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Carbon-14 in Methane Sources and in Atmospheric Methane: The Contribution from Fossil Carbon

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Measurements of carbon-14 in small samples of methane from major biogenic sources, from biomass burning, and in "clean air" samples from both the Northern and Southern hemispheres reveal that methane from ruminants contains contemporary carbon, whereas that from wetlands, peat bogs, rice fields, and tundra is somewhat, depleted in carbon-14. Atmospheric $^{14}CH_4$ seems to have increased from 1986 to 1987, and levels at the end of 1987 were 123.3 ± 0.8 percent modern carbon (pMC) in the Northern Hemisphere and 120.0 ± 0.7 pMC in the Southern Hemisphere. Model calculations of source partitioning based on the carbon-14 data, CH_4 concentrations, and $\delta^{13}C$ in CH_4 indicate that 21 ± 3% of atmospheric CH_4 was derived from fossil carbon at the end of 1987. The data also indicate that pressurized water reactors are an increasingly important source of $^{14}CH_4$.

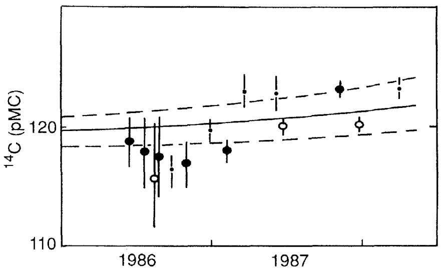

Fig. 1. Atmospheric $^{14}CH_4$ concentration for the sampling period 1986 to 1988. Large data points represent average values and SD for sample series of ocean surface air (Table 2), with the number of samples as in Table 2. Filled circles, Northern Hemisphere data; open circles, Southern Hemisphere data; small data points represent single Northern Hemisphere "clean" land air samples, except for December 1986 (five samples) and March 1988 (two samples). Solid line, model prediction for global average value from one-box model; broken lines, same for Northern Hemisphere (upper) and Southern Hemisphere (lower) average values from two-box model (see text).

METHANE IS A STRONG INFRARED absorber that directly and indirectly affects atmospheric temperature (*1*). It also influences tropospheric and stratospheric ozone concentrations (*2*) and is a major source of stratospheric water (*3*). The atmospheric concentration has more than doubled during the past 200 years (*4*). This increase, mostly attributed to human activities, is about three times as great as the natural concentration variations that occurred between glacial and interglacial times (*5*). The concentration continues to increase by about 1% per year (*6*). Destruction of CH_4 occurs mainly through reaction with OH radicals, and the tropospheric lifetime is 8 to 12 years. Methane is produced bacterially from wet environments (wetlands, rice fields, and tundra) and from ruminants and possibly termites. Additional contributions are from natural gas, coal mining, and biomass burning. The annual production rate and the magnitude of the individual source terms are not well known. Various estimates have come from flux measurements (*7*), atmospheric chemistry (*8*), biostatistical surveys (*9*), and modeling of atmospheric concentration data (*10*).

Derivation of a quantitative budget of CH_4 from ^{13}C, deuterium, and ^{14}C is an approach similar to that proposed for ^{13}C by Stevens and Rust (*11*). If methane from the various sources can be distinguished and characterized isotopically, then in principle a budget can be obtained from comparison of the isotopic composition of source methane to that of the atmosphere. The $^{14}CH_4$ content of the atmosphere is particularly sensitive to the contribution from fossil carbon (^{14}C free), which is thought to come from losses during exploration and distribution of natural gas, from coal mining, and from natural seepage from gas reservoirs. We have measured ^{14}C and ^{13}C in CH_4 from the atmosphere in both the Northern and Southern hemispheres and from various sources and used this data to determine a global CH_4 budget from 1950 to 1987.

Large volume air samples (about 0.5 to 1.5 m^3) were collected into Al gas tanks with three-stage Al air compressors. Methane from ecosystems was sampled in various ways, either retrieved as above from large volume (5 to 10 m^3 and 10 to 20 m^2) flux-box enclosures, from beneath near-surface atmospheric inversion over strong sources (up to two times the background atmospheric CH_4 concentration has been observed over bogs and rice fields), or from bubbles collected with an inverted funnel. Major and minor trace gas concentrations in the samples were measured by gas chromatography. In order to collect other trace constituents (for example, ^{85}Kr), CH_4 and Kr were completely separated from the air samples with adsorption-desorption and gas chromatographic techniques (*12*). The separated CH_4 was then combusted to CO_2 (*13*) and analyzed (*14–19*).

