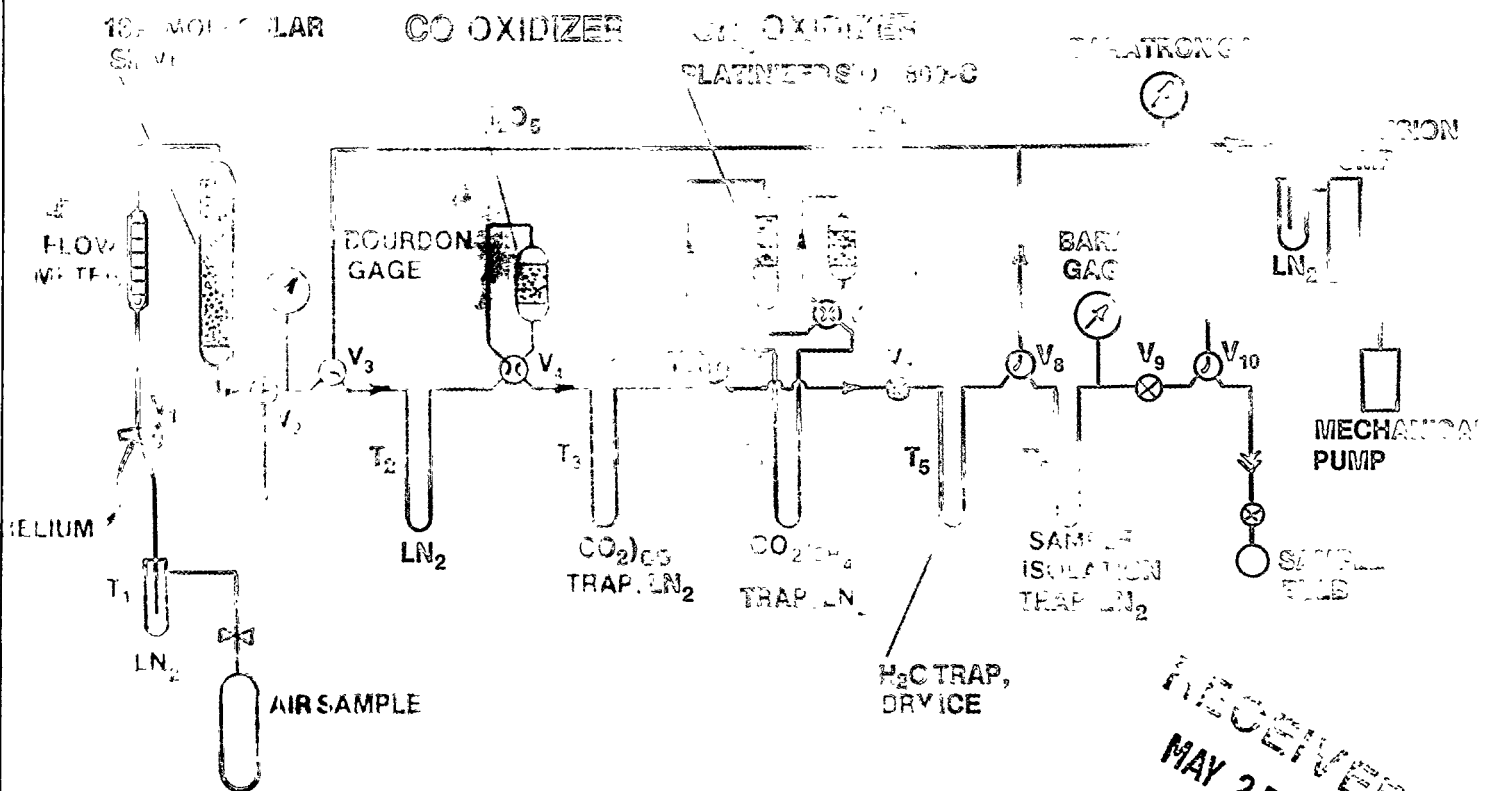


Carbon-13 Isotopic Abundance and Concentration of Atmospheric Methane for Background Air in the Southern and Northern Hemispheres From 1978 to 1989



DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

GH

RECEIVED
MAY 25 1995
OSTI

C. M. Stevens
Chemical Technology Division
Argonne National Laboratory
Argonne, Illinois

This report has been reproduced directly from the best available copy.

Available to DOE and DOE contractors from the Office of Scientific and Technical Information, P.O. Box 62, Oak Ridge, TN 37831; prices available from (615) 576-8401, FTS 626-8401.

Available to the public from the National Technical Information Service, U.S. Department of Commerce, 5285 Port Royal Rd., Springfield, VA 22161.

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

CARBON-13 ISOTOPIC ABUNDANCE AND CONCENTRATION
OF ATMOSPHERIC METHANE FOR BACKGROUND AIR IN THE SOUTHERN
AND NORTHERN HEMISPHERES FROM 1978 TO 1989

C. M. Stevens[†]
Chemical Technology Division
Argonne National Laboratory
Argonne, Illinois

Prepared by:
Robert J. Sepanski*
Laura J. Morris

* Energy, Environment, and Resources Center
The University of Tennessee
Knoxville, Tennessee

Environmental Sciences Division
Publication No. 4388

Date Published: March 1995

Prepared for the
Global Change Research Program
Environmental Sciences Division
Office of Health and Environmental Research
U.S. Department of Energy
(KP 05 02 00 0)

Prepared by the
Carbon Dioxide Information Analysis Center
OAK RIDGE NATIONAL LABORATORY
Oak Ridge, Tennessee 37831-6335
managed by
MARTIN MARIETTA ENERGY SYSTEMS, INC.
for the
U.S. DEPARTMENT OF ENERGY
under contract DE-AC05-84OR21400

[†]Work supported by the U.S. Department of Energy under contract W-31-109-ENG-38

CONTENTS

LIST OF FIGURES	v
LIST OF TABLES	vii
ACKNOWLEDGMENTS	ix
ABSTRACT	xi

PART I: OVERVIEW

1. BACKGROUND AND SOURCE INFORMATION	3
2. METHODOLOGY	3
3. LIMITATIONS AND RESTRICTIONS	6
4. DATA CHECKS PERFORMED BY CDIAC	7
5. HOW TO OBTAIN THE DATA	8
6. REFERENCES	8

PART II. CONTENT AND FORMAT OF DATA FILES

1. FILE DESCRIPTIONS	11
----------------------------	----

"ndp049.des" (descriptive file that complements the written documentation and provides details about the data files provided on the floppy diskette or other transfer medium).

"ndp049.dat" (atmospheric methane concentrations and carbon-13 isotopic abundances at globally distributed sites from 1978 through 1989)

"ndp049.for" (FORTRAN 77 data retrieval program to read and write the atmospheric methane concentration and carbon-13 isotopic abundance data)

"ndp049.sas" (SAS® data retrieval program to read and write the
atmospheric methane concentration and carbon-13 isotopic abundance
data)

APPENDIX A. Carbon-13 Isotopic Abundance and Concentration of Atmospheric Methane.	A-1
--	-----

APPENDIX B. Reprint of Pertinent Literature	B-1
---	-----

Isotopic abundances in the atmosphere and sources, by C.M. Stevens.
1993.

LIST OF FIGURES

<u>Figure</u>	<u>Page</u>
1. Schematic outline of gas train system for oxidizing CH ₄ in air samples to CO ₂ and separating for isotopic analysis	5

LIST OF TABLES

<u>Table</u>	<u>Page</u>
1. Content, size, and format of data files	16

ACKNOWLEDGMENTS

Measurements were carried out in the Chemistry Division, Argonne National Laboratory, Argonne, IL and supported by the Office of Basic Energy Sciences, Division of Mathematical and Geosciences, U.S. Department of Energy, Contract W-31-109-Eng-38 and the Interdisciplinary Research Program in Earth Sciences, National Aeronautics and Space Administration, Order No. W-16188.

ABSTRACT

Stevens, C.M. 1995. Carbon-13 Isotopic Abundance and Concentration of Atmospheric Methane for Background Air in the Southern and Northern Hemispheres from 1978 to 1989. ORNL/CDIAC-80, NDP-049. Carbon Dioxide Information Analysis Center, Oak Ridge National Laboratory, Oak Ridge, Tennessee, U.S.A. 60 pp.

This document presents atmospheric CH₄ concentration and carbon-13 isotopic abundance data derived from air samples collected over the period 1978–1989 at globally distributed clean-air sites. The data set comprises 201 records, 166 from the Northern Hemisphere and 35 from the Southern Hemisphere. The air samples were collected mostly in remote rural or marine locations, far from large sources of CH₄, and are considered representative of tropospheric background conditions. The air samples were processed by isolation of CH₄ from air and conversion to CO₂ for isotopic analysis by isotope-ratio mass spectrometry. These data represent one of the earliest records of carbon-13 isotopic data for atmospheric methane and have been used to refine estimates of CH₄ emissions, calculate annual growth rates of emissions from changing sources, and provide evidence for changes in the rate of atmospheric removal of CH₄.

The data records consist of sample collection date; number of samples combined for analysis; sampling location; analysis date; CH₄ concentration; carbon-13 isotopic abundance; and flag codes to indicate data outliers, repeated analyses, and other information. The data are available free of charge as a numeric data package (NDP) from the Carbon Dioxide Information Analysis Center. The NDP consists of this document and a floppy diskette (or other medium, upon request) containing machine-readable files. This document provides a complete listing of the atmospheric CH₄ concentration and carbon-13 isotopic abundance data. This document also contains retrieval program listings (in FORTRAN and SAS® languages), furnishes information on analysis methods, defines limitations and restrictions of the data, and provides a reprint of a pertinent paper from the literature.

Keywords: air samples, atmospheric methane, carbon-13, global distribution, isotope, mass spectrometry, trends

PART I

OVERVIEW

1. BACKGROUND AND SOURCE INFORMATION

Atmospheric methane (CH_4) may become an increasingly important contributor to global warming in future years. Its atmospheric concentration has risen, doubling over the past several hundred years, and additional methane is thought to have a much greater effect on climate, on a per molecule basis, than additional CO_2 at present day concentrations (Shine et al. 1990). The causes of the increase of atmospheric CH_4 have been difficult to ascertain because of a lack of quantitative knowledge of the fluxes (i.e., net emissions) from the numerous anthropogenic and natural sources. The goal of CH_4 isotopic studies is to provide a constraint (and so reduce the uncertainties) in estimating the relative fluxes from the various isotopically distinct sources, whose combined fluxes must result in the measured atmospheric isotopic composition, after the fractionating effect of the atmospheric removal process is considered. In addition, knowledge of the spatial and temporal changes in the isotopic composition of atmospheric CH_4 , along with estimates of the fluxes from some of the major sources, makes it possible to calculate growth rates for sources whose temporal emissions trends would be difficult to measure directly. A detailed discussion of the use of carbon isotopic data to elucidate CH_4 source fluxes and growth rates is given in Stevens (1993), a reprint of which is included as Appendix B.

The atmospheric CH_4 concentration and carbon-13 isotopic abundance data presented in this package are derived from air samples collected over the period 1978–1989 at globally distributed clean-air sites. The data set (presented in its entirety in hard copy form as Appendix A) comprises 201 records, 166 from the Northern Hemisphere and 35 from the Southern Hemisphere. The air samples were collected mostly in remote rural or marine locations, far from large sources of CH_4 , and are considered representative of tropospheric background conditions. Sampling locations in the Northern Hemisphere included 32 Pacific Ocean sites and 11 land-based sites. In the Southern Hemisphere, locations included 18 Pacific Ocean sites and 4 land-based sites. At many locations, air samples were collected by C.M. Stevens and his colleagues. For some Southern Hemisphere and Pacific Ocean measurements, and all measurements at Cape Meares, Oregon, samples were obtained from stored air cylinders contributed by R.A. Rasmussen from the sample bank at the Oregon Graduate Institute of Science and Technology (formerly the Oregon Graduate Center), Portland, Oregon, U.S.A.

These data represent one of the earliest records of carbon-13 isotopic measurements for atmospheric methane at globally distributed clean-air sites. Additional information, including measurements of the isotopic composition of CH_4 sources, estimates of the atmospheric lifetime of CH_4 , measurements of carbon-14 abundances in atmospheric CH_4 , and some CH_4 source flux estimates derived from emissions inventories, are provided in Stevens (1993). Together with these additional data, the atmospheric $^{13}\text{CH}_4$ data presented in this package have been used to refine estimates of the global CH_4 fluxes from combined rice and cattle production and from biomass burning, to calculate growth rates in CH_4 fluxes from biomass burning in the Southern Hemisphere and from natural wetlands in the Northern Hemisphere, and to provide evidence of changes in the rate of the atmospheric removal process (Stevens, 1993).

2. METHODOLOGY

Sampling Techniques and Conditions

The sampling in both hemispheres occurred in two main phases:

Phase 1: Samples collected during 1978–83 were, with few exceptions, obtained from the air sample bank of the Oregon Graduate Center in collaboration with R.A. Rasmussen. The samples in the bank had been stored from 1 to 5 years in cleaned and treated stainless steel cylinders of various sizes (approximately 2 to 30 liters) and at various high pressures (up to 25 atmospheres). These cylinders were shipped to Argonne National Laboratory and then transferred by expansion to atmospheric pressure into 33-liter evacuated stainless steel cylinders (untreated WWII-surplus oxygen cylinders) of accurately known volume and analyzed within 1 to 2 days. The air in these stored samples had been collected either at sea or at land stations upwind of any urban or anthropogenic sources of CH₄. During this period, some of the Northern Hemisphere samples were collected at the Cape Meares station of the Oregon Graduate Center; the others were taken at sea in the Pacific. Beginning in 1983, samples were also collected in Northern Illinois. The average $\delta^{13}\text{C}$ values of 36 samples collected in Northern Illinois during 1983 were compared with the average of seven samples collected at Cape Meares during the same year and were found to agree within 0.01 per mil.

Phase 2: From 1984 through 1989 all samples were collected in Argonne 33-liter evacuated stainless steel cylinders (untreated WWII-surplus oxygen cylinders), either at rural sites in Northern Illinois or, in the case of the Southern Hemisphere samples, at rural sites upwind of Canberra (Australia), or at the shore near the NOAA observatory in American Samoa. A special set of analyses was carried out in 1988 on four samples which had been collected in 1978 and analyzed in 1983, in order to compare results after another five years of storage. The results of these reanalyses are found in the data set (see data for samples collected at Cape Meares, dated 4-4-78, 4-7-78, 10-5-78, and 10-5-78).

The Illinois samples were collected mostly in the afternoon on days with winds in excess of 10 mph. Collections in the morning were avoided because of overnight temperature inversions. Typically, only one flask sample was collected at each site. An exception occurred on 9-8-88, when six different samples in six different flasks were collected simultaneously and analyzed at intervals over a six week period in order to ascertain the integrity of samples stored in Argonne cylinders. Multiple samples were combined only when it was necessary to combine air stored in several small cylinders (obtained from the Oregon Graduate Institute) in order to make enough for the 33 liters required for isotopic analysis. Multiple analyses from a single flask occurred in several cases, as in the samples with collection times denoted 11-00-81 (Tasmania) and 05-00-82 (Pacific). (Days denoted as 00, as in 11-00-81, indicate that the exact day of sampling is not known.)

Analytical Methods

Air samples were processed by the oxidation of the CH₄ in the air to CO₂ after quantitative removal of atmospheric CO₂ and CO₂ from oxidation of atmospheric CO by Schutze reagent. (The experimental apparatus used to carry out this procedure is shown schematically in Figure 1.) The CO₂ from CH₄ oxidation was quantitatively separated from the air by distillation and analyzed isotopically. Details of the experimental procedures are as follows.

