

Final Report

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Carbon and Hydrogen Isotope Composition and ¹⁴C Concentration
in Methane from Sources and from the Atmosphere:
Implications for a Global Methane Budget

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C-14 CONCENTRATION IN METHANE FROM
SOURCES AND FROM THE ATMOSPHERE:
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Biogenic Methane Studies

Wetland studies.

Sample analysis and data work up has been completed in a study of the isotopic composition of emitted methane started in 1990 by our group in the Moosonee, Ontario, Canada, region in conjunction with Nigel Roulet, York University, and Carol Kelly, University of Manitoba, with the Canadian Northern Wetlands Study (NOWES), and ongoing NASA ABLE 3B research. We measured $\delta^{13}\text{C}$, δD and ^{14}C in CH_4 from bubble samples and large volume flux box samples taken at the Coastal Fen, Interior Fen, and Kinosheo Lake sampling sites. The sites cover a progression in degree of water saturation, ecological development and age of stored carbon (N. Roulet pers. comm.).

The data presented in figure 1 (also included are data from tundra sites near Churchill, Manitoba, Canada) shows that the $\delta^{13}\text{C}$ and δD of methane from dislodged bubbles is different at each site reflecting either differences in the substrate carbon composition or changes in the microbiology with respect to acetate fermentation/ CO_2 reduction. Unfortunately measurements of $\delta^{13}\text{C}$ in carbon pools from the bog soils have not yet been made, so differences in the source carbon can only be hypothesized as a cause for the differences. Differences in the microbiology are possible, but a substantial shift in the acetate fermentation versus CO_2 reduction pathway would result in sizable differences in the δD values (Whiticar et al., 1986; Alperin et al., 1992; Kelly et al., 1992). The observed δD values for CH_4 at all 4 sites are similar, as the δD value is a consequence of the source δD from precipitation (Wahlen et al., 1990) and the fractionation in the acetate fermentation/ CO_2 reduction processes.

A comparison can also be made between the isotopic composition of bubble methane and the total emitted methane from the sites as collected in large flux box like enclosures (tarp samples). The latter includes the sum of CH_4 emanating by ebullition, diffusion and venting through plant stems (Figure 2). At only one of the three Moosonee sites (the interior fen) the $\delta^{13}\text{C}$ in total emitted

methane is heavier (more positive) than that of the bubble CH_4 which is what would be expected as a result of fractionation if CH_4 oxidation is occurring in the oxic surface zone of the soil. This anomaly is shown most strongly in the data from the Kenosheo site where methane is significantly lighter both for $\delta^{13}\text{C}$ and δD in the enclosure methane relative to the bubble samples. The Churchill data and Costal fen data also show a distinct trend in lighter $\delta^{13}\text{C}$ values in the enclosure samples as compared to the dislodged bubbles. The exact reason for these trends has not yet been determined but possible candidates are: discrepancies in the method of sample collection and the non-synoptic nature of the samples. To help resolve this issue continued research will be conducted under the BOREAS investigations.

The ^{14}C composition of the emitted methane is an indication of the average age of the carbon being consumed by the methanogens. The average values of $\delta^{13}\text{C}$ and ^{14}C in the methane from bubbles show distinct differences between the sites. This data is presented in figure 3, and shows that the separation in values between the sites is quite remarkable. The age progression from coastal to inland to the Kinoshoo sites is supported by the ^{14}C values of the methane. While we have previously noted some depletion of biogenic $^{14}\text{CH}_4$ with respect to contemporary levels, we have never observed depletions as large as from some of the Moosonee sites, indicating CH_4 production from very old carbon. An explanation is that, at least for the dislodged bubbles, old carbon is being decayed and in some areas there is a sizable flux of methane from an underlying zone containing old carbon. The present BOREAS project will allow us to continue $^{14}\text{CH}_4$ investigations from high northern latitude environments to resolve the imbalance between fossil methane budgets derived via $^{14}\text{CH}_4$ and those derived from statistical considerations (Barns and Edmonds, 1990), the latter being smaller than the former. Biogenic methane from considerably older carbon from the northern environments could make up the difference.

Forest soil methane uptake.

We have completed the sample analysis and data work up of an experiment on forest soil methane consumption conducted in 1990. The consumption of methane by tundra, forest, and grassland soils has been noted by several investigators (Born et al., 1990; Mosier et al., 1991; Whalen and Reeburgh, 1990; Whalen et al., 1991; Yavitt et al., 1990; 1990b; Koschorreck and Conrad, 1992). In the tundra and in variously saturated soils methane production occurs in the lower anaerobic layers and methane oxidation occurs in the top aerobic layers. The balance between production and consumption was observed by Yavitt et al. (1990) for temperate forest soils. Methane oxidation was also investigated in drier forest soils by Born et al. (1990). In the above studies CH_4 consumption by oxidation has been found to be low compared to methane production, resulting in net methane fluxes to the atmosphere. Consumption rates are typically less than $3 \text{ mg CH}_4 \text{ m}^{-2} \text{ d}^{-1}$. Global methane consumption by oxidation has been estimated to be 1 to 15% of the total annual methane production (Born et al. (1990)).

Studies on the isotopic fractionation of methane by soil oxidation are limited. King et al. (1989) reported a methane consumption of 0.6 to $1.2 \text{ mg CH}_4 \text{ m}^{-2} \text{ d}^{-1}$ and an enrichment factor for $^{13}\text{C}/^{12}\text{C}$ of $\epsilon = 16$ to 26 permil observed in an Alaskan tundra soil. In 1990 we measured temperate forest soil methane consumption rates of 2 to $4 \text{ mg CH}_4 \text{ m}^{-2} \text{ d}^{-1}$, with an enrichment factor of $\epsilon = 16$ permil (Figure 4). Samples were obtained by installing a large flux box enclosure over the site. We monitored the mixing ratio of CH_4 in the enclosure as a function of time, and a continuous decrease from the ambient atmospheric value was observed, indicating CH_4 consumption and/or oxidation. Samples for $\delta^{13}\text{CH}_4$ analyses were retrieved at different times after closure, and $\delta^{13}\text{CH}_4$ was observed to increase (become isotopically heavier) with time. From the measured changes of $\delta^{13}\text{CH}_4$ ($\Delta\delta^{13}\text{CH}_4$) in the remnant CH_4 and in the CH_4 mixing ratio we determined the enrichment factor according to $\epsilon = \Delta\delta^{13}\text{CH}_4 / \ln f$, where f is the fraction of remaining CH_4 . In this case, the enrichment factor for deuterium in methane was about 6

times that for ^{13}C . At this site we also obtained depth profiles of CH_4 (Figure 5). The profiles are similar to those obtained by Born et al. (1990) and subsequent work by this group and others on forest soils (Deck et al., 1993) and support the evidence for CH_4 oxidation.