The atmospheric surface air samples were primarily collected over the oceans. We considered land surface air samples to be uncontaminated by local sources if the measured methane concentration did not exceed by more than 3% the one expected for that latitude and time from worldwide measurements (*20*). The atmospheric $^{14}CH_4$ activity increased during the time period covered at a rate of about 2 to 3% per year (Fig. 1). We cannot exclude the possibility that part of the exhibited variability may be seasonal. We detected a small interhemispheric difference of about 3 pMC; the $^{14}CH_4$ activity was 123.3 ± 0.8 pMC in the mid-latitude

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Northern Hemisphere, and 120.0 ± 0.7 pMC in the Southern Hemisphere at the end of 1987. This difference was expected because of the rapidly rising contribution of $^{14}CH_4$ from pressurized light-water reactors (PWR). This emission began around 1960, is a predominantly Northern Hemisphere source, and currently contributes substantially to the atmospheric $^{14}CH_4$ burden. The PWRs operate with H_2 as cover gas. Thus the ^{14}C produced from the $^{17}O(n,\alpha)^{14}C$ and $^{14}N(n,p)^{14}C$ reactions in water and in nitrogen impurities tends to form reduced species, mainly $^{14}CH_4$.

The $^{14}CH_4$ data for CH_4 sources (Tables 1 and 2) show that the ^{14}C concentrations of CH_4 from rumen gas of cows were the same as that of contemporary atmospheric $^{14}CO_2$ [119 pMC in 1986 to 1987 (*21*)]. This result was also expected as the animals feed on this or last year's forage. The data from the remaining important biogenic sources are all somewhat depleted in ^{14}C with respect to contemporary C, indicating that the organisms also are utilizing older C. The partitioning probably depends on the availability of decomposed recent organic C in the system. This observation is similar to that for $^{14}CO_2$ from soils (*22*), where the decomposition of organic matter can be characterized by a fast (recent C) and slow (older C) component. The ^{14}C concentrations in methane emitted from peat bogs and tundra are low because large amounts of C are stored in these systems, and decomposition is slow. We did not expect that the ^{14}C activity would also be low for CH_4 from rice production, where C cycling was thought to be rapid. Most CH_4 in wet environments is produced from acetate, with a smaller contribution from CO_2 and H_2; if carbonate were present in the system, some ^{14}C-free carbon could be introduced by isotopic exchange via CO_2. The results for CH_4 from fires varied considerably and indicated that a large fraction of the burnt wood was of moderate age.

The above data were used to reconstruct the turnover of C from atmospheric CO_2 via organic C into atmospheric CH_4 and to extract the contribution of CH_4 from fossil carbon to the atmospheric inventory. This reconstruction is facilitated by the atmospheric $^{14}CO_2$ spike caused by atmospheric nuclear testing. However, we required information not only on the $^{14}CH_4$ activity of today's atmosphere and CH_4 sources, but also on that of the atmosphere since 1960. Three air samples from this period were obtained from stored air in scuba tanks used for diving or firefighting (collected in urban areas), and two samples were obtained from stored pressurized oxygen tanks (even high purity oxygen from liquefaction of atmospheric oxygen contains trace amounts of CH_4). Krypton-85 (half-life 10.8 years), which is produced mostly from nuclear fuel reprocessing in the Northern Hemisphere, was also separated from these samples, and the ^{85}Kr activity was determined by proportional counting. By comparing the present ^{85}Kr activity in these samples to the atmospheric ^{85}Kr activity for various times in the past (*23*), we could date these samples to ±0.5 years. In addition, ^{85}Kr is a chemically conservative tracer, in many ways analogous to CH_4, and may be used to determine whether chemical or transport effects produced the temporal variations observed in atmospheric CH_4 concentration. The $\delta^{13}C$ values from the oxygen tank CH_4 were close to the present atmospheric average, indicating that fractionation did not occur during the liquefaction process. The CH_4 concentrations of all the stored air samples were higher than those expected for the collection time and latitude (*20*). Because several contaminated modern air samples from urban areas were depleted in ^{14}C and enriched in ^{13}C (CH_4 ranged from 1860 to 2030 ppbv, $^{14}CH_4$ from 119 to 99 pMC, and $\delta^{13}CH_4$ from −47.2 to −43.2 per mil), indicative of contamination from fossil CH_4, we corrected the $^{14}CH_4$ values of the stored samples under the assumption that the excess CH_4 was free of ^{14}C (Fig. 2 and Table 2).