The air pressure in the sampling flask was first measured, then the flask was connected to the air intake line and air was passed through a low-efficiency, high-flow liquid N₂ trap to remove water, most of the atmospheric CO₂, and non-methane hydrocarbons. Next, the samples were passed through molecular sieve 13X and another liquid N₂ trap of high efficiency to further remove any CO₂ present. The air stream was then passed through a granular Schutze reagent made up of I₂O₅ on silica gel, by which the atmospheric CO was oxidized to CO₂. Another liquid N₂ trap then removed this CO₂. The gas was then passed through an electrically heated quartz combustion tube containing platinized silica, which quantitatively oxidizes the CH₄ to CO₂ and H₂O, which are then trapped in high-efficiency, liquid N₂

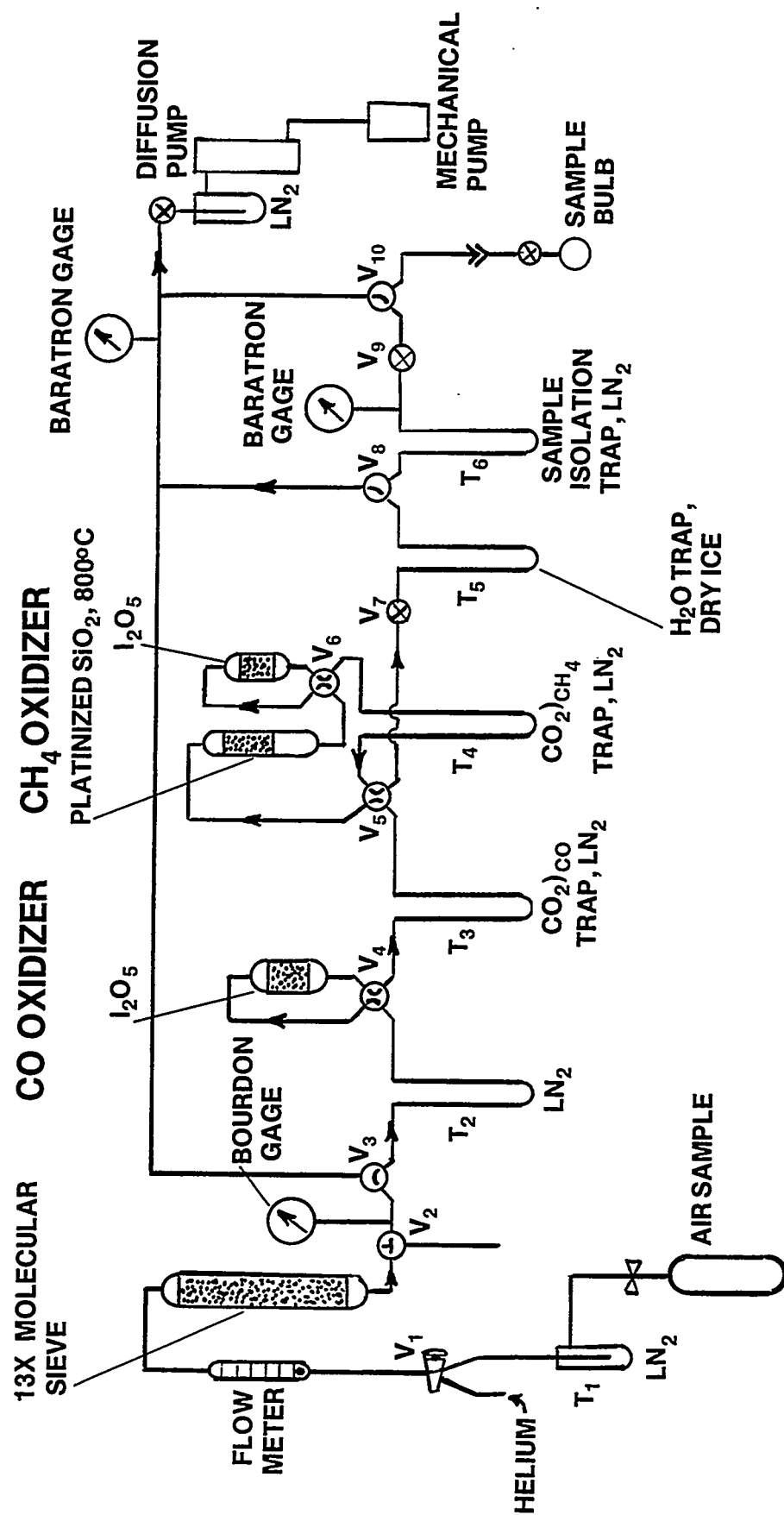


Figure 1. Schematic outline of gas train system for oxidizing CH₄ in air samples to CO₂ and separating for isotopic analysis

traps. The air in the original cylinder was passed through this treatment until the pressure was reduced to approximately 5% of atmospheric pressure. The flow rate was maintained at a constant flow of approximately 0.5 liters/min by adjustment of the valve on the cylinder until the valve was wide open and the pressure was reduced to approximately 25% of atmospheric pressure; the flow then gradually decreases until terminated at 5% of atmospheric pressure. The line beyond the CH₄ combustion section was pumped to a good vacuum and then isolated. The trap with the CO₂ and H₂O from CH₄ oxidation was warmed with a hot water bath, and the CO₂ and H₂O were transferred with a controlled helium flow through a trap cooled by dry ice/methanol to remove the H₂O. The CO₂ was condensed in a trap in the micromanometer section, which was then pumped to a good vacuum and isolated. The trap containing the CO₂ from CH₄ oxidation was then warmed, and the CO₂ pressure was measured with a precision of $\pm 0.3\%$. Finally, the CO₂ was distilled to a sample tube for isotopic analysis on a Consolidated-Nier isotope-ratio mass spectrometer. The concentration of CH₄ was calculated stoichiometrically with a precision of $\pm 0.5\%$. The $\delta^{13}\text{C}$ values of the CO₂ samples were measured with a precision of ± 0.05 per mil. A correction of -0.11 per mil was made for an impurity of N₂O produced in the combustion train. The overall uncertainties in the analyzed values of CH₄ concentration and isotopic composition are estimated to be 0.02 parts per million (ppm) for the concentration values, 0.2 per mil for isotopic values prior to 1985, and 0.1 per mil for isotopic values after 1985.

3. LIMITATIONS AND RESTRICTIONS

The isotopic results for the samples of stored air from 1978 through 1983 were all analyzed during 1982–83 in random order and using a laboratory isotopic standard which had been accurately measured at -24.8 per mil. This standard had been used for many years and was replenished without fractionation 2–3 times per year. The order of processing and analysis of samples was random for both the hemisphere of origin and the chronology of collection; therefore, it is unlikely that there are any systematic errors in the set of samples from this period. The same cannot be said for the samples from 1984 through 1989. During this period, new isotopic working standards were started, having a value nearly the same as the isotopic composition of the CH₄ samples in order to reduce the mass spectrometer error resulting from measuring large differences, sometimes called the "memory" effect. There may have been some drift of the value of the isotopic standard due to fractionation while it was consumed during the analysis process, as these standards were not prepared in large amounts as had been the case for the standard used for the earlier samples. The repeat analyses done in 1988 on second aliquots of four of the stored air samples showed an average difference of $+0.3$ per mil compared to the first analysis done five years earlier using the -24.8 per mil isotopic standard. This difference is attributed to background CH₄ contamination from the cylinder during storage. The analyses of all stored air samples were therefore corrected by -0.067 per mil per year of storage time between the collection and analysis dates (see column 9 of the data set, included as Appendix A). Another check of the last isotopic standard used for the 1988–89 samples indicated a possible drift of about $+0.5$ per mil.

The most important feature of the isotopic data is the measured interhemispheric trend, which is independent of the individual hemispheric trends because the analyses were done with the same standard at more or less the same time period. Mathematical analysis of the hemispheric trends shows that the difference of the hemispheric trends is the most important term in the calculation of the trends of the fluxes in each hemisphere. The average trend of each hemisphere is of secondary importance in the analysis. Hence, systematic errors such as fractionation of the isotopic standard would have only a small effect on the final application of the results.

Additional uncertainties may affect the ability to compare isotopic ratios in atmospheric CH₄ from clean-air sites with isotopic ratios from the various source types for the purpose of resolving uncertainties in the global methane budget. Perhaps the largest uncertainty is the determination by inventory estimates of the globally averaged isotopic ratio of individual sources such as biomass burning or methane from ruminants. This uncertainty arises because the CH₄ from these sources is made up of contributions of uncertain relative amounts globally from metabolically distinct plant types (i.e., C₃ and C₄ plants), which have large isotopic variations. The globally averaged isotopic composition of CH₄ sources from coal mining and natural gas losses are subject to large uncertainties of $\pm 4\%$ because of large variations among the many individual sources.

4. DATA CHECKS PERFORMED BY CDIAC

The Carbon Dioxide Information Analysis Center (CDIAC) endeavors to provide quality assurance (QA) of all data before their distribution. To ensure the highest possible quality in the data, CDIAC conducts extensive reviews for reasonableness, accuracy, completeness, and consistency of form. While having common objectives, the specific form of these reviews must be tailored to each data set; this tailoring process may involve considerable programming efforts. The entire QA process is an important part of CDIAC's effort to assure accurate, usable data for researchers.

For the atmospheric methane concentration and carbon-13 isotopic abundance data, the QA procedure consisted of the following:

1. The format of all information was checked to ensure consistency throughout each data record.
2. Data values were examined for reasonableness, absence of typographical errors, and absence of outliers.

No errors or inconsistencies of the types described above were found in the atmospheric methane concentration and carbon-13 isotopic abundance data received by CDIAC. All data values in the file distributed by CDIAC are identical to those received from C.M. Stevens. However, in order to enhance their value and their ease of use, the data records were reformatted and appended in the following way:

1. The latitude and longitude of each sampling site, which were absent for most locations in the original data set, were obtained from C.M. Stevens and appended to each data record.
2. The conventions for missing values and repeated analyses were altered in order to create a consistent format for all data records. New flag codes were created to identify any of the following: (1) uncertainties in the analysis date, (2) records that represent repeated measurements, and (3) records that represent averages of two or more previous measurements.

5. HOW TO OBTAIN THE DATA

This documentation and the data described herein are available from:

Carbon Dioxide Information Analysis Center
Oak Ridge National Laboratory
Post Office Box 2008
Oak Ridge, TN 37831-6335, U.S.A.
Telephone (615) 574-3645 or (615) 241-4851

The following citation should be used for referencing this archive and/or this documentation report:

Stevens, C.M. 1995. Carbon-13 Isotopic Abundance and Concentration of Atmospheric Methane for Background Air in the Southern and Northern Hemispheres from 1978 to 1989. ORNL/CDIAC-80, NDP-049. Carbon Dioxide Information Analysis Center, Oak Ridge National Laboratory, Oak Ridge, Tennessee, U.S.A.

6. REFERENCES

- Rust, F., and C.M. Stevens. 1980. Carbon kinetic isotope effect in the oxidation of methane by hydroxyl. *International Journal of Chemical Kinetics* 12:371-77.
- Shine, K.P., R.G. Derwent, D.J. Wuebbles, and J-J. Morcrette. 1990. Radiative forcing of climate. pp. 41-68. In J.T. Houghton, G.J. Jenkins, and J.J. Ephraums (eds.), *Climate Change: the IPCC Scientific Assessment*. Cambridge University Press, Cambridge.
- Stevens, C.M. 1993. Isotopic abundances in the atmosphere and sources. pp. 62-88. In M.A.K. Khalil (ed), *Atmospheric Methane: Sources, Sinks, and Role in Global Change*. Proceedings of the NATO Advanced Research Workshop on the Atmospheric Methane Cycle: Sources, Sinks, Distributions, and Role in Global Change, held at Mt. Hood near Portland, OR, U.S.A., October 7-11, 1991. NATO ASI Series I: Global Environmental Change, Vol. 13. Springer-Verlag, Berlin and Heidelberg.
- Stevens, C.M. 1988. Atmospheric methane. *Chemical Geology* 71:11-21.
- Stevens, C.M., and A. Engelkemeir. 1988. Stable carbon isotopic composition of methane from some natural and anthropogenic sources. *Journal of Geophysical Research* 93(D1): 725-33.
- Stevens, C.M., and A. Engelkemeir. 1985. Causes of increasing methane fluxes based on carbon isotopic studies. Special Environmental Report No. 16, WMO 647. WMO Technical Conference on Observation and Measurement of Atmospheric Contaminants. World Meteorological Organization, Geneva.

PART II

CONTENT AND FORMAT OF DATA FILES

1. FILE DESCRIPTIONS

Filename: ndp049.des

This file contains a detailed description of both the data set and the digital data file. It is intended to serve as a digital version of Sects. I-1-I-6 and II-1 of this printed document (figure excluded).

Filename: ndp049.dat

This 21.5 kB file presents 201 records (166 records from Northern Hemisphere sites and 35 records from Southern Hemisphere sites) of atmospheric methane concentrations and carbon-13 isotopic abundances from background (clean-air) samples collected at globally distributed sites from 1978 through 1989.

Each data record presents the following variables: sample collection date; number of samples combined for analysis; sampling location (site name, latitude, and longitude); analysis date; CH₄ concentration; carbon-13 isotopic abundance (uncorrected and corrected); and flag codes to indicate outliers, repeated analyses of a sample, and other information. The file can be read by using the following FORTRAN code:

```
C FORTRAN data retrieval routine to read and write the file named
C "ndp049.dat".
C
C Unit 1 is input.
C
      CHARACTER NSAMP, LOCN*27, LAT*9, LON*11, AFLAG, OFLAG, AVCODE*2
      INTEGER CMONTH, CDAY, CYEAR, AMONTH, ADAY, AYEAR
      REAL CONC, C13MEAS, C13CORR
      OPEN (UNIT=1, FILE='ndp049.dat')
      READ (1,10) CMONTH, CDAY, CYEAR, NSAMP, LOCN, LAT, LON, AMONTH,
1         ADAY, AYEAR, AFLAG, CONC, C13MEAS, OFLAG, C13CORR,
2         AVCODE
10  FORMAT (////////I2,1X,I2,1X,I2,2X,A1,2X,A26,2X,A9,2X,A11,2X,I2,1X,
2         I2,1X,I2,1X,A1,2X,F5.3,2X,F6.2,1X,A1,2X,F6.2,1X,A2)
20  READ (1,30,END=99) CMONTH, CDAY, CYEAR, NSAMP, LOCN, LAT, LON,
2         AMONTH, ADAY, AYEAR, AFLAG, CONC, C13MEAS,
3         OFLAG, C13CORR, AVCODE
30  FORMAT (I2,1X,I2,1X,I2,2X,A1,2X,A26,2X,A9,2X,A11,2X,I2,1X,I2,1X,
2         I2,1X,A1,2X,F5.3,2X,F6.2,1X,A1,2X,F6.2,1X,A2)
      GO TO 20
99  STOP
      END
```

The data can also be read by using the following SAS® code:

```
* SAS data retrieval routine to read and write the file named
"ndp049.dat";
*;
DATA NDP049;
  INFILE 'ndp049.dat';
```

```

IF _N_=1 THEN INPUT ////////// CMONTH 1-2 CDAY 4-5 CYEAR 7-8 NSAMP $ 11
    @14 LOCN $CHAR26. @42 LAT $CHAR9. @53 LON $CHAR11. AMONTH 66-67
    ADAY 69-70 AYEAR 72-73 AFLAG $ 75 @78 CONC 5.3 @85 C13MEAS 6.2
    OFLAG $ 92 @95 C13CORR 6.2 AVCODE $ 102-103;
ELSE INPUT CMONTH 1-2 CDAY 4-5 CYEAR 7-8 NSAMP $ 11 @14 LOCN $CHAR26.
    @42 LAT $CHAR9. @53 LON $CHAR11. AMONTH 66-67 ADAY 69-70 AYEAR 72-73
    AFLAG $ 75 @78 CONC 5.3 @85 C13MEAS 6.2 OFLAG $ 92 @95 C13CORR 6.2
    AVCODE $ 102-103;
RUN;

```

where

CMONTH	is the numeric month of the year in which the air sample was collected;
CDAY	is the numeric day of the month on which the air sample was collected;
CYEAR	is the final two digits of the year (since 1900) in which the air sample was collected;
NSAMP	is the number of samples combined from different locations for a single analysis;
LOCN	is a descriptive character string consisting of (1) the location of the sampling site and, in some cases, (2) the sample number(s), denoted as one or more numbers following a "#" sign and referring to the identity of the stored air sample(s) contributed from the sample bank at the Oregon Graduate Institute of Science and Technology, Portland, Oregon, U.S.A., by R.A. Rasmussen;
LAT	is the estimated latitude (or range of latitudes) of the sampling site(s), given in decimal degrees;
LON	is the estimated longitude (or range of longitudes) of the sampling site(s), given in decimal degrees;
AMONTH	is the numeric month of the year in which the air sample was analyzed;
ADAY	is the numeric day of the month on which the air sample was analyzed;
AYEAR	is the final two digits of the year (since 1900) in which the sample was analyzed;
AFLAG	is a one-character flag code providing additional information about the sample analysis: 'R' — entry represents one of two or more repeated analyses carried out on the same air sample; 'C' — identifies samples where the actual date of analysis is not given but was within one week of the date of collection;
CONC	is the CH ₄ concentration in the air sample, given in parts per million (1×10^6) by volume;
C13MEAS	is the measured $\delta^{13}\text{C}$ (per mil), corrected by +0.10 per mil for N ₂ O contamination but uncorrected for water vapor contamination;

- OFLAG is a one-character flag code denoting values of C13MEAS that are considered as outliers and not included in any subsequent averages; the symbol for the flag code is "*";
- C13CORR is a corrected value of $\delta^{13}\text{C}$ (per mil), calculated only for samples stored for a considerable time before analysis; values represent an addition of -0.067 per mil per year for background contamination (from the cylinder walls) that accumulated between the collection and analysis dates;
- AVCODE is a two-character code denoting an entry whose C13CORR value is an average of those of the previous 2 to 5 entries [i.e., the immediately preceding entries containing AFLAG values of 'R' (excluding outliers, denoted by OFLAG="*")]: A2, A3, and A5 signify entries representing averages of 2, 3, and 5 previous entries, respectively.

