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Stable carbon isotopic composition of atmospheric methane: A comparison of surface level and free tropospheric air

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Abstract. We report CH₄ mixing ratios and δ¹³C of CH₄ values for remote air at two ground-based atmospheric sampling sites for the period December 1994 to August 1998 and similar data from aircraft sampling of air masses from near sea level to near tropopause in September and October of 1996 during the Global Tropospheric Experiment Pacific Exploratory Mission (PEM)-Tropics A. Surface values of δ¹³C-CH₄ ranged from -47.02 to -47.52‰ at Niwot Ridge, Colorado (40°N, 105°W), and from -46.81 to -47.64‰ at Montaña de Oro, California (35°N, 121°W). Samples for isotopic analysis were taken from 2° to 27°S latitude and 81° to 158°W longitude and from sea level to 11.3 km in altitude during the PEM-Tropics A mission. They represent the first study of ¹³CH₄ in the tropical free troposphere. At ~11 km, δ¹³C-CH₄ was ~1‰ greater than surface level values. Methane was generally enriched in ¹³C as altitude increased and as latitude increased (toward the South Pole). Using criteria to filter out stratospheric subsidence and convective events on the basis of other trace gases present in the samples, we find evidence of a vertical gradient in δ¹³C-CH₄ in the tropical troposphere. The magnitude of the isotopic shifts in atmospheric CH₄ with altitude are examined with a two-dimensional tropospheric photochemical model and experimentally determined values for carbon kinetic isotope effects in chemical loss processes of CH₄. Model-calculated values for δ¹³C-CH₄ in both the troposphere and lower stratosphere significantly underpredict the enrichment in ¹³CH₄ with altitude observed in our measurement data and data of other research groups.

1. Introduction

The importance of atmospheric methane (CH₄) is well established (see reviews by *Ehhalt* [1974] and *Cicerone and Oremland* [1988]). Over the past decade several studies established its role as a radiative trace gas in global warming [e.g., *Ramanathan et al.*, 1985; *Dickinson and Cicerone*, 1986; *Kiehl and Dickinson*, 1987] and determined its chemistry in the troposphere and stratosphere [e.g., *Levy*, 1971; *Levine et al.*, 1985; *Thompson and Cicerone*, 1986; and *Crutzen* 1987]. Methane has a projected global warming potential (GWP) of ~56 relative to CO₂ over the next 20 years [*Shine et al.*, 1996]. Because of this, an increase in CH₄ causes a large change in radiative forcing relative to its atmospheric mixing ratio; that is, since preindustrial times, radiative forcing by CH₄ has increased 0.5 W m⁻², whereas for CO₂, radiative forcing has increased 1.56 W m⁻² [*Shine et al.*, 1995]. Furthermore, an increase in

atmospheric CH₄ affects the oxidizing capacity of the atmosphere by its reaction with hydroxyl (OH) and may indicate human impacts on the global carbon cycle brought about by land-usage change.

Ehhalt [1974] first determined a budget relating sources and sinks of CH₄ to its atmospheric burden. Since then, studies of its emission to the atmosphere (see review by *Cicerone and Oremland* [1988]) and atmospheric observations [e.g., *Dlugokencky et al.*, 1994] have increased in number. The global budget of CH₄ has been revised several times on the basis of new emissions data [e.g., *Ehhalt and Schmidt*, 1978; *Sheppard et al.*, 1982; *Seiler et al.*, 1984; and *Cicerone and Oremland*, 1988] and of information such as observations of trends in atmospheric values and seasonal cycles and latitudinal gradient of CH₄ mixing ratio [*Fung et al.*, 1991].

Determinations of the budget for CH₄ have also been constrained by information gained from measurements of stable and radiocarbon isotopes of atmospheric CH₄ and its sources and sink processes (i.e., CH₄ loss from reactions with OH, Cl, O(¹D), and soil bacteria). Numerous published studies of stable isotope measurements in CH₄ sources detail one or several aspects of emission or pathways of production (for a review see *Tyler* [1991]). Recent studies of stable and radiocarbon isotopes of atmospheric CH₄ are fewer but include work by *Wahlen et al.*

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[1989], Quay *et al.* [1991], Lowe *et al.* [1991, 1994, 1997], Lassey *et al.* [1993], Thom *et al.* [1993], and Gupta *et al.* [1996]. A few measurements of stable carbon isotope fractionation in CH₄ sink processes also exist [e.g., Coleman *et al.*, 1981; King *et al.*, 1989; Cantrell *et al.*, 1990; Tyler *et al.*, 1994a, b, 1998; Saueressig *et al.*, 1995]. In addition, calculations of kinetic isotope effects (KIEs) in chemical sink processes of CH₄ have also been made [i.e., Lasaga and Gibbs, 1991; Melissas and Truhlar, 1993; Tanaka *et al.*, 1996; Gupta *et al.*, 1997; and Roberto-Neto *et al.*, 1998]. These theoretical calculations have in some cases revealed inconsistencies among atmospheric observations, laboratory results, and theory with respect to the KIEs in chemical loss processes of CH₄. It is important to resolve these differences in order to maximize the value of isotope data in studying the atmospheric CH₄ budget and to examine current and future trends in CH₄ sources and sinks.

We report a record of surface CH₄ mixing ratios and $\delta^{13}\text{C}$ of CH₄ for remote air at a midcontinental site near Niwot Ridge, Colorado, and a coastal site at Montaña de Oro, California, and from tropospheric samples between ~3 and ~11 km collected during the Global Tropospheric Experiment Pacific Exploratory Mission-Tropics A (PEM-Tropics A) program in September and October 1996. The period of surface measurements includes dates from December 29, 1994, to August 1, 1998. Surface samples were collected twice monthly (approximately) during this interval. Our highest altitude samples from PEM-Tropics A (~11 km) corroborate earlier measurements by others that indicate upper tropospheric and lower stratospheric CH₄ carbon isotope ratios have been shifted by as much as 1‰ toward heavier (¹³C-enriched) CH₄ values, presumably because of chemical loss processes. To the best of our knowledge, measurements of $\delta^{13}\text{C}$ of CH₄ from PEM-Tropics A samples are the first to be reported from air masses in the tropical free troposphere (~3--9 km). They provide evidence that a vertical gradient in $\delta^{13}\text{C}$ -CH₄ values exists in the tropical troposphere in addition to the stratospheric subsidence and fast mixing brought about by convective events from the surface. The causes of the isotopic shifts in atmospheric CH₄ with altitude are examined using a two-dimensional (~11 km) corroborate earlier measurements by others that indicate upper tropospheric and lower stratospheric CH₄ carbon isotope ratios have been shifted by as much as 1‰ toward heavier (¹³C-enriched) CH₄ values, presumably because of chemical loss processes. To the best of our knowledge, measurements of $\delta^{13}\text{C}$ of CH₄ from PEM-Tropics A samples are the first to be reported from air masses in the tropical free troposphere (~3--9 km). They provide evidence that a vertical gradient in $\delta^{13}\text{C}$ -CH₄ values exists in the tropical troposphere in addition to the stratospheric subsidence and fast mixing brought about by convective events from the surface. The causes of the isotopic shifts in atmospheric CH₄ with altitude are examined using a two-dimensional tropospheric photochemical model. We compare model-calculated $\delta^{13}\text{C}$ -CH₄ values in both the troposphere and stratosphere to available measurement data reported here and by other research groups.

2. Experimental Methods

2.1. Sample Site Descriptions

Surface air samples were collected at two locations. One is near Niwot Ridge, Colorado, part of the continental divide for North America, with an altitude of ~3.75 km. The collection site itself is located at latitude 40°N and longitude 105°W, ~4 km southeast of Niwot Ridge at an altitude of ~3.15 km. It is situated

on land owned by the Mountain Research Station (MRS) of the University of Colorado and used as a long-term ecological research site by the National Science Foundation. It is ~1 km northwest of the MRS building and 40 km west of Boulder, Colorado. Air samples were collected at the National Oceanic and Atmospheric Administration/Climate Monitoring and Diagnostics Laboratory (NOAA/CMDL) compressor shed and tower located at the site. Wind patterns at Niwot Ridge are dominated by westerlies [Barry, 1973; Haagenson, 1979], although, at times, upslope flow from the south or southeast transports air from the Denver metropolitan area (located ~70 km to the southeast) to the site [Hahn, 1981; Johnson and Toth, 1982]. In our study all samples were collected before noon in order to increase the likelihood of sampling when the prevailing wind was from the west. Samples taken in this manner have the best chance of representing well-mixed background air from over the western United States without interference from regional contamination.

A second site used for collections of surface air samples is located along the coast of California in Montaña de Oro State Park near San Luis Obispo (35°N, 121°W). This site is protected from the city of San Luis Obispo by low-lying foothills forming a ridge running parallel to the coast. The city of Morro Bay is northeast of the site, while the Diablo Canyon nuclear power plant is ~2 km to the southeast. According to the *California Energy Commission* [1985], which compiled measurements at two wind stations near to the site, Diablo Canyon, California (years 1967-1981), and Santa Maria, California (years 1948-1978), average annual wind speeds were ~16.1 and ~12.7 km h⁻¹, respectively, at the two stations. Additional data given for Santa Maria indicate that the months from March to June exhibited the highest winds, although only 20% or so above the mean wind speed, while late afternoon to early evening hours exhibited nearly twice the wind speed found for other times of the day. Accordingly, our air samples from Montaña de Oro were collected in late afternoon or early evening during periods when prevailing winds were from the west or northwest.

A third set of samples was from upper tropospheric air collected during the PEM-Tropics A program as part of NASA's Global Tropospheric Experiment (GTE). Air samples used in our study were collected from either a DC-8 or P3-B aircraft over the central and southern Pacific Ocean between 2° and 27°S latitude and between 81° and 158°W longitude. These were collected at average altitudes of between 11.4 and 3.40 km. PEM-Tropics A consisted of a variety of flight patterns, including constant altitude, constant latitude, and vertical-climb flights to study vertical profiles at constant latitude and longitude. We obtained samples from all three types of flight patterns.

2.2. Sample Collection Procedures

At each site a different equipment system was used for air sampling. Niwot air samples were collected into passivated aluminum gas cylinders (Scott Marin, Inc., Riverside, California) pressurized using an RIX model SA-3 compressor [Lang *et al.*, 1990]. The volume of gas in these cylinders was ~793 L (STP) when pressurized to ~13,800 kPa by the compressor. Air was drawn through a stainless steel tube that had its inlet secured to a 10 m tower at a height ~6.5 m above ground level. Each cylinder was filled to ~3450 kPa from the surrounding air and then purged to ambient pressure before the final fill to ~13,800 kPa. Two drying tubes in series, each filled with magnesium perchlorate (Mg(ClO₄)₂), were located on the high-pressure side of the compressor just before the cylinder inlet. These were used to

remove water vapor from air during the purging stages and while the air was collected.

At Montaña de Oro, air was collected into a 32 L stainless steel electropolished canister (Chicago Float Works, Elk Grove, Illinois) after passing through a 1.27 cm diameter plastic tubing with a nonreactive inner lining of ethylene copolymer (Dekabon tubing, Furon Dekoron, Aurora, Ohio). The tube inlet, which was pointed into the wind, had a passive particle filter and was raised ~1 m above ground level. Air was drawn through the tube using an oilless, greaseless, battery-operated piston pump (model 415CDC30/12B, Thomas, Co., Sheboygan, Wisconsin) that forced air to enter a 2.54 cm diameter stainless steel drying tube filled with $\text{Mg}(\text{ClO}_4)_2$ as above. The drying tube was located on the high-pressure side of the compressor to remove water before the air was flushed through or collected using the canister. The canisters, which had double-valved inlet/outlet ports to allow for continuous air flow when needed, were flushed with the surrounding air for ~25 minutes and then pressurized to ~690 kPa by closing the outlet port while filling.

PEM-Tropics A air samples were collected as whole air samples in 2 L stainless steel canisters. Air from outside either the DC-8 or P-3B aircraft was drawn into a gas-handling manifold in the cabin using a metal bellows pump [Blake *et al.*, 1996]. Canisters were filled to a pressure of 275 kPa with a filling time ranging from 10 (boundary layer air) to 75 s (~11.5 km). The canisters used in this study were fabricated at University of California (UC), Irvine, and prepared for use by a technique developed to maintain sample integrity over a period of several weeks for nonmethane hydrocarbons (D. Blake, unpublished data, 1996). Sample integrity for CH_4 and other relatively long-lived trace gases was maintained for time scales much longer than our time interval from sampling to analysis using these canisters.

The PEM-Tropics A program flights took place over a period of 6 weeks during September and October 1996 and comprised 40 individual missions using both DC-8 and P-3B aircraft. On all flights aboard either aircraft, 2 L canister samples were taken by members of the D. Blake/F. S. Rowland research group of UC, Irvine, approximately every 4 min (constant altitude flights) or every 90 s (vertical climbs). However, we were able to analyze for $\delta^{13}\text{C}$ of CH_4 on only a small portion of the number of samples taken during PEM-Tropics A flights because of sampling logistics and the time constraints on laboratory analyses of samples. In practice, from 6 to 12 individual canisters collected in sequence were processed as a group (simultaneously) for isotope analysis by our laboratory. This procedure was used to provide a large enough sample for isotope ratio analysis of CH_4 . Effectively each set of canisters combined as a group represented an integration over the period of flight time elapsed during sample collection. Overall, the time period of collection for grouped samples was comparable to that of air samples collected for ^{13}C content in other studies that used relatively large air sample volumes in single cylinders or canisters for each individual sample measurement (i.e., ~9-15 min collection time per cylinder as reported by Brenninkmeijer *et al.* [1995] and ~25-30 min collection time per canister for Airborne Arctic Stratospheric Experiment (AASE)-II samples discussed by Gupta *et al.* [1996]).