A one-box, time-dependent, global model was used with the data to determine the contribution of fossil C–derived CH_4 to the atmospheric burden. The input data consisted of individual source terms (biogenic and fossil, biomass burning, reactors) with their measured isotopic composition. The contribution from wet environments (wetlands,

Table 1. Concentrations of CH_4 (*36*) and $^{14}CH_4$ in samples from biogenic sources and from burning. The experimental uncertainties of the ^{14}C results are the combined measurement error of standard, blank, and sample measurements. All ^{14}C data are corrected to $\delta^{13}C = -25$ per mil (*37*). Percent modern carbon (pMC) was obtained according to pMC = $(\Delta^{14}C/1000 + 1) \times 100$ (*37*).

Date or source	CH_4 (ppmV)	^{14}C (pMC)
	Wetland (New York, 43°N, 77°W)	
6-11-86	2.79 ± 0.01	119.4 ± 1.3
11-6-86	9.27 ± 0.04	113.3 ± 1.8
6-21-88	14.64 ± 0.05	116.8 ± 1.0
6-21-88	73.44 ± 0.28	114.4 ± 1.5
6-22-88	2.02 ± 0.01	119.7 ± 1.0
6-22-88	20.09 ± 0.08	111.0 ± 1.0
	Tundra (Manitoba, Canada, 59°N, 96°W)	
7-29-87	6.71 ± 0.02	113.5 ± 1.1
7-29-87	6.18 ± 0.02	115.5 ± 0.9
7-30-87	9.28 ± 0.02	115.2 ± 1.2
7-31-87	10.75 ± 0.02	110.8 ± 1.3
8-2-87	30.50 ± 0.09	112.7 ± 1.6
7-30-87	bubbles	113.8 ± 1.5
	Rice (Louisiana, 30°N, 93°W)	
5-12-87	6.02 ± 0.02	110.4 ± 1.0
5-14-87	25.80 ± 0.15	114.4 ± 1.3
5-14-87	bubbles	112.3 ± 1.1
5-14-87	bubbles	118.1 ± 1.0
6-16-87	249.60 ± 0.01	111.7 ± 1.9
6-16-87	2.69 ± 0.01	110.6 ± 0.9
6-16-87	52.40 ± 0.20	116.1 ± 1.5
	Peat bog (West Virginia, 39°N, 80°W)	
5-21-86	28.90 ± 0.37	115.6 ± 1.7
8-26-86	76.60 ± 0.60	120.3 ± 0.9
8-27-86	18.90 ± 0.25	115.6 ± 1.9
8-27-86	41.00 ± 0.45	116.5 ± 1.7
	Rumen gas	
Cow	7230 ± 350	121.0 ± 2.0
Cow	16,300 ± 500	119.7 ± 1.6
Cow	3540 ± 111	118.5 ± 1.3
Cow	295 ± 8	119.8 ± 1.6
Sheep	17,000 ± 600	117.6 ± 1.3
Barn air*	4.33 ± 0.01	121.2 ± 1.4
	Termites	
	902 ± 20	123.8 ± 1.8
	Fires	
Forest, brush	3.14 ± 0.05	140.3 ± 1.5
Forest, stumps	22.2 ± 0.1	116.5 ± 1.2
Brush fire	49.5 ± 0.5	128.0 ± 1.1

*No cows.

peat bogs, and tundra) was kept constant with time. The contributions of all other sources except PWRs were increased at 1.1 to 1.2% per year from 1950 values (Fig. 3) and the model runs were started in 1950 with a prebomb $^{14}CH_4$ concentration of 85 pMC. The model had to account properly for (i) the atmospheric burden of CH_4 [4700 teragrams (Tg)] (*6, 20, 24*), (ii) the atmospheric values of $^{14}CH_4$ (121 to 122 pMC), and $\delta^{13}CH_4$ (−46.7 per mil) for the global atmosphere at the end of 1987. The biogenic sources were added by treating each as a two-component carbon system, consisting of a "rapid" fraction with contemporary ^{14}C, and an "aged" fraction with 95% of the prebomb $^{14}CO_2$ value. Together both had to add up to the measured $^{14}CH_4$ for each source. The contemporary $^{14}CO_2$ used in the rapid fraction was obtained from (*21*). Incorporation was delayed by 5 years for CH_4 from wet environments (wetlands, peat bogs, tundra, and rice) and by 13 years for CH_4 from biomass burning. No delay was used for ruminant CH_4. The ^{13}C balance took into account the average $\delta^{13}CH_4$ values (Table 2); additional data on $\delta^{13}CH_4$ for fossil methane was obtained from (*25*). Estimates of the relative contributions of various types of fossil gases from Cicerone and Oremland (*26*) and from Fung (*27*) were considered, and an average $\delta^{13}CH_4$ of −42 per mil was adopted for the fossil gas mix. An enrichment factor of 10 per mil for the CH_4 destruction reaction by OH was applied for ^{13}C (*28*) and 20 per mil for ^{14}C.