We earlier measured the fractionation of ^{13}C by methane oxidation in the oxic soil cover over a landfill to be 28 permil. Continued work on dry forest soils conducted in 1992-93 has confirmed the importance of methane uptake and supported the above fractionation factors. Initial results from the BOREAS site indicate that northern forest show significant methane uptake.

The enrichment factor ϵ determined in these studies is comparable to or greater than the fractionation determined for methane destruction by the OH radical in the atmosphere as variously measured in laboratory studies by Davidson et al. (1987) $\epsilon = 10$ permil, Rust and Stevens, (1980) of $\epsilon = 3$ permil, Cantrell et al. (1990) $\epsilon = 5$ permil, and the data presented by Wahlen et al. (1989). The stratospheric data on isotopic methane (discussed later), yield an enrichment factor for $^{13}\text{CH}_4$ in the lower stratosphere of $\epsilon = 14$ permil (at stratospheric temperatures). Recent measurements of the enrichment factor for δD in methane in the laboratory for the OH oxidation of methane of 160 permil (DeMore 1993) compare very favourably with our stratospheric measurements for the singly deuterated methane enrichment factor of 161 permil. Discrepancies between the $^{13}\text{CH}_4$ fractionation determined in various laboratory experiments can have severe consequences for an isotopic budget of the global methane.

Rice field methane sources.

An initial set of samples from the International Rice Research Institute in the Philippines were returned in 1991. The gas composition and methane $\delta^{13}\text{C}$ and δD measurements have been made (Table 1). These samples were taken to determine the effects different cultivation methods make on the isotopic composition of

the emitted methane. The initial $\delta^{13}\text{CH}_4$ values for three sites of -59.1, -61.2 and -68.6 permil are comparable to other values made by this group (in Louisiana) and those reported by other investigators (Cicerone et al, 1992). Additional samples were returned in 1993 with additional analyses being made. Sampling will be continued.

Atmospheric Measurements

Churchill, Manitoba Canada.

Atmospheric methane isotope determinations have been continued at several sites over the last year. Mixing ratio data on methane from Churchill, Manitoba, Canada was obtained throughout much of 1991 (Figure 6). The data show a large degree of variability. The single high data point, above 2000 ppbv, is most probably from local source anthropogenic contamination at this sampling time. The results show a remarkable drop in the methane mixing ratio in mid summer which has been observed at other high northern latitude sampling stations (Pt. Barrow, Quay et al. 1990). This may possibly be the result of downward mixing of stratospheric air in conjunction with the breakdown of the polar vortex, which would be consistent with a period of very cold dry air from the north observed at this time. Other influences could also be possible (massive consumption of methane by the high northern latitude soils). In either case, analysis of the air at this time for the isotopic composition in methane, trace gas composition and ^{85}Kr would have been extremely important and would confirm what process was occurring. Unfortunately, although several large volume samples were taken at this site in 1991, none was taken during this time period. An FID gas chromatograph at this site (Churchill Northern Studies Centre), as well as the equipment to collect large volume air samples, was on hand in 1992, but the work was impeded by frequent change in personnel due to a funding crisis at this Centre. Large volume samples were taken in 1992 but continuous GC data were not available.

South Pole, Antarctica.

Large volume air samples taken at the South Pole in 1990, which should have been analyzed during the time period of this grant, were held up in shipment and only returned to our lab in April 1992. The analysis of the samples has begun with the results indicating that methane mixing ratio at the south pole has increased from approximately 1645 ppbv to approximately 1690 ppbv between the end of 1987 and summer of 1990, or approximately 1% per year. The $\delta^{13}\text{C}$ in the methane, as determined on initial analysis, does not appear to have changed over this time period and was found to be -46.6 ± 0.2 permil. The initial measurements of ^{85}Kr show an continued increase in atmospheric concentration from the values measured by our group in 1987.

California, USA.

A time series for stable isotopes and ^{14}C in methane of large volume air samples was initiated in 1991 near our lab site, on Scripps pier, La Jolla, CA. Sampling was performed in conjunction with continuous measurements of CO_2 being made by Dr. C. D. Keeling and his group. In collaboration with Dr. Keeling's group we plan to make continuous measurements of the mixing ratio of methane (and of carbon monoxide) at this site. Initial data obtained by our group indicates that low CO_2 mixing ratios at this site do not always correspond to low CH_4 mixing ratios. Initial isotope determinations for $\delta^{13}\text{C}$ in methane and ^{85}Kr confirm that these samples are representative of samples taken at similar latitude in the northern hemisphere atmosphere.

Germany.

A series of samples from Germany were taken and analyzed in 1991. The samples represent both clean (German clean air site, Schauinsland, (Sil, Table 2)) and industrially contaminated background air masses (Heildberg (HD)). The concentration results (Table 2) show the clear differences between the air sample sites. Isotopic analysis of the samples continues and will allow the quantification of the anthropogenic methane isotopic signature.

Stratospheric samples.