Stated in tabular form, the contents include the following.

Variable*	Variable type	Variable width**	Starting column	Ending column
CMONTH	Numeric	I2	1	2
CDAY	Numeric	I2	4	5
CYEAR	Numeric	I2	7	8
NSAMP	Character	A1	11	11
LOCN	Character	A26	14	39
LAT	Character	A9	42	50
LON	Character	A11	53	63
AMONTH	Numeric	I2	66	67
ADAY	Numeric	I2	69	70
AYEAR	Numeric	I2	72	73
AFLAG	Character	A1	75	75
CONC	Numeric	F5.3	78	82
C13MEAS	Numeric	F6.2	85	90
OFLAG	Character	A1	92	92
C13CORR	Numeric	F6.2	95	100
AVCODE	Character	A2	102	103

* Missing values for numeric variables are represented as follows — CMONTH, CDAY, CYEAR, AMONTH, ADAY, AYEAR: 00; CONC: 9.999; C13MEAS, C13CORR: 999.99. Missing values for character variables (NSAMP, AFLAG, OFLAG, AVCODE) are represented as blanks.

** Values for variable width are entered as FORTRAN 77 format codes.

Filename: ndp049.for

This file contains a FORTRAN 77 data retrieval routine to read and write the file "ndp049.dat". The following is a listing of this program. For additional information regarding variable definitions and format statements, please see the file description for "ndp049.dat" on pages 11-13.

```
C FORTRAN data retrieval routine to read and write the file named
C "ndp049.dat".
C
C Unit 1 is input.
C Unit 2 is output.
C
      CHARACTER NSAMP, LOCN*27, LAT*9, LON*11, AFLAG, OFLAG, AVCODE*2
      INTEGER CMONTH, CDAY, CYEAR, AMONTH, ADAY, AYEAR
      REAL CONC, C13MEAS, C13CORR
      OPEN (UNIT=1, FILE='ndp049.dat')
      OPEN (UNIT=2, FILE='output')
      READ (1,10) CMONTH, CDAY, CYEAR, NSAMP, LOCN, LAT, LON, AMONTH,
2          ADAY, AYEAR, AFLAG, CONC, C13MEAS, OFLAG, C13CORR,
3          AVCODE
10 FORMAT (////////I2,1X,I2,1X,I2,2X,A1,2X,A26,2X,A9,2X,A11,2X,I2,1X,
2          I2,1X,I2,1X,A1,2X,F5.3,2X,F6.2,1X,A1,2X,F6.2,1X,A2)
20 WRITE (2,30) CMONTH, CDAY, CYEAR, NSAMP, LOCN, LAT, LON, AMONTH,
2          ADAY, AYEAR, AFLAG, CONC, C13MEAS, OFLAG, C13CORR,
3          AVCODE
30 FORMAT (I2.2,1X,I2.2,1X,I2.2,2X,A1,2X,A26,2X,A9,2X,A11,2X,I2.2,
2          1X,I2.2,1X,I2.2,1X,A1,2X,F5.3,2X,F6.2,1X,A1,2X,F6.2,1X,
3          A2)
      READ (1,40,END=99) CMONTH, CDAY, CYEAR, NSAMP, LOCN, LAT, LON,
2          AMONTH, ADAY, AYEAR, AFLAG, CONC, C13MEAS,
3          OFLAG, C13CORR, AVCODE
40 FORMAT (I2,1X,I2,1X,I2,2X,A1,2X,A26,2X,A9,2X,A11,2X,I2,1X,I2,1X,
2          I2,1X,A1,2X,F5.3,2X,F6.2,1X,A1,2X,F6.2,1X,A2)
      GO TO 20
99 CLOSE (1)
      CLOSE (2)
      STOP
      END
```

Filename: ndp049.sas

This file contains a SAS® data retrieval routine to read and write the file "ndp049.dat". The following is a listing of this program. For additional information regarding variable definitions and format statements, please see the file description for "ndp049.dat" on pages 11-13.

```
* SAS data retrieval routine to read the file named "ndp049.dat";
*;
DATA NDP049;
  INFILE 'ndp049.dat';
  IF _N_=1 THEN INPUT ////////// CMONTH $ 1-2 CDAY $ 4-5 CYEAR $ 7-8
    NSAMP $ 11 @14 LOCN $CHAR26. @42 LAT $CHAR9. @53 LON $CHAR11.
    AMONTH $ 66-67 ADAY $ 69-70 AYEAR $ 72-73 AFLAG $ 75
    @78 CONC 5.3 @85 C13MEAS 6.2 OFLAG $ 92 @95 C13CORR 6.2
    AVCODE $ 102-103;
  ELSE INPUT CMONTH $ 1-2 CDAY $ 4-5 CYEAR $ 7-8 NSAMP $ 11
    @14 LOCN $CHAR26. @42 LAT $CHAR9. @53 LON $CHAR11.
    AMONTH $ 66-67 ADAY $ 69-70 AYEAR $ 72-73 AFLAG $ 75
    @78 CONC 5.3 @85 C13MEAS 6.2 OFLAG $ 92 @95 C13CORR 6.2
    AVCODE $ 102-103;
  FILE 'output';
  PUT CMONTH 1-2 CDAY 4-5 CYEAR 7-8 NSAMP 11 @14 LOCN $CHAR26.
    @42 LAT $CHAR9. @53 LON $CHAR11. AMONTH 66-67 ADAY 69-70
    AYEAR 72-73 AFLAG 75 @78 CONC 5.3 @85 C13MEAS 6.2 OFLAG 92
    @95 C13CORR 6.2 AVCODE 102-103;
RUN;
```

Table 1. CONTENT, SIZE, and FORMAT of DATA FILES

File number and name	Logical records	File size in kB	Block size ¹	Record length
1. ndp049.des	555	45.0	8000	80
2. ndp049.for	31	2.5	8000	80
3. ndp049.sas	18	1.5	8000	80
4. ndp049.dat	207	21.5	8000	103
Total:	811	70.5		

¹ The block size pertains only to files on magnetic tape.

APPENDIX A.

Carbon-13 Isotopic Abundance and Concentration of Atmospheric Methane

Date of Sample Collection		No. 1	Sampling Location and Reference No.		Latitude	Longitude	Date of Sample Analysis		CH ₄ Conc. (ppmv)	Measured $\delta^{13}\text{C}$ (‰)	Corrected $\delta^{13}\text{C}$ (‰)	No. of Analyses Averaged ²
Mo	Da	Yr	Mo	Da	Yr	Mo	Da	Yr				
05 00	78	7	Pacific, Gamestag		13 - 57 S		01	11	83	1.484	-47.66	-47.98
05 00	78	4	Pacific, Gamestag		1 N - 6 S		01	13	83	1.514	-47.70	-48.02
12 04	78		South Pole		89.98 S	24.80 W	11	28	83	1.511	-47.63	-47.98
12 04	78		South Pole		89.98 S	24.80 W	05	29	84	1.474	-47.60	-47.97
05 06	80		Samoa #164		14.25 S	170.57 W	05	25	83	1.546	-47.55	-47.75
09 15	80		Tasmania #174		40.68 S	144.68 E	11	01	81	1.513	-47.35	-47.42
09 15	80		Tasmania #156		40.68 S	144.68 E	08	10	81	1.503	-47.43	-47.50
04 05	81		Samoa #216		14.25 S	170.57 W	05	24	83	1.546	-47.46	-47.59
04 02	81	7	Pacific off Peru		10 S	90 W	03	27	83†	1.561	-46.80*	999.99
04 02	81	7	Pacific off Peru		10 S	90 W	04	08	83†	1.553	-47.15*	999.99
11 00	81	8	Tasmania		40.68 S	144.68 E	03	11	83†	1.578	-47.06*	999.99
11 00	81	8	Tasmania		40.68 S	144.68 E	04	07	83†	1.571	-47.33	-47.43
11 00	81	8	Tasmania		40.68 S	144.68 E	04	19	83†	1.561	-47.40	-47.50
11 00	81	8	Tasmania		40.68 S	144.68 E	04	21	83†	9.999	-47.42	-47.52
11 00	81	8	Tasmania		40.68 S	144.68 E	00	00	00	9.999	999.99	-47.48
05 00	82	9	Pacific		0 - 4 N	125 (+-15) W	03	15	83†	1.583	-47.20	-47.25
05 00	82	9	Pacific		0 - 4 N	125 (+-15) W	04	07	83†	1.569	-47.33	-47.39
05 00	82	9	Pacific		0 - 4 N	125 (+-15) W	07	21	83†	1.583	-47.30	-47.37
05 00	82	9	Pacific		0 - 4 N	125 (+-15) W	08	19	83†	1.571	-47.27	-47.35
05 00	82	9	Pacific		0 - 4 N	125 (+-15) W	08	23	83†	1.561	-47.22	-47.31
05 00	82	9	Pacific		0 - 4 N	125 (+-15) W	00	00	00	9.999	999.99	-47.33
09 10	82	5	Tasmania		40.68 S	144.68 E	03	29	83	1.591	-47.28	999.99
12 17	82	2	Samoa #059+067		14.25 S	170.57 W	07	13	83	1.568	-47.33	999.99
02 19	83		Samoa #205		14.25 S	170.57 W	05	24	83	1.570	-47.39	999.99
02 26	84		South Pole.		89.98 S	24.80 W	11	22	85	1.580	-47.15	999.99
06 27	86		Canberra		35.12 S	148.75 E	09	10	86	1.602	-47.02	999.99
06 30	86		Canberra		35.12 S	148.75 E	09	09	86	1.650	-46.59	999.99
09 08	86		Samoa		14.25 S	170.57 W	09	30	86	1.602	-46.71	999.99
09 10	86		Samoa		14.25 S	170.57 W	10	22	86	1.645	-46.52	999.99
02 18	87		Samoa		14.25 S	170.57 W	03	20	87	1.626	-46.52	999.99
02 24	87		Canberra		35.12 S	148.75 E	03	24	87	1.638	-46.96	999.99
02 25	87		Canberra		35.12 S	148.75 E	03	25	87	1.619	-46.78	999.99
02 27	87		Samoa		14.25 S	170.57 W	03	22	87	1.639	-46.60	999.99
04 22	88		Samoa		14.25 S	170.57 W	05	06	88	1.634	-46.81	999.99
04 25	88		Samoa		14.25 S	170.57 W	05	10	88	1.638	-46.50	999.99
05 20	88		Samoa		14.25 S	170.57 W	06	03	88	1.659	-46.51	999.99

Date of Sample Collection	Mo Da Yr	No. 1	Sampling Location and Reference No.	Latitude	Longitude	Date of Sample Analysis		CH ₄ Conc. (ppmv)	Measured $\delta^{13}\text{C}$ (‰)	Corrected $\delta^{13}\text{C}$ (‰)	No. of Analyses Averaged ²
						Mo	Da Yr				
05 27 88			Samoa	14.25 S	170.57 W	06	08 88	1.661	-46.25	999.99	
06 15 88			Samoa	14.25 S	170.57 W	07	07 88	1.647	-46.39	999.99	
06 22 88			Samoa	14.25 S	170.57 W	07	03 88	1.640	-46.48	999.99	
03 21 89			Samoa	14.25 S	170.57 W	04	28 89	1.656	-46.34	999.99	
03 24 89			Samoa	14.25 S	170.57 W	04	27 89	1.616	-46.30	999.99	
04 04 78			Cape Meares, OR #032	45.48 N	123.97 W	05	24 84†	1.562	-47.61	-48.00	
04 04 78			Cape Meares, OR #032	45.48 N	123.97 W	06	14 88†	1.608	-47.31	-48.00	
04 04 78			Cape Meares, OR #032	45.48 N	123.97 W	00	00 00	9.999	999.99	-48.00	2
04 07 78			Cape Meares, OR #035	45.48 N	123.97 W	05	23 84†	1.557	-47.71	-48.11	
04 07 78			Cape Meares, OR #035	45.48 N	123.97 W	06	15 88†	1.609	-47.16	-47.83	
04 07 78			Cape Meares, OR #035	45.48 N	123.97 W	00	00 00	9.999	999.99	-47.97	2
05 00 78	7		Pacific	16 - 70 N	130 - 140 W	01	05 83	1.567	-47.35	-47.67	
10 05 78			Cape Meares, OR #010	45.48 N	123.97 W	02	16 83†	1.648	-47.42	-47.71	
10 05 78			Cape Meares, OR #010	45.48 N	123.97 W	06	13 88†	1.628	-47.33	-47.64	
10 05 78			Cape Meares, OR #010	45.48 N	123.97 W	00	00 00	9.999	999.99	-47.67	2
11 03 78			Cape Meares, OR #041	45.48 N	123.97 W	02	24 83†	1.616	-47.64	-47.95	
11 03 78			Cape Meares, OR #041	45.48 N	123.97 W	06	17 88†	1.623	-47.43	-48.07	
11 03 78			Cape Meares, OR #041	45.48 N	123.97 W	00	00 00	9.999	999.99	-48.01	2
04 20 79			Cape Meares, OR #061	45.48 N	123.97 W	06	28 84	1.585	-47.56	-47.89	
04 25 79			Cape Meares, OR #064	45.48 N	123.97 W	06	20 84	1.583	-47.79	-48.12	
04 25 80			Cape Meares, OR #096	45.48 N	123.97 W	06	29 84	1.606	-47.71	-47.98	
04 29 80			Cape Meares, OR #104	45.48 N	123.97 W	06	29 84	1.619	-47.60	-47.88	
03 14 80	2		Pacific off OR #018	45 N	125 - 130 W	05	18 83	1.648	-47.79	-47.99	
08 28 80			Pacific off OR #159	45 N	125 - 130 W	00	00 00	9.999	999.99	999.99	
07 08 80			Cape Meares, OR #113	45.48 N	123.97 W	03	01 83	1.660	-47.76	-47.94	
07 17 80			Cape Meares, OR #115	45.48 N	123.97 W	02	25 83	1.606	-47.43	-47.60	
12 04 80	2		Pacific #197+203	50 N	140 W	04	18 83	1.650	-47.68	-47.83	
12 13 80	2		Pacific #180+221	48 N	132 W	07	14 83†	1.644	-47.76	-47.93	
12 13 80	2		Pacific #180+221	50 N	140 W	07	18 83†	1.652	-47.60	-47.75	
12 13 80	2		Pacific #180+221	50 N	140 W	00	00 00	9.999	999.99	-47.84	2
12 23 80			Cape Meares, OR #1	45.48 N	123.97 W	05	03 83†	1.644	-47.63	-47.80	
12 23 80			Cape Meares, OR #2	45.48 N	123.97 W	03	31 83†	1.650	-47.52	-47.67	
12 23 80	2		Cape Meares, OR #1+2	45.48 N	123.97 W	07	15 83†	1.641	-47.76	-47.93	
12 23 80	2		Cape Meares, OR #1+2	45.48 N	123.97 W	00	00 00	9.999	999.99	-47.80	3
02 04 81	2		Mauna Loa, HI #192+210	19.53 N	155.58 W	04	01 83	1.549	-47.42	-47.55	
02 04 81	2		Cape Kumukahi, HI #183+196	19.52 N	154.82 W	05	17 83	1.625	-47.24	-47.39	