2.3. Analytical Procedures (Mixing Ratios)

At UC, Irvine, CH_4 mixing ratios were measured using a Hewlett Packard 5880A gas chromatograph (GC) with packed columns and a flame ionization detector (FID). The main

separation column was 1.83 m (3.2 mm OD) of molecular sieve 5A. It was preceded by a 30.4 cm precolumn (3.2 mm o.d.) of the same material. Both columns were at 100°C and used nitrogen carrier gas. Our working CH_4 standard was a cylinder of whole air certified by direct intercalibration with standards maintained by the NOAA/CMDL air-sampling program [Lang *et al.*, 1990]. Relative to the National Institute of Standards and Technology (NIST) scale, atmospheric CH_4 mixing ratios measured using the NOAA/CMDL standards are 0.023 ppm lower. Our measurement precision was ~0.005 ppm. The uncertainty in our measurements was 0.25-0.50% for CH_4 . All CH_4 mixing ratio data reported are from determinations made at UC, Irvine.

Samples collected at Niwot Ridge were also analyzed for CH_4 and CO by NOAA/CMDL in collaboration with our lab. Methods and standard gases used for these analyses are detailed by Steele *et al.* [1987], Lang *et al.* [1990], and Novelli *et al.* [1991, 1992]. Although CO in Montaña de Oro samples was not measured directly, an approximate value for CO concentration was obtained by a calculation that divided the recovered CO in the vacuum line as determined by manometric measurement to the total amount of air processed assuming 100% recovery of CO.

2.4. Analytical Procedures (Sample Preparation)

Preparation of the samples for isotopic analysis was done on a combustion vacuum line that separates CH_4 , CO, and CO_2 trace gases from whole air (and from each other) while further converting CH_4 to CO_2 and H_2O and converting CO to CO_2 as the air stream moves toward the pump. Most of the details regarding the vacuum line design and procedure as well as improvements made over time have been reported previously [i.e., Lowe *et al.*, 1991; Tyler *et al.*, 1994a, b]. In brief, a series of cryo traps condensed trace gases such as CO_2 , H_2O vapor, and N_2O at liquid N_2 temperature, leaving CO and CH_4 in the air stream. The CO was converted to CO_2 using I_2O_5 on silica gel, also known as Schütze reagent (Leco Corp., St. Joseph, Michigan), before its removal using cryo trapping with liquid N_2 . The CH_4 was then converted to CO_2 using platinumized alumina pellets heated to 740°C, prior to its recovery using cryo trapping with liquid N_2 .

Two kinds of sample preparation tests were also made routinely. Taken together, they served to help ascertain the suitability of our analytical methods for keeping measurement data intercalibrated over the long time periods necessary to study isotopic trends. One test consisted of running dry zero air (<0.003 ppm CH_4 as judged by our GC measurements) through the vacuum line and checking for possible accumulation of condensable gases in each of the trapping sections of the vacuum line used to recover CO_2 . This test helps determine the stability of the vacuum line by checking for potential contamination from either leaks into the line or outgassing of impurities from the combustion oven or Schütze reagent. The second test consisted of routinely preparing and then processing on the vacuum line calibration gases of CH_4 in zero air using the same source of CH_4 each time. This test helps assess the long-term stability of our vacuum line, isotope ratio standards, and mass spectrometer and serves as an overall check on our precision of measurement for samples processed using the vacuum line.

2.5. Analytical Procedures (Sample Measurement)

The converted CO_2 from recovered CH_4 in air samples was measured by a Finnigan-Mat model 252 isotope ratio mass spectrometer to determine $^{13}\text{C}/^{12}\text{C}$ ratios. The units of

measurement are ‰ per mil for $\delta^{13}\text{C}$ with values for both gas standards and samples reported versus Peedee belemnite (PDB) carbonate [Craig, 1957]. The precision of measurement on clean dry CO_2 gas standards was $\pm 0.01\text{‰}$. Overall measurements of an individual CH_4 sample from field collections had a precision of $\pm 0.05\text{‰}$. The reproducibility of isotope measurements from like samples (i.e., multiple samples collected simultaneously) when all possible errors associated with sampling, processing, and measurement were taken into account was $\leq \pm 0.10\text{‰}$ for $\delta^{13}\text{C}$ of CH_4 .

Our working carbon isotope standard was CO_2 gas purchased from Oztech Gas Co. (Dallas, Texas). They certified it to be -39.78‰ versus PDB. We compared it to two other CO_2 isotope reference materials. One was a CO_2 working reference gas obtained from the National Institute of Water and Atmospheric Research (NIWA) in New Zealand that had been assigned a value of $-47.56 \pm 0.01\text{‰}$ versus PDB by NIWA. The other was a barium carbonate powder recently made available by the International Atomic Energy Agency (IAEA) for use as a CO_2 standard following prescribed methods for its preparation. Designated as IAEA-CO-9, it was reported to have a value of $-47.12 \pm 0.12\text{‰}$ (2σ , $n=10$, results of a blind test interlaboratory comparison), although isotope measurements reported by the producer were reported as $\delta^{13}\text{C} = -47.23 \pm 0.03\text{‰}$ [Stichler, 1995]. Versus our Oztech gas standard, the NIWA CO_2 gas standard had a value of $-47.61 \pm 0.03\text{‰}$ while CO_2 gas made in our laboratory from IAEA-CO-9 carbonate obtained directly from the original producer had a value of $-47.18 \pm 0.04\text{‰}$ (from five prepared standards totaling 11 measurements). Our measured values for atmospheric CH_4 are reported without a correction to account for any offset in our values versus either the NIWA working reference gas or IAEA carbon isotope standard.

3. Sample Processing Tests

3.1. Vacuum Line Tests

Contamination or "blank" tests of the vacuum line consisted of running zero air (determined to have < 0.003 ppm CH_4 by GC measurements) through the vacuum line and checking for possible accumulation of condensable gases in each of the trapping sections of the vacuum line used to recover CO_2 . This test was run every few weeks during 1995 and early 1996 and once a week routinely beginning July 1996. The average total recovered gas from blanks was 1-2 μL accumulated in the CH_4 traps and 2-5 μL in the CO traps for ~ 300 L of air processed each time. Blanks for smaller volumes of air processed were smaller. During dates when PEM-Tropics A air samples were processed, blanks were run on 25-45 L of air and found to have ~ 0.7 μL of accumulated product in the CH_4 traps.

As judged from the mass spectrometer analysis, these contamination blanks were quite variable in content; that is, they were a mixture of CO_2 and H_2O , and had $\delta^{13}\text{C}$ values of anywhere from -25 to -50‰ . The accuracy of $\delta^{13}\text{C}$ measurements on these blanks was not sufficient to assign a reasonable value to the contamination. A calculated worst possible case scenario for the relatively smaller air samples collected during PEM-Tropics A can be made assuming a fixed blank volume of 0.7 μL at -25‰ mixed with recovered CO_2 from either 25 or 45 L of sample air. The calculation indicates that the smaller CH_4 samples measured (i.e., CH_4 as CO_2 recovered from 25 L of air) would be artificially heavier than the larger samples (~ 45 L of air) by 0.15‰. Furthermore, air samples of 45 L

volume would be $\sim 0.07\text{‰}$ heavier in $\delta^{13}\text{C}$ of CH_4 than samples where 300 L of air were processed with a corresponding 2 μL blank. However, on the basis of the sample blank size relative to amounts of CH_4 recovered as CO_2 , inaccuracy in measuring its $\delta^{13}\text{C}$ value and lack of conclusive proof that the blank observed in zero air processing also appears in air sample processing we made no correction to our $\delta^{13}\text{C}$ - CH_4 data. Overall, the worst possible case scenario for vacuum line contamination revealed that neither random nor systematic errors in processing affected our ability to discern differences in $\delta^{13}\text{C}$ - CH_4 values of the order of the several tenths of per mil potentially caused by the spatial and temporal variability of air samples.

Tests of the efficiency of the Schütze reagent in the vacuum line were made to determine if incomplete reaction between it and CO could cause some CO to be oxidized to CO_2 by the platinized alumina and subsequently mixed with CO_2 from CH_4 oxidation. A series of calibration gases were made by pressurizing 32 L canisters with zero air to an appropriate pressure after first adding an aliquot of CO from a control lecture bottle of research grade CO (99.97% purity, Linde Division, Union Carbide Industrial Gases, Inc., Somerset, New Jersey). These tests revealed that $< 1.6\%$ of all CO present in a 100 L volume of calibration gas with a CO mixing ratio of ~ 1 ppm went unreacted in passing through the Schütze reagent in our vacuum line. Less than 1% of all CO in a 220 L volume of calibration gas with a CO mixing of ~ 200 ppb went unreacted. From these tests we concluded that the amount of CO breaking through the Schütze reagent and combining with recovered CH_4 using our vacuum line was negligible for our purposes.

3.2. Isotope Gas Standard Tests

Throughout the time period of sample line processing of atmospheric samples we analyzed a series of calibration gases of CH_4 in air. These calibration air samples were made in one of two methods. One method was to remove an aliquot of CH_4 from a control cylinder of research grade CH_4 (99.99% purity, Linde Division, Union Carbide Industrial Gases, Inc., Somerset, New Jersey) and to inject it into an air canister. It was then diluted using zero air to obtain ~ 30 -60 ppmv CH_4 . Using this method, canisters were measured 18 times between June 1995 and August 1997 and found to have a $\delta^{13}\text{C}$ - CH_4 value of $-35.28 \pm 0.012\text{‰}$ (1σ) for all measurements. A second method used a cylinder of zero air with an added component of 60.2 ppmv CH_4 (Scott-Marin, Inc., Riverside, California). This cylinder was analyzed 10 times between February 1996 and July 1997 and found to have a $\delta^{13}\text{C}$ - CH_4 value of $-19.53 \pm 0.07\text{‰}$ (1σ) for all measurements. These results are a good indication of the stability of our processing line over time. They confirm that there were no contamination processes occurring that were varying with time and shifting measured $\delta^{13}\text{C}$ of CH_4 values from samples significantly.

3.3. Air Sample Tests

On two Niwot Ridge air samples, duplicate aliquots from the same air cylinder were analyzed. The sample from March 15, 1996, was processed and measured twice and had a $\delta^{13}\text{C}$ - CH_4 of -47.38‰ each time. The sample from April 12, 1996, was analyzed in a similar manner and had $\delta^{13}\text{C}$ - CH_4 values of -47.37‰ and -47.38‰ . These tests showed that processing multiple aliquots of air sample and/or multiple measurements of an air sample on the mass spectrometer were unnecessary to obtain sufficient measurement precision for our study.

3.4. Intercalibration of Air Sample Measurements With Another Laboratory

Our CH₄ data sets from Niwot Ridge and Montaña de Oro are intercalibrated with data obtained by NIWA at Scott Base, Antarctica, and Baring Head, New Zealand [e.g., Lowe *et al.*, 1991, 1994, 1997; Lassey *et al.*, 1993] through an on-going intercalibration program. The intercalibration program includes not only the isotopic standards mentioned earlier but also the effects of sample containers, collection procedures, and trace gas processing prior to isotopic measurements of CH₄. A subset of the air samples collected at Montaña de Oro and Baring Head are measured by both laboratories while still in their original canisters through a sample exchange program.

For 16 air samples processed and measured by both laboratories (eight samples from Montaña de Oro and eight from Baring Head) the level of agreement for δ¹³C-CH₄ was +0.01±0.12‰. This determination excludes one sample from Montaña de Oro for which the measured difference in δ¹³C of CH₄ found by the two laboratories was 0.29‰. If we further exclude the largest outlier in the average of 16, from a sample collected at Baring Head, the level of agreement between the two labs becomes -0.01±0.09‰ (*n*=15) with the negative value indicating that our reporting of δ¹³C is lighter by 0.01‰ for the same sample measured by the New Zealand researchers.

In principle, we could adjust either Montaña de Oro or Baring Head data by 0.05‰ (making our determinations 0.04‰ heavier for the same samples measured by NIWA) to account for the offset between the two labs in measuring the NIWA reference gas. However, the uncertainty in the direct comparison of air samples (±0.09‰) is larger than the offset. Furthermore, our offset in measuring barium carbonate provided by the original producer is 0.05‰ in the opposite direction from the NIWA gas when compared to the original value assigned by the producer (i.e., not the IAEA value). We prefer to ignore corrections of the order of a few hundredths of a per mil until we participate in an appropriate blind test interlaboratory comparison.

4. Sample Data

4.1. Recovery of CH₄ From Air Samples

The yield on the vacuum line for recovery of CH₄ converted to CO₂ by combustion was 100.0±1.2% (1σ, *n*=42) for all Niwot Ridge samples processed. A similar type of yield calculated for all samples processed from Montaña de Oro was 99.6±1.3% (1σ, *n*=108). Typical volumes of CH₄ recovered were ~540 μL from processing ~300 L of air from Niwot Ridge. The amount of CH₄ recovered from Montaña de Oro air samples were correspondingly smaller because only ~180 L of air were processed using 32 L canisters.