Stratospheric air samples obtained in December 1990 (HOU 7) have been analyzed for CH_4 , CO_2 , N_2O , CO (Table 3). The results indicate that this set of samples correlates well with previous sampling flights (Figures 7 and 8). The Isotopic determinations in 1991 were delayed until the capability to measure ^{85}Kr was completed. As this was achieved in 1992, the isotope composition is presented. Sample flights in 1991 were not possible due to lack of flying time on the aircraft. A sample flight in April 1992 was attempted but sampling problems on the aircraft prevented the collection of useful samples, but a subsequent sample flight in December was made. ^{14}C data from the available samples (HOU 1 through HOU 6) have been analyzed. The results show a ^{14}C methane composition in the lower stratosphere very close to that in the troposphere (Figure 9). This work was intended to detect the time delay between stratospheric $^{14}\text{CO}_2$ and stratospheric $^{14}\text{CH}_4$. Apparently the time changes of tropospheric $^{14}\text{CH}_4$ by bomb ^{14}C are too slow to manifest themselves in the stratosphere profiles.

Work was initiated, under separate funding from the Max Plank Institute, to augment the large volume sampling system with a cleaner system so that the analysis of the isotopic composition of CO_2 , CO , Freons and other trace gases can be made with the WB-57F airplane.

A series of stratospheric air samples collected by cryogenic techniques on balloons from 1988 by the group of Drs. Ehhalt and Schmidt (KFA Juelich, FRG) over northern Sweden to a height of 25 km, and over southern France to a height of 22 km, were analyzed for $\delta^{13}\text{C}$ in methane. Since the samples collected were small (18-28 L STP) the $\delta^{13}\text{C}$ in methane determinations had to await the completion of calibration of our micro bleed and micro combustion racks. The determinations now have been made (Table 3) and show similar values, but larger uncertainties than those measured from large air samples collected by the WB-57F aircraft. The data in

figure 10 do, however, support the trend of $\delta^{13}\text{CH}_4$ with altitude observed previously (Wahlen et al., 1990).

In conjunction with the above research intercalibration with other investigators has been made. Our move to Scripps Institution of Oceanography has allowed collaboration with Dr. C. D Keeling and his group in the concentration measurement and isotopic composition of CO_2 , and with Dr. R. Weiss for methane and nitrous oxide intercalibration. This association has aided in the collection of background methane samples at Scripps pier as mentioned above and the intercomparison of standards (which identified a major problem with a Scott methane standard).

Our group has also been asked to participate in an international intercomparison of ^{14}C and $\delta^{13}\text{C}$ in methane conducted by the NOAA Environmental Research Lab, Boulder, and CSIRO (Australia). The results released in January 1994 indicate that our lab performed very well with respect to the other investigators.

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Table 1

Samples: Rice, International Rice Research Inst. Phil.

Tank	Label	CH4 ppm +/-	CO2 ppm +/-	CO ppb +/-	H2 ppb +/-	N2O ppb +/-	C-13 permil +/-	C-14 %mod +/-	D permil +/-
LL21203	IRRI,1 IR72	118.9 1.4 123.0 5.6 121.0 4.1	290 12	2354 29	2521 28	310 6	-59.1 0.5	119.5 0.6	-277 10
LL21143	IRRI,2 IR70	942.4 19.8 918.5 33.1 930.5 27.2	7211 299	1848 25	3521 46	296 6	-60.8 0.5 -61.6 0.5	114.2 0.7	-322 10
LL22863	IRRI,3 IR74 P., Laguna	94.2 2.6 100.5 2.1	241 10	718 12	1483 15	321 6	-68.6 0.5	117.9 0.6	-274 10

TABLE 2

Samples: German clean / polluted land air samples 90-91

Tank	Date	Label	CH4 ppb +/-	CO2 ppm +/-	CO ppb +/-	H2 ppb +/-	N2O ppb +/-
LL21121	082190	SIL 1	1786 20	340 31	194 2	2065 5	307 3
			1833 23	356 20			
LL21047	082290	SIL 2	1822 21	344 37	164 2	1066 6	313 3
			1812 15	361 50			
LL21063	043091	SIL 3	1851 19	364 39	228 1	305 3	311 4
			1850 23	357 21			
LL21161	043091	SIL 4	1843 18	359 31	195 1	309 3	309 5
			1850 15	361 24			
LL21200	051491	HD 1	1923 22	387 33	358 5	340 8	312 2
			1948 26	387 25			
LL21140	051491	HD 2	1969 21	406 43	360 5	346 5	315 5
			1963 16	398 26			
LL21068	052791	HD 3	1977 22	390 36	345 4	312 5	314 2
			1986 13	391 54			
LL21055	052791	HD 4	1971 25	387 33	337 2	305 2	311 5
			1984 16	377 42			

Table 3

Samples: Stratosphere sample flight Dec. 6, 1990, Hou 7

Tank	Height Kf Km Km^Tp	Height Lable	CH4 ppb +/-	CO2 ppm +/-	CO ppb +/-	H2 ppb +/-	N2O ppb +/-	C-13 permil +/-
176	50 k 15.2 km 3.3 km	37.0 - 39.5 N -35 C	1682 16 1660 19	348 2	416 69	319 3	293 4 283 5	-46.8 0.5
			(1671) (19)					
315	55k 16.8 km 5.5 km	42.1 - 42.3 N -27.5 C	1591 10 1582 20	350 2	769 18	330 6	276 2 272 5	-46.27 0.5
			(1587) (17)					
278	57k 17.4 km 6.4 km	39.92 - 41.63 N -27 C	1520 22 1519 17	356 2	3534 34	332 4	266 1 258 5	-46.1 0.5
			(1520) (18)					
047	58k 17.7 km 7.0 km	45.6 - 46.3 - 44.9 N -25.5 C	1504 17 1497 17	356 2	3213 31	366 10	258 2 253 5	-46.2 0.5

