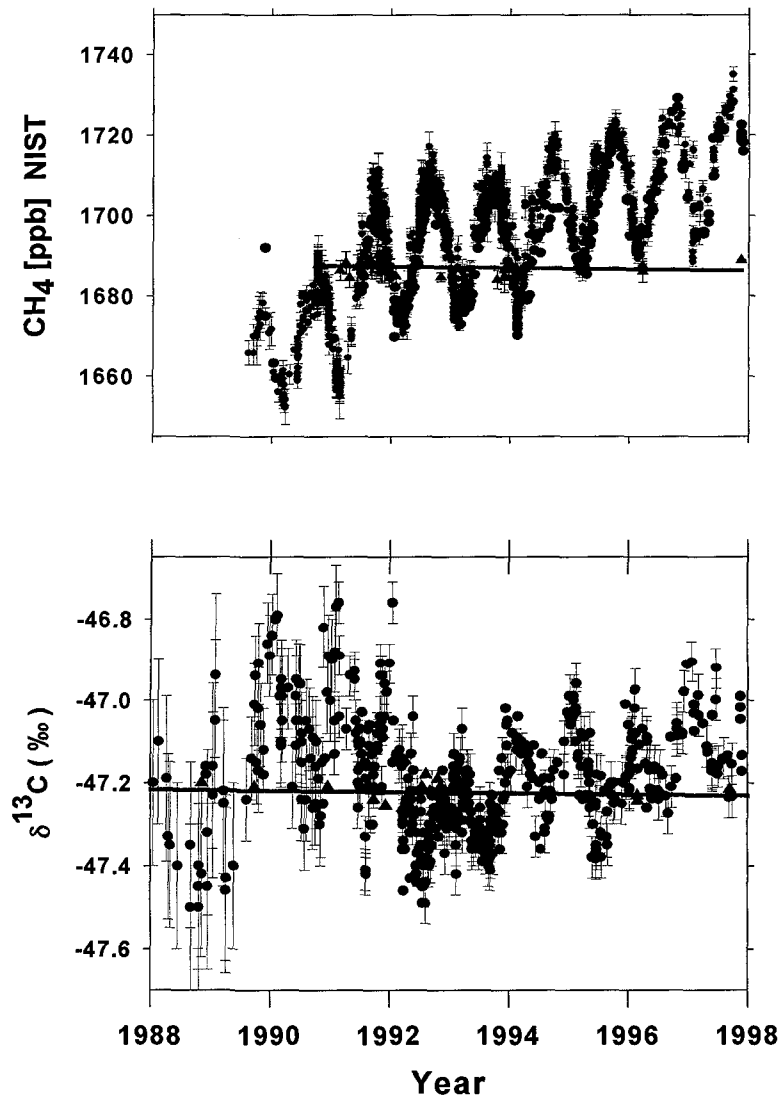

Figure 2: Atmospheric mixing ratio and ^{13}C data from Baring Head and Scott Base are shown as the solid circles with vertical error bars (1 sigma). The horizontal solid lines are regression lines fitted through the quality control "archive" tanks (triangles) referred to in the text.
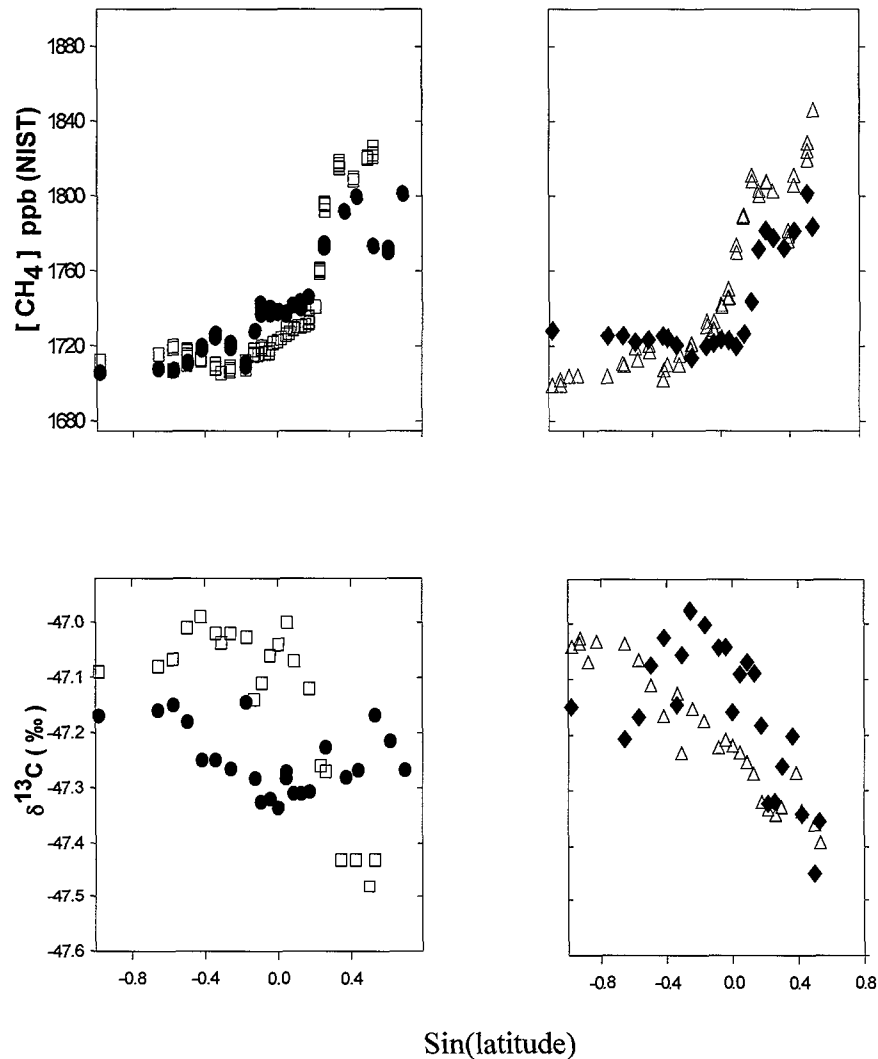
Sin(latitude)

Figure 3: Adapted from [21] Methane mixing ratio and δ¹³CH₄ data from clean air samples collected on four Pacific voyages. The left hand panels show data from June 1996 (filled circles) and November 1996 (open squares) and the right hand panels show data from February 1997 (open triangles) and September 1997 (filled diamonds). For clarity data from Scott Base and Baring Head are not marked differently, but they can be located on the plot by their latitude.

The $\delta^{13}CH_4$ data shown in Figure 3 clearly exhibit marked seasonal behaviour with cycles quite unlike those observed for the concurrent methane mixing ratio data or similar shipboard atmospheric methane mixing ratio data reported for the Pacific by Dlugokencky et al. [6]. Examination of the data shows that the maximum of a cycle at 33°N in June 1996 is about − 47.25‰ which is similar in magnitude to the seasonal minimum observed at Baring Head and Scott Base. Since the tropical data show a minimum of about −47.30‰ at this time, no pronounced inter-hemispheric gradient in $\delta^{13}CH_4$ data on the voyage in June 1996 was observed. For the November 1996 voyage, however, the situation was quite different with the minimum of seasonal cycles