We evaluated the contribution of $^{14}CH_4$ from PWRs by use of measured production and emission rates, as well as the world nuclear energy production (*29*). On the basis of continuous measurements of effluent gases from PWRs in New York State, Kunz (*30*) determined that the ^{14}C production rate was 8.8 Ci/GW-year (electric) and that 95% was discharged as $^{14}CH_4$. Howles (*31*) listed the cumulative power of 394 reactors (worldwide, without U.S.S.R.) from their start-up date to the end of 1986, of which 61% was from PWRs. We differentiated the cumulative power data, and with the discharge rate from (*30*) derived an annual $^{14}CH_4$ emission history (Fig. 3). We treated the remaining 55 Soviet reactors in the same manner, using the information in (*29*). The total global reactor contribution for 1987 was extrapolated from the data on additional plants in service by the end of 1987 (*32*). The $^{14}CH_4$ discharge for 1986 derived from the differentiated data compared well with that obtained from the listed PWR power data for 1986. The cumulative $^{14}CH_4$ contribution at the end of 1987 was 6370 Ci, of which 3590 Ci remained in the atmosphere, for a CH_4 lifetime of 8.7 years (as derived below). This estimate is in reasonable agreement with an independent estimate obtained from European reactors (*33*).

The model was iteratively run, and the split between biogenic and fossil methane sources, as well as the partitioning among the biogenic sources, were adjusted to fit the measured atmospheric $^{14}CH_4$ data and to satisfy the methane mass balance and the ^{13}C budget. The best fit to the data (solid lines in Figs. 1 and 2) was obtained with an atmospheric lifetime of CH_4, τ_{atm} of 8.7 to 8.8 years, and a corresponding annual total CH_4 input of 590 to 580 Tg/year, of which 21% or 123 Tg were from fossil CH_4 at the end of 1987 and the remainder were from biogenic sources (25 to 26% from wetlands, peat bogs, and tundra, 19 to 22% from ruminants, 23 to 24% from rice production) and biomass burning (9 to 10%). A similar

Table 2. Summary of ^{14}C and ^{13}C data. Listed are the average values and 1 SD for ^{14}C and $\delta^{13}C$ for the various groups of atmospheric and biogenic samples as well as the range of CH_4 concentrations for the atmospheric samples (numbers of samples is in parentheses). Specific data are available from authors upon request.