Tundra Bubbles

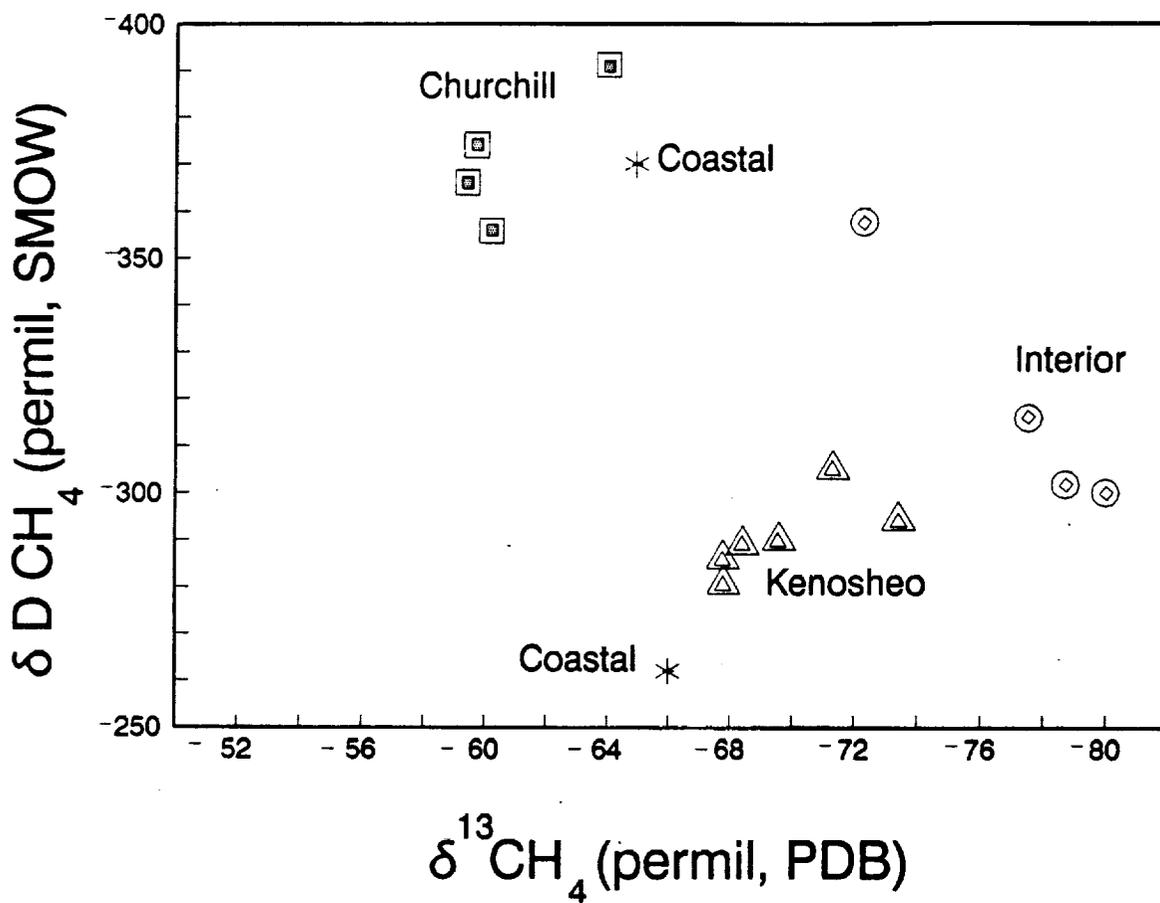


Figure 1. The isotopic δD vs $\delta^{13}C$ of methane in dislodged bubbles from fen sites in the Northern Wetlands study area and Churchill, Manitoba, Canada.

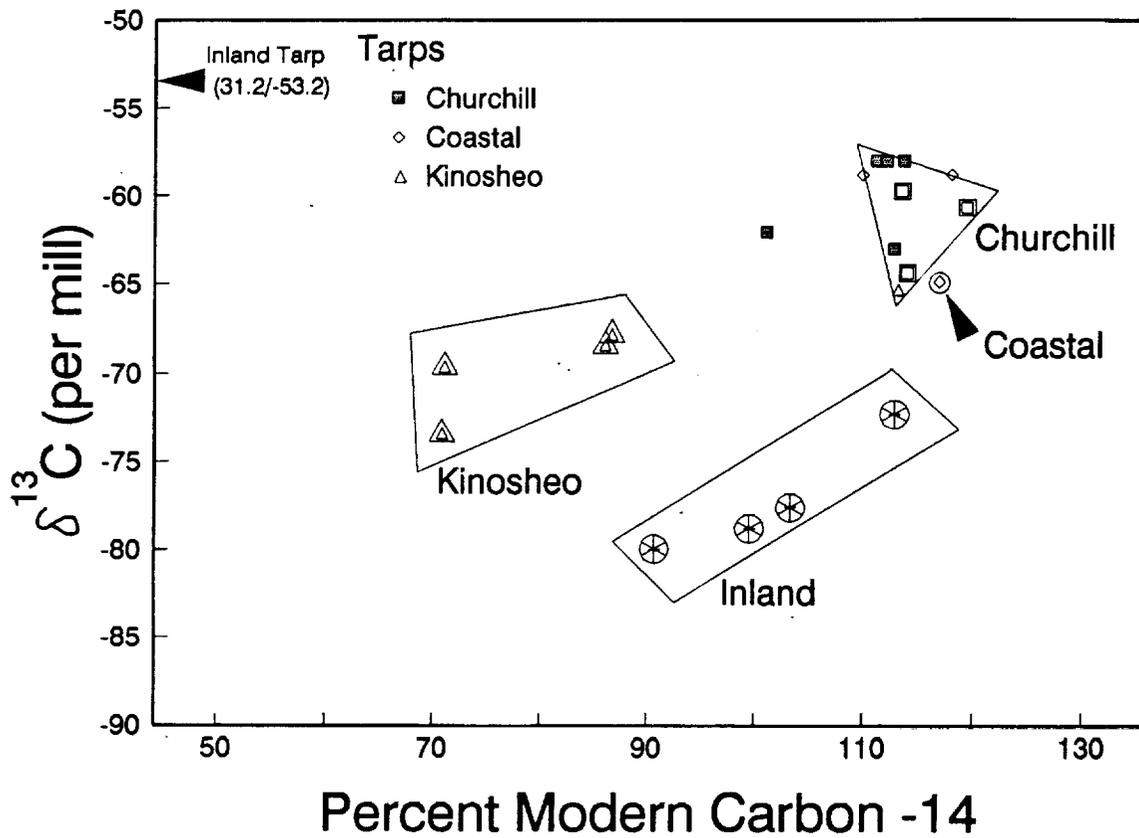


Figure 3. Isotopic $\delta^{13}\text{C}$ in methane vs the ^{14}C value for dislodged bubbles and surface enclosure samples at the wetland sites. (Note the shift in direction of the ordinate axis.)