Date of Sample Collection		No. 1	Sampling Location and Reference No.	Latitude	Longitude	Date of Sample Analysis		CH ₄ Conc. (ppmv)	Measured $\delta^{13}\text{C}$ (‰)	Corrected $\delta^{13}\text{C}$ (‰)	No. of Analyses Averaged ²
Mo	Da	Yr				Mo	Da	Yr			
04	29	81	Cape Meares, OR #160	45.48 N	123.97 W	05	24	84	1.596	-47.57	-47.69
12	08	81	Cape Meares, OR #190	45.48 N	123.97 W	05	29	84	1.639	-48.22*	999.99
04	07	82	Cape Meares, OR #207	45.48 N	123.97 W	05	30	84	1.627	-47.94	-48.02
05	00	82	Pacific (NOAA)	8 - 50 N	105 - 135 W	03	16	83†	1.637	-47.47	-47.52
05	00	82	Pacific (NOAA)	8 - 50 N	105 - 135 W	07	28	83†	1.638	-47.39	-47.47
05	00	82	Pacific (NOAA)	8 - 50 N	105 - 135 W	00	00	00	9.999	999.99	-47.50
09	08	82	Alaska, Portage Glacier	60.67 N	147 W	05	24	84	1.639	-47.84	-47.96
01	27	83	Cape Meares, OR #209A	45.48 N	123.97 W	03	15	83	1.670	-47.64	999.99
01	27	83	Cape Meares, OR #209B	45.48 N	123.97 W	05	03	83	1.674	-47.54	999.99
01	27	83	Cape Meares, OR #209A+209B	45.48 N	123.97 W	05	04	83	1.689	-47.61	999.99
01	27	83	Cape Meares, OR #225	45.48 N	123.97 W	03	23	83†	1.658	-47.48	999.99
01	27	83	Cape Meares, OR #225	45.48 N	123.97 W	04	29	83†	1.672	-47.76	999.99
01	27	83	Cape Meares, OR #225	45.48 N	123.97 W	00	00	00	9.999	-47.62	999.99
04	06	83	Cape Meares, OR #253	45.48 N	123.97 W	06	26	84	1.634	-47.65	-47.73
05	18	83	Cape Meares, OR #260	45.48 N	123.97 W	07	02	84	1.652	-47.47	-47.55
09	28	83	Cape Meares, OR #275	45.48 N	123.97 W	07	02	84	1.638	-47.82	-47.85
10	12	83	Cape Meares, OR #277	45.48 N	123.97 W	06	28	84	1.692	-47.38	-47.41
01	06	83	Clow airport, IL	41.72 N	88.22 W	00	00	00†	1.897	-47.79	999.99
01	11	83	Clow airport, IL	41.72 N	88.22 W	00	00	00†	1.734	-47.84	999.99
01	13	83	Clow airport, IL	41.72 N	88.22 W	00	00	00†	1.769	-47.87	999.99
01	19	83	Kenosha, WI	42.57 N	87.83 W	00	00	00†	1.731	-47.62	999.99
01	28	83	Clow airport, IL	41.72 N	88.22 W	00	00	00†	1.796	-47.26	999.99
02	01	83	Argonne, IL	41.72 N	88 W	00	00	00†	1.867	-47.49	999.99
03	03	83	Clow airport, IL	41.72 N	88.22 W	03	18	83	1.790	-47.50	999.99
04	04	83	Clow airport, IL	41.72 N	88.22 W	00	00	00†	1.758	-47.56	999.99
04	10	83	Clow airport, IL	41.72 N	88.22 W	00	00	00†	1.708	-47.62	999.99
04	21	83	Argonne, IL	41.72 N	88 W	00	00	00†	1.705	-47.60	999.99
05	22	83	Clow airport, IL	41.72 N	88.22 W	00	00	00†	1.713	-47.58	999.99
06	01	83	Chicago, IL lakefront	41.83 N	87.63 W	00	00	00†	1.724	-47.62	999.99
07	01	83	Clow airport, IL	41.72 N	88.22 W	00	00	00†	1.610	-47.61	999.99
07	05	83	Argonne, IL	41.72 N	88 W	00	00	00†	1.692	-47.58	999.99
07	07	83	Clow airport, IL	41.72 N	88.22 W	00	00	00†	1.668	-47.57	999.99
07	07	83	Clow airport, IL	41.72 N	88.22 W	00	00	00†	1.795	-47.67	999.99
07	11	83	Clow airport, IL	41.72 N	88.22 W	00	00	00†	1.740	-47.75	999.99
07	20	83	Clow airport, IL	41.72 N	88.22 W	00	00	00†	1.660	-47.20	999.99
07	22	83	Clow airport, IL	41.72 N	88.22 W	00	00	00†	1.820	-47.90	999.99

Date of Sample Collection		No. 1	Sampling Location and Reference No.		Date of Sample Analysis		CH ₄ Conc. (ppmv)	Measured $\delta^{13}\text{C}$ (‰)		Corrected $\delta^{13}\text{C}$ (‰)		No. of Analyses Averaged ²
Mo	Da	Yr	Mo	Da	Yr	Mo	Da	Yr	Mo	Da	Yr	
07	25	83	Chicago, IL lakefront	41.83 N		00	00	00†	1.720	-47.86	999.99	
07	27	83	Clow airport, IL	41.72 N		00	00	00†	1.720	-47.76	999.99	
07	28	83	Clow airport, IL	41.72 N		00	00	00†	1.685	-47.81	999.99	
08	02	83	Clow airport, IL	41.72 N		00	00	00†	1.692	-47.49	999.99	
08	03	83	Clow airport, IL	41.72 N		00	00	00†	1.704	-47.62	999.99	
08	10	83	Clow airport, IL	41.72 N		00	00	00†	1.680	-47.51	999.99	
08	11	83	Clow airport, IL	41.72 N		00	00	00†	1.682	-47.49	999.99	
08	17	83	Clow airport, IL	41.72 N		00	00	00†	1.744	-47.44	999.99	
11	01	83	Clow airport, IL	41.72 N		00	00	00†	1.785	-47.11	999.99	
11	06	83	Clow airport, IL	41.72 N		00	00	00†	1.840	-47.31	999.99	
11	11	83	Clow airport, IL	41.72 N		00	00	00†	1.717	-47.65	999.99	
11	20	83	Clow airport, IL	41.72 N		00	00	00†	1.753	-47.82	999.99	
11	21	83	Clow airport, IL	41.72 N		00	00	00†	1.746	-47.71	999.99	
11	23	83	Clow airport, IL	41.72 N		00	00	00†	1.729	-47.65	999.99	
11	24	83	Clow airport, IL	41.72 N		00	00	00†	1.739	-47.55	999.99	
12	17	83	Clow airport, IL	41.72 N		00	00	00†	1.757	-47.93	999.99	
12	19	83	Clow airport, IL	41.72 N		00	00	00†	1.810	-47.64	999.99	
05	10	84	Clow airport, IL	41.72 N		00	00	00†	1.785	-47.29	999.99	
05	12	84	Clow airport, IL	41.72 N		00	00	00†	1.760	-47.33	999.99	
05	18	84	Clow airport, IL	41.72 N		00	00	00†	1.700	-47.63	999.99	
05	23	84	Clow airport, IL	41.72 N		00	00	00†	1.670	-47.86	999.99	
06	01	84	Clow airport, IL	41.72 N		00	00	00†	1.660	-47.24	999.99	
10	17	84	Clow airport, IL	41.72 N		00	00	00†	1.780	-47.57	999.99	
10	26	84	Clow airport, IL	41.72 N		00	00	00†	1.810	-48.60*	999.99	
10	27	84	Clow airport, IL	41.72 N		00	00	00†	1.690	-48.77*	999.99	
01	22	85	Clow airport, IL	41.72 N		00	00	00†	1.744	-47.79	999.99	
01	22	85	Clow airport, IL	41.72 N		00	00	00†	1.718	-47.85	999.99	
01	23	85	Clow airport, IL	41.72 N		00	00	00†	1.710	-48.01*	999.99	
01	24	85	Clow airport, IL	41.72 N		00	00	00†	1.700	-48.12*	999.99	
10	22	85	Cape Meares, OR	45.48 N		00	00	00†	1.728	-47.31	999.99	
11	07	85	Clow airport, IL	41.72 N		00	00	00†	1.787	-47.61	999.99	
11	16	85	Clow airport, IL	41.72 N		00	00	00†	1.807	-47.61	999.99	
11	21	85	Naperville, IL	41.75 N		00	00	00†	1.892	-47.62	999.99	
11	22	85	Clow airport, IL	41.72 N		00	00	00†	1.790	-47.52	999.99	
12	02	85	Clow airport, IL	41.72 N		00	00	00†	1.780	999.99	999.99	
03	26	86	Clow airport, IL	41.72 N		00	00	00†	1.777	-47.26	999.99	

Date of Sample Collection	Mo Da Yr	No. 1	Sampling Location and Reference No.	Latitude	Longitude	Date of Sample Analysis Mo Da Yr	CH ₄ Conc. (ppmv)	Measured δ ¹³ C (‰)	Corrected δ ¹³ C (‰)	No. of Analyses Averaged ²
03 28 86			Clow airport, IL	41.72 N	88.22 W	00 00 00†	1.811	-46.98	999.99	
04 07 86			Clow airport, IL	41.72 N	88.22 W	00 00 00†	1.852	-47.10	999.99	
04 19 86			Clow airport, IL	41.72 N	88.22 W	00 00 00†	1.852	-47.27	999.99	
04 22 86			Clow airport, IL	41.72 N	88.22 W	00 00 00†	1.780	-47.32	999.99	
04 25 86			Clow airport, IL	41.72 N	88.22 W	00 00 00†	1.864	-47.32	999.99	
04 28 86			Clow airport, IL	41.72 N	88.22 W	00 00 00†	1.741	-47.14	999.99	
05 01 86			Clow airport, IL	41.72 N	88.22 W	00 00 00†	1.776	-47.68	999.99	
05 23 86			Chicago, IL lakefront	41.83 N	87.63 W	00 00 00†	1.789	-47.44	999.99	
07 13 86			Clow airport, IL	41.72 N	88.22 W	00 00 00†	1.704	-47.00	999.99	
09 05 86			Clow airport, IL	41.72 N	88.22 W	00 00 00†	1.780	-46.62*	999.99	
09 17 86			Clow airport, IL	41.72 N	88.22 W	00 00 00†	1.758	-46.77*	999.99	
09 26 86			Clow airport, IL	41.72 N	88.22 W	00 00 00†	1.716	-46.81*	999.99	
10 12 86			Clow airport, IL	41.72 N	88.22 W	00 00 00†	1.785	-46.50*	999.99	
10 14 86			Clow airport, IL	41.72 N	88.22 W	00 00 00†	1.778	-47.22	999.99	
10 21 86			Clow airport, IL	41.72 N	88.22 W	00 00 00†	9.999	-47.19	999.99	
11 08 86			Clow airport, IL	41.72 N	88.22 W	00 00 00†	1.761	-47.26	999.99	
11 09 86			Clow airport, IL	41.72 N	88.22 W	00 00 00†	1.740	-47.07	999.99	
11 18 86			Clow airport, IL	41.72 N	88.22 W	00 00 00†	1.850	-47.20	999.99	
11 27 86			Clow airport, IL	41.72 N	88.22 W	00 00 00†	1.762	-47.18	999.99	
12 04 86			Clow airport, IL	41.72 N	88.22 W	02 02 87	1.783	-47.66	999.99	
01 23 87			Clow airport, IL	41.72 N	88.22 W	00 00 00†	1.790	-47.32	999.99	
01 26 87			Clow airport, IL	41.72 N	88.22 W	00 00 00†	1.789	-47.07	999.99	
02 08 87			Clow airport, IL	41.72 N	88.22 W	00 00 00†	1.762	-47.23	999.99	
02 17 87			Chicago, IL lakefront	41.83 N	87.63 W	00 00 00†	1.812	-47.01	999.99	
03 09 87			Chicago, IL lakefront	41.83 N	87.63 W	09 11 87	1.855	-46.53*	999.99	
03 11 87			Chicago, IL lakefront	41.83 N	87.63 W	00 00 00†	1.960	-46.65*	999.99	
09 17 87			Clow airport, IL	41.72 N	88.22 W	11 11 87	1.769	-47.23	999.99	
09 19 87			Clow airport, IL	41.72 N	88.22 W	11 11 87	1.751	-47.16	999.99	
09 23 87			Clow airport, IL	41.72 N	88.22 W	11 16 87	1.763	-47.21	999.99	
11 11 87			Clow airport, IL	41.72 N	88.22 W	00 00 00†	1.804	-47.23	999.99	
11 17 87			Clow airport, IL	41.72 N	88.22 W	00 00 00†	1.736	999.99	999.99	
11 21 87			Clow airport, IL	41.72 N	88.22 W	00 00 00†	1.790	-47.17	999.99	
11 23 87			Clow airport, IL	41.72 N	88.22 W	00 00 00†	1.793	-47.37	999.99	
12 09 87			Clow airport, IL	41.72 N	88.22 W	03 21 87	1.835	-47.19	999.99	
01 30 88			Clow airport, IL	41.72 N	88.22 W	04 15 88	1.843	-46.97	999.99	
02 06 88			Clow airport, IL	41.72 N	88.22 W	04 13 88	1.890	-46.99	999.99	

Date of Sample Collection	Mo Da Yr	No. ¹	Sampling Location and Reference No.	Latitude	Longitude	Date of Sample Analysis		CH ₄ Conc. (ppmv)	Measured $\delta^{13}\text{C}$ (‰)	Corrected $\delta^{13}\text{C}$ (‰)	No. of Analyses Averaged ²
						Mo	Da Yr				
03 26 88			Clow airport, IL	41.72 N	88.22 W	04	14 88	1.843	-47.15	999.99	
04 05 88			Clow airport, IL	41.72 N	88.22 W	00	00 00†	1.822	-46.89	999.99	
04 27 88			Clow airport, IL	41.72 N	88.22 W	00	00 00†	1.793	-47.11	999.99	
05 09 88			Clow airport, IL	41.72 N	88.22 W	00	00 00†	1.790	-46.83	999.99	
06 04 88			Clow airport, IL	41.72 N	88.22 W	00	00 00†	1.782	-46.78	999.99	
06 11 88			Clow airport, IL	41.72 N	88.22 W	00	00 00†	1.790	-47.01	999.99	
07 17 88			Clow airport, IL	41.72 N	88.22 W	00	00 00†	1.753	-47.06	999.99	
07 29 88			Clow airport, IL	41.72 N	88.22 W	00	00 00†	1.812	-47.05	999.99	
09 08 88			Plainfield, IL	41.60 N	88.08 W	09	09 88	1.785	-46.97	999.99	
09 08 88			Plainfield, IL	41.60 N	88.08 W	09	21 88	1.778	-47.07	999.99	
09 08 88			Plainfield, IL	41.60 N	88.08 W	10	11 88	1.798	-47.04	999.99	
09 08 88			Plainfield, IL	41.60 N	88.08 W	10	12 88	1.794	-47.27	999.99	
09 08 88			Plainfield, IL	41.60 N	88.08 W	10	13 88	1.807	-47.01	999.99	
09 08 88			Plainfield, IL	41.60 N	88.08 W	10	17 88	1.810	-47.08	999.99	
10 27 88			Clow airport, IL	41.72 N	88.22 W	03	03 89	1.810	-47.12	999.99	
12 04 88			Clow airport, IL	41.72 N	88.22 W	03	03 89	1.818	-47.02	999.99	
01 08 89			Clow airport, IL	41.72 N	88.22 W	03	03 89	1.842	-47.11	999.99	
02 07 89			Clow airport, IL	41.72 N	88.22 W	03	02 89	1.899	-47.09	999.99	
04 08 89			Clow airport, IL	41.72 N	88.22 W	05	02 89	1.794	-47.03	999.99	
05 02 89			Clow airport, IL	41.72 N	88.22 W	05	05 89	1.799	-46.77	999.99	
05 07 89			Book Road, DuPage Cty, IL	41.75 N	88.08 W	05	11 89	1.778	-46.90	999.99	

¹ Number of samples from different locations combined for a single analysis.

² An entry other than blank denotes a record whose $\delta^{13}\text{C}$ value is an average of those of the previous 2 to 5 entries (indicated by the symbol "+").

† Entry represents one of two or more repeated analyses carried out on the same air sample.

‡ Actual date of analysis is not given but was within one week of the date of collection.

* The measured value of $\delta^{13}\text{C}$ is considered to be an outlier and is not included in any subsequent averages.

Missing values for dates of collection or analysis are represented as 00. Missing values for CH₄ concentration are represented as 9.999. Missing values for $\delta^{13}\text{C}$ are represented as 999.99. Missing values for all other variables are represented as blanks.

APPENDIX B.

Reprint of Pertinent Literature

Isotopic abundances in the atmosphere and sources, by C.M. Stevens. 1993.