Samples	Date (month-year)	Location	CH_4 (ppbv)	^{14}C (pMC)	$\delta^{13}C$ (per mil PDB)
North Atlantic	6-1986	50° to 42°N, 8° to 62°W	1726 to 1789 (12)	118.6 ± 2.3 (10)	−46.7 ± 0.5 (12)
North Atlantic	2-1987	37° to 44°N, 1° to 60°W	1757 to 1793 (9)	118.5 ± 1.7 (7)	−46.4 ± 0.3 (5)
North Atlantic	11-1987	37° to 39°N, 11° to 58°W	1747 to 1792 (6)	123.3 ± 0.8 (5)	−46.6 ± 0.3 (6)
Equatorial Atlantic south	8 to 9-1986	5°N to 9°S, 30° to 10°W	1657 to 1676 (5)	115.9 ± 4.5 (5)	−46.0 ± 0.7 (5)
Equatorial Atlantic north	9-1986	9° to 22°N, 16° to 51°W	1680 to 1784 (3)	117.5 ± 3.9 (2)	−46.6 ± 0.5 (3)
North Pacific	7-1986	50° to 40°N, 134° to 144°W	1696 to 1766 (6)	117.7 ± 3.2 (6)	−47.2 ± 0.6 (5)
Mediterranean and Indian Ocean	10 to 11-1986	7° to 23°N, 37° to 81°E	1697 to 1777 (10)	116.9 ± 1.7 (8)	−46.4 ± 0.5 (7)
South Pacific	6-1987	10° to 32° S, 90° to 100°E	1641 to 1690 (2)	120.0 ± 0.4 (2)	−45.2 ± 0.3 (2)
South Pole	12-1987	90° S	1641 to 1648 (4)	120.0 ± 0.9 (4)	−46.6 ± 0.3 (4)
"Clean" land air	1986 to 1988	9° to 65°N, 44° to 80°W	1772 to 1856 (14)	120.4 ± 2.1 (9)	−46.7 ± 0.7 (12)
Contaminated land air	1986 to 1987	30° to 59°N, 74° to 96°W	1860 to 1996 (9)	115.0 ± 2.6 (9)	−46.3 ± 0.5 (8)
	1988	35° S, 138°E	2030 (1)	99.1 ± 0.9 (1)	−45.5 ± 0.2 (1)
Stored air samples	1977	42°N, 73°W	1722 (1)	103.7 ± 1.4 (1), 113.7 ± 1.5*	−46.9 ± 0.2 (1)
	1976	43°N, 74°W	1851 (1)	97.4 ± 1.6 (1), 116.2 ± 1.9*	−47.3 ± 0.2 (1)
	1978	43°N, 74°W	1640 (1)	110.3 ± 1.4 (1), 113.6 ± 1.5*	−46.5 ± 0.2 (1)
CH_4 from oxygen tanks	1966	Unknown	20540 (1)	87.6 ± 1.4 (1)	−47.3 ± 0.2 (1)
	1984	Unknown	8740 (1)	119.5 ± 1.6 (1)	−45.8 ± 0.2 (1)
Wetland (New York)	1986 to 1988	43°N, 77°W	See Table 1	115.8 ± 3.5 (6), 112.7 ± 2.5‡	−58.3 ± 2.4 (8)†
Tundra (Manitoba, Canada)	7-1987	59°N, 96°W		113.6 ± 1.7 (6), 112.2 ± 2.0‡	−62.9 ± 1.9 (8)†
Rice (Louisiana)	5 to 6-1987	30°N, 93°W		113.4 ± 2.9 (7), 109.7 ± 9.2‡	−63.2 ± 2.9 (8)†
Peat bog (West Virginia)	5 to 11-1986	39°N, 80°W		117.0 ± 2.2 (4), 116.9 ± 2.4‡	−56.7 ± 3.3 (8)†
Cows	1986 to 1988			119.8 ± 1.0 (4)	−71.3 ± 4.1 (4)†
Termites	1987			123.8 ± 1.8 (1)	−68.0 ± 0.2 (1)†
Fires	1987			128.3 ± 11.9 (3), 137.1 ± 26.4‡	−26.6 ± 0.4 (2)†

*Corrected as explained in text. †Average values for emitted CH_4 from sources, corrected for ambient air content using the average clean air value of −46.7 ± 0.5 per mil (*n* = 66). ‡Average values for emitted CH_4 from sources, corrected for ambient air content using average Northern Hemisphere clean air $^{14}CH_4$ values for sampling periods.

lifetime was obtained from a simple two-box model and the observed interhemispheric CH_4 concentration difference. Examination of lifetimes τ and corresponding global annual CH_4 production rates P as functions of the interhemispheric exchange times τ_e and of the North-South production ratio P_N/P_S yielded similar results for $\tau_e = 1.1$ to 1.4 years and $P_N/P_S = 3.0$ to 3.3.

The results were most sensitive to the fossil CH_4 input and to $^{14}CH_4$ from reactors. Different distributions among the biogenic and biomass burning sources had little effect on the ^{14}C fit because their ^{14}C content is rather similar, but had a great effect on the ^{13}C fit. Different splits between fast and slow components in each biogenic source and use of different ages for the slowly incorporated carbon also had little effect on ^{14}C. An assumption of "dead" carbon for the slow component would require 1 to 2% more fossil carbon in 1987, but would result in an overestimate of the $^{14}CH_4$ between 1966 and 1978 of about 3 pMC. Other choices for the prebomb atmospheric $^{14}CH_4$ value did not yield significantly different results after 1970. Larger or smaller values for the delay in incorporating contemporary carbon are not consistent with the 1966 to 1978 data. Doubling the annual increase of the fossil CH_4 contribution would require an additional 10 Tg/year of fossil CH_4. A different version of the model in which only the troposphere was treated gave virtually identical results with respect to lifetime, annual input, and source distribution when we assumed that 5.6% of tropospheric CH_4 per year was lost to the stratosphere. This value was determined from ^{85}Kr measurements.