Forest Soil Methane Consumption June - July 1990

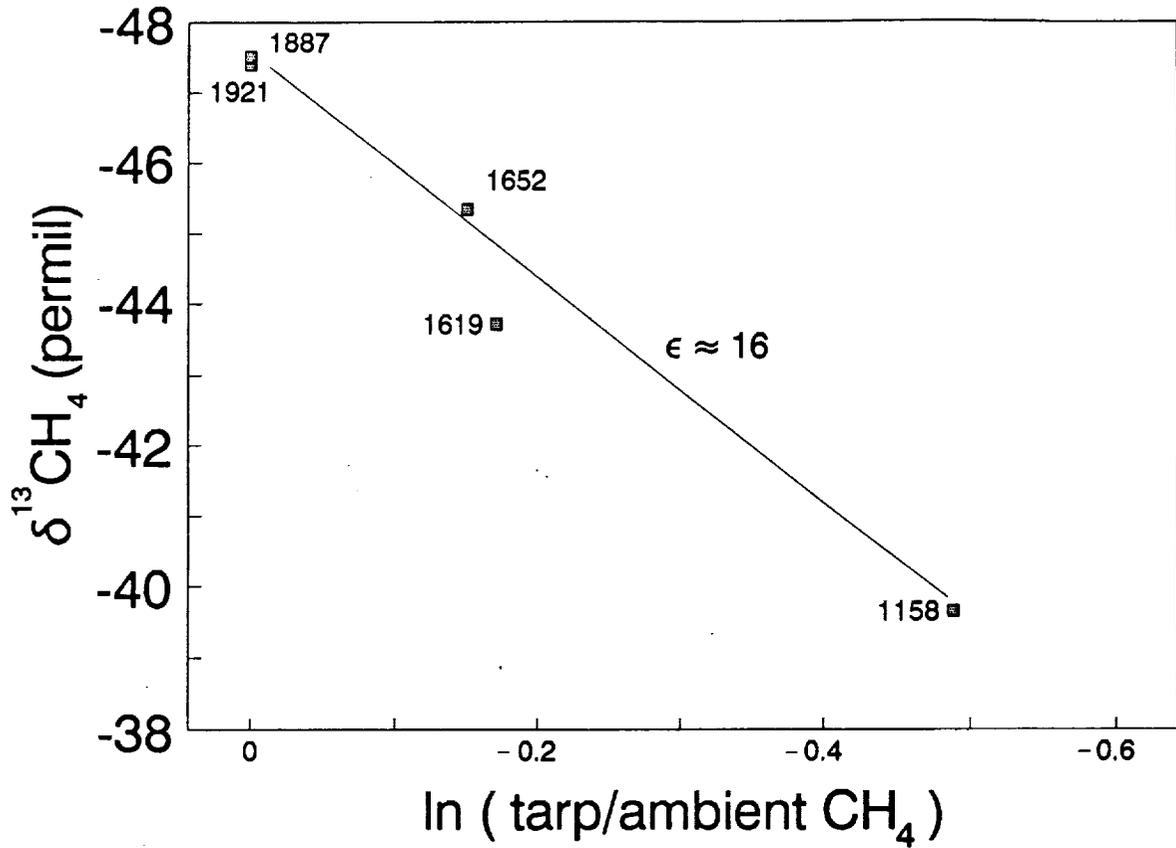


Figure 4. Isotopic $\delta^{13}\text{C}$ of methane in a surface enclosure over a moist temperate forest soil as a function of decreasing concentration over two hours. The line describes a fractionation enrichment factor, ϵ , of 16 permil.

Carpenters Farm Soil Methane Profiles

Aug 13, 1990

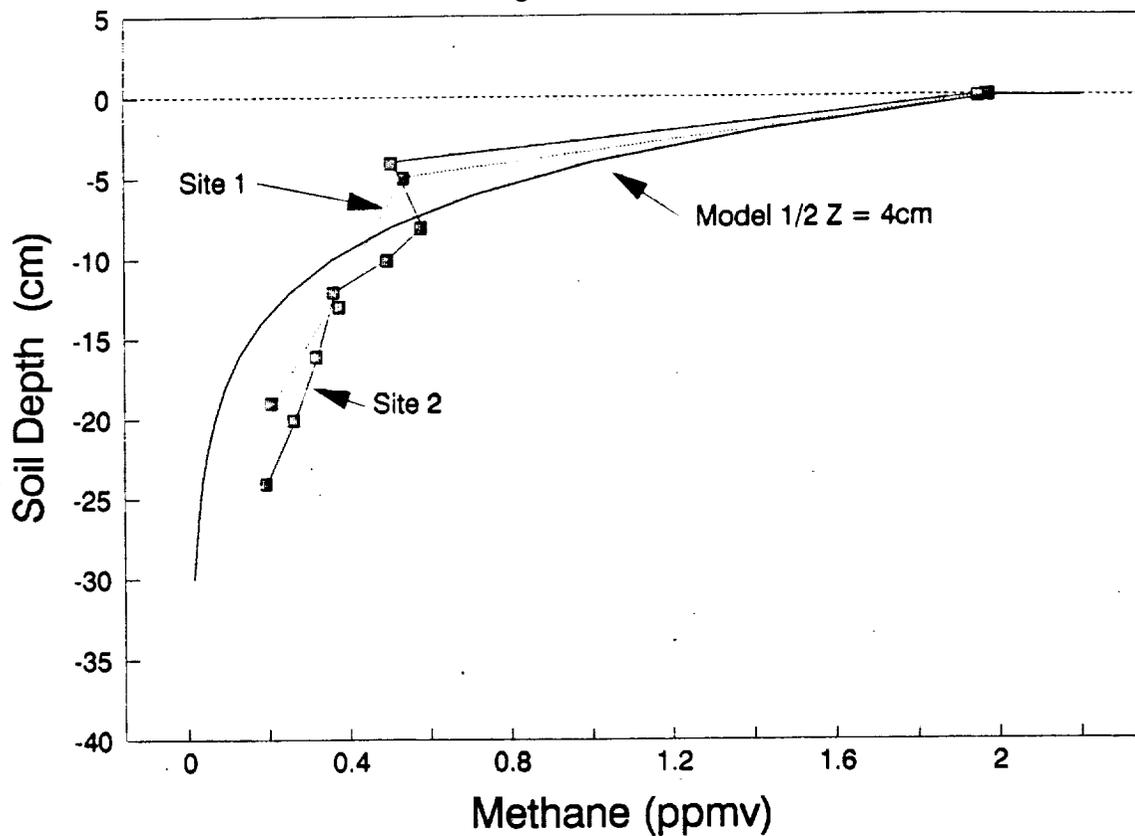


Figure 5. Methane mixing ratio in a temperate forest soil as a function of depth.