4.2. Methane Measurements at Surface Sites

Methane mixing ratios and δ¹³C of CH₄ values from Niwot Ridge are plotted for the December 1994 to April 1997 in Figures 1a and 1b. Each point represents an individual air sample. Similar data from Montaña de Oro are plotted for the period July 1995 to August 1998 in Figures 2a and 2b; only in this case each point represents the average of all samples (usually two) collected on each date. At both locations the first several months exhibited relatively more scatter in measurements than later months. This is most probably a result of our having had to develop a protocol

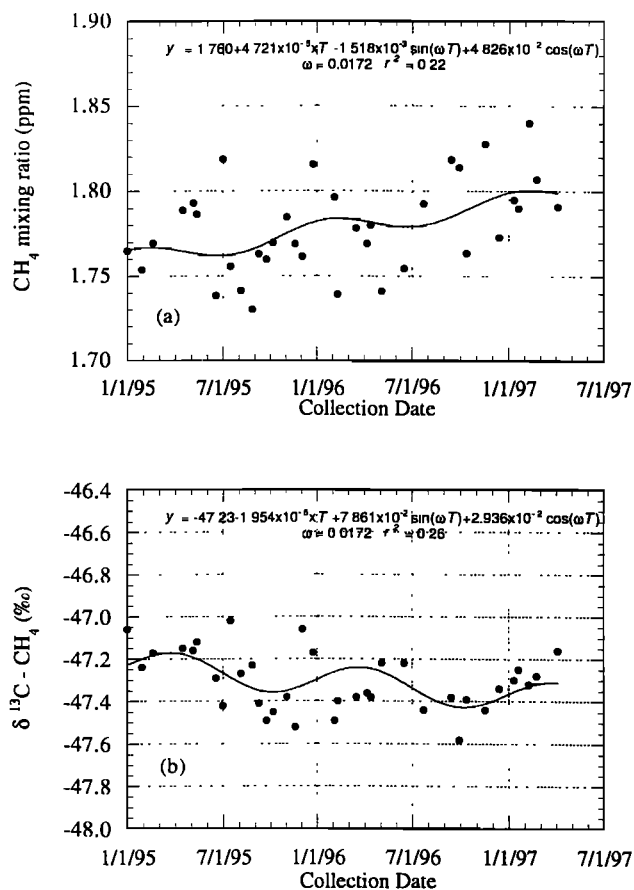


Figure 1. (a) CH₄ mixing ratio and (b) δ¹³C-CH₄ versus time at Niwot Ridge, Colorado, from December 29, 1994, to April 3, 1997. Each δ¹³C-CH₄ data point represents the result of one sample measurement made with a precision of ±0.05‰. Curves fit to data are unweighted least squares fits (1-harmonic) of form $y = a + bT + c \sin(\omega T) + d \cos(\omega T)$ with *T* in days relative to January 1, 1994, and $\omega = 2\pi/365$.

for sampling times and procedures during the first few months of sample collections at each site.

Using the measurement data, we looked for relationships between the isotope or mixing ratios and source and sink changes such as simple seasonal changes from winter/summer differences in OH abundance. In both Figures 1 and 2 the data were fit with an unweighted least squares fit (1-harmonic) by setting the periodicity at 1 year ($\omega = 2\pi/365$) but allowing for four parameters to be calculated from the best fit to a general equation of the form

$$y = a + bx + c \sin(\omega x) + d \cos(\omega x)$$

Trends in the data can be seen both from a visual inspection of the data points and from the calculated curve fits shown.

At Montaña de Oro (Figure 2), CH₄ mixing ratio data exhibited seasonality ($r^2=0.39$ for curve fit) with higher values in the winter than in the summer over 3 full years. The δ¹³C-CH₄ values were also seasonal with higher (less negative) values during summers compared to lower values in winter months. The curve fit to δ¹³C-CH₄ had a correlation of $r^2=0.14$ that improved to $r^2=0.50$ if only the last 2 years of data are used. The relative change in CH₄ mixing ratio with time was -0.23% yr⁻¹. The average δ¹³C of CH₄ using all dates for the last 3 years was -47.28±0.21‰ (1σ, *n*=46) with a peak-to-peak amplitude of ~0.6‰ (~0.25‰ from the curve fit). The CH₄ mixing ratio

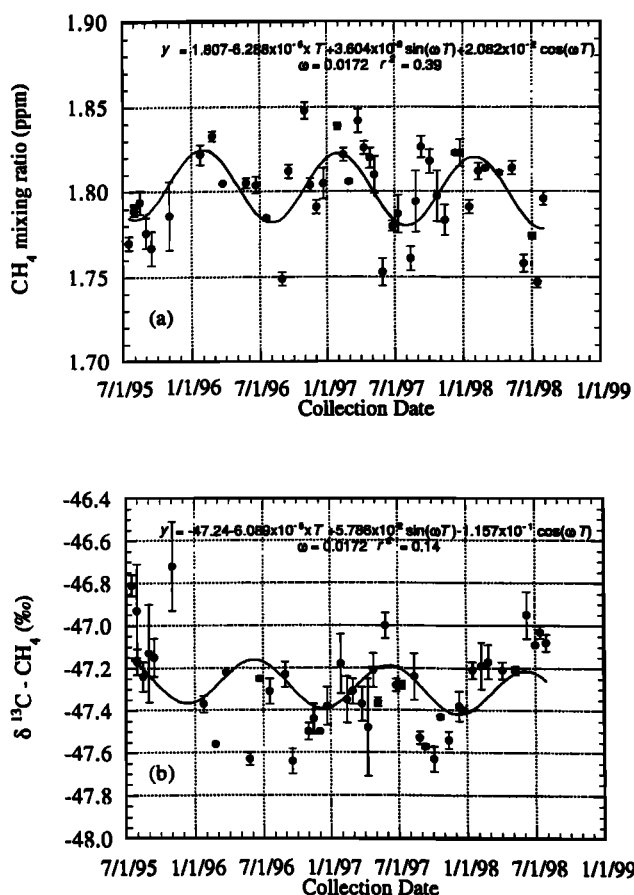


Figure 2. (a) CH₄ mixing ratio and (b) $\delta^{13}\text{C}-\text{CH}_4$ versus time at Montaña de Oro, California, from July 15, 1995, to August 3, 1998. Error bars are 1 standard deviation from the average of multiple samples. Curves fit to data are unweighted least squares fits (1-harmonic) of form $y = a + bT + c \sin(\omega T) + d \cos(\omega T)$ with T in days relative to January 1, 1995, and $\omega = 2\pi/365$. The correlation in Figure 2b improves to $r^2 = 0.50$ if only the last 2 years of data are used.

seasonality was similar to that reported in other studies of Northern Hemispheric air with more extensive data sets [e.g., *Dlugokencky et al.*, 1994]. A likely explanation for coupled CH₄ mixing ratio and $\delta^{13}\text{C}$ behavior is seasonal changes in OH concentrations that lessen atmospheric CH₄ concentrations while increasing $\delta^{13}\text{C}-\text{CH}_4$ when more OH is present.

At Niwot Ridge (Figure 1) the curve fits for CH₄ mixing ratio and $\delta^{13}\text{C}$ were less well correlated with season ($r^2 = 0.22$ for mixing ratio and $r^2 = 0.26$ for $\delta^{13}\text{C}$) than those of Montaña de Oro. However, the seasonal timing of high and low values for both CH₄ mixing ratio and $\delta^{13}\text{C}$ were similar to those of Montaña de Oro. The relative change in CH₄ mixing ratio with time was $0.97\% \text{ yr}^{-1}$, while the average $\delta^{13}\text{C}$ of CH₄ for the last 2 years was $-47.30 \pm 0.14\%$ (1σ , $n=36$). The peak-to-peak amplitude of $\delta^{13}\text{C}$ was $\sim 0.4\%$ ($\sim 0.20\%$ from the curve fit). The relatively lower correlation with season at Niwot Ridge compared to Montaña de Oro may indicate that the frequency of collection at this site was not sufficient to reveal seasonal characteristics clearly over the relatively short time span of sample collections. Another potential explanation may be a complexity in the Niwot Ridge site characteristics that goes beyond a simple seasonality driven by the OH sink.

The results from the $\delta^{13}\text{C}-\text{CH}_4$ measurements can be compared to studies of air samples from other locations over similar time frames. *Gupta et al.* [1996] reported on measurements of $\delta^{13}\text{C}-\text{CH}_4$ at Niwot Ridge for the period 1989–1992. In those data the latter 2 years showed a distinct difference between winter and summer values, with the $\delta^{13}\text{C}$ of CH₄ being $\sim 0.5\%$ lighter in winter than in summer (a curve fit of the form of (1) above had an $r^2 = 0.63$ with seasonal amplitude 0.3%). *Lowe et al.* [1991, 1994, 1997] have consistently reported easily discernible seasonality in CH₄ mixing ratio and $\delta^{13}\text{C}$ of CH₄ from Baring Head, New Zealand (41°S), for the period 1988–1993. Their data show a seasonal amplitude variation with a range of 0.6% . However, at three different Northern Hemispheric sites, *Quay et al.* [1991] saw varying degrees of winter/summer differences in $\delta^{13}\text{C}-\text{CH}_4$. The amplitude of the seasonal cycle at the three locations reported by Quay et al. was $\sim 0.5\%$ at Point Barrow, Alaska (71°N), $\sim 0.35\%$ at Olympic Peninsula, Washington (48°N), and $\sim 0.15\%$ at Mauna Loa, Hawaii (19°N), a site with an altitude (~ 3.4 km) similar to Niwot Ridge.

Measurements of CH₄ mixing ratios made by NOAA/CMDL at comparable latitudes were used to help determine whether air

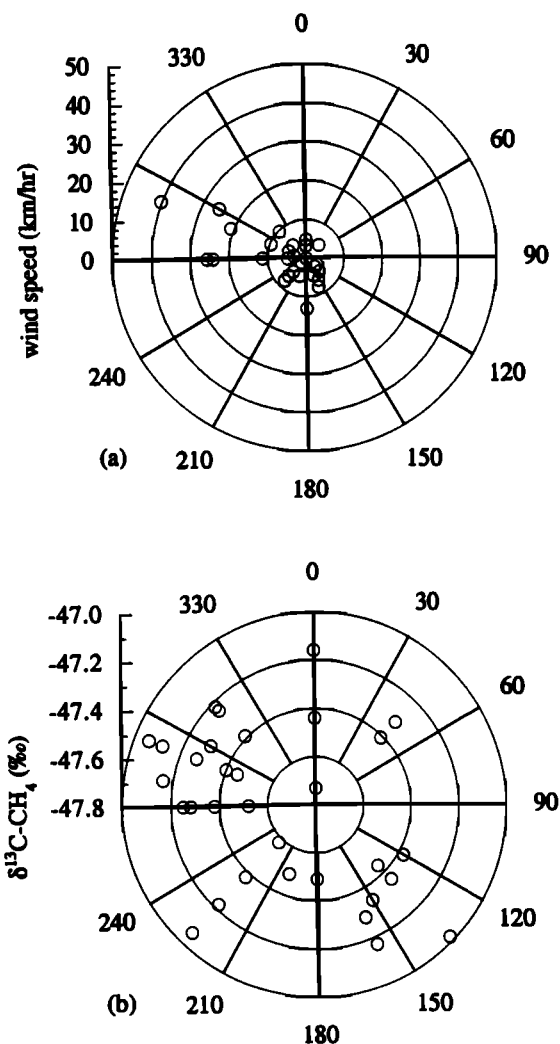


Figure 3. Windrose plots of the (a) windspeed and (b) $\delta^{13}\text{C}-\text{CH}_4$ value versus direction of wind taken at the time of sampling at Niwot Ridge. In this polar plot the radial coordinate is either $\delta^{13}\text{C}-\text{CH}_4$ for Figure 3a or windspeed for Figure 3b, and the polar angle is the wind direction.

sampled at either Niwot Ridge or Montaña de Oro was representative of background air at the site [Dlugokencky *et al.*, 1994, 1996]. We reasoned that local or regional contamination from nearby urban sources might influence CO and CH₄ mixing ratios similarly. On this basis one sampling date at Montaña de Oro with values of 1.95 ppm (CH₄) and ~319 ppb (CO) and four dates at Niwot Ridge with pairwise values of CH₄ and CO of 1.83 ppm and 217 ppb, 1.85 ppm and 172 ppb, 1.86 ppm and 174 ppb, and 1.89 ppm and 182 ppb, respectively, were not used in our calculations and analyses. Excluding these samples, CO values ranged from 123 to 210 ppb at Montana de Oro (estimated using the amount of CO recovered from our vacuum line processed as described earlier) and from 86 to 164 ppb at Niwot Ridge (as determined from NOAA/CMDL measurements of our samples).

4.3. Surface Wind Speed and Direction Measurements

At both surface sites, wind speed and direction were measured in order to help determine whether data at either site were affected by local sources. Figures 3a and 3b are windrose plots of measured windspeed and $\delta^{13}\text{C-CH}_4$ versus wind direction corresponding to sample collection times at Niwot Ridge using meteorological equipment of NOAA/CMDL at the site. Figures 4a and 4b plot similar data for Montaña de Oro obtained using a hand held compass and wind meter (Dwyer Instruments, Inc., Michigan City, Indiana).

At Niwot Ridge, where all samples were taken before noon, wind was usually from the west and was most often $<8 \text{ km h}^{-1}$ (see Figure 3a). More importantly, even when wind was from a southern or southeastern direction, it did not appear to affect the $\delta^{13}\text{C-CH}_4$ values (see Figure 3b). In contrast, *Bollinger et al.* [1984] studied NO_x mixing ratios at Niwot Ridge and determined that there was a strong correlation between meteorological conditions and NO_x at the site. Low NO_x was associated with westerly winds (more likely in winter), while high NO_x was clearly associated with Denver metropolitan pollution (more likely in summer). Events driving high-NO_x periods included daytime warming causing a valley-to-mountain circulation with accompanying upslope winds (winter) and increased convection with easterly winds (summer).

