JOURNAL OF GEOPHYSICAL RESEARCH, VOL. 97, NO. D15, PAGES 16,689–16,701, OCTOBER 30, 1992

Carbon and Hydrogen Isotopic Characterization of Methane From Wetlands and Lakes of the Yukon-Kuskokwim Delta, Western Alaska

CHRISTOPHER S. MARTENS, CHERYL A. KELLEY AND JEFFREY P. CHANTON[1]

Marine Sciences Program, University of North Carolina, Chapel Hill

WILLIAM J. SHOWERS

Department of Marine, Earth, and Atmospheric Sciences, North Carolina State University, Raleigh

The total methane flux to the troposphere from tundra environments of the Yukon-Kuskokwim Delta is dominated by emissions from wet meadow tundra (~75%) and small, organic-rich lakes (~20%). The mean $\delta^{13}C$ value of methane diffusing into collar-mounted flux chambers from wet meadow environments near Bethel, Alaska, was -65.82 ± 2.21‰ (±1 sigma, n = 18) for the period July 10 to August 10, 1988. Detritus-rich sediments of Delta lakes, including margins of large lakes and entire submerged areas of smaller ones, are laden with gas bubbles whose methane concentration ranges from 11% to 79%. Lowest methane concentrations are found along heavily vegetated lake edge environments and highest throughout organic-rich, fibrous sediments of small lakes. A minimum ebullition flux estimated for the 5% of total Delta area comprised of small lakes ranges from 0.34 to 9.7 x 10^{10} g CH_4 yr^{-1}, which represents 0.6% to 17% of the total Delta methane emission. The $\delta^{13}C$ and δD values of this ebullitive flux are -61.41 ± 2.46‰ (n = 38) and -341.8 ± 18.2‰ (n = 21), respectively. The methane in gas bubbles from two lakes is of modern, bomb carbon enriched, radiocarbon age. Gas bubble $\delta^{13}C$ values varied from 2 to 5‰ seasonally, reaching heaviest values in midsummer; no such variations in δD values were observed. Combined isotope data reveal that higher $\delta^{13}C$ values in heavily vegetated areas correlate with lower δD values, suggesting enhanced methane production via acetate fermentation. Spatial isotopic variations in lakes appear to be controlled by variations in production rather than oxidation processes.

INTRODUCTION

In this paper we report the results of a study of the carbon and hydrogen isotopic composition of methane from tundra environments of the Yukon-Kuskokwim Delta of western Alaska (Figure 1). The work was conducted as part of NASA's Global Tropospheric Experiment/Arctic Boundary Layer Experiment (GTE/ABLE 3A), which included ground-based studies of methane production, distribution, and fluxes [*Sass et al.*, 1989; *Bartlett et al.*, this issue] as well as the effect of macrophytes on these fluxes [*Chanton et al.*, this issue]. The overall study included methane emission measurements, which were performed using static chambers as well as by eddy correlation flux techniques used at a micrometeorological tower site [*Fan et al.*, this issue] and on board the NASA Electra aircraft [*Ritter et al.*, this issue].

Recent measurements of ^{14}C in methane from various sources and in atmospheric methane [*Wahlen et al.*, 1989] indicate that approximately 79% of the methane reservoir in the atmosphere in 1987 is of recent biogenic origin. This finding is in reasonable agreement with previous budget estimates for identified sources of atmospheric methane [e.g., *Ehhalt and Schmidt*, 1978]. In a recent review of such budgets, *Cicerone and Oremland* [1988] estimate that natural wetlands could account for 100 to 200 x 10^{12} g CH_4 yr^{-1} of the total 400 to 640 x 10^{12} g CH_4 yr^{-1} flux to the atmosphere.

High-latitude wetland ecosystems appear to be important atmospheric methane sources based on budgets and direct flux measurements [*Sebacher et al.*, 1986; *Matthews and Fung*, 1987; *Aselman and Crutzen*, 1989; *Whalen and Reeburgh*, 1990; *Crill*, 1992; *Bartlett et al.*, this issue]. The wet peats and soils of tundra and boreal ecosystems contain huge quantities of organic carbon [*Schlesinger*, 1977; *Aitjay et al.*, 1979; *Post et al.*, 1982], the tundra alone representing over 10% of the total global reservoir [*Billings*, 1987]. This organic carbon is readily decomposed to carbon dioxide and methane via microbial processes during warmer periods [e.g., *Svensson*, 1976; *Svensson and Rosswall*, 1984].

Methane fluxes to the atmosphere from tundra environments are controlled by both temperature and moisture conditions. Over 90% of the net flux occurs during the warm season when soils overlying permafrost are thawed [*Whalen and Reeburgh*, 1988]. However, *Sebacher et al.* [1986], *Whalen and Reeburgh* [1988], *Crill* [1992], *Bartlett et al.* [this issue], and others have found a relatively poor correlation between temperature and methane flux from tundra; soil moisture content appears to be the controlling factor. High methane fluxes are observed only when soils are water saturated. Small-scale patchiness in plant distribution and topography of the tundra surface is also important [*Whalen and Reeburgh*, 1988].

Stable carbon isotopes can be utilized to help quantify the relative importance of natural wetlands and other sources of methane to the atmosphere [e.g., *Stevens and Engelkemeir*, 1988; *Craig et al.*, 1988; *Quay et al.*, 1988; *Tyler*, 1989; *Wahlen et al.*, 1989]. The $^{13}C/^{12}C$ isotopic ratio of methane for the global atmosphere using the $\delta^{13}C$ notation was -47.7‰ in 1980 [*Stevens and Engelkemeir*, 1988] and -46.7‰ at the end of 1987 [*Wahlen et al.*, 1989]. The $\delta^{13}C$ value is defined as the relative difference between the sample $^{13}C/^{12}C$ isotopic

[1]Now at Florida State University, Tallahassee.

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