Churchill Manitoba, Air Methane 1991

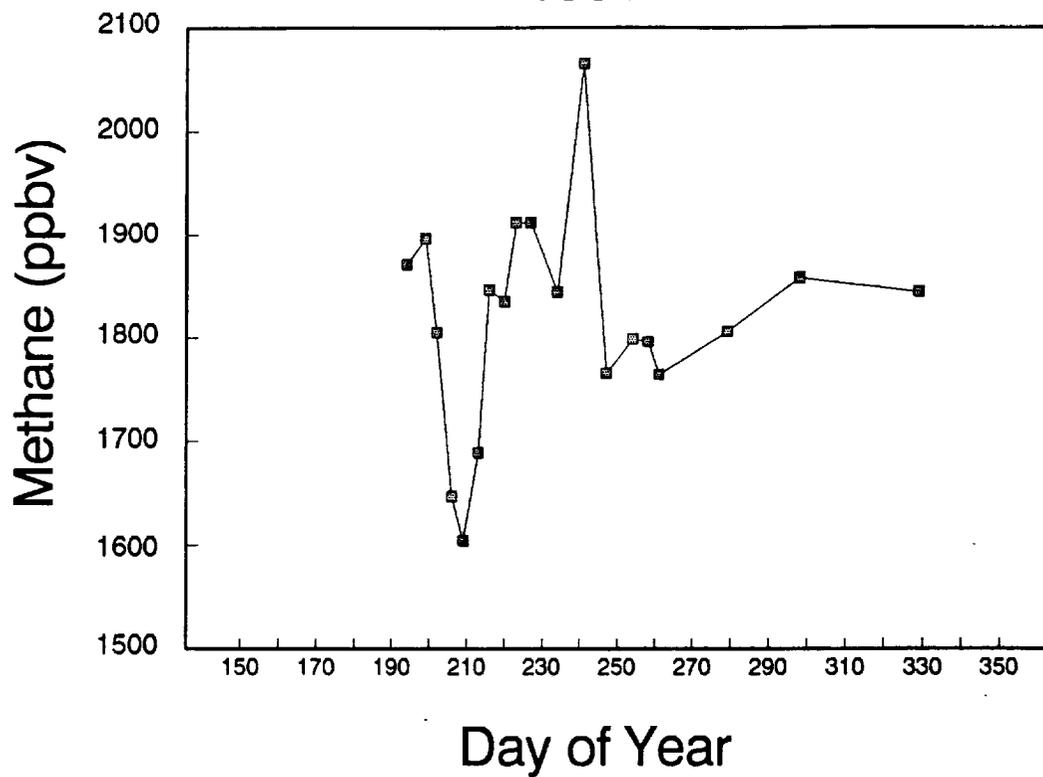


Figure 6. Methane mixing ratio in ambient air samples taken at Churchill, Manitoba, Canada as a function of day of the year.