A two-box model was used to predict the interhemispheric $^{14}CH_4$ difference caused by the rapidly increasing $^{14}CH_4$ source from PWRs. On the basis of the Northern Hemisphere input (Fig. 3), the 8.8-year CH_4 lifetime, and an interhemispheric exchange constant $k = 1/\tau_e$ between 1.0 and 0.56 per year, the predicted interhemispheric difference for 1987 was 2.7 to 5.0 pMC, in agreement with the observed difference. The observed $^{14}CH_4$ increase and the indication of a small interhemispheric difference confirm that the PWR $^{14}CH_4$ contribution is substantial today; it almost quantitatively compensates the ^{14}C dilution from the fossil CH_4 input. The PWR contribution can be more precisely quantified with future atmospheric $^{14}CH_4$ measurements, as the levels will increase faster and lead to a larger interhemispheric difference than at present.

There are few data available for comparison. Ehhalt and Schmidt (*34*) and Ehhalt (*3*) have presented five measurements of $^{14}CH_4$ of various origins from 1949 to 1960 between 75 and 102 pMC (average 83 pMC); they derived a fossil CH_4 contribution of 10 to 15% for this time. These authors mentioned that some of the samples from urban areas could be contaminated. This uncertainty, together with the large spread in these data, precludes quantitative estimation of the evolution of the relative source strength for fossil CH_4 between 1950 and today. Recent $^{14}CH_4$ data (*35*) from the Southern Hemisphere (New Zealand; 32% fossil CH_4) are not in agreement with our data. Out of 18 samples with $^{14}CH_4$ values between 92 and 131 pMC (and $\delta^{13}C$ between −38.3 and −58.5 per mil), 10 were identified as "clean" air samples from 1987; $^{14}CH_4$ in these samples averaged 106 ± 3 pMC ($\delta^{13}C = -47.0 \pm 1.6$ per mil). Our measurements for the same time indicate 120.0 ± 0.7 pMC for the well-mixed Southern Hemisphere. However, the minimum fossil contribution derived from this data (23%) conforms to our estimate. Thus, the fossil contribution to the CH_4 budget is clearly at least 20% of the total; this contribution is underestimated in recent budgets of others (*26*). The difference could be due to seepage from land based and nearshore gas and oil deposits or from clathrate CH_4.

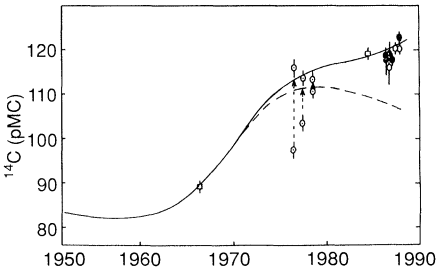

Fig. 2. Atmospheric $^{14}CH_4$ concentration and SD of the measurements from 1966 to 1987, including stored air samples (⊙) and methane extracted from oxygen tanks (☐). For the stored air samples (1976 to 1978) both the measured (lower) and the corrected (upper) values are given (see text). Solid line is the best fit of the one-box model prediction and includes the $^{14}CH_4$ contribution by PWRs; broken line is without the reactor contribution; filled circles, Northern Hemisphere data; open circles, Southern Hemisphere data.

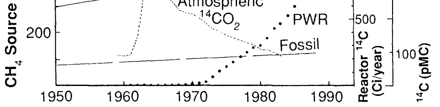

Fig. 3. Annual methane input in teragrams per year, as used in the one-box model. Upper solid line, biogenic sources and biomass burning; lower solid line, fossil methane; dots, derived $^{14}CH_4$ contribution by PWRs in Curies per year; broken line, atmospheric $^{14}CO_2$.