in the northern Pacific coinciding with maximum values in the Southern Hemisphere. This, coupled with the fact that, on average, $\delta^{13}CH_4$ is lower in the Northern than the Southern Hemisphere, led to a relatively large inter-hemispheric gradient of 0.5‰. Interpolation of data from all four voyages suggests that the annual average inter-hemispheric gradient in $\delta^{13}CH_4$ in the Pacific is about 0.2–0.3‰.

The principal removal mechanism for methane from the atmosphere is believed to be chemical destruction by the OH radical and hence, because $^{12}CH_4$ reacts faster with OH than $^{13}CH_4$, methane remaining in the atmosphere becomes enriched in ^{13}C relative to the global source. This process has been investigated under laboratory conditions and a kinetic isotope effect (KIE) defined as the ratio of the rate constants of the reaction of OH with $^{12}CH_4$ and with $^{13}CH_4$ has been measured at 1.0054, or 5.4‰, by Cantrell et al. [23] and recently by Saueressig et al. [24] at 3.9‰ at 296K. Consequently as methane "ages" after emission to the atmosphere, it becomes progressively enriched in ^{13}C as it is oxidised by OH. Hence an inter-hemispheric exchange time of about 1 year, 1/10 of the atmospheric methane lifetime, implies that methane reaching the southern hemisphere from the northern hemisphere will be enriched in ^{13}C by about 0.5‰. When contributions by southern hemisphere sources of methane are taken into account, this enrichment is consistent with the average inter-hemispheric gradient, 0.2–0.3‰, deduced from the data in shown in Figure 3.