Our current wind data from Niwot Ridge also contrast with our previous experience at the site from samples collected between 1989 and 1992. At that time, morning winds were routinely stronger, and upslope winds from the southeast, biased by urban air, were likely if we sampled in afternoon or evening. However, in our 1995-1997 data set, removing data from samples taken during southerly and easterly winds does not appreciably change the results. Overall, it appears that the combination of taking early to late morning samples only during 1995-1997 and having mostly relatively calm days, thus far, has resulted in an unbiased data set with smaller differences between winter and summer values of CH₄.

Wind at the time of sampling at Montaña de Oro was nearly always from a westerly to northwesterly direction and was generally variable in speed with values between 8 and 24 km h⁻¹ (see Figure 4a). Winds from other directions were also in this range of speed. The three samples taken during southeasterly winds had values of $\delta^{13}\text{C-CH}_4$ that were midrange between the values (-46.7 to -47.6‰) for samples collected during winds from the predominant west and northwest directions (see Figure 4b). Therefore, because wind direction and $\delta^{13}\text{C-CH}_4$ were not well correlated, we did not exclude any samples from analysis on the basis of wind direction.

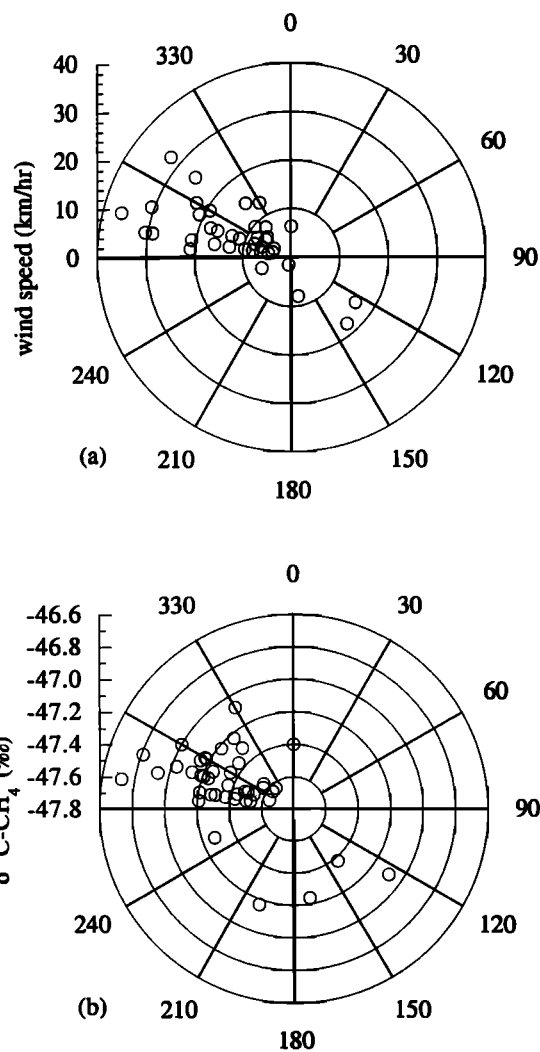


Figure 4. Windrose plots of the (a) windspeed and (b) $\delta^{13}\text{C-CH}_4$ value versus direction of wind taken at the time of sampling at Montaña de Oro, California. In this polar plot the radial coordinate is either $\delta^{13}\text{C-CH}_4$ for Figure 4a or windspeed for Figure 4b, and the polar angle is the wind direction.

4.4. PEM-Tropics Air Samples

We measured air samples from six different flights during the PEM-Tropics A program. The data appear in Table 1. An explanation of Table 1's format follows. As mentioned earlier, we combined air samples from several 2 L canisters collected sequentially to obtain enough air for $\delta^{13}\text{C-CH}_4$ analysis. Because of this, the location and altitude of each group of samples providing a $\delta^{13}\text{C-CH}_4$ value in Table 1 are listed as a range of values. Similarly, the CH₄ mixing ratio for each $\delta^{13}\text{C-CH}_4$ value is the average value of all canisters combined as a group as determined by a calculation that divided recovered CH₄ from vacuum line sample processing by the total amount of sample processed assuming 100% recovery of CH₄. In-flight determinations of CH₄ mixing ratio of individual canisters were unavailable at the time we made our analyses, and sampling logistics prevented us from making these measurements ourselves.

Ideally, we would have liked to analyze air samples from groups of canisters collected at nearly constant altitude because

Table 1. Measurement Data From Air Samples Collected During the Pacific Exploratory Mission-Tropics A (PEM-Tropics A), September and October 1996

Reference Number	Date	Latitude, deg	Longitude, deg	Altitude, km	CH ₄ vol., μ L	CH ₄ Concentration, ppm	$\delta^{13}\text{C}_{\text{CH}_4}$, ‰
1	Sept. 10	23.1 - 26.6	110	10.85 - 11.29	45.4	1.66	-45.96
2	Sept. 10	26.4 - 26.6	110	6.27 - 8.30	56.2	1.71	-46.69
3	Sept. 10	18.2 - 21.8	110	9.45	41.8	1.73	-46.24
4	Sept. 14	18.3 - 20.3	98 - 101	4.57 - 6.10	76.1	1.69	-46.56
5	Sept. 14	16.0 - 18.0	96 - 98	4.57 - 5.49	67.3	1.69	-46.61
6	Sept. 14	10.7 - 11.2	91	3.96 - 6.40	60.0	1.74	-46.91
7	Sept. 14	5.2 - 6.8	85 - 87	5.85 - 7.32	55.8	1.74	-46.80
8	Sept. 14	8.5 - 9.8	88 - 90	2.80 - 3.96	69.8	NM	-47.16
9	Sept. 14	11.5 - 14.2	91 - 94	6.10 - 7.32	62.5	1.71	-46.34
10	Sept. 18	2.2 - 2.5	81 - 83	6.59 - 7.93	50.6	1.74	-46.80
11	Oct. 3	15.7 - 19.3	154	10.45 - 10.67	68.7	1.72	-46.31
12	Oct. 3	16.9 - 17.3	154	8.11 - 10.09	48.5	1.71	-46.38
13	Oct. 5	5.6 - 9.4	146	9.44	50.1	1.71	-47.13
14	Oct. 5	9.9 - 13.7	146 - 148	9.44	48.1	1.71	-46.48
15	Oct. 5	15.2 - 16.8	149	3.67 - 7.70	45.9	1.69	-46.73

our primary goal was to look for changes in $\delta^{13}\text{C}$ of CH₄ with altitude. In practice, because of the relatively small number of samples available to us, some analyses were made on samples taken during vertical climbs. We therefore tried to minimize the amount of averaging over altitude inherent in grouping samples from different altitudes. Criteria were set up for combining multiple samples for analysis. The first criterion used was simply to combine canisters collected in sequence at near-constant altitude and near-constant latitude. For samples collected sequentially during changing elevation the criterion was based on monthly mean OH concentrations calculated by our

two-dimensional global tropospheric photochemical model [Gupta, 1996; Gupta *et al.*, 1998]. Air from individual canisters was combined such that within a group of canisters the lowest and highest calculated OH concentrations in grid points corresponding to those of the canisters were within 10% of each other.

It is helpful to look at the data in Table 1 graphically. In Figure 5a, a two-dimensional (2-D) plot of median altitude versus median latitude for all longitudes held arbitrarily constant shows the approximate location of air parcels used to make each measurement. Numbers in Figure 5a marking each air parcel

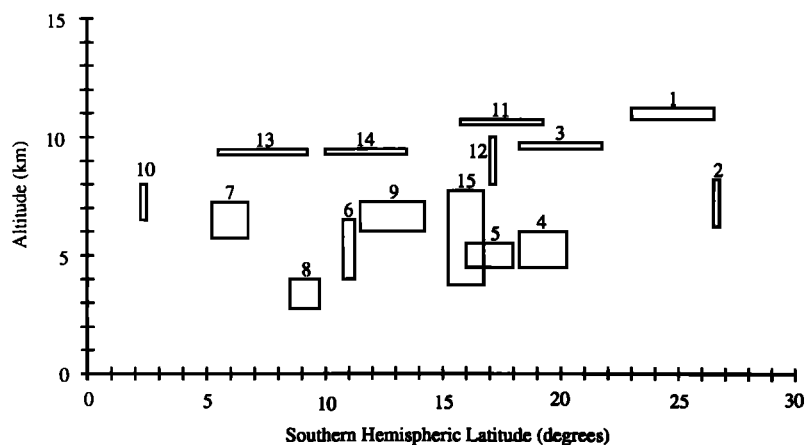


Figure 5a. The two-dimensional plot of median altitude versus median latitude for all longitudes held arbitrarily constant to show the approximate air parcels used to make each measurement in Pacific Exploratory Mission (PEM)-Tropics A air samples.

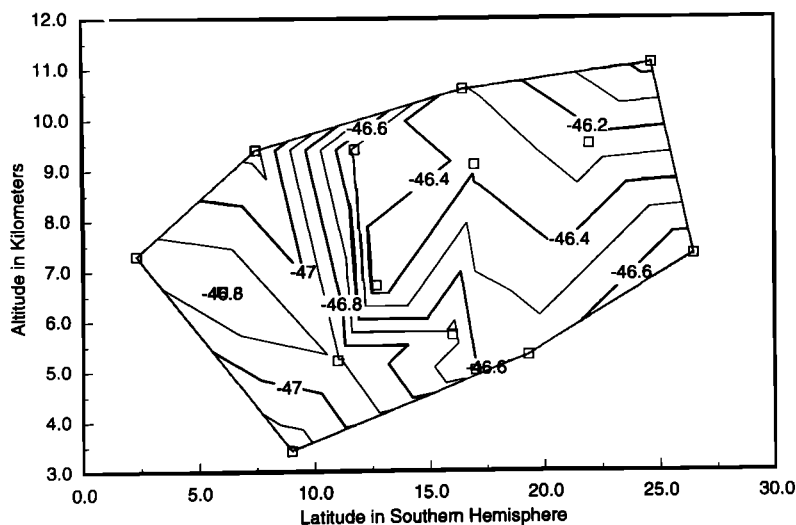


Figure 5b. Three-parameter plot showing lines of equal $\delta^{13}\text{C-CH}_4$ generated as a function of median altitude and median latitude using data from PEM-Tropics A air samples (contour lines generated using DeltaGraph, Macintosh version 2.02, DeltaPoint, Inc., Monterey, California).

correspond to the reference numbers in Table 1. In Figure 5b a three-parameter plot shows lines of equal $\delta^{13}\text{C-CH}_4$ generated as a function of median altitude and median latitude (DeltaGraph, Macintosh version 2.02, DeltaPoint, Inc., Monterey, California).

Several features of the data stand out in Figure 5b. For example, values of $\delta^{13}\text{C-CH}_4$ were generally heavier in ^{13}C as altitude increased and as latitude increased (toward the South Pole). An exception to this occurred at $\sim 2^\circ\text{S}$ where the $\delta^{13}\text{C-CH}_4$ value at ~ 9.5 km was as isotopically light as near-surface values. At ~ 11 km, $\delta^{13}\text{C-CH}_4$ was -46.0 and -46.3‰ for two data points, $\sim 1.3\text{‰}$ greater than surface level values measured in the Northern Hemisphere (NH) at both Niwot Ridge (-47.4‰) and Montaña de Oro (-47.6‰). The value of $\delta^{13}\text{C-CH}_4$ at Baring Head, New Zealand, during fall of 1996 (intercalibrated with our own measurements as mentioned earlier) was $\sim -47.2\text{‰}$ [Lowe *et al.*, 1997], making it $\sim 1\text{‰}$ less than the 11 km values we report for the Southern Hemisphere (SH) tropics. One can infer from this that enrichment in $\delta^{13}\text{C-CH}_4$ at 11 km compared to surface values in the SH tropics will also be at least 1‰ since the hemispherically averaged NH/SH gradient in $\delta^{13}\text{C-CH}_4$ and the change in $\delta^{13}\text{C-CH}_4$ across the equator at the surface are well known from both measurement [e.g., Quay *et al.*, 1991; Manning *et al.*, 1998] and modeling [Gupta *et al.*, 1996] studies to lie within a few tenths of a per mil of the NH and SH averages for $\delta^{13}\text{C-CH}_4$ at any given season.

Our PEM-Tropics A data can be compared to other CH_4 data sets reported from aircraft samples. For example, Lowe *et al.* [1991] measured aircraft samples at altitudes of ~ 5.0 – ~ 9.0 km at latitudes ranging from 47.6° to 88.4°S in 1989 and 1990. These were compared to surface measurements at Scott Base Antarctica (77.7°S) and the South Pole. The data indicated no significant correlation between increasing altitude and either CH_4 concentration or $\delta^{13}\text{C-CH}_4$. Lowe *et al.* noted that disregarding small seasonal effects, the Southern Hemisphere atmosphere from temperate to polar latitudes was quite uniform in $\delta^{13}\text{C}$ of CH_4 , a finding that paralleled CH_4 mixing ratio data reported by Steele *et al.* [1987]. However, with the data in their Table 3 we calculate that increasing $\delta^{13}\text{C-CH}_4$ and decreasing CH_4 mixing ratio were correlated ($r^2=0.51$).