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12. The samples were first concentrated in a bleed-down train at flow rates of ≤2.5 l min^{-1} (measured with a digital integrating mass-flow meter). After H_2O, CO_2, N_2O, and other condensibles were removed at −196°C in traps, each sample was passed through ~60 g of granular charcoal (at $\leq 2 \times 10^4$ Pa to prevent liquefaction of O_2). This process quantitatively retained CH_4 and Kr. Most of the trapped air (~12 liters) was then removed by pumping on the charcoal at −80°C. Desorption of CH_4 and Kr was achieved by heating to 250°C. The sample, containing at this point CH_4, Kr, and several cubic centimeters of air, was trapped on a small amount of molecular sieve 5A (MS) and transferred to the inlet loop (containing charcoal) of a separation gas chromatograph that was equipped with a 10-m column (10% charcoal, 90% MS), a thermal conductivity detector, and parallel collection traps with MS at the exit. On desorption by heating, the sample was injected with He carrier into the column, which completely separated O_2, N_2, Kr, CH_4, and trace amounts of CO and CO_2. The effluent was routed through the collection traps, where CH_4 and Kr were individually trapped on MS at −196°C. The product CH_4 was yielded manometrically, and the average yield of this separation process was 98 ± 1%.
13. The product CH_4 was transferred to a platinum-coated combustion tube, oxygen was added, and the CH_4 was converted at 600°C to H_2O and CO_2, which were collected on coils at −80°C and −196°C, respectively. The combustion yield for CO_2 was 96 ± 1%. The recovered CO_2 was split for analysis of ^{13}C and ^{14}C, and the recovered H_2O was later reduced to H_2 for analysis of deuterium.
14. Radiocarbon analyses were done by the Simon Fraser University accelerator mass spectrometry group (RIDDL), using the McMaster University Tandem Van de Graaff (*15, 16*). The ^{13}C analyses were performed with standard techniques (*17, 18*) on a Finnigan MAT-251 isotope ratio mass spectrometer at Lamont Doherty Geological Observatory. The experimental procedures were extensively tested for sample contamination and for isotopic fractionation (*19*). The samples for ^{14}C measurements were transported as CO_2 in glass tubes. The CO_2 was converted to filamentous graphite on a cobalt substrate; see (*15*) for details. In each wheel, 12 to 13 samples were measured against the three oxalic acid I standards from the National Bureau of Standards (NBS). The SDs of these sample measurements were 1 to 2%. Samples of well-known materials served as secondary standards. The ANU (Aus-

tralian National University) sugar secondary standard, with a ^{14}C activity of 150.8 ± 0.2 pMC (*16*), averaged 149.7 pMC with an SD of 3.0 pMC (number of samples, $n = 62$). The other two secondary standards ($n = 31$, and 49) also had accuracies within the precisions of the measurements. Duplicate sputter targets from the graphites of 23 CH_4 samples and single sputter targets from 14 CH_4 samples were remeasured on widely different occasions. These measurements had an SD of 1.4 pMC.