Large-scale biomass burning occurs in the tropics and subtropics, particularly the southern tropics during the dry period of August to October [15, 25, 26]. These regions contain tropical rain forests comprising C3 plants with $\delta^{13}C$ about –28‰, and Savannah regions with C4 plants, $\delta^{13}C$ about –13‰ [14]. Methane produced during biomass burning is known to have a $\delta^{13}C$ value near that of the carbon in the parent material [13] and is therefore considerably more enriched in ^{13}C than atmospheric methane. The $\delta^{13}CH_4$ data from the voyage of September 1997 show a large broad peak in the southern tropics with a maximum at about 12°S consistent with the release of methane enriched in ^{13}C from biomass burning in the dry season in the Southern Hemisphere. These data were coincident with large fires and wide spread areas of smoke reported from Kalimantan to Sumatra caused by an intense El Nino induced drought in the latter part of 1997 [27] and similar to the situation caused in the El Nino southern oscillation event of 1991 [28].

4.   CONCLUSIONS

Measurements of methane $\delta^{13}C$ and mixing ratio at Baring Head, New Zealand, and Scott Base, Antarctica, from 1989 to 1998 show both seasonal and secular variability. The secular growth rate caused by the imbalance of methane sources and sinks is quite variable with a maximum growth rate of 16 ppb.year^{-1} observed in 1991 and a minimum of close to zero in 1993. $\delta^{13}CH_4$ data at both sites show a variable seasonal cycle with an amplitude of 0.1–0.3‰ superimposed on a rather variable increasing secular trend of about 0.04‰.year^{-1}. This cycle is approximately six months out of phase with the corresponding methane mixing ratio cycle. In 1990/91 a large positive anomaly of about 0.2‰ was observed in $\delta^{13}CH_4$ at both Baring Head and Scott Base. The causes of the anomaly remain unresolved but, during 1992 when it disappeared, the decrease in $\delta^{13}C$ was approximately coincident with a decrease in growth rate consistent with a decrease in biomass burning sources that are relatively enriched in $^{13}CH_4$.

The shipboard data reported here show that the methane distribution in the Southern Hemisphere appears to be largely determined by inter-hemispheric transport with about a 5% difference in mixing ratio between the hemispheres and an abrupt gradient at the ITCZ. Significant variations in mixing ratio distributions between the ITCZ and the SPCZ were observed on the 4 voyages reported here and related to the intensity and position of the SPCZ. In June 1996, a well defined SPCZ and ITCZ led to a confined region of well mixed air around the equator showing methane mixing ratios midway between the extra tropical southern and northern hemispheres. However a relatively weak SPCZ in September 1997 led

to uniform mixing ratios extending throughout the extra tropical southern hemisphere and SPCZ to the ITCZ region. Complex tropical meteorology which results in changes in the intensity and position of the convergence zones clearly plays a major role in the distribution of atmospheric methane in tropical regions and its transport to the extra-tropical southern hemisphere.

The inter-hemispheric gradient for $\delta^{13}CH_4$ is highly dependent on season, varying from a minimum of less than 0.1‰ in June 1996 to a maximum of more than 0.5‰ in November 1996. Lower values for $\delta^{13}CH_4$ were observed in the Northern Hemisphere north of the ITCZ. Interpolation of the data suggests that the average inter-hemispheric gradient in $\delta^{13}CH_4$ in the Pacific is 0.2–0.3‰.

The small gradients between the ITCZ and 35°S as well as the broad peak observed in $\delta^{13}CH_4$ in the southern tropics in September 1997 suggest that the seasonal cycles observed in the extra tropical southern hemisphere are influenced by the southward transport of ^{13}C enriched methane from tropical biomass burning.

The cycles in the extra tropical southern hemisphere can be used to estimate a value for the apparent KIE of methane oxidation of 12–15‰ which is much larger than current laboratory measurements of the KIE of CH_4 + OH.

The data reported here demonstrate the value of simultaneous high precision measurements of $\delta^{13}CH_4$ and methane mixing ratios as tools to probe latitudinal and seasonal structures in the Pacific region. However, far more high precision $\delta^{13}CH_4$ data are needed to increase the scope of the method and to constrain 3-D chemical tracer models used to predict the global distribution of atmospheric methane.

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