Brenninkmeijer *et al.* [1995] measured $\delta^{13}\text{C}$ of CH_4 from eight samples of air taken by aircraft between 10 and 12 km in the Southern Hemisphere in June 1993. All samples were collected between 43° and 85°S latitude and were judged to be of stratospheric air on the basis of companion data of potential vorticity. However, a range of $\delta^{13}\text{C-CH}_4$ values was reported that was attributed at least partially to differing degrees of mixing between stratospheric and tropospheric air among the individual samples. Within the relatively narrow range of altitudes sampled, CH_4 mixing ratios ranged from ~ 1.69 to ~ 1.62 ppmv. Measured $\delta^{13}\text{C-CH}_4$ values showed a linear relationship with CH_4 mixing ratio (with one outlier) such that the heaviest measured air sampled at altitude (with $\delta^{13}\text{C-CH}_4$ value $\sim -46.8\text{‰}$) was 0.6‰ heavier than surface air sampled at Baring Head, New Zealand (41°S), at the same time.

Gupta *et al.* [1996] reported on samples taken during the AASE-II program during January and February of 1992. In that data set, six air samples from 11.3 to 12.6 km altitude (latitudinal range of 8°S to 73°N) were measured to have an average $\delta^{13}\text{C-CH}_4$ value of $-46.44 \pm 0.21\text{‰}$, almost 1‰ heavier than Northern Hemispheric air from Niwot Ridge sampled at the same time. Similar to findings by Brenninkmeijer *et al.* [1995], enriched $\delta^{13}\text{C-CH}_4$ values were strongly correlated with low CH_4 mixing ratios ($r^2 = 0.74$) even within the narrow range of altitudes sampled (S. Tyler, unpublished data, 1995).

In our PEM-Tropics A samples, increasing $\delta^{13}\text{C}$ of CH_4 and increasing altitude were correlated ($r^2 = 0.39$) as were increasing $\delta^{13}\text{C}$ of CH_4 and decreasing mixing ratio ($r^2 = 0.40$). However, a plot of CH_4 mixing ratio versus altitude (figure not shown) indicated only a very weak correlation ($r^2 = 0.08$). If data from two PEM-Tropics A samples are removed from the analysis, measured at $\sim 2.3^\circ\text{S}$ with ~ 7.3 km altitude (point 10) and at $\sim 7.5^\circ\text{S}$ with ~ 9.4 km altitude (point 13), the correlation of $\delta^{13}\text{C-CH}_4$ with altitude improves from $r^2 = 0.39$ to $r^2 = 0.72$, although the correlation of mixing ratio versus altitude barely improves.

Of course, justification for filtering out specific samples depends on a detailed analysis of the upper air data presented here. In earlier Global Tropospheric Experiment Pacific Exploratory Missions (PEM-West A and PEM-West B) both

stratospheric subsidence and convection were frequently in evidence [Newell *et al.*, 1996; Wu *et al.*, 1997]. Even so, the troposphere was found to have a layered structure [e.g., Newell *et al.*, 1996] under certain conditions with some of the layering arising from the very events (e.g., convection) known to provide fast mixing. For that reason we implemented criteria to filter out stratospheric subsidence and convective events on the basis of other trace gases present in the samples.

We looked for corroborating evidence for convective plumes and stratospheric subsidence in air samples from Table 1 using companion measurements of O₃, CO, H₂O vapor, C₂H₆, C₃H₈, and C₂Cl₄ made at the time of sampling (NASA PEM-Tropics A, archived data, 1997). We assumed that instances of high O₃ with accompanying low CO, H₂O vapor, and CH₄ mixing ratios at a given altitude were an indication of stratospheric subsidence, while instances of high O₃ with elevated mixing ratios of CH₄, CO, C₂H₆, C₃H₈, and C₂Cl₄ (present in urban plumes but not in biomass burning plumes) at a given altitude were an indication of convective events. Low O₃ and surface level mixing ratios of CH₄, CO, C₂H₆, C₃H₈, and C₂Cl₄ were assumed to arise from convective events without accompanying biomass burning or urban air plumes. The degree of change in these values from that expected at altitude provides a measure of the strength of the influence of that event on the air sample. On each flight for which we had samples we plotted the observed concentrations for these compounds versus time for the entire flight track as well as for the portion of the track from which our samples were collected (data not shown).

Using the chemical data described above, we determined that several air parcels providing data points in Table 1 were indicative of some degree of transport from another region. As identified by reference number in Table 1, stratospheric subsidence had affected points 1 (strongly) and 11 (weakly), while convection from the surface had affected points 6, 7, 9, and 14 (all weakly, from urban plume), points 8 and 10 (moderately, from biomass burning), and point 13 (weakly, from a clean convective event). Although these determinations are qualitative, they aid in interpreting Table 1 and Figure 5b. For instance, the greatest value of $\delta^{13}\text{C-CH}_4$ was observed not only at the highest altitude but also during stratospheric subsidence (point 1). Some of the lowest values of $\delta^{13}\text{C-CH}_4$ were observed at a relatively midrange altitude (point 7) or high altitude (point 13) because of convection. Convection appeared to affect two samples differently that had been collected close together both spatially and temporally. There is no obvious explanation why the two samples (points 13 and 14) had such different $\delta^{13}\text{C-CH}_4$ values from each other.

We must stress that in comparing the levels of mixing ratio for various compounds to that expected for air unaffected by fast mixing events the use of terms such as strongly, moderately, and weakly is subjective. In no case were CH₄ mixing ratios in our PEM-Tropics A samples elevated appreciably above levels for background southern tropical tropospheric air at the surface. This result belies the likelihood that surface sources of CH₄ from other regions appreciably influenced the $\delta^{13}\text{C-CH}_4$ values of our PEM-Tropics A samples. In our judgement, except for point 1, for which O₃ data provided strong evidence of stratospheric subsidence, a majority of the points in Figure 5b represent CH₄ in air largely unaffected by fast mixing of air from other regions. Thus our PEM-Tropics A air samples measured for ¹³C-CH₄ content provide evidence that a pattern of $\delta^{13}\text{C-CH}_4$ values exists in the southern tropical troposphere that follows a trend toward isotopically heavier CH₄ with increasing latitude and altitude.

5. Modeling Results and Discussion

New measurement data reported here for the years 1995-1998 corroborate the basic features of the observational data discussed by Gupta *et al.* [1996], i.e., that there is a large $\delta^{13}\text{C-CH}_4$ difference (~1‰) between surface and near-tropopause values and an even larger difference between surface and aged air in the stratosphere. They also extend the observational evidence because of the direct comparison of intercalibrated surface and upper air samples measured by our laboratory and NIWA and because they indicate that a gradient in $\delta^{13}\text{C}$ of CH₄ at Southern hemispheric low-latitude tropospheric altitudes exists as well. Previous model-calculated $\delta^{13}\text{C-CH}_4$ values have shown poor agreement with observations in determining the difference between surface and higher-altitude air [Bergamaschi *et al.*, 1996; Gupta *et al.*, 1996, 1997]. In this section we use the latest determinations of carbon KIEs and available observational data, including the most recently reported, to see if a better fit between observations and calculations is now possible and to determine what the causes for any remaining discrepancy might be.

5.1. Kinetic Isotope Effects on Atmospheric Methane

Qualitatively, the difference in $\delta^{13}\text{C}$ of CH₄ found in comparing surface to higher-altitude air is largely because CH₄, which has only surface sources, is increasingly exposed to chemical sink processes as it ages. Some of these sinks isotopically fractionate CH₄ carbon because of kinetic isotope effects during chemical oxidation. The KIE of O(¹D) is very small (i.e., ~1.001 [Davidson *et al.*, 1987]), while the KIE from bacterial consumption of CH₄ in soils is reasonably well known (e.g., ~1.022 at 296 K [King *et al.*, 1989; Tyler *et al.*, 1994b]) and takes place only at the surface of the earth. The most influential effects come from CH₄ reactions with OH (the largest sink process) and Cl (the sink with the largest carbon KIE).

Gupta *et al.* [1996] explored the effect of all four CH₄ loss processes and their KIEs while attempting to reconcile the large difference in $\delta^{13}\text{C}$ of CH₄ between observed surface and upper tropospheric values reported through 1992. They used experimentally determined KIEs of $K_{12}/K_{13} = 1.0054$ at 300 K with no temperature dependence from 273 to 350 K for the OH sink [Cantrell *et al.*, 1990] and $K_{12}/K_{13} = 1.043 \cdot \exp(6.455/T)$ for the Cl sink [Saueressig *et al.*, 1995]. The Cl sink KIE expression indicates an enormous effect of $K_{12}/K_{13} = 1.066$ at 297 K relative to the effect from OH. Use of these KIEs yielded poor agreement between observed and calculated atmospheric CH₄ values above the surface when a reasonable CH₄ source function was used to match observed and calculated surface values in each hemisphere. Agreement became worse when a theoretical calculation leading to $K_{12}/K_{13} = 1.026$ [Tanaka *et al.*, 1996] was substituted for the Cl sink KIE.

Since the initial experimental determination by Saueressig *et al.* [1995] several more determinations of the Cl sink KIE have been made, including both theoretical calculations and experimental measurements. Some of those studies reported much lower Cl sink KIE values than that of Saueressig *et al.* [1995], but no two of them were in reasonable agreement. Gupta *et al.* [1997] used quite different theoretically calculated KIEs for CH₄ reactions with OH and Cl from those of Cantrell *et al.* [1990] and Saueressig *et al.* [1995] to model data reported through 1992 again. However, the most recent theoretically calculated value of $K_{12}/K_{13} = 1.06$ at 297 K [Roberto-Neto *et al.*, 1998] and experimentally determined value of $K_{12}/K_{13} = 1.0621$

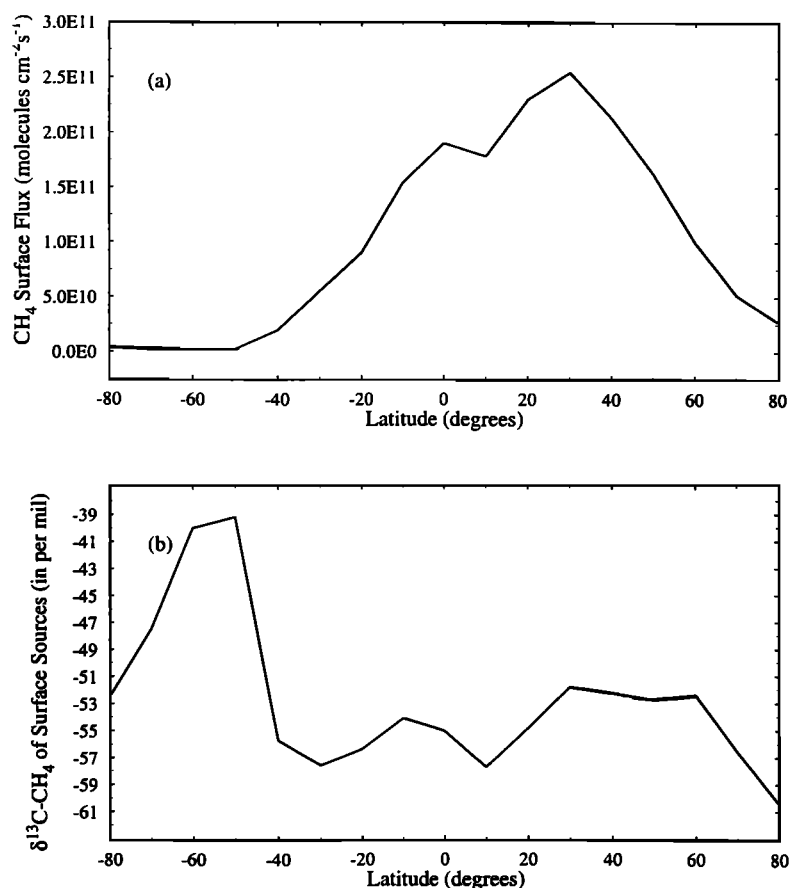


Figure 6. Latitudinal distributions of (a) surface CH₄ flux and (b) corresponding δ¹³C-CH₄ values used as input in model calculations.

at 299 K [Tyler *et al.*, 1998] corroborate data of Saueressig *et al.* [1995] and indicate convergence toward consensus values for the Cl sink KIE.

Reaching a consensus for each KIE is very important because any proposed significant change in the KIEs of the sink processes alters the isotopic balance of the summed CH₄ sources and estimates of the various strengths and distributions of CH₄ sources to the atmosphere. Changes in the two most important KIEs also alter the calculated vertical profile of δ¹³C of CH₄ significantly. Gupta *et al.* [1996] show that although Cl radicals are more concentrated in the stratosphere, some effect on CH₄ from reaction with Cl will be observed at lower altitudes because of vertical mixing between higher and lower altitudes. Although the OH reaction dominates CH₄ loss at all altitudes, beginning at ~16 km, Cl abundance is great enough that direct reactions with CH₄ cause some of the ¹³C enrichment in CH₄. The effect of Cl on δ¹³C-CH₄ may be quite disproportionate relative to its abundance compared to OH at all altitudes depending on the KIEs of the two reactions in question.