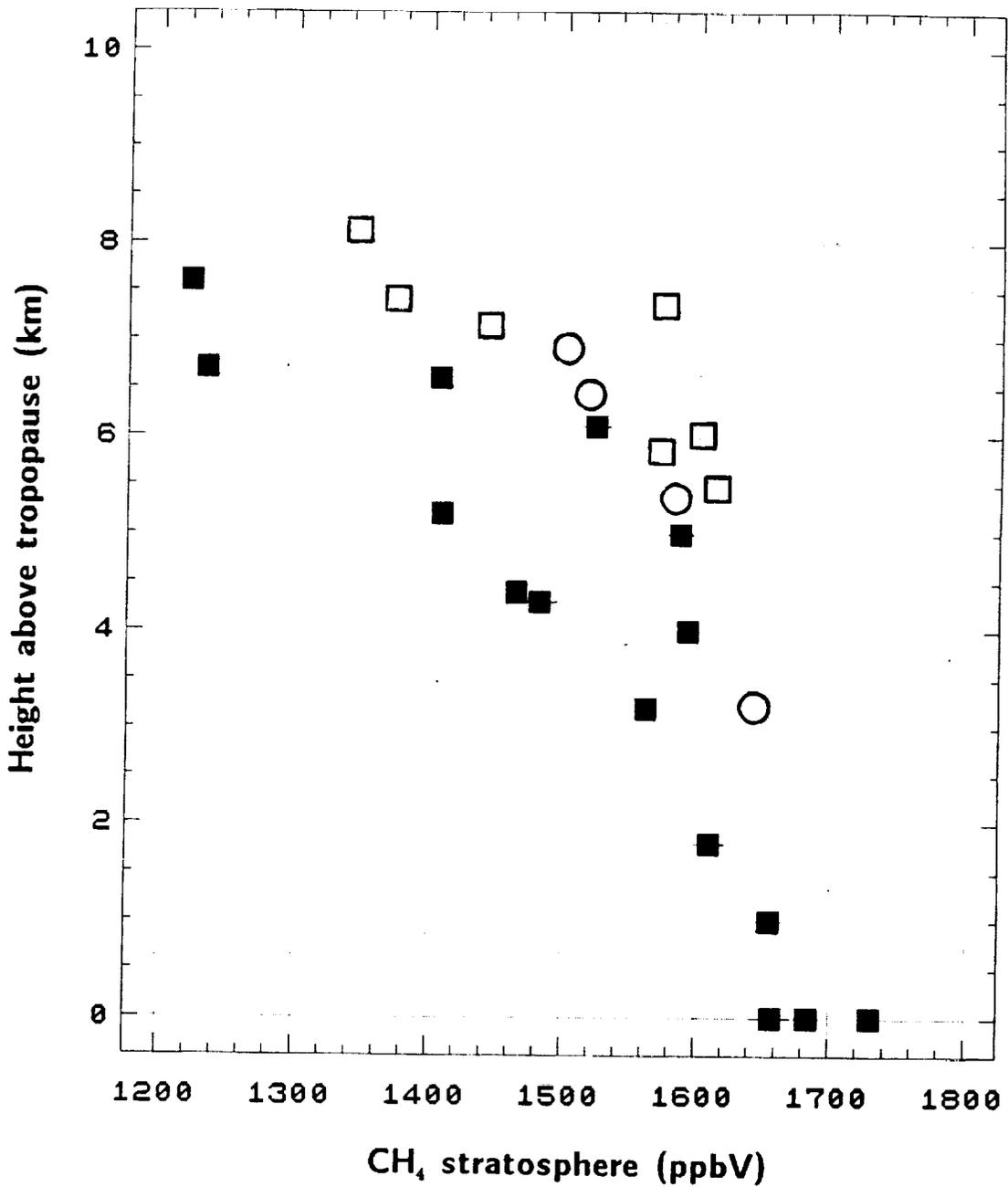


Figure 7. Methane mixing ratios in stratospheric air samples as a function of height above the local tropopause. Solid symbols flights HOU 1-4, open squares flights HOU 5 and 6, circles HOU 7.

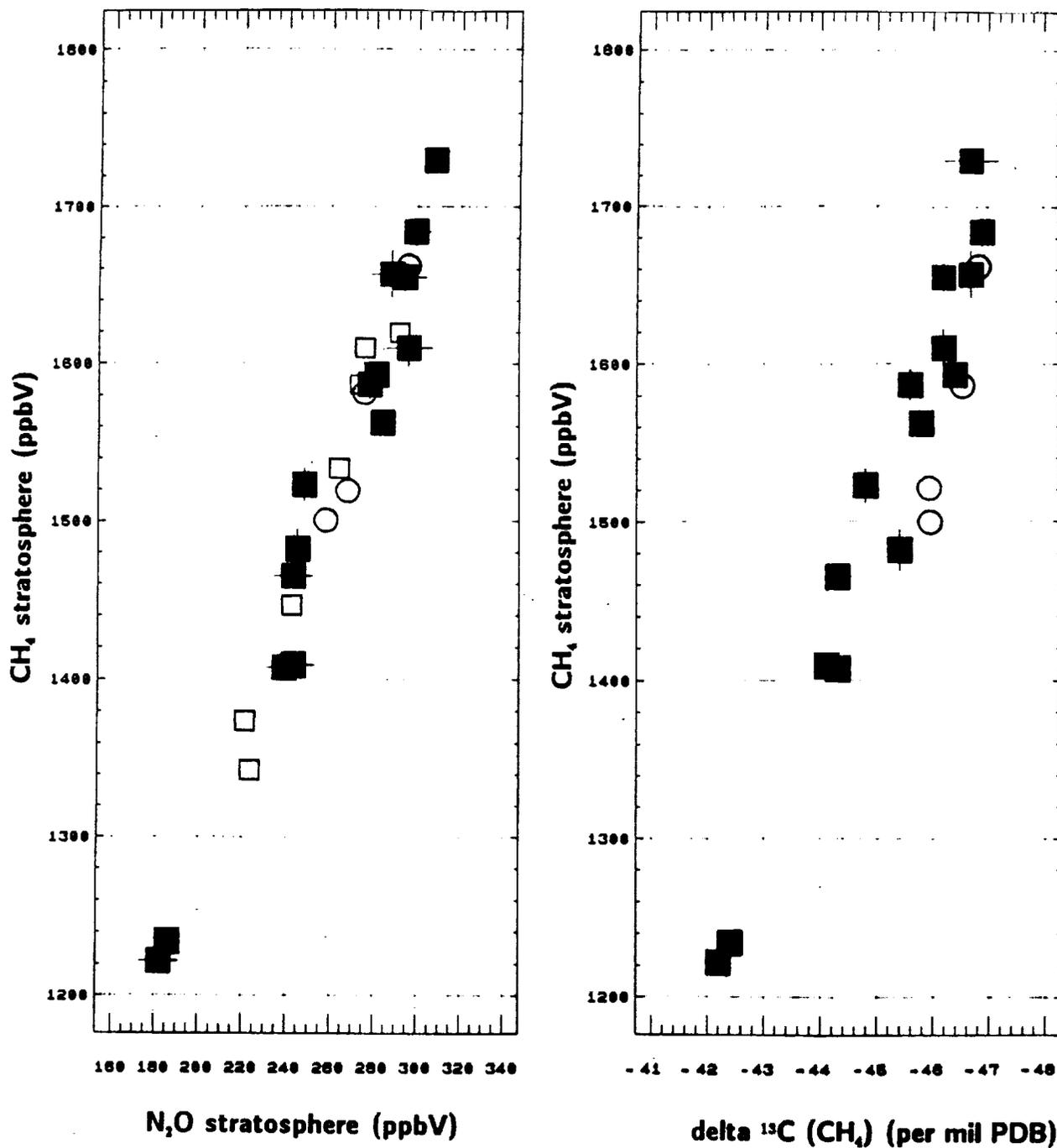


Figure 8. (a.) Methane mixing ratios as a function of Nitrous Oxide mixing ratio. (b.) As a function of $\delta^{13}\text{C}$ in methane ratio. Symbols as that for figure 7.