Chapter 4

Isotopic Abundances in the Atmosphere and Sources

C.M. STEVENS

Chemical Technology Division, Argonne National Laboratory, Argonne, IL 60439

1. Introduction

The ultimate goal of isotopic studies of atmospheric CH_4 is to contribute to the understanding of the atmospheric CH_4 cycle by determining the relative fluxes from various categories of sources and the causes of the increasing concentration (Stevens and Engelkemeir, 1988; Quay et al., 1988; Wahlen et al., 1989). Because the large number of generic anthropogenic source types makes it impossible to determine their relative strengths based on carbon-13 data alone, Stevens and Engelkemeir (1988) and Craig et al. (1988) used the isotopic data to calculate the flux of the source with the greatest uncertainty, namely biomass burning, making use of the estimated fluxes for the other sources from emission inventories. This method determined the flux and isotopic composition of the natural sources from the concentration and isotopic composition of CH_4 in old polar ice cores assuming the same lifetime as now. The lifetime was mostly determined by the fluxes based on the emissions inventories. This approach does not use the lifetime as a constraint nor contribute to the knowledge of the major sources, which have significant uncertainties in the estimates based on emissions inventories. A better approach is to start with the constraint of the lifetime value based on the methyl chloroform cycle (see Mayer et al., 1982; Khalil and Rasmussen, 1983; Prinn et al., 1987; Cicerone and Oremland, 1988). Then it is possible to calculate the fluxes of the two most isotopically different sources, providing an estimate based on emissions inventories for one of the anthropogenic sources is used as a constraint. A source is chosen that introduces the least error, namely landfills, which is one of the smallest and has an isotopic composition closest to the average.

Whiticar (this volume) discusses the overall cycles of CH_4 formation from the fundamental standpoint of the biogenic and thermogenic pathways and the isotopic fractionation effects at all stages from source generation to loss processes. The diverse and variable conditions for these fractionation effects hinder the isotopic characterization of the various generic sources and therefore the determination of a budget by this method. Examination of the measured values of the CH_4 produced by the various generic sources except fossil fuel sources (see Table 2) shows that they seem to fall in a narrow enough range to permit solving the budget with the practical approach of using these values directly, bypassing the fractionation effects of the formation pathways.

The following sections will summarize the knowledge about the flux strengths of the major anthropogenic sources using only the carbon isotopic results. Use is made of the carbon-14 results for the flux of "dead" CH_4 from fossil fuel sources as reported by others; the application of deuterium isotopic data to the atmospheric CH_4 is mentioned but not discussed in detail. The average measured isotopic compositions of the CH_4 produced by the various generic sources and released to the atmosphere are used to make up a budget whose isotopic composition is constrained to agree with the value determined from the atmospheric composition modified by the fractionation effect of the atmospheric removal process. The most recent determination of the kinetic isotope effect of the reaction $\text{CH}_4 + \text{OH}$ (Cantrell et al., 1990) is used. The results of calculations for the determination of the relative fluxes of the generic sources are shown subject to conditions for the lifetime. Measurements of the isotopic temporal trends, when considered with the constraints for the unequal distribution between hemispheres of the anthropogenic fluxes, lead to estimates of large increasing fluxes from biomass burning in the southern hemisphere and from natural fluxes in the northern hemisphere.

2. Isotopic composition of the sources

Table 1 lists the categories of the major sources of atmospheric CH_4 and the averages of the measured values of $\delta^{13}\text{C}$ reported by several laboratories.

Table 2 lists the measurements of $\delta^{13}\text{C}$ for the anthropogenic sources and the average values and 1 standard deviation (SD). These uncertainties were generally about $\pm 0.2\text{‰}$, except in the case of rice (± 0.05). The uncertainty for the value for rice has been made greater, $\pm 0.2\text{‰}$, to reflect an uncertainty from the lack of samples in the principal global rice growing areas. The uncertainty for the $\delta^{13}\text{C}$ of CH_4 from fossil fuels has been increased ($\pm 0.4\text{‰}$) from the indicated SD ($\pm 0.2\text{‰}$) of the measured values because of the very wide spread in the values and the uncertain distribution of a global emissions inventory. The non-anthropogenic source, sometimes called the "natural source," is not directly related to man's activities and consists of natural wetlands of all types, forest and savanna fires caused by lightning, oceans and lakes, any possible leakages from natural gas deposits, and termites. Natural wetlands constitute the major natural source.

Table 1. The carbon-13 isotopic composition of the sources of atmospheric CH₄. The uncertainty is estimated at ± 0.2 ‰, except (a), which is ± 0.4 ‰.

Source	$\delta^{13}\text{C}$
Natural (all non-anthropogenic)	-56.7
Rice Paddies	-64
Herbivores	-60
Landfills	-52
Natural Gas	-43 (a)
Coal Mining	-37 (a)
Biomass Burning	-22

Table 2. The carbon isotopic compositions of the anthropogenic sources of atmospheric CH₄.

Source	Method and number of samples	Mean $\delta^{13}\text{C}$ and range (‰)	Reference
RICE PADDIES			
California	Inversion (4)	-67 (-66 to -68)	Stevens and Engelkemeir, 1988
Louisiana	Flux Chamber (8)	-63.2 $\pm$ 2.9	Wahlen et al., 1989
Kenya	Flux Chamber (10)	-59.4 (-57 to -63)	Tyler et al., 1988
Vercelli, Italy	Flux Chamber (7)	-65.4 $\pm$ 1.6	
Average		-63.8 $\pm$ 1.5	Levin et al., 1993
RUMINANTS C₃ Diet			
Cattle	Fistula (5)	-63.7 (-61 to -76)	Rust, 1981
Cattle	Barn (1)	-61.1	Rust, 1981
Sheep	Fistula (2)	-68.6 (-67 to -70)	Rust, 1981
Cattle	Barn (4)	-71.3 $\pm$ 4	Wahlen et al., 1989
Cattle	Bag (1)	-65.1 $\pm$ 1.7	Levin et al., 1993
Sheep	Bag (1)	-70.6	Levin et al., 1993
Goat	Bag (1)	-65.2	Levin et al., 1993
Average		-63 $\pm$ 1.0	
RUMINANTS C₄ Diet			
Cattle	Fistula (3)	-50.3 (-47 to -51)	Rust, 1981
Cattle	Barn (1)	-45.4	Rust, 1981
Cattle (60-80% C ₄ diet)	Bag (3)	-55.6 $\pm$ 1.4	Levin et al., 1993
Average		-50 $\pm$ 3	
LANDFILLS			
Indiana		-50 (-48 to -52)	Games & Hayes, 1976
Colorado	Flux chamber (2)	-53 (-51 to -55Z)	Tyler, 1986
Heidelberg	Upper layers (1)	-52	Levin et al., 1993
Average		-52 $\pm$ 2	
NATURAL GAS			
Thermogenic 20%		-38 (-25 to -52)	Schoell, 1980
Biogenic 80%		-65 (-60 to -70)	Rice & Claypool, 1981
Average		-43 $\pm$ 4(a)	

Table 2. The carbon isotopic compositions of the anthropogenic sources of atmospheric CH₄.

Source	Method and number of samples	Mean $\delta^{13}\text{C}$ and range (‰)	Reference
COAL MINING		-37 $\pm$ 4 (-14 to -60)	Deines, 1980
BIOMASS BURNING			
Wood fire	Plume (3)	-27 (-24 to -32)	Stevens & Engelkemeir, 1988
Grass fire	Plume (1)	-32	"
Brush fire	Plume (2)	-26.6	Wahlen et al., 1989
Wood fire	Plume (1)	-26.4	Levin et al., 1993

Table 3 lists the measurements of the isotopic composition of CH₄ emitted from or contained in the sediment gases of the various natural wetlands, such as the arctic tundra, Amazon floodplain, peatlands, Everglades marsh and temperate marshes, lakes and ponds, and estuaries. However, it would be difficult to

Table 3. The carbon isotopic composition of CH₄ emitted from or contained in sediments of various natural wetlands.

Wetlands	Sampling Method	Mean $\delta^{13}\text{C}$ and Range (‰)	Reference
Alaska tundra	Flux chamber	-66 (-55 to -73)	Quay et al., 1988
"	Bubbles	-62 (-57 to -72)	Quay et al., 1988
Canadian tundra	Surface	-63 $\pm$ 1.9	Wahlen et al., 1989
USSR marshes	Not specified	-64 (-52 to -69)	Ovsyannikov & Lebedev, 1967
New England Lakes	Mud gases	-69 (-57 to -80)	Oona & Deevey, 1960
New York wetlands	Surface	-58 $\pm$ 2.4	Wahlen et al., 1989
Minnesota peat bog	Inversion	-67 (-64 to -71)	Stevens & Engelkemeir, 1988
"	Flux chamber	-66 (-57 to -77)	Quay et al., 1988
"	Bubbles	-66 (-50 to -86)	Quay et al., 1988
Amazon River	Surface	-64	Tyler, 1986
Kenya papyrus swamp	Flux chamber	-51 (-31 to -62)	Tyler et al., 1988
Kenya river	Flux chamber	-54	Tyler et al., 1988
Kenya lake	Flux chamber	-48 (-44 to -50)	Tyler et al., 1988
Amazon flood plain	Bubbles, 1985	-62 (-47 to -73)	Quay et al., 1988

Table 3. The carbon isotopic composition of CH₄ emitted from or contained in sediments of various natural wetlands.

Wetlands	Sampling Method	Mean $\delta^{13}\text{C}$ and Range (‰)	Reference
"	Bubbles, 1987	-52 (-42 to -60)	"
"	Dissolved in lakes	-56 (-41 to -66)	"
"	Flux chamber	-51 (-42 to -73)	"
"	Inversion	-52 (-49 to -56)	"
Florida Everglades	Inversion	-55 (-53 to -58)	Stevens & Engelkemeir, 1988
"	Sediment bubbles	-65 (-63 to -70)	Chanton et al., 1988
Florida, Crescent Lake	Flux chamber	-64 (-79 to -71)	Burke & Sackett, 1986
Florida, Mirror Lake	"	-55 (-52 to -56)	"
Florida, Lake Dias	"	-63 (-60 to -67)	"
Miss. River Delta	"	-60 (-59 to -60)	"
South Carolina pond	"	-53 (-51 to -55)	"
Florida, Tampa Bay estuary	"	-66 (-63 to -71)	"
Colorado pond	"	-53 (-52 to -54)	Tyler, 1986
North Carolina marine basin	Bubbles	-60 + 2 (summer)	Chanton & Martens, 1988
"	Flux chamber	-67 (-66 to -70)	"
Illinois slough	Flux chamber	-50 (-49 to -51)	Stevens & Engelkemeir, 1988
"	Sediment gases	-56 (-55 to -58)	"
Swamp, Heidelberg, Germany	Flux chamber	-57 $\pm$ 2	Levin et al., 1993

determine the global average isotopic composition of all of the natural sources from these data because the relative emission inventories of the contributions from the various natural wetlands types, as well as other natural sources such as forest fires, cannot be easily ascertained. A direct measure of this average value can be taken from the isotopic composition of atmospheric CH₄ for a time when anthropogenic emissions were negligible, assuming the makeup of the natural sources has remained the same. Methane in the air contained in 100- to 300-year-old ice cores has $\delta^{13}\text{C} = -49.6 \pm 0.7$ ‰ (Craig et al., 1988); this leads to the average value for all the natural sources at that time of -55.7 ‰, after applying the correction $\Theta = -6.0$ for the fractionating factor $\alpha = 0.994$ (Cantrell et al.,

1990) of the atmospheric loss processes, where $\Theta = (\alpha - 1)(1 + 10^{-3}\delta^{13}\text{C}_{\text{atm}})$. The fractionation factor of the atmospheric loss processes is the ratio of the loss rates of $^{13}\text{CH}_4$ and $^{12}\text{CH}_4$, mainly the relative oxidation rates of the reaction of CH_4 by OH radicals. Assuming that the fluxes of all the component natural sources have not changed in the interim, the value at the present time would be -56.7‰ due to a small correction of -1‰ for the decreasing carbon-13 abundance of atmospheric CO_2 caused by contributions from fossil fuel burning (Keeling et al., 1979; Friedli et al., 1986).

The major natural source is the emission from the natural wetlands. The isotopic composition of the northern wetlands, including the regions of the arctic tundra and peatlands and some of the Amazon flood plains and Florida Everglades, falls in the range -60 to -70‰ with an average of about -65‰ (Table 3). More enriched values of CH_4 , up to -50‰ , are observed for some northern mid-latitude lakes and ponds and some regions of the Amazon and the Florida Everglades. It is likely that the difference between -57‰ , the average for all natural sources derived from the atmospheric CH_4 in old polar ice cores, and -65‰ , for the major natural wetlands, is at least partially accounted for by isotopically heavy CH_4 emissions from natural forest and savanna fires.

The value of -64‰ shown for rice is the average of the measurements by Stevens and Engelkemeir (1988), Tyler et al. (1988), Wahlen et al. (1989), and Levin et al. (1993) and is very close to the average value for CH_4 from the majority of natural wetlands. For CH_4 from herbivores the value -60‰ is used, which is based on the comprehensive study by Rust (1981). The values of -43‰ for natural gas and -37‰ for coal mining are based on the means of the extensive compilations of Schoell (1980), Deines (1980), and Rice and Claypool (1981). These values are averages of available data and not weighted for the geographic flux distributions except for an estimated ratio of thermogenic and biogenic gas sources. For CH_4 from biomass burning a value of $\delta^{13}\text{C} = -22\text{‰}$ is used. This value is the weighted average of 80% due to C_3 plants and trees with an average isotopic composition of -25‰ (Craig, 1953) and 20% due to C_4 plants of tropical savanna fires with $\delta^{13}\text{C} = -12\text{‰}$. The measured values show little fractionation by the burning process from the isotopic composition of the biomass (Stevens and Engelkemeir, 1988; Wahlen et al., 1989). In order to reduce the number of independent variables, the CH_4 from rice paddies and herbivores are combined as a single generic source with an average $\delta^{13}\text{C}$ of -62‰ , based on the emissions inventories of the relative fluxes. The fluxes from natural gas and coal mining can be combined into one generic fossil fuel source with an average value of -41‰ , since the isotopic compositions are similar and both contain 100% "dead" carbon, i.e., no carbon-14.

3. Isotopic composition of atmospheric methane

Measurements of $\delta^{13}\text{C}$ of atmospheric CH_4 that have been done by various groups are listed in Table 4 and plotted in Figure 1. They agree well enough to determine the average value of the sources but not well enough to compare with

Table 4. Comparison of measurements of the carbon-13 isotopic composition of atmospheric CH₄; errors are 1 SD with numbers of samples in parentheses.

Laboratory	Year	$\delta^{13}\text{C}$ ‰ Southern Hemisphere	$\delta^{13}\text{C}$ ‰ Northern Hemisphere
A	1978.5	-47.84 ± .05 (4)	
	1978.8		-47.88 ± .14 (7)
"	1980.5	-47.52 ± .09 (3)	-47.78 ± .08 (5)
"	1981.5	-47.49 ± .09 (3)	-47.69 ± .02 (7)
"	1982.5	-47.35 ± .04 (4)	-47.74 ± .26 (4)
"	1983.25		-47.60 ± .05 (20)
"	1983.5		-47.61 ± .05 (7)
"	1983.75		-47.61 ± .04 (20)
"	1984.2	-47.15 ± .15 (1)	
"	1984.5		-47.53 ± .10 (5)
"	1985.5		-47.66 ± .08 (5)
"	1986.25		-47.28 ± .06 (11)
"	1986.75		-47.25 ± .06 (10)
"	1986.9	-46.71 ± .08 (6)	
"	1987.5		-47.21 ± .10 (6)
"	1988.25		-46.98 ± .05 (15)
"	1988.3	-46.49 ± .09 (6)	
"	1989.25		-47.00 ± .10 (7)
"	1989.3	-46.32 ± .10 (2)	
B	1976.5		-47.3 ± .2 (1)
"	1977.5		-46.9 ± .2 (1)
"	1978.5		-46.5 ± .2 (1)
"	1986.5		-46.7 ± .3 (27)
"	1986.8	-46.0 ± .2 (5)	
"	1987.5	-45.2 ± .3 (2)	-46.5 ± .2 (11)
"	1988.0	-46.6 ± .3 (4)	
C	1987 to 1989	-47.04 ± .2 (5)	-47.35 to -47.20 ± .13 (208)
D	1985.5		-46.5
E	1989.6 to 1991.8	-47.14 ± .03 (90)	

* A: Stevens, 1988. B: Wahlen et al., 1989. C: Quay et al., 1988. D: Tyler, 1986. E: Lassey et al., 1993.

each other for temporal trends or latitude gradients. There may be small real differences among these values due to different locations of sample collection, but the main differences are most likely caused by differences in sample preparation and calibration of the working isotopic standards used in the mass spectrometric analysis. Accurate calibration is a difficulty inherent in trying to establish to ± 0.1 ‰ the absolute accuracy of samples that differ by the large amount of -47 ‰ from the Peedee belemnite carbonate used as the common reference.