5.2. Description of the Model and Basic Inputs

All models calculations were made using a modified version of the Oslo 2-D global tropospheric model of Isaksen and Rohde [1978]. Because our 2-D model has been described in detail previously by Gupta [1996] and Gupta *et al.* [1998], only a broad description is provided here. The model has a horizontal resolution of 10° and extends from the surface to 24.5 km with a

vertical resolution of 0.5 km. Transport coefficients (advective and diffusive) are derived from the Geophysical Fluid Dynamics Laboratory general circulation model [Plumb and Mahlman, 1987]. A reasonably complete gas-phase photochemical scheme containing only CH₄ as a parent hydrocarbon with parameterized tropospheric heterogeneous losses is included. All species including CH₄ and its isotopic species are calculated with the time-dependent photochemical scheme up to 16.5 km. Above 16.5 km, hydroxyl and chlorine radical concentrations are prescribed on a monthly basis, and their values are adopted from the Oslo 2-D tropospheric-stratospheric global model. This model includes simplified polar stratospheric cloud and sulfur chemistry (I. Isaksen, University of Oslo, Norway, personnel communication, 1995).

Only slight changes were made to the annual surface CH₄ source used to initialize the model by Gupta *et al.* [1996]. Magnitudes of the individual sources and their corresponding averaged δ¹³C-CH₄ values were modified slightly to reflect recent information about sources and their distributions and to provide global and hemispheric averages in CH₄ mixing ratio and δ¹³C that approximate 1995 data. Equal portions of the total annual source of 535 Tg (Tg = 10¹² grams) were applied uniformly throughout the year on a daily basis using the distributions for magnitude and δ¹³C-CH₄ shown in Figure 6. The adopted source magnitude and δ¹³C-CH₄ data appear in Table 2.

It is important to realize that any reasonable set of source magnitudes and distributions will be sufficient to study mixing

Table 2. Estimated Annual Global Emission Strengths and Corresponding $\delta^{13}\text{C}$ Values for Various Categories of CH_4 Sources Used in the Model Calculations

Source	Emission Strength, Tg yr^{-1}	$\delta^{13}\text{C}$, ‰
Lake	74	-59*
Swamps	95	-56*
Tundra	5	-65
Rice paddies	60	-61
Animals	90	-63
Landfills	45	-52
Gas venting and leakage	55	-38
Oceans	6	-40
Coal minings	30	-37
Biomass burning	45	-25
Termites	30	-57

The average $\delta^{13}\text{C}$ of these sources is -52.25‰. Values appearing are adapted from source budgets by Cicerone and Oremland [1988], Fung *et al.* [1991], and Tyler [1991].

*Between 60°N and 90°N, $\delta^{13}\text{C}$ values were decreased to -65‰.

and isotope ratios of CH_4 both vertically and latitudinally as shown by Gupta *et al.* [1996]. It is not necessary to use a source function that provides an exact match to observed values for these ratios at the few locations reported on globally in order to do a study of the vertical gradient of CH_4 . In fact, the source function chosen to approximate observed values at the surface will depend heavily on the choices of magnitudes of the various loss processes and their associated KIEs, which are also subject to uncertainty.

Values of CH_4 mixing ratio and $\delta^{13}\text{C}\text{-CH}_4$ were calculated by running the model until it obtained steady state with respect to $^{13}\text{CH}_4$. Steady state was defined as the condition under which for all 12 months of the year and for all model grid points, $^{13}\text{CH}_4$ mixing ratios were within $\pm 0.01\%$ of their values for the previous year. Once steady state was obtained we examined the CH_4 mixing and carbon isotope ratios calculated at appropriate grid points, months, and altitudes and compared them to observational data.

5.3. Model Results and a Comparison to Observations

The experimentally determined KIEs of Cantrell *et al.* [1990] and Saueressig *et al.* [1995] along with the source strengths and carbon isotope ratios in Table 2 provided global and hemispheric surface values in CH_4 mixing ratio and $\delta^{13}\text{C}$ of CH_4 reasonably close to September 1996 measurement data fit to curves at Niwot Ridge, Colorado (1.79 ppm, -47.30‰), Montaña del Oro, California (1.81 ppm, -47.40‰), and Baring Head, New Zealand (1.72 ppm, -47.2‰) [Lowe *et al.*, 1997]. The model-calculated mixing ratios and $\delta^{13}\text{C}\text{-CH}_4$ values for September were 1.79 ppm and -47.86‰ at 40°N, 1.79 ppm and -47.87‰ at 35°N (interpolated from values at 40° and 30°N), and 1.69 ppm and -47.72‰ at 40°S. Other calculated values for $\delta^{13}\text{C}\text{-CH}_4$ in the Southern Hemisphere included -47.91‰ (0°S), -47.84‰ (10°S), -47.79‰ (20°S), and -47.76‰ (30°S), indicating agreement within a few tenths of a per mil for calculated and measured surface values at all latitudes based on observed latitudinal gradients reported by others [e.g., Quay *et al.*, 1991; Lowe *et al.*, 1994]. Therefore the source function chosen to initialize the model was appropriate for our study of the vertical gradient in $\delta^{13}\text{C}\text{-CH}_4$. We then compared the calculated Southern Hemispheric surface values to corresponding values at higher

altitudes in the range 0 to 30°S to see how well the model results agreed with experimental data.

Figure 7 plots the calculated monthly averaged latitudinal variations in the relative enrichment of $\delta^{13}\text{C}\text{-CH}_4$ in going from the surface to a given altitude. For instance, Figure 7b results show an increase in $\delta^{13}\text{C}\text{-CH}_4$ of 0.11‰ (0°S), 0.05‰ (10°S), 0.02‰ (20°S), and 0.00‰ (30°S) at 10.25 km altitude for September. These $^{13}\text{CH}_4$ enrichments are much smaller than the observed enrichments ($\sim 1.3\%$) found by comparing our NH surface data to PEM-Tropics A data between 2° and 27°S and ~ 11 km altitude. The calculated $\delta^{13}\text{C}\text{-CH}_4$ values are also $\sim 1\%$ greater than SH surface values calculated from our model. Furthermore, the calculated enrichments at 3.25 km (Figure 7a) were nearly identical to those at 10.25 km for the same months and latitudes. For any given month of the year, differences of as much as 1‰ or more between surface and upper atmospheric values were not calculated to have occurred until ~ 18.25 km altitude and then only at higher latitudes (see Figure 7c). The region between 2° and 27°S latitude continued to show only a small relative $^{13}\text{CH}_4$ enrichment for all months of the order of those at lower altitudes in the same latitude range, i.e., an increase in $\delta^{13}\text{C}\text{-CH}_4$ of 0.23‰ (0°S), 0.15‰ (10°S), 0.10‰ (20°S), and 0.08‰ (30°S) at 18.25 km altitude for September. Overall, the relationship between surface and higher-altitude $\delta^{13}\text{C}\text{-CH}_4$ data shown here is similar to that reported by Gupta *et al.* [1996], where only a small vertical gradient in $\delta^{13}\text{C}\text{-CH}_4$ values was calculated to exist up to 24 km in spite of measurement evidence to the contrary.

Differences found in comparing model-calculated CH_4 mixing ratios throughout the troposphere to the surface were very small. For example, at an altitude of 3.25 km in September, no changes toward lower mixing ratios were calculated to have occurred over the southern high latitudes (i.e., 0.00 ppm below 40°S); only very small changes toward lower mixing ratio were calculated for the tropics (-0.01 ppm between $\sim 30^\circ$ and 20°S, -0.02 ppm between $\sim 10^\circ$ S and 10°N, and -0.02 ppm from 10° to 20°N) and from -0.02 to -0.04 ppm at higher northern latitudes. At 10.25 km in September, changes of -0.02 ppm at southern high latitudes and changes in the tropics very similar to those found in going from the surface to 3.25 km (0.00 to -0.02 ppm between $\sim 30^\circ$ S and 10°N) were found. The northern high latitudes, however, showed a larger decrease in mixing ratio with increasing altitude (~ -0.05 to ~ -0.06 ppmv between 20° and 80°N) such that the difference between 10.25 km and the surface was larger than that between 3.25 km and the surface.

The relative change in mixing ratio calculated for Southern Hemispheric latitudes is reasonably close to data reported here and by Lowe *et al.* [1991]; neither set of measurement data shows appreciable change in mixing ratio with altitude up to ~ 10 km. Measurements reported by Brenninkmeijer *et al.* [1995], Gupta *et al.* [1996], and our data for point 1 from air samples taken in the tropopause or lower stratosphere (i.e., $\sim 11\text{--}13$ km), however, showed that mixing ratios can be decreased from surface values by appreciable amounts (~ 0.05 to ~ 0.10 ppm). Our model calculates appreciable September changes in mixing ratio at high latitudes and 18.25 km with respect to the surface of -0.07 ppm (between 60° and 80°S) and -0.16 to -0.25 ppm (between 60° and 80°N). Changes are smaller at lower latitudes even at 18.25 km (i.e., ~ -0.01 ppm between 40° and 10°S, ca. -0.03 to -0.06 ppm between 10°S and 30°N, and -0.08 to -0.12 ppm between 30° and 50°N). The agreement in CH_4 mixing ratio between our model-calculated values and observed values reported in several studies

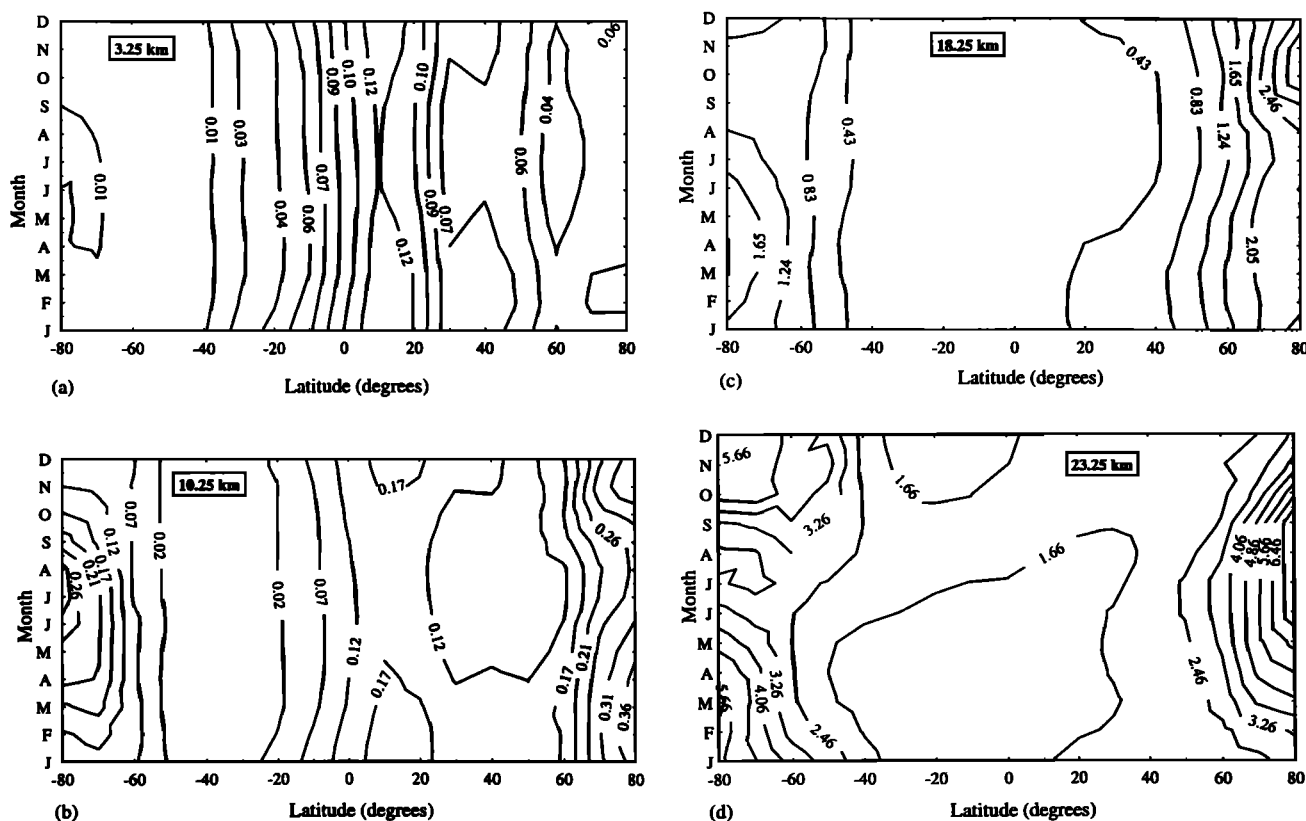


Figure 7. Calculated monthly latitudinal variations in the relative enrichment of $\delta^{13}\text{C-CH}_4$ in going from the surface to altitude (a) 3.25, (b) 10.25, (c) 18.25, and (d) 23.25 km.

at altitudes in our model domain is therefore much better than it is for $\delta^{13}\text{C}$ of CH_4 values.

Another effort was made to obtain agreement between model-calculated and observed values of $\delta^{13}\text{C}$ of CH_4 as a function of altitude. Using the same KIEs for Cl and OH as before, two model runs were made with a modified Cl field to increase the effect of the relatively large KIE in its reaction with CH_4 . All model runs described previously had between 7×10^3 and 4×10^4 molecules cm^{-3} between 16.5 and 24.5 km with no Cl lower than 16.5 km. In the first model run with a modified Cl field we increased the Cl concentration between 10 and 16 km altitude from 0 to 7×10^3 molecules cm^{-3} . This had virtually no effect on the relative difference between $\delta^{13}\text{C-CH}_4$ at the surface and at either 10.25 or 18.25 km. For instance, for September, increases of $\delta^{13}\text{C-CH}_4$ in comparison to surface values were 0.11‰ (0°S), 0.05‰ (10°S), 0.02‰ (20°S), and 0.00‰ (30°S) at 10.25 km altitude and were 0.23‰ (0°S), 0.15‰ (10°S), 0.10‰ (20°S), and 0.08‰ (30°S) at 18.25 km altitude.