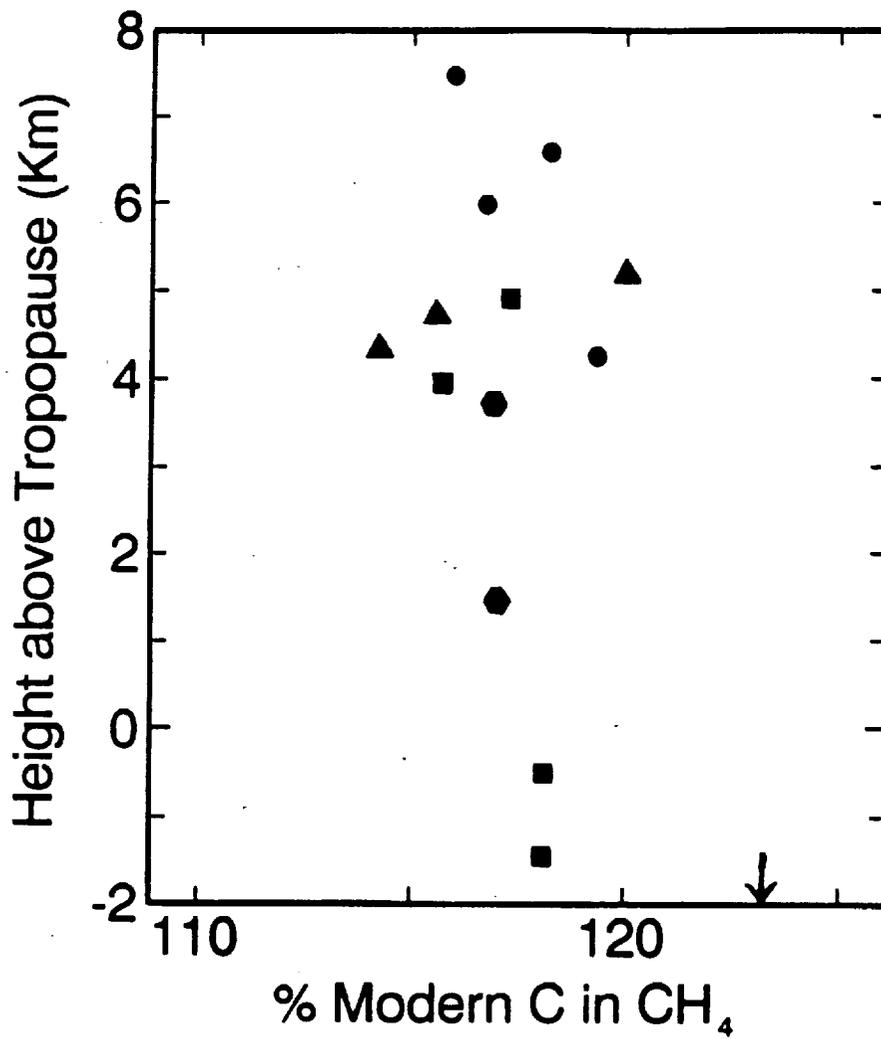


Figure 9. ¹⁴C in methane as a function of height above the local tropopause.

German Balloon Stratospheric Samples

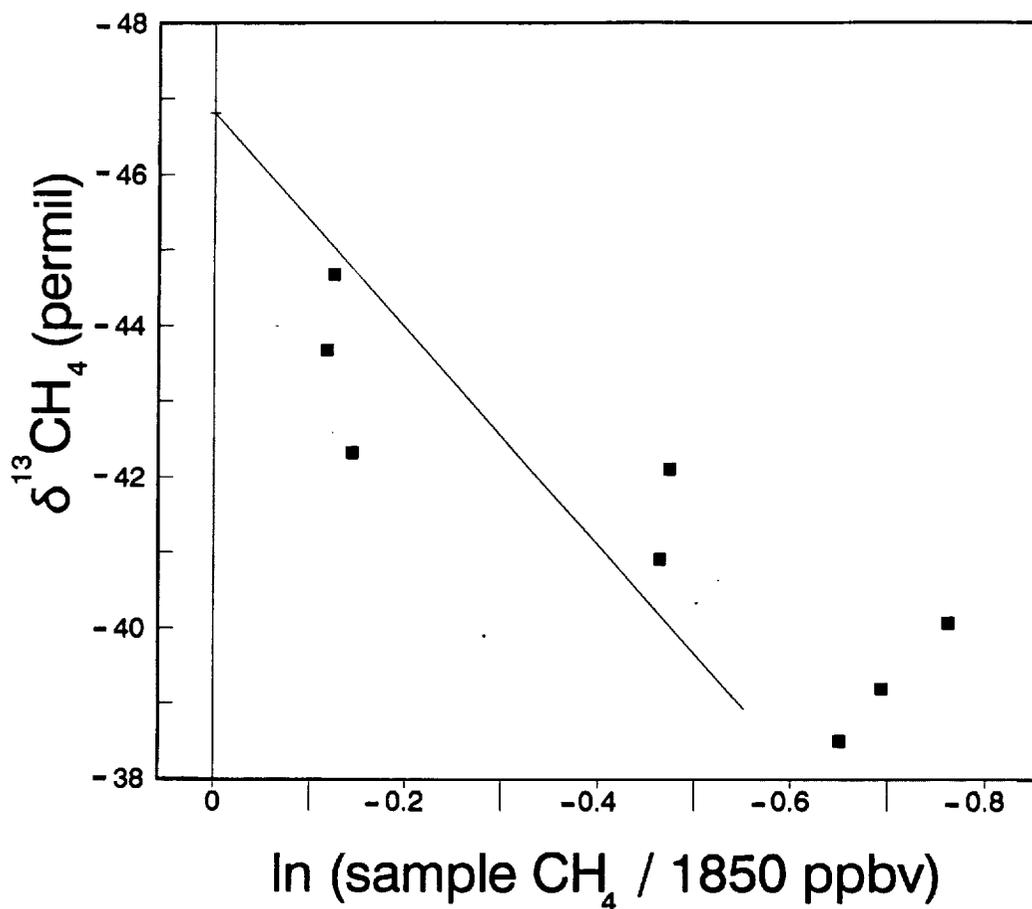


Figure 10. Methane $\delta^{13}\text{C}$ in stratospheric balloon samples as a function of sample mixing ratio compared to 1850 ppbv. The line is representative of previous stratospheric samples, enrichment factor $\epsilon = \text{approx. } 15 \text{ permil}$ (Wahlen et al., 1989).