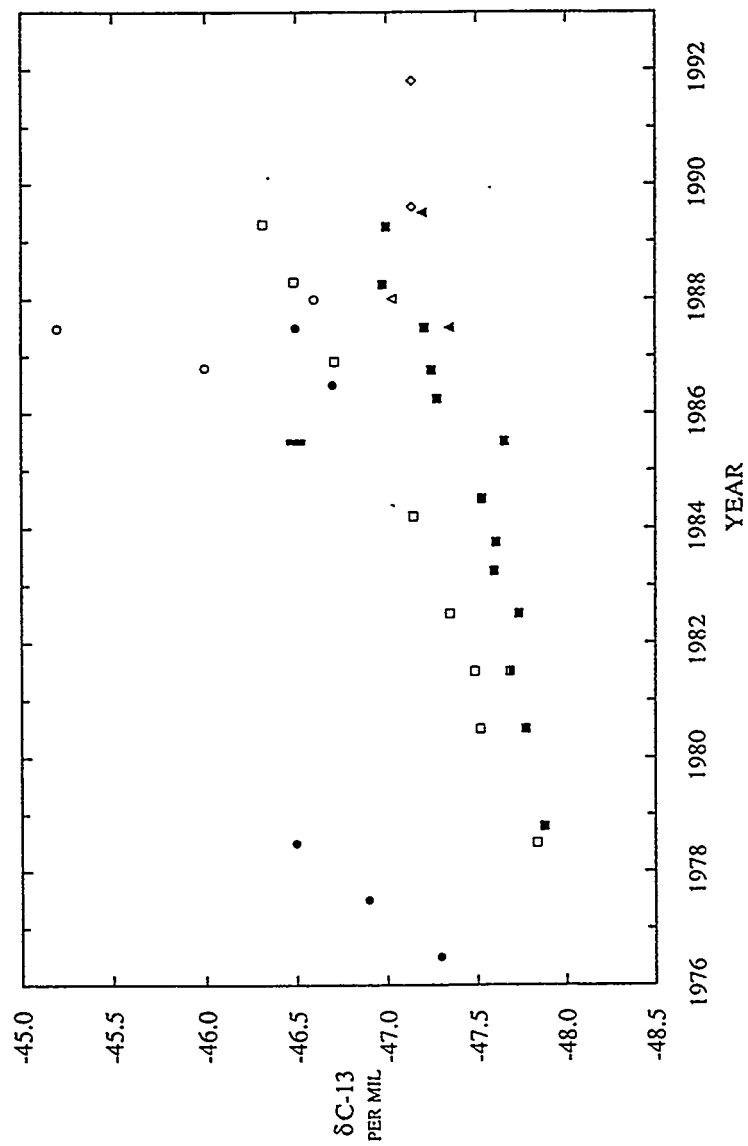


Figure 1. Comparison of measured values of $\delta^{13}\text{C}$ for atmospheric CH_4 in both hemispheres; open symbols SH, solid symbols NH, squares lab A, circles lab B, triangles lab C, upside down triangles lab D, diamonds lab E; Laboratory reference same as in Table 3. Error bars are 1 SD; numbers of samples are in parentheses. For location and source of samples see references cited in Table 4.

4. Calculation of source budgets

The overall objective is to determine the relative, if not absolute, fluxes of the five generic types of sources of atmospheric CH_4 . There are only three constraints based on measurable quantities of the overall CH_4 cycle; two of them are the two mass balance equations for $^{12}\text{CH}_4$ and $^{13}\text{CH}_4$ for the current (1978) condition of atmospheric CH_4 .

$$dC/dt = \sum F_i - C/\tau \quad (1)$$

$$d(C\delta_A)/dt = \sum F_i\delta_i - C(\delta_a + \Theta)/\tau \quad (2)$$

where C is the atmospheric burden in teragrams, F_i the individual fluxes, δ_i the isotopic composition of the sources, δ_A the average atmospheric isotopic composition, τ the lifetime and Θ the average fractionation factor of the atmospheric loss processes (-6.0‰). A third constraint is the abundance of $^{14}\text{CH}_4$ in atmospheric CH_4 , which determines the fraction of CH_4 from fossil fuel sources at 16 to 21% of the total flux in 1987 (Wahlen et al., 1989; Quay et al., 1991; Lowe et al., 1991). The reference year for these calculations is 1978; back correcting for the growth rates of 2.75 %/yr of both global natural gas and coal production (see Figure 2) exceeding the concentration growth by 1.75 %/yr, the flux from these combined sources in 1978 would have been 13 to 17 % of the total flux or 60 to 80 Tg/yr if the total flux was 460 Tg/yr for a lifetime of 10 years. The mass balance equations for $^{12}\text{CH}_4$ and $^{13}\text{CH}_4$ 100 to 300 years ago, based on measurements of CH_4 in old polar ice cores when the concentration was 45% of that in 1978 and representing mainly natural sources (Craig and Chou, 1982; Craig et al., 1988), are important for determining the average isotopic composition of the natural sources, $\delta^{13}\text{C} = -56.7\text{‰}$. The $^{12}\text{CH}_4$ mass balance might seem to supply another constraint for the natural flux, but the lifetime at that time is another unknown, making for no net change in the number of degrees of freedom. Using the constraints cited above, the solution for the unknown fluxes is under-determined with an excess of three degrees of freedom, the unknown lifetime for the ice-core CH_4 and the fluxes of the following sources: combined rice and herbivores, landfills, and biomass burning. Assuming the lifetime at the time the methane was trapped in the polar ice was the same as now, then the fluxes of two of the sources can be expressed in terms of a third. This is as far as the calculation of a budget can be done based on carbon isotopic data alone. To proceed further the emissions inventories estimate for one of the sources is used. Using the estimate for landfills introduces the least uncertainty. This estimate is 50 ± 20 Tg/yr (Bingemer and Crutzen, 1987). On this basis Table 5 lists the fluxes calculated for the fluxes of all the sources. These results show that for a lifetime of ten years the calculated combined fluxes from rice and herbivores of 110 Tg/yr disagrees by a large amount with the emissions inventory estimate of 180 ± 60 Tg/yr. Also, the values for the natural fluxes based on the CH_4 in polar ice cores are much greater than the emissions inventory estimate by Matthews and Fung (1987). With a lifetime of 8 years, the discrepancy

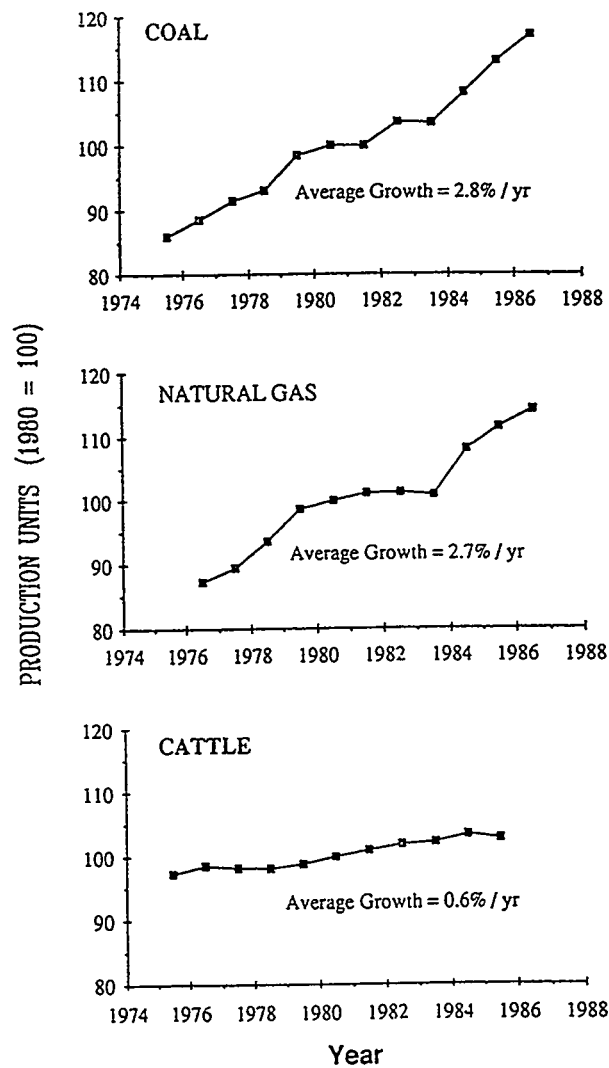


Figure 2. The growth rate for the global production of hard coal, natural gas, and cattle. Production units are based on setting the values for the year 1980 equal to 100 (from United Nations Statistical Yearbooks).

between the calculated values and the emissions inventory estimate becomes smaller for the combined rice and cattle flux and much larger for the natural fluxes. Figure 3 shows the calculated flux from the combined rice and herbivores versus the ratio of the lifetime in 1978 to the lifetime in pre-industrial times for lifetimes of 8 and 10 years in 1978. If the emissions inventory estimates for the combined fluxes of rice and herbivores are correct, then the lifetime has been decreasing since pre-industrial times by as much as 33%. The existing uncertainties for the lifetime as well as for the emissions inventory estimates of fluxes from rice and herbivores are the limiting factors in determining the natural fluxes, or the lifetime in pre-industrial times. There is other evidence that the

CALCULATED COMBINED FLUXES FROM RICE AND CATTLE

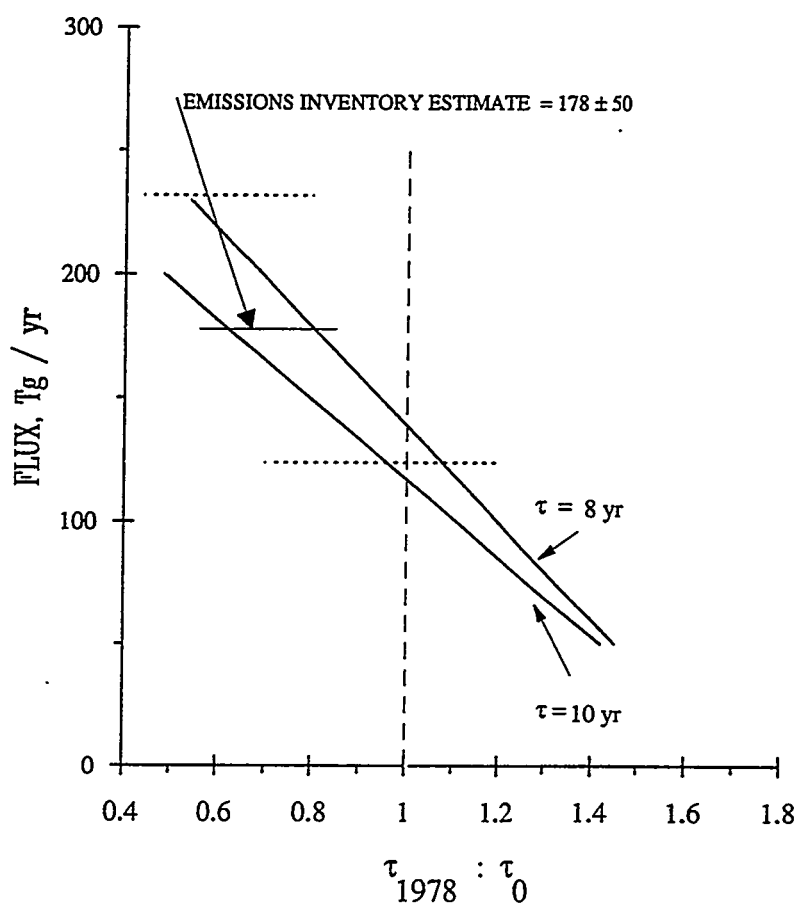


Figure 3. The calculated combined fluxes from rice and herbivores versus the ratio of the lifetime in 1978 to the lifetime in pre-industrial times for lifetimes of 8 and 10 years in 1978.

concentration of tropospheric ozone, the precursor of OH radicals that scavenge CH_4 , has been increasing in recent decades as well as in the past century (Logan, 1985; Hough and Derwent, 1990). In the following section on isotopic trends, other evidence is presented that shows that the sink rate in the northern hemisphere has been increasing in the past decade.

The flux from biomass burning that is calculated from the isotopic data in the above treatment falls in the narrow range of 37 to 50 Tg/yr if the flux from rice and herbivores is in the range of 110 to 178 Tg/yr. This is illustrated in Figure 4, which gives the fluxes from rice and herbivores versus the flux from biomass burning for a lifetime of ten years. A higher upper limit for the latter would seem unlikely since this would lead to unreasonably small fluxes for the natural sources.

Table 5. The fluxes of the sources of atmospheric CH₄ in 1978, assuming a constant lifetime over the age of the ice cores in which the concentration and isotopic composition were measured and based on the flux from landfills of 50 Tg/yr.

Source	% of total	Flux Tg/yr		
		10-year lifetime	8-year lifetime	Estimate by emissions inventory
Natural	41	189 (a)	236 (a)	100 (b)
Rice + Herbivores	24	110	146	178 ± 54 (c) ranges
Landfills	10.8	50	50	50 ± 20 (d) ranges
Fossil Fuel	17 ± 3	78	85	60 (e)
Biomass Burning	7.5	35	50	15 to 71 (f)

a. Lifetime assumed constant. b. Matthews and Fung, 1987. c. Schütz et al., 1989; Khalil and Rasmussen, 1991; Crutzen et al., 1986. d. Bingemer and Crutzen, 1987. e. Holzapfel-Pschorn and Seiler, 1986; Hitchcock and Wechsler, 1972. f. Crutzen and Andreae, 1990.

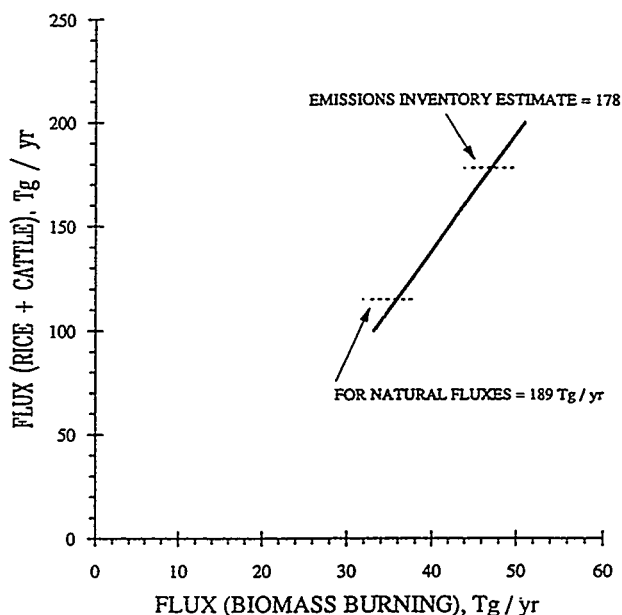


Figure 4. The calculated relationship between the combined fluxes from rice and herbivores and the fluxes from biomass burning for a lifetime of 10 years and the fluxes of the natural sources undetermined.

The isotopic abundance of deuterium in atmospheric CH₄ and its sources provide an additional constraint for a global CH₄ budget as shown by Wahlen et al. (1990). Their measurements show the global average δD for atmospheric CH₄ is -82 ‰, while δD for the biogenic CH₄ from the major wet environments sources is -290 to -360 ‰. The deuterium data provide additional constraints for calculating a budget of fluxes: first, the δD of the CH₄ from wet environments correlates with the δD of the local precipitation, which is latitude-dependent. This makes it possible to distinguish CH₄ from tropical and arctic

wetlands; secondly, the δD of fossil fuel CH_4 has a different relative composition compared to the value for CH_4 from wetlands than in the case for the carbon isotopes. The fractionation factor of $(\alpha - 1) = -0.330$ measured by Gordon and Mulac (1975) for the oxidation of CH_3D/CH_4 by OH radicals seems too large, leading to an average value for the sources more depleted than the value of the most depleted source. Wahlen et al. (1990) derives a value of -0.150 to -0.170 based on the enrichment of CH_3D in the stratosphere where the concentration decreases with altitude because of OH oxidation.

5. Temporal trends of the $\delta^{13}C$ ratio in atmospheric methane

The ice core data showed that the isotopic composition remained constant for 200 years while the concentration had increased from 0.65 to 1.2 ppm 3 to 5 decades ago (Craig et al., 1988). The 2 ‰ enrichment since then is attributed mainly to the heavy CH_4 from biomass burning and fossil fuel sources that must be increasing more rapidly than the increase in light CH_4 from rice and cattle.