In the second model run with a modified Cl field we reverted to the usual model condition where no Cl was present below 16.5 km, but we increased Cl between 16.5 and 24.5 km by a factor of 5. This had the effect of barely changing the increase in $\delta^{13}\text{C-CH}_4$ values in going from surface to 10.25 km but nearly tripling the increase in going from surface to 18.25 km when compared to the results obtained using the original set of parameters described (Figure 7). For comparison, for September, increases of $\delta^{13}\text{C-CH}_4$ in comparison to surface values were 0.18‰ (0°S), 0.09‰ (10°S), 0.01‰ (20°S), and 0.00‰ (30°S) at 10.25 km altitude and were 0.62‰ (0°S), 0.48‰ (10°S), 0.39‰ (20°S), and 0.35‰

(30°S) at 18.25 km altitude. For any given month of the year, differences of as much as 1‰ or more between surface and upper atmospheric values were not calculated to have occurred until 10.25 km and then only at 80°N during winter and spring (between November and May).

Using the theoretically calculated KIEs of Gupta *et al.* [1997] with the 1994–1997 data also resulted in poor agreement with observed vertical changes in $\delta^{13}\text{C-CH}_4$. As an example, for September, increases of $\delta^{13}\text{C-CH}_4$ at 10.25 km in comparison to surface values were 0.18‰ (0°S), 0.12‰ (10°S), 0.06‰ (20°S), and 0.03‰ (30°S). These are nearly identical to the very slight increases calculated before and shown in Figure 7b. By comparing calculations using the two sets of KIEs an interesting result was discovered. The effect of using the theoretically calculated KIEs of Gupta *et al.* [1997] was to change absolute $\delta^{13}\text{C-CH}_4$ values roughly equally at the surface and at higher altitudes without much change in the relationship between isotopic CH_4 at various altitudes. The lessening of the KIE effect of Cl by ~32‰ (which matters mostly above 16 km but affects the total column CH_4 to some extent) is approximately balanced by the increase of the KIE effect of OH by ~5‰ (which is the most important loss process at all altitudes).

5.4. Model Results Compared to Another Model

Bergamaschi *et al.* [1996] have made similar calculations regarding the implications of the relatively large carbon KIE in the reaction of CH_4 with Cl. They used a 2-D photochemical model that calculates OH and Cl interactively and extends from

the surface to 60 km altitude with a vertical resolution of ~2 km. Methane mixing ratio was distributed with a north/south hemispheric gradient and a fixed $\delta^{13}\text{C}\text{-CH}_4$ surface value of -47.0‰ for all latitudes and months. Their calculations were made with the measured KIEs from laboratory experiments, i.e., the same ones *Gupta et al.* [1996] used in their calculations.

Bergamaschi et al.'s [1996] vertical profiles of $\delta^{13}\text{C}\text{-CH}_4$ calculated for June 1993 at all latitudes showed that the relative enrichments in $\delta^{13}\text{C}\text{-CH}_4$ in going from the surface to higher altitudes were very similar to those calculated using our 2-D model for altitudes up to 24 km. For example, *Bergamaschi et al.* [1996, Figure 1] indicated that at 10°S, values for $\delta^{13}\text{C}\text{-CH}_4$ should be ~-46.95‰ (3 km), ~-46.85‰ (10 km), ~-46.65‰ (18 km), and ~-46.2‰ (24 km) as judged by interpolating between contour lines of equal $\delta^{13}\text{C}\text{-CH}_4$ value. Similarly, at 40°N the values were ~-46.95‰ (3 km), ~-46.8‰ (10 km), ~-46.55‰ (18 km), and ~-45.6‰ (24 km). These values amount to calculated enrichments of ~0.1‰, 0.2‰, 0.4‰, and 1.1‰ (based on an average of values at both 10°S and 40°N) for 3, 10, 18, and 24 km, respectively. The agreement between the two models is a good indication that our upper boundary condition for CH_4 and our Cl distribution throughout our model domain are reasonable.

5.5. Model Results Compared to Midstratospheric Data

Comparisons between observed and calculated data $\delta^{13}\text{C}\text{-CH}_4$ values obtained either from our model or that of *Bergamaschi et al.* [1996] can be made for $\delta^{13}\text{C}\text{-CH}_4$ values at altitudes higher than aircraft data sets provide. These rely on measurement data by *Sugawara et al.* [1997], which provide information on $^{13}\text{CH}_4$ enrichment above surface level values at midstratospheric altitudes. *Sugawara et al.* sampled air over northern Japan (~38.5°-40°N) in the summer of 1994. The value of $\delta^{13}\text{C}\text{-CH}_4$ was -47.0‰ just above the tropopause (~16 km) and increased to ~-39‰ at 34.7 km. Although the data are not intercalibrated with our own, the average tropospheric value at this time was roughly -47.5‰ according to *Sugawara et al.* [1997], a value in good agreement with our own value for surface CH_4 irrespective of spatial and temporal variability. At 24 km, *Sugawara et al.* [1997] measured a $\delta^{13}\text{C}\text{-CH}_4$ value of ~-42.7‰. This means that comparisons between model-calculated enrichments with altitude and observed enrichments with altitude, already discrepant in the tropopause, worsen with increased altitude. At 24 km the discrepancy is several per mil as compared to ~1‰ at 10 km (see Figure 7d).

5.6. Further Discussion of PEM-Tropics A Samples and Vertical Gradients

In general, we expect the lower troposphere to be wellmixed vertically because of convective events and air mass subsidence as well as diffusion. *Ehhalt* [1974] first showed that vertical profiles of CH_4 mixing ratio were uniform from monthly samples taken both 200 km offshore from Santa Barbara in the Pacific Ocean and over Scottsbluff, Nebraska, in 1965-1967. Nevertheless, the influence of subsidence and convection events on air samples measured to determine CH_4 mixing and $\delta^{13}\text{C}$ value depends on how much time has elapsed and how far away the event is from the air parcel sampled. The underlying chemical composition in the absence of such events may still provide a structure for the $\delta^{13}\text{C}\text{-CH}_4$ gradient that is measureable in the troposphere.

Our PEM-Tropics A air samples measured for $^{13}\text{CH}_4$ content provided evidence that a pattern of $\delta^{13}\text{C}\text{-CH}_4$ values exists in the

tropical troposphere that follows a discernable trend both vertically and latitudinally. Although the vertical trend was not seen by *Lowe et al.* [1991] in samples taken at and near the South Pole, both the PEM-Tropics A data and South Pole data show a moderate correlation between $\delta^{13}\text{C}\text{-CH}_4$ and mixing ratio at all altitudes. Therefore both data sets are consistent with the well-known phenomenon of isotopically enriched CH_4 from chemical loss processes. Only the degree to which both CH_4 ratio and $\delta^{13}\text{C}\text{-CH}_4$ are affected by loss at different altitudes is different in the two regions studied.

One plausible explanation why there might exist a tropospheric gradient in $\delta^{13}\text{C}\text{-CH}_4$ when no appreciable one exists for the CH_4 mixing ratio comes from the great difference in the KIEs of CH_4 reaction with OH and Cl. It may be that $\delta^{13}\text{C}\text{-CH}_4$ values in the troposphere are more sensitive to changes in chemical loss processes than CH_4 mixing ratio values are because of the indirect effect of stratospheric Cl on tropospheric air. Stratospheric-tropospheric air exchange can bring aged CH_4 into the troposphere from above with a ^{13}C content relatively more affected than its mixing ratio by the Cl chemical loss process in the stratosphere. In effect, stratospheric Cl, with its very large carbon KIE compared to OH, has an increasingly important and more easily detectable effect on tropospheric $\delta^{13}\text{C}\text{-CH}_4$ values as altitude increases or as all forms of chemical loss take place in the troposphere since it affects the troposphere only indirectly through exchange of stratospheric and tropospheric air. However, a corresponding situation for the vertical gradient of tropospheric mixing ratios of CH_4 does not exist because the effect of stratospheric Cl on tropospheric mixing ratios is too small to be detected in comparison to the effect from tropospheric OH.

6. Conclusions

Air samples from surface sites at Niwot Ridge, Colorado and Montaña de Oro, California, showed a seasonality in $\delta^{13}\text{C}\text{-CH}_4$ values, although only the Montaña de Oro site showed a seasonality in CH_4 mixing ratio data. These features are characteristic of CH_4 seasonality reported at other sites worldwide and probably are driven significantly by seasonality in the OH sink.

Two of the most important features of the data at Niwot Ridge and Montaña de Oro are (1) that each of their average $\delta^{13}\text{C}\text{-CH}_4$ values over the time period of measurements had a relatively small peak-to-peak range (~0.5‰ at Niwot Ridge and ~0.8‰ at Montaña de Oro) and (2) that the average values for all measurements at each site had small standard deviations around a mean of roughly -47.3‰. These features establish a surface level value for $\delta^{13}\text{C}\text{-CH}_4$ in marked contrast to data from upper air samples at ~11 km altitude taken in the SH during PEM-Tropics A. PEM-Tropics A data revealed that $\delta^{13}\text{C}\text{-CH}_4$ values at or near 11 km were ~1.3‰ enriched in comparison to our NH surface measurements taken at the same time and ~1.1‰ enriched in $\delta^{13}\text{C}\text{-CH}_4$ in comparison to SH surface values both from observations reported by others and from our model calculations. The enrichments are much larger than can be explained by our 2-D photochemical model whether using measured or theoretically calculated KIEs for the reactions of CH_4 with OH and Cl.

Measurements of $\delta^{13}\text{C}\text{-CH}_4$ in air collected from PEM-Tropics A revealed a trend in $\delta^{13}\text{C}\text{-CH}_4$ both vertically and latitudinally in the free tropical troposphere that is discernible in spite of any stratospheric subsidence and fast transport effects such as convective events. Such a vertical trend is theoretically possible on the basis of the larger KIE associated with CH_4 loss

through reaction with Cl than through reaction with OH and on the fact that unlike CH₄ loss from reaction with OH, which occurs at all altitudes and accounts for almost all CH₄ loss, direct loss of CH₄ by reaction with Cl occurs only in the stratosphere. Hence the long-term effect of the slow exchange between stratospheric air and tropospheric air may be to bring highly ¹³C enriched CH₄ in stratospheric air to lower altitudes in a layered pattern in spite of stratospheric subsidence and convection.

Currently, no multidimensional photochemical model calculates values for δ¹³C-CH₄ in reasonable agreement with observations at any altitude appreciably above the surface, even with CH₄ source functions that provide good isotopic agreement at the surface. This is true even though the models can be made to provide excellent to very good agreement between calculated and observed mixing ratios at all altitudes. The model and parameters we have used here, which match calculated and observed data well at the surface, badly undercalculate the enrichment of isotopic CH₄ with altitude well into the stratosphere. Our model does not provide a verification for the δ¹³C-CH₄ gradient with altitude observed in the tropical free troposphere from PEM-Tropics A samples.

It will be very important to obtain more isotopic data from both air samples collected at fixed surface sites and aircraft samples. Continued measurements at surface sites will provide information on long-term trends and seasonal changes in atmospheric CH₄ that can be related to its sources and sink processes. More upper air samples (such as those obtained by aircraft and balloon-borne cryogenic samplers) will help resolve current problems in establishing the proper magnitudes of KIEs for various CH₄ sink processes and reconcile measurements and model calculations involving δ¹³C-CH₄ and mixing ratios. Isotopic measurements of CH₄ made by each research group must be intercalibrated with others to fully make use of all available data.