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17. The $^{13}C/^{12}C$ ratio is expressed in the well-known δ notation; see H. Craig, *Geochim. Cosmochim Acta* **3**, 53 (1953). Standardization was obtained from NBS-16 and NBS-17 standards. A control sample of −48.9 per mil was commonly included in the sample batches, and the SD of these measurements was 0.07 per mil. To check on the extremely light values, we also processed and measured CH_4 samples, which are used in the isotopic analysis of natural gases, for which the $\delta^{13}C$ values have been determined in an interlaboratory comparison study (*18*). From a series of measurements we determined the stable isotope fractionation of the sample separation and combustion steps. Both processes fractionate isotopes, resulting in lighter $\delta^{13}C$ and lower yields (Y), according to $\epsilon = [\delta^{13}C(Y) - \delta^{13}C(Y = 1)]/\ln Y$, with an enrichment factor ϵ of 7.5 per mil for the separation process, and of 2.2 per mil for the combustion process. As the measured yields for individual samples were generally high, the resulting corrections applied to the results were small; 22 samples were processed and analyzed in duplicate or triplicate, and the average SD of these data sets was 0.23 per mil. We therefore adopted an experimental uncertainty of ±0.2 per mil for all individual samples. No correction was required for N_2O as it was completely removed from the samples.
18. We measured an average $\delta^{13}C$ of −29.0 ± 0.1 per mil ($n = 2$), −44.4 ± 0.2 per mil ($n = 4$), and −72.0 ± 0.6 per mil ($n = 2$), respectively, for natural gas standards NGS-1A, NGS-2A, and NGS-3A, in good agreement with data in an intercomparison study [G. Hut, *Stable Isotope Reference Samples for Geochemical and Hydrological Investigations (IAEA Rep.*, International Atomic Energy Agency, Vienna, 1987).
19. Any errors associated with the compressor were investigated by compressing an already collected sample into a second tank, with the assumption that this incremental sampling would reveal any changes introduced by this procedure. We also compared samples separated from outside air directly piped into the separation train to samples simultaneously collected by compression. The results from these tests, which were conducted throughout the period of study, showed that the CH_4 concentration ratio for twice-compressed versus once-compressed samples was 1.003 ± 0.003 ($n = 5$), and the ratio for $\delta^{13}C$ was 0.998 ± 0.004 ($n = 4$), which indicates that the sampling process produced no statistically significant alteration. However, the concentration of ^{14}C was found to be lowered in the twice compressed samples by an average of 1.7 ± 0.6 pMC ($n = 4$). We do not understand how to reconcile these findings, but have applied such a correction to all the ^{14}C data. The combustion blank was determined intermittently between samples with UHP CH_4 (natural gas). The average contamination due to combustion was about 0.7 pMC ($n = 6$). We tested the separation procedure blank periodically by processing spiked air samples (mixture of ambient air and UHP methane, with a total CH_4 concentration of 22.5 ± 0.2 ppmv). The average blank from the separation procedure was about 0.9 pMC ($n = 10$). All the data were corrected for the contamination as measured. In addition, we have verified the experimental uncertainties, which were between ±0.9 and ±2.0 pMC for the individual samples. Nine samples were processed (entire procedure and measurement) in duplicate or triplicate and yielded an average SD of 1.4 pMC. Thus we conclude that the SD, including components for processing and analytical error for ^{14}C, was 1.5 pMC and that our total possible systematic error was of similar value. These tests demonstrate that the employed techniques produce accurate results, even though the sample size used (0.1 to 0.5 mg of carbon) was small.
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36. Methane concentration was determined by gas chromatography with flame ionization defector on at least four splits of each sample on at least two different dates against a series of NBS or NBS–traceable standards covering the entire concentration range. Samples with ≥ 250 ppmv of CH_4 were measured with a small-volume TC detector. For atmospheric concentrations the average SD was 0.57%. This does not include a systematic error from the gas standards (±1% relative error).
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38. This work was supported by National Aeronautics and Space Administration grant (NAGW-843). We thank Trans Freight Lines and the officers and crews of the MVs *TFL Liberty*, *TFL Freedom*, *TFL Independence*, and *TFL Franklin* for transatlantic passages for sampling, and T. Yoshinari, S. R. Piotrowicz, P. Quay, M. Koehn, A. Herczeg, J. Yavitt, G. Lang, J. Samson, S. Barnard, D. Carpenter, the Smithsonian Tropical Research Institute, the Churchill Northern Studies Centre (Churchill, Manitoba, Canada), D. Carpenter, the Matheson Company, and the Rice Research Station (Crowley, Louisiana), for samples and support in the field. M. Schoell provided natural gas standards. We thank N. Blair, R. Cicerone, P. Crutzen, D. Ehhalt, H. Doerr, I. Fung, S. King, C. Kunz, I. Levin, C. Martens, E. Matthews, K. O. Muennich, E. Nelson, P. Quay, U. Schmidt, W. Rheeburg, M. Rubin, M. Schoell, C. Stevens, M. Wolin, and J. Yavitt for valuable discussions.

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Sex Pheromones in Snakes

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The majority of pheromones identified to date are insect pheromones, which are volatile in nature. Identification of nonvolatile pheromones have been relatively rare, especially in vertebrates. Male and female garter snakes use pheromones to mediate sexual behavior. The female sex attractiveness pheromone of the Canadian red-sided garter snake, *Thamnophis sirtalis parietalis*, consists of a novel series of nonvolatile saturated and monounsaturated long-chain methyl ketones, whereas the male sex recognition pheromone contains squalene. These compounds were isolated, identified, and partially synthesized, and field tests show them to be biologically active.

More than 50 years ago, Noble (*1*) showed that tongue-flicking behavior in male garter snakes serves to deliver nonvolatile sex pheromones sequestered on the female's dorsum to the male's vomeronasal organ. Unlike the majority of insect pheromones studied to date, garter snake pheromones are not produced by a discrete gland (*2*); rather, they are components of the integumental skin lipids found in all terrestrial vertebrates and similar to the cuticular lipids of insects that often also serve a pheromonal function (*3*). In garter snakes, if the pheromones are not present on the female's skin or the male is unable to perceive them, males will not exhibit courtship behavior (*1, 4*). Previous investigations (*2*) on the isolation and identification of the sex attractiveness pheromone indicated that the pheromone is chemically related to the yolking protein vitellogenin, or lipid-rich subunits of this molecule, and is sequestered in the female skin. Subsequent research (*5*) on the transport, immunoreactivity, and field tests of

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