Figure 5 shows the temporal trend of the carbon-13 isotopic composition of atmospheric CH_4 from 1978 to 1989 in both hemispheres. These plots are an update of earlier data reported by Stevens et al. (1985) and Stevens (1988). These data consist of analyses of 29 samples in the southern hemisphere (SH) and 129 in the northern hemisphere (NH), which are presented in this plot as annual averages. The slopes of these trends are greater by 0.04 ‰/yr than shown in an earlier publication of the same data up to 1987 (Stevens, 1988) because of a correction factor applied to the results of analyses done in 1983 of samples collected as far back as 1978 and stored. The oldest of these samples from 1978 collections were analyzed again five years later in 1988 and showed a small increase of $\delta^{13}C$ compared to the 1983 value, averaging 0.2 ‰, as well as slightly higher concentrations. The differences are interpreted as contamination with isotopically heavier CH_4 from the walls of the storage cylinders accumulating over the 5-year interval between analyses, amounting to a correction of -0.04 ‰ per year of the interval between collection and analysis of the stored air samples. This correction makes only a small change in the calculated trends of the isotopic composition of the sources in each hemisphere because the principal term in this calculation is the rate of change of the difference between the atmospheric $\delta^{13}C$ trends, which is not altered by this correction (see equations 3 and 4 below). The correction increases the slopes of the trends in both hemispheres somewhat, but the difference between them remains the same.

The results in Table 4 and Figure 1 show that laboratory B measured a difference in the isotopic values between hemispheres of 0.7 ± 0.3 ‰ in 1986-87 versus 0.5 ± 0.2 ‰ for laboratory A for the same years. The results of Lassey et al. (1993) (E) showed no change in the $\delta^{13}C$ of the SH from late 1989 to late 1991 with much smaller uncertainties and many more analyses per year (40 to 50) than any other group. This does not necessarily conflict with the increasing trend observed by lab A since the two studies do not overlap, and it is possible that there could have been a change in the trend as happened after 1983 in the NH data of laboratory A in Figure 5. A decrease in the trend of $\delta^{13}C$ in the SH

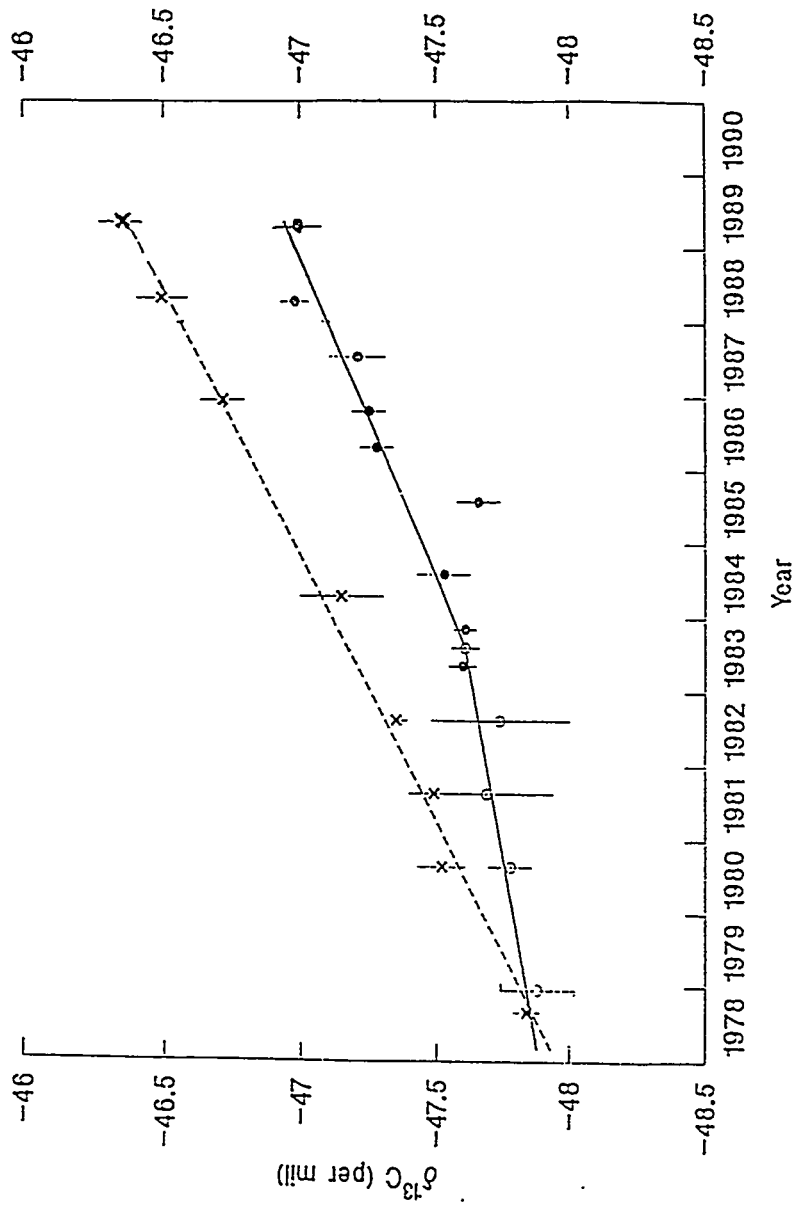


Figure 5. The stable carbon isotopic composition of atmospheric methane for the northern hemisphere (solid line) and southern hemisphere (dashed line) from 1978 to 1989. The points are the average values of annual or semi-annual sets of 4 to 15 measurements.

would result if there was a significant reduction in biomass burning in the Amazon in recent years.

During the decade 1978-88 the trend of $\delta^{13}\text{C}$ for atmospheric CH_4 was 0.14 ‰/yr in the SH and averaged 0.08 ‰/yr in the NH; there was a change in the slope in the NH after 1983 from 0.054 ± 0.017 to 0.112 ± 0.008 ‰/yr. The difference of 0.058 ± 0.019 ‰/yr between these trends is more than three times the standard deviation.

The trends of the average isotopic composition of the source fluxes in each hemisphere can be derived using a two box model of the atmosphere, with the mass balance equations for $^{13}\text{CH}_4$ and $^{12}\text{CH}_4$ taking into account the interhemispheric exchange. They are

$$d\delta_{\text{NS}}/dt = d\delta_{\text{NA}}/dt - \frac{\eta_{\text{ex}}(C_{\text{S}}/C_{\text{N}})[d(\delta_{\text{SA}} - \delta_{\text{NA}})/dt]}{\eta + dC/Cdt + \eta_{\text{ex}}C_{\text{N}}/C_{\text{S}} - 1} \quad (3)$$

$$d\delta_{\text{SS}}/dt = d\delta_{\text{SA}}/dt + \frac{\eta_{\text{ex}}(C_{\text{N}}/C_{\text{S}})[d(\delta_{\text{SA}} - \delta_{\text{NA}})/dt]}{\eta + dC/Cdt - \eta_{\text{ex}}[1 - C_{\text{S}}/C_{\text{N}}]} \quad (4)$$

where δ_{NA} and δ_{SA} are $\delta^{13}\text{C}$ of atmospheric CH_4 in the NH and SH respectively, δ_{SS} and δ_{NS} are $\delta^{13}\text{C}$ of the average CH_4 sources, and C_{N} and C_{S} are the concentrations in the respective hemispheres, η and η_{ex} are the loss rate and interhemispheric exchange rate. The $^{13}\text{C}/^{12}\text{C}$ ratio of the sources in the SH increased at an average rate of 0.63 ‰/yr for the decade (Figure 6). In that hemisphere, biomass burning is the major anthropogenic source; rice and cattle production are estimated at only 20 and 25%, respectively (Khalil and Rasmussen, 1983), of the global production, while losses from natural gas systems, coal mining, and landfills are negligible. The increasing trend can most plausibly be attributed to the increasing fluxes from the isotopically very heavy CH_4 from biomass burning associated with the rapid deforestation in that hemisphere in recent decades. The magnitude of the isotopic trend gives a quantitative measure of the rate of increase of biomass burning in the southern hemisphere from the relationship

$$\begin{aligned} dF_{\text{BB}}/dt &= \frac{F_{\text{S.H.}}[d(\delta_{\text{S.H.}})/dt]}{(\delta_{\text{BB}} - \delta_{\text{AVG}})} \\ &= 3.5 \text{ Tg/yr}^2 \end{aligned} \quad (5)$$

where F_{BB} is the flux from biomass burning in the southern hemisphere, $F_{\text{S.H.}}$ the total flux in the southern hemisphere of ca. 180 Tg/yr, and δ_{BB} , the isotopic composition for CH_4 from biomass burning, -22 ‰. This rate would be 0.2 Tg/yr² greater taking into account the increasing rates (1 to 2%/yr) of the small fluxes of light CH_4 from rice and cattle in this hemisphere. Since the increasing global concentration of atmospheric CH_4 is 1 ‰/yr (Blake and Rowland, 1988;

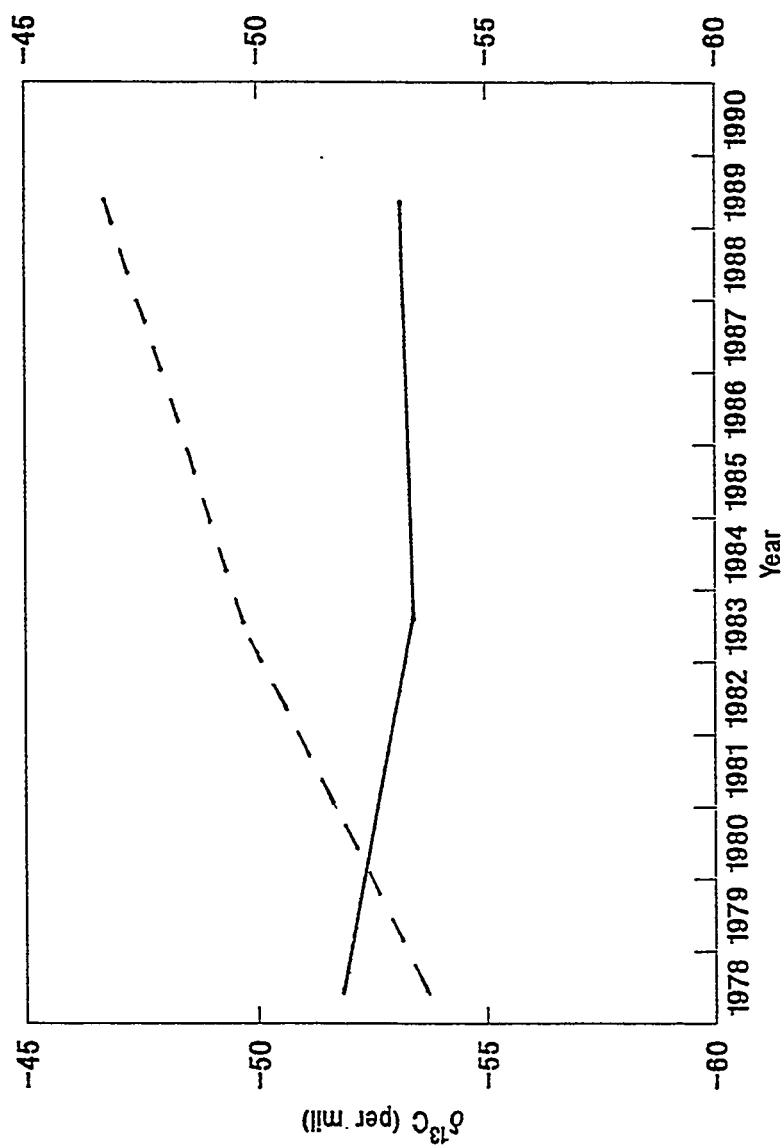


Figure 6. The trends of $\delta^{13}\text{C}$ for the SOURCES of CH_4 in the southern hemisphere (dashed line) and northern hemisphere (solid line) from 1978 to 1988, calculated for a lifetime of 10 years.

Khalil and Rasmussen, 1990) and the global flux is about 500 Tg/yr, the increasing fluxes from biomass burning in the southern hemisphere account for 50% of the increasing concentration and must be its leading cause, assuming the other 50% is due to increasing fluxes of all the anthropogenic sources in the northern hemisphere and the sink rate and fluxes of the natural sources are constant. Analysis of the trends in the northern hemisphere will show that both the fluxes of the natural sources and the loss rate are probably increasing; however, biomass burning in the southern hemisphere is the major anthropogenic source contributing to the increase in the concentration.

The trend of the $\delta^{13}\text{C}$ of the sources in the northern hemisphere averaged -0.17 ± 0.03 ‰/yr over the decade. The slope was -0.36 ‰/yr until 1983, when it changed to $+0.02$ ‰/yr. Table 6 lists the calculated average rate of change for the decade based on estimates of the rates of growth of the isotopically light and heavy CH_4 fluxes of the anthropogenic sources in this hemisphere as $+0.02$ to $+0.08$ ‰/yr; the measured trend is significantly different by -0.19 to -0.25 ‰/yr. The disparity with the average measured trend is too large to be explained by uncertainties in the factors involved in the calculation, namely, rates of growth and fluxes. The difference implies that there was a much greater increase in the fluxes of isotopically light CH_4 than can be reasonably accounted for by the increases in the production of rice and cattle, the only light anthropogenic sources. A plausible explanation is that the fluxes of the natural sources were changing (i.e., some combination of increasing light CH_4 or decreasing heavy CH_4 fluxes). The former possibility seems more likely because the temperate zone wetlands in the subarctic regions of the NH account for a major fraction of the global natural sources (Matthews and Fung, 1987) and produce light CH_4 (Quay

Table 6. The calculated contribution of the increasing fluxes of the anthropogenic sources to the trend of the average isotopic composition of the sources for the northern hemisphere from 1978 to 1989 and comparison with the measured change.

Source	Flux (Tg/yr)	Growth Rate (%/yr)	$(\delta^{13}\text{C}_i - \delta^{13}\text{C}_{\text{avg}})$ (‰)	$d(\delta^{13}\text{C})/dt$ (‰/yr)
Rice	80	0.5 to 1.0?	-12	-0.016 to
Cattle	68	0.6	- 8	-0.032?
Landfills	50	2.0 (a)	+ 2	-0.009
Fossil Fuel	69	2.75	+12	+0.003
Biomass	20 (b)	0 to 2 (a)	+22	+0.06
Burning				+0 to 0.04

Calculated Total = $+0.02$ to $+0.08$ ‰/yr

Measured rate = -0.17 ‰/yr

DIFFERENCE = -0.19 to -0.25 ‰/yr

The indicated difference corresponds to 4 to 6 Tg/yr^2 in the rate of increase of a flux of CH_4 having $\delta^{13}\text{C} = -65$ ‰.

a. Assumed rate equals population growth.

b. Flux in the northern hemisphere assumed to be half of the lower limit of the range calculated for biomass burning shown in Figure 3, 40 Tg/yr.

et al., 1988). There was an increase in global temperature from 1975 to 1982 that could have caused increases in fluxes from these wetlands (Harriss, 1989), as well as increasing fluxes from rice paddies that were not accounted for by increasing acreage. The change in slope for the NH in 1983 coincides with a decrease in the slope of the global concentration trend after 1983 (Khalil and Rasmussen, 1990); thus, for the two phenomena to be caused by the same event would require a relatively rapid change over a few years of either a decrease of isotopically light fluxes or an increase in the loss rate. Based on the ratio of the change in slope of the isotopic trend to the change in slope of the concentration trend, the former possibility is more likely. This is further supported by the evidence of a pronounced cooling of 1°C during 1984-85 for the northern temperate zone (Angell, personal communication), which might have caused decreased fluxes from these northern wetlands and the change in the slope of the isotopic trend observed after 1983. The trend of the isotopic composition of atmospheric CH_4 might be a simple indicator of average temperature trends in the regions of the northern temperate zone wetlands. There is evidence that the arctic regions have undergone amplified warming (Lachenbruch and Marshall, 1986), which is predicted in models of climate change. Continuous monitoring of the isotopic trends in both hemispheres over the coming decades might be a means of indicating these changes. The results of the trend data show increasing fluxes of biomass burning in the SH of 3.5 Tg/yr and increasing light CH_4 fluxes in the NH of 4.2 Tg/yr . Adding these to the increasing fluxes from the other anthropogenic sources from increasing production of rice (1.0 Tg/yr), cattle (0.4 Tg/yr), and fossil fuel (1.7 Tg/yr) gives a total of 10.8 to 15.1 Tg/yr , or two to three times the total based on the increasing concentration of $1\text{ \%/yr}$ for an annual flux of 460 Tg/yr in 1978. From this it is deduced that the loss rate must be increasing by about 1 to $2\text{ \%/yr}$.

6. Summary

Carbon isotopic data have been used to elucidate three features of the atmospheric CH_4 cycle: (1) the magnitude of the fluxes from the combined rice and cattle source and from biomass burning, (2) annual rates of change for the fluxes of biomass burning in the SH and natural wetlands in the NH, and (3) indirect evidence of changes in the loss rate.

The sources of atmospheric CH_4 have been divided into five categories (Table 5) based on a combination of similar isotopic composition or source characteristics. The fraction of the annual flux due to fossil fuel sources can be determined from carbon-14 measurements. The flux of the natural source is based on the concentration of CH_4 in pre-industrial times as measured in polar ice cores with the caveat of possible changes in the lifetime. Taking the flux of the less important source of landfills based on emissions inventory data, then the carbon-13 data are limited to the determination of the ratio of the fluxes of the two remaining and isotopically different sources, namely those of heavy CH_4 from biomass burning and light CH_4 from the combined sources of rice paddies and

ruminants. This ratio is subject to the possibility of changes in the lifetime (increasing loss rate) as shown in Figures 3 and 4.