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References

- Barry, R. B., A climatological transect on the east slope of the front range, Colorado, *Arct. Alp. Res.*, **5**, 89-110, 1973.
- Bergamaschi, P., C. Brühl, C. A. M. Brenninkmeijer, G. Saueressig, J. N. Crowley, J. U. Grob, H. Fischer, and P. J. Crutzen, Implications of the large carbon kinetic isotope effect in the reaction CH₄ + Cl for the ¹³C/¹²C ratio of stratospheric CH₄, *Geophys. Res. Lett.*, **23**, 2227-2230, 1996.
- Blake, D. R., T.-Y. Chen, T. W. Smith, C. J.-L. Wang, O. W. Wingenter, N. J. Blake, F. S. Rowland, and E. W. Mayer, Three-dimensional distribution of nonmethane hydrocarbons and halocarbons over the northwestern Pacific during the 1991 Pacific Exploratory Mission (PEM-West A), *J. Geophys. Res.*, **101**, 1763-1778, 1996.
- Bollinger, M. J., C. J. Hahn, D. D. Parrish, P. C. Murphy, D. L. Albritton, and F. C. Fehsenfeld, NO_x measurements in clean continental air and analysis of the contributing meteorology, *J. Geophys. Res.*, **89**, 9623-9631, 1984.
- Brenninkmeijer, C. A. M., D. C. Lowe, M. R. Manning, R. J. Sparks, and P. F. J. van Velthoven, The ¹³C, ¹⁴C, and ¹⁸O isotopic composition of CO, CH₄, and CO₂ in the higher southern latitudes lower stratosphere, *J. Geophys. Res.*, **100**, 26,163-26,172, 1995.
- California Energy Commission, *Wind Atlas*, contract P500-82-002, Calif. Dep. of Water Resour., Sacramento, April 1985.
- Cantrell, C. A., R. E. Shetter, A. H. McDaniel, J. G. Calvert, J. A. Davidson, D. C. Lowe, S. C. Tyler, R. J. Cicerone, and J. P. Greenberg, Carbon kinetic isotope effect in the oxidation of methane by the hydroxyl radical, *J. Geophys. Res.*, **95**, 22,455-22,462, 1990.
- Cicerone, R. J., and R. S. Oremland, Biogeochemical aspects of atmospheric methane, *Global Biogeochem. Cycles*, **2**, 299-327, 1988.
- Coleman, D. D., J. B. Risatti, and M. Schoell, Fractionation of carbon and hydrogen isotopes by methane-oxidizing bacteria, *Geochim. Cosmochim. Acta*, **45**, 1033-1037, 1981.
- Craig, H., Isotopic standards for carbon and oxygen and correction factors for mass-spectrometric analysis of carbon dioxide, *Geochim. Cosmochim. Acta*, **12**, 133-149, 1957.
- Crutzen, P. J., Role of the tropics in the atmospheric chemistry, in *The Geophysiology of Amazonia*, edited by R.E. Dickinson, pp. 107-130, John Wiley, New York, 1987.
- Davidson, J. A., C. A. Cantrell, S. C. Tyler, R. E. Shetter, R. J. Shetter, and J. G. Calvert, Carbon kinetic isotope effect in the reaction of CH₄ with OH, *J. Geophys. Res.*, **92**, 2195-2199, 1987.
- Dickinson, R. E., and R. J. Cicerone, Future global warming from atmospheric trace gases, *Nature*, **319**, 109-115, 1986.
- Dlugokencky, E. J., L. P. Steele, P. M. Lang, and K.A. Masarie, The growth rate and distribution of atmospheric methane, *J. Geophys. Res.*, **99**, 17,021-17,043, 1994.
- Dlugokencky, E. J., E. G. Dutton, P. C. Novelli, P. P. Tans, K. A. Masarie, K. O. Lantz, and S. Madronich, Changes in CH₄ and CO growth rates after the eruption of Mt. Pinatubo and their link with changes in tropical tropospheric UV flux, *Geophys. Res. Lett.*, **23**, 2761-2764, 1996.
- Ehhalt, D. H., The atmospheric cycle of methane, *Tellus*, **26**, 58-70, 1974.
- Ehhalt, D. H., and U. Schmidt, Sources and sinks of atmospheric methane, *Pure Appl. Geophys.*, **116**, 452-464, 1978.
- Fung, I., J. Jehn, E. Lerner, E. Matthews, M. Prather, L.P. Steele, and P.J. Fraser, Three-dimensional model synthesis of the global methane cycle, *J. Geophys. Res.*, **96**, 13,033-13,065, 1991.
- Gupta, M. L., Modeling the role of selected light nonmethane hydrocarbons on the chemical composition of natural and perturbed troposphere, Ph.D. thesis, Univ. of Calif., Irvine, 1996.
- Gupta, M., S. Tyler, and R. Cicerone, Modeling atmospheric δ¹³C-CH₄ and the causes of recent changes in atmospheric CH₄ amounts, *J. Geophys. Res.*, **101**, 22,923-22,932, 1996.
- Gupta, M. L., M. P. McGrath, R. J. Cicerone, F. S. Rowland, and M. Wolfsberg, ¹²C/¹³C kinetic isotope effects in the reactions of CH₄ with OH and Cl, *Geophys. Res. Lett.*, **24**, 2761-2764, 1997.
- Gupta, M. L., R. J. Cicerone, D. Blake, and F. S. Rowland, Global atmospheric distributions and source strengths of light hydrocarbons and perchloroethylene, *J. Geophys. Res.*, **103**, 28,219-28,235, 1998.
- Haagensohn, P. L., Meteorological and climatological factors affecting Denver air quality, *Atmos. Environ.*, **13**, 79-85, 1979.
- Hahn, C. J., A study of the diurnal behavior of boundary-layer winds at the Boulder Atmospheric Observatory, *Boundary Layer Meteorol.*, **21**, 231-245, 1981.
- Isaksen, I. S. A., and H. Rodhe, A two-dimensional model for the global distribution of gases and aerosol particles in the troposphere, *Rep. AC-47*, Dep. Meteorol., Univ. of Stockholm, Sweden, 1978.
- Johnson, R. H., and J. J. Toth, A climatology of the July 1981 surface flow over northeast Colorado, *Atmos. Sci. Pap.* **342**, Dep. Atmos. Sci., Colo. State Univ., Ft. Collins, 1982.
- Kiehl, J. T., and R. E. Dickinson, A study of the radiative effects of enhanced atmospheric CO₂ and CH₄ on early Earth surface temperatures, *J. Geophys. Res.*, **92**, 2991-2998, 1987.
- King, S.L., P.D. Quay, and J.M. Lansdown, The ¹³C/¹²C kinetic isotopic effect for soil oxidation of methane at ambient atmospheric concentrations, *J. Geophys. Res.*, **94**, 18,273-18,277, 1989.

- Lang P. M., L. P. Steele, and R. C. Martin, Atmospheric methane data for the period 1986-1988 from the NOAA/CMDL global cooperative flask sampling network, in *NOAA Tech. Mem. ERL CMDL-2*, 1990.
- Lasaga, A. C., and G. V. Gibbs, *Ab initio* studies of the kinetic isotope effect of the $\text{CH}_4 + \text{OH}$ atmospheric reaction, *Geophys. Res. Lett.*, **18**, 1217-1220, 1991.
- Lassey, K. R., D. C. Lowe, C. A. M. Brenninkmeijer, and A. J. Gomez, Atmospheric methane and its carbon isotopes in the Southern Hemisphere: Their time series and an instructive model, *Chemosphere*, **26**, 95-109, 1993.
- Levine, J. S., C. P. Rinsland, and G. M. Tenille, The photochemistry of methane and carbon monoxide in the troposphere in 1950 and 1985, *Nature*, **318**, 254-257, 1985.
- Levy, H., II, Normal atmosphere: Large radical and formaldehyde concentrations predicted, *Science*, **173**, 141-143, 1971.
- Lowe, D. C., C. A. M. Brenninkmeijer, S. C. Tyler, and E. J. Dlugokencky, Determination of the isotopic composition of atmospheric methane and its application in the Antarctic, *J. Geophys. Res.*, **96**, 15,455-15,467, 1991.
- Lowe, D. C., C. A. M. Brenninkmeijer, G.W. Brailsford, K.R. Lassey, and A.J. Gomez, 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, 1994.
- Lowe, D. C., M. R. Manning, G. W. Brailsford, and A. M. Bromley, The 1991-1992 atmospheric methane anomaly: Southern Hemispheric ^{13}C decrease and growth rate fluctuations, *Geophys. Res. Lett.*, **24**, 857-860, 1997.
- Manning, M. R., W. Allan, A. J. Gomez, and D. C. Lowe, How well do we know the distribution and variability of methane sources to the atmosphere?, paper presented at Joint International Symposium of Global Atmospheric Chemistry, Comm. Atmos. Chem. and Global Pollut./Int. Global Atmos. Comm., Seattle, Washington, August 22-25, 1998.
- Melissas, V., and D. G. Truhlar, Deuterium and carbon-13 isotope effects for the reaction of OH with CH_4 , *J. Chem. Phys.*, **99**, 3542-3553, 1993.
- Newell, R. E., Z.-X. Wu, Y. Zhu, W. Hu, E. V. Browell, G. L. Gregory, G. W. Sachse, J. E. Collins Jr., K. K. Kelly, and S. C. Liu, Vertical fine-scale atmospheric structure measured from NASA DC-8 during PEM-West A, *J. Geophys. Res.*, **101**, 1943-1960, 1996.
- Novelli, P. C., J. W. Elkins, and L. P. Steele, The development and evaluation of a gravimetric reference scale for measurements of atmospheric carbon monoxide, *J. Geophys. Res.*, **96**, 13,109-13,121, 1991.
- Novelli, P. C., L. P. Steele, and P. P. Tans, Mixing ratios of carbon monoxide in the troposphere, *J. Geophys. Res.*, **97**, 20,731-20,750, 1992.
- Plumb, R. A., and J. M. Mahlman, The zonally averaged transport characteristics of the GFDL general circulation/transport model, *J. Atmos. Sci.*, **44**, 298-327, 1987.
- Quay, P. D., et al., Carbon isotopic composition of atmospheric CH_4 : Fossil and biomass burning source strengths, *Global Biogeochem. Cycles*, **5**, 25-47, 1991.
- Ramanathan, V., R. J. Cicerone, H. B. Singh, and J. T. Kiehl, Trace gas trends and their potential role in climate change, *J. Geophys. Res.*, **90**, 5547-5566, 1985.
- Roberto-Neto, O., E. L. Coitiño, and D. G. Truhlar, Dual-level direct dynamics calculations of deuterium and carbon-13 kinetic isotope effects for the reaction $\text{Cl} + \text{CH}_4$, *J. Phys. Chem. A*, **102**, 4568-4578, 1998.
- Saueressig, G., P. Bergamaschi, J.N. Crowley, H. Fischer, and G.W. Harris, Carbon kinetic isotope effect in the reaction of CH_4 with Cl atoms, *Geophys. Res. Lett.*, **22**, 1225-1228, 1995.
- Seiler, W., A. Holzappel-Pschorn, R. Conrad, and D. Scharffe, Methane emission from rice paddies, *J. Atmos. Chem.*, **1**, 241-268, 1984.
- Sheppard, J. C., H. Westberg, J. F. Hopper, K. Ganesan, and P. Zimmerman, Inventory of global methane sources and their production rates, *J. Geophys. Res.*, **87**, 1305-1312, 1982.
- Shine, K. P., Y. Fouquart, V. Ramaswamy, S. Solomon, and J. Srinivasan, Radiative forcing, Ch. 4, in *Climate Change 1994: Radiative Forcing of Climate Change and an Evaluation of the IPCC IS92 Emission Scenarios*, pp. 163-203, Sci. Assess. Work. Group I of Intergov. Panel on Clim. Change, World Meteorol. Org., Cambridge, Great Britain, 1995.
- Shine, K. P., Y. Fouquart, V. Ramaswamy, S. Solomon, J. Srinivasan, Radiative forcing of climate change, in *Climate Change 1995: The Science of Climate Change*, pp. 108-118, Sci. Assess. Work. Group I of Intergov. Panel on Clim. Change, World Meteorol. Org., Cambridge, Great Britain, 1996.
- Steele, L. P., P. J. Fraser, R. A. Rasmussen, M. A. K. Khalil, T. J. Conway, A. J. Crawford, R. H. Gammon, K. A. Masarie, and K. W. Thoning, The global distribution of methane in the troposphere, *J. Atmos. Chem.*, **5**, 125-171, 1987.
- Stichler, W., Interlaboratory comparison of new materials for carbon and oxygen isotope ratio measurements, in *Reference and Intercomparison Materials for Stable Isotopes of Light Elements, IAEA-TECDOC-825*, pp. 67-74, Int. Atomic Energy Agency, Vienna, Austria, 1995.
- Sugawara, S., T. Nakazawa, Y. Shirakawa, K. Kawamura, S. Aoki, T. Machida, and H. Honda, Vertical profiles of the carbon isotopic ratio of stratospheric methane over Japan, *Geophys. Res. Lett.*, **24**, 2989-2992, 1997.
- Tanaka, N., Y. Xiao, and A. C. Lasaga, *Ab initio* study on carbon kinetic isotope effect (KIE) in the reaction of $\text{CH}_4 + \text{Cl}$, *J. Atmos. Chem.*, **23**, 37-49, 1996.
- Thom, M., R. Bösinger, M. Schmidt, and I. Levin, The regional budget of atmospheric methane of a highly populated area, *Chemosphere*, **26**, 143-160, 1993.
- Thompson, A. M., and R. J. Cicerone, Possible perturbations to atmospheric CO , CH_4 , and OH , *J. Geophys. Res.*, **91**, 10,853-10,864, 1986.
- Tyler, S. C., The global methane budget, in *Microbial Production and Consumption of Greenhouse Gases: Methane, Nitrogen Oxides, and Halomethanes*, edited by J. E. Rogers and W. B. Whitman, pp. 7-38, Am. Soc. for Microbiol., Washington, D. C., 1991.
- Tyler, S. C., G. W. Brailsford, K. Yagi, K. Minami, and R. Cicerone, Seasonal variations in methane flux and $\delta^{13}\text{C}$ values for rice paddies in Japan and their implications, *Global Biogeochem. Cycles*, **8**, 1-12, 1994a.
- Tyler, S. C., P. M. Crill, and G. W. Brailsford, $^{13}\text{C}/^{12}\text{C}$ fractionation of methane during oxidation in a temperate forested soil, *Geochim. Cosmochim. Acta*, **58**, 1625-1633, 1994b.
- Tyler, S. C., H. O. Ajie, A. L. Rice, R. J. Cicerone, and E. C. Tuazon, Experimentally determined kinetic isotope effects in the reaction of CH_4 with Cl: Implications for atmospheric CH_4 , *Eos Trans. AGU*, **79**(45), Fall Meet. Suppl., F102, 1998.
- Wahlen, M., N. Tanaka, R. Henry, B. Deck, J. Zeglen, J. S. Vogel, J. Southon, A. Shemesh, R. Fairbanks, W. Broecker, Carbon-14 in methane sources and in atmospheric methane: The contribution from fossil carbon, *Science*, **245**, 286-290, 1989.
- Wu, Z., R. E. Newell, Y. Zhu, B. E. Anderson, E. V. Browell, G. L. Gregory, G. W. Sachse, and J. E. Collins Jr., Atmospheric layers measured from the NASA DC-8 during PEM-West B and comparison with PEM-West A, *J. Geophys. Res.*, **102**, 28,353-28,365, 1997.

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