The different isotopic trends for the two hemispheres are analyzed with the following conclusions: The isotopic composition of the overall sources in the southern hemisphere is becoming heavier and is most likely due to heavy CH_4 from the only important anthropogenic source in this hemisphere, burning of biomass, which has been increasing rapidly in recent decades in this hemisphere. The northern hemisphere showed an increasing net depletion of $^{13}\text{CH}_4$ of the source CH_4 during the past decade after taking account of increasing anthropogenic fluxes, as well as an abrupt increase of $^{13}\text{CH}_4$ in 1984-85. These changes are interpreted as caused by changing emissions of the isotopically light CH_4 from the natural northern wetlands as well as rice paddies due to climate changes.

Finally, there are indications from both the budget calculations and trend results that the sink rate has been increasing. Because of these important findings, especially the possibility of the natural fluxes changing with climate change, there should be continuing measurements of the isotopic trends in both hemispheres. It would be best to have these analyses for both hemispheres done by the same laboratory using the same processing techniques and isotopic measurement standards in order to avoid the difficult calibration problems between different laboratories.

Acknowledgements. The preparation of the graphics was by Carter Lewis. Work performed under the auspices of the Interdisciplinary Research Program in Earth Sciences, National Aeronautics and Space Administration, Order No. W-16188, and the Office of Basic Energy Sciences, Division of Mathematical and Geosciences, U. S. Department of Energy, under Contract No. W-31-109-Eng-38, and the U.S. Environmental Protection Agency through Interagency Agreement, Reference No. DW 89934989-01-0.

References

- Bingemer, H.G., P.J. Crutzen. 1987. The production of methane from solid wastes. *J. Geophys. Res.*, 92:2,181-2,187.
- Blake, D.R., F.S. Rowland. 1988. Continuing worldwide increase in tropospheric methane. *Science*, 239:1,129-1,131.
- Burke, R.A., W.M. Sackett. 1986. Stable hydrogen and carbon isotopic compositions of biogenic methane from several shallow aquatic environments. In: *Organic Marine Geochemistry* (M.L. Sohn, ed.), American Chemical Society, Washington, D.C., p. 297.
- Cantrell, C.A., R.E. Shetter, A.H. McDaniel, J.G. Calvert, J.A. Davidson, D.C. Lowe, S.C. Tyler, R.J. Cicerone, J.P. Greenberg. 1990. Carbon kinetic isotope effect in the oxidation of methane by hydroxyl radicals. *J. Geophys. Res.*, 95:22,455-22,462.
- Chanton, J.P., C.S. Martens. 1988. Seasonal variations in ebullitive flux and carbon isotopic composition of methane in a tidal freshwater estuary. *Global Biogeochem. Cycles*, 2:289.

- Chanton, J.P., G.G. Pauly, C.S. Martens, N.E. Blair. 1988. Carbon isotopic composition of methane in Florida Everglades soils and fractionation during its transport to the troposphere. *Global Biogeochem. Cycles*, 2:245.
- Cicerone, R.J., R.S. Oremland. 1988. Biogeochemical aspects of atmospheric methane. *Global Biogeochemical Cycles*, 2:299-327.
- Craig, H. 1953. The geochemistry of the stable carbon isotopes. *Geochim. Cosmochim. Acta*, 3:53-92.
- Craig, H., C.C. Chou. 1982. Methane: The record in polar ice cores. *Geophys. Res. Lett.*, 9:1,212-1,224.
- Craig, H., C.C. Chou, C.M. Stevens, A. Engelkemeir. 1988. Isotopic composition of methane in polar ice cores. *Science*, 242:1,535-1,539.
- Crutzen, P.J., M.O. Andreae. 1990. Biomass burning in the tropics: Impact on atmospheric chemistry and biogeochemical cycles. *Science*, 250:1,669.
- Crutzen, P.J., I. Aselmann, W. Seiler. 1986. Methane production by domestic animals, wild ruminants, other herbivorous fauna, and humans. *Tellus*, 38B:271-284.
- Deines, P. 1980. The isotopic composition of reduced organic carbon. In: *Handbook of Environmental Isotope Geochemistry, Vol. 1* (P. Fritz and J.C. Fontes, eds.), Elsevier Scientific, Chapter 9, p. 329-406.
- Friedli, H., H. Lotscher, H. Oeschger, U. Siegenthaler, B. Stauffer. 1986. Ice core record of the $^{13}\text{C}/^{12}\text{C}$ ratio of Atmospheric CO_2 in the past two centuries. *Nature*, 324:237.
- Games, L.M., J.M. Hayes. 1976. On the mechanisms of CO_2 and CH_4 production in natural anaerobic environments. In: *Proc. of the 2nd International Conference on Environmental Biogeochemistry, Vol. 1* (J.O. Nriague, ed.), Butterworth, Stoneham, Mass., p 51.
- Gordon, S., W.A. Mulac. 1975. Reactions of the OH (X^2II) radical produced by the pulse radiolysis of water vapor. *Int. J. Chem. Kinet.*, 7:289.
- Harriss, R.C. 1989. Historical trends in atmospheric methane concentration and the temperature sensitivity of methane outgassing from boreal and polar regions. In: *Proceedings of a Joint Symposium by the Board on Atmospheric Sciences and Climate and the Committee on Global Change Commission on Physical Sciences, Mathematics and Resources*. National Academic Press, Washington D.C., p. 79.
- Hitchcock, D.R., A.E. Wechsler. 1972. Biological cycling of atmospheric trace gases. Contr. Rep. NASA-CR 126663. Natl. Aeron. Space Adm., Washington D.C., p. 117.
- Holzappel-Pschorn, A., W. Seiler. 1986. Methane during a cultivation period from an Italian rice paddy. *J. Geophys. Res.*, 91:11,803.
- Hough, A., R.G. Derwent. 1990. Changes in the global concentration of tropospheric ozone due to human activities. *Nature*, 344:645.
- Keeling, C.D., W.G. Mook, P.P. Tans. 1979. Recent trends in the $^{13}\text{C}/^{12}\text{C}$ ratio of atmospheric carbon dioxide. *Nature*, 277:121.
- Khalil, M.A.K., R.A. Rasmussen. 1983. Sources, sinks, and seasonal cycles of atmospheric methane. *J. Geophys. Res.*, 88:5,131-5,144.
- Khalil, M.A.K., R.A. Rasmussen. 1990. Atmospheric methane: Recent global trends. *Environ. Sci. Technol.*, 24:549.
- Khalil, M.A.K., R.A. Rasmussen. 1991. Methane emissions from rice fields in China. *Environ. Sci. Technol.*, 25:979.
- Lachenbruch, A.H., B.V. Marshall. 1986. Changing climate: Geothermal evidence from permafrost in the Alaskan Arctic. *Science*, 234:689.
- Lassey, K.R., D.C. Lowe, C.A.M. Brenninkmeijer, A.J. Gomez. 1993. Atmospheric methane and its carbon isotopes in the southern hemisphere: Their time series and an instructive model. *Chemosphere*, 26 (1-4):95-110.

- Levin, I., P. Bergamaschi, H. Dörr, D. Trapp. 1993. Stable isotopic signature of methane from different sources in western Europe. *Chemosphere*, 26 (1-4):161-178.
- Logan, J.A. 1985. Tropospheric ozone: Seasonal behavior, trends and anthropogenic influence. *J. Geophys. Res.*, 90:10,463.
- Lowe, D.C., C.A.M. Brenninkmeijer, S.C. Tyler, E.J. Dlugokencky. 1991. Determination of the isotopic composition of atmospheric methane and its application in the antarctic. *J. Geophys. Res.*, 96:15,455-15,467.
- Matthews, E., I. Fung. 1987. Methane emissions from natural wetlands: Global distribution area, and environmental characteristics of sources. *Global Biogeochem. Cycles*, 1:61.
- Mayer, E.W., D.R. Blake, S.C. Tyler, Y. Makide, D.C. Montague, F.S. Rowland. 1982. Methane: interhemispheric concentration gradient and atmospheric residence time. *Proc., Natl. Acad. Sci.*, 79:1,366-1,370.
- Oona, S., E.S. Deevey. 1960. Carbon 13 in lake waters and its possible bearing on paleolimnology. *Am. J. Sci.*, 258A:253.
- Ovsyannikov, V.M., V.S. Lebedev. 1967. Isotopic composition of carbon in gases of biogenic origin. *Geochem. Int.*, 4:453.
- Prinn, R., D. Cunnold, R.A. Rasmussen, P. Simmonds, F. Alyea, A. Crawford, P. Fraser, R. Rosen. 1987. Atmospheric trends in methylchloroform and the global average for the hydroxyl radical. *Science*, 238:945.
- Quay, P., S.L. King, J.M. Lansdown, D.O. Wilbur. 1988. Isotopic composition of methane released from wetlands: Implications for the increase in atmospheric methane. *Global Biogeochem. Cycles*, 2:385.
- Quay, P., S.L. King, J. Stutsman, D.O. Wilbur, L.P. Steele, I. Fung, R.H. Gammon, T.A. Brown, G.W. Farwell, P.M. Grootes, F.H. Schmidt. 1991. Carbon isotopic composition of atmospheric CH₄: fossil and biomass burning source strengths. *Global Biogeochem. Cycles*, 5:25.
- Rice, D.D., G.E. Claypool. 1981. Generation, accumulation and resource potential of biogenic gas. *Bull. Am. Assoc. Pet. Geol.*, 65:5.
- Rust, F.E. 1981. Ruminant methane $\delta(^{13}\text{C}/^{12}\text{C})$ values: Relationship to atmospheric methane. *Science*, 211:1,044-1,046.
- Schoell, M. 1980. The hydrogen and carbon isotopic composition of methane from natural gases of various origins. *Geochem. Cosmochim. Acta*, 44:649.
- Schütz, H., A. Holzapfel-Pschorn, R. Conrad, H. Rennenberg, W. Seiler. 1989. A 3-year continuous record on the influence of daytime, season, and fertilizer treatment on methane emission rates from an Italian rice paddy. *J. Geophys. Res.*, 94:16,405.
- Stevens, C. 1988. Atmospheric methane. *Chem. Geol.*, 71:11.
- Stevens, C., A. Engelkemeir. 1988. Stable carbon isotopic composition of methane from some natural and anthropogenic sources. *J. Geophys. Res.*, 93:725.
- Stevens, C., A. Engelkemeir, R. Rasmussen. 1985. Causes of increasing methane fluxes based on carbon isotope studies. In: *Special Environmental Report No. 16 (WMO-No.647)*; Lectures presented at the WMO Technical Conference on Observations and Measurement of Atmospheric Contaminants. World Meteorol. Org., Geneva, Switzerland, p. 237.
- Tyler, S.C. 1986. Stable carbon isotope ratios in atmospheric methane and some of its sources. *J. Geophys. Res.*, 91:13,232.
- Tyler, S.C., P.R. Zimmerman, C. Cumberbatch, J. Greenberg, C. Westberg, J.P.E.C. Darlington. 1988. Measurements and interpretation of $\delta^{13}\text{C}$ of methane from termites, rice paddies, and wetlands in Kenya. *Global Biogeochem. Cycles*, 2:341.
- United Nations Statistical Yearbook. 1988.

- Wahlen, M., N. Tanaka, R. Henry, B. Deck, Zeglan, J.S. Vogel, J. Southon, A. Shemesh, R. Fairbanks, W. Broecker. 1989. Carbon-14 in methane sources and in atmospheric methane: The contribution from fossil carbon. *Science*, 245:286.
- Wahlen, M., N. Tanaka, B. Deck, R. Henry. 1990. δD in CH_4 : Additional constraints for a global budget. *EOS*, 71 (43):1,249.

INTERNAL DISTRIBUTION

1. L. D. Bates
2. B. A. Berven
3. T. A. Boden
4. B. A. Berven
5. R. B. Cook
6. J. H. Cushman
7. R. M. Cushman
8. V. H. Dale
9. N. T. Edwards
10. M. P. Farrell
11. D. E. Fowler
12. S. G. Hildebrand
13. G. K. Jacobs
14. S. B. Jones
15. P. Kanciruk
16. J. M. Loar
17. L. J. Morris
18. D. E. Reichle
19. R. J. Sepanski
20. F. E. Sharples
21. D. S. Shriner
22. L. D. Voorhees
- 23-222. CDIAC
223. Central Research Library
- 224-239. ESD Library
- 240-241. Laboratory Records Department
242. Laboratory Records, RC
243. ORNL Patent Section
244. ORNL Y-12 Technical Library

EXTERNAL DISTRIBUTION

245. D. Alvic, EERC/UT, Pellissippi Office, Ste. 100, 10521 Research Drive, Knoxville, TN 37932
246. Donald R. Blake, Department of Chemistry, University of California, Irvine, CA 92717
247. Roger C. Dahlman, Global Change Research Program, Environmental Sciences Division, Office of Health and Environmental Research, ER-74, U.S. Department of Energy, Washington, DC 20585

249. Edward J. Dlugokencky, Carbon Cycle Division, National Oceanic and Atmospheric Administration, Climate Monitoring and Diagnostics Laboratory, 325 Broadway, Boulder, CO 80303-3328
250. R. N. Farvolden, Professor, Department of Earth Sciences, University of Waterloo, Waterloo, Ontario N2L 3G1 Canada
251. Dr. Diana W. Freckman, Director, College of Natural Resources, 101 Natural Resources Building, Colorado State University, Fort Collins, CO 80523
252. Ian R. Gross, Rights and Permissions Administrator, Springer-Verlag New York, Inc., 175 Fifth Avenue, New York, NY 10010-7858
253. M.A.K. Khalil, Oregon Graduate Institute of Science and Technology, Global Change Research Center, P.O. Box 91000, Portland, OR 97291-1000
254. Ingeborg Levin, University of Heidelberg, Inst. für Umweltphysik, Im Neuenheimer Feld 366, 6900 Heidelberg, Germany
255. Martin R. Manning, National Institute of Water and Atmospheric Research, Ltd., Climate Division, Gracefield Road, Gracefield, P.O. Box 31-311, Lower Hutt, New Zealand
256. Bobbi Parra, Global Change Research Program, Environmental Sciences Division, Office of Health and Environmental Research, ER-74, U.S. Department of Energy, Washington, DC 20585
257. Paul D. Quay, University of Washington, School of Oceanography, WB-10, Seattle, WA 98195
258. G. Y. Jordy, Director, Office of Program Analysis, Office of Energy Research, ER-30, G-226, U.S. Department of Energy, Washington, DC 20585
259. Ari Patrinos, Acting Director Office of Health and Environmental Research, ER-74, U.S. Department of Energy, Washington, DC 20585
260. R. A. Rasmussen, Oregon Graduate Institute of Science and Technology, Global Change Research Center, P.O. Box 91000, Portland, OR 97291-1000
261. Michael R. Riches, Acting Director, Environmental Sciences Division, Office of Health and Environmental Research, ER-74, U.S. Department of Energy, Washington, DC 20585
262. G. S. Sayler, Professor, 10515 Research Drive, Suite 100, The University of Tennessee, Knoxville, TN 37932-2567
263. L. Paul Steele, Commonwealth Scientific and Industrial Research Organization, Division of Atmospheric Research, Private Bag No. 1, Mordialloc, Victoria 3195, Australia
- 264-268. Charles M. Stevens, Analytical Chemistry Laboratory, Chemical Technology Division, Argonne National Laboratory, 9700 South Cass Avenue, Argonne, IL 60439-4831

- 269. Pieter P. Tans, Carbon Cycle Division, National Oceanic and Atmospheric Administration, Climate Monitoring and Diagnostics Laboratory, 325 Broadway, Boulder, CO 80303-3328
- 270. Martin Wahlen, Scripps Institute of Oceanography, University of California, La Jolla, CA 92093-0220
- 271. F. J. Wobber, Environmental Sciences Division, Office of Health and Environmental Research, Office of Energy Research, ER-74, U.S. Department of Energy, Washington, DC 20585
- 272. Douglas E. J. Worthy, Environment Canada, Atmospheric Environment Service, 4905 Dufferin Street, Downsview, Ontario M3H 5T4, Canada
- 273. Office of Assistant Manager for Energy Research and Development, U.S. Department of Energy Oak Ridge Operations, P. O. Box 2001, Oak Ridge, TN 37831-8600
- 274-275. Office of Scientific and Technical Information, P. O. Box 62, Oak Ridge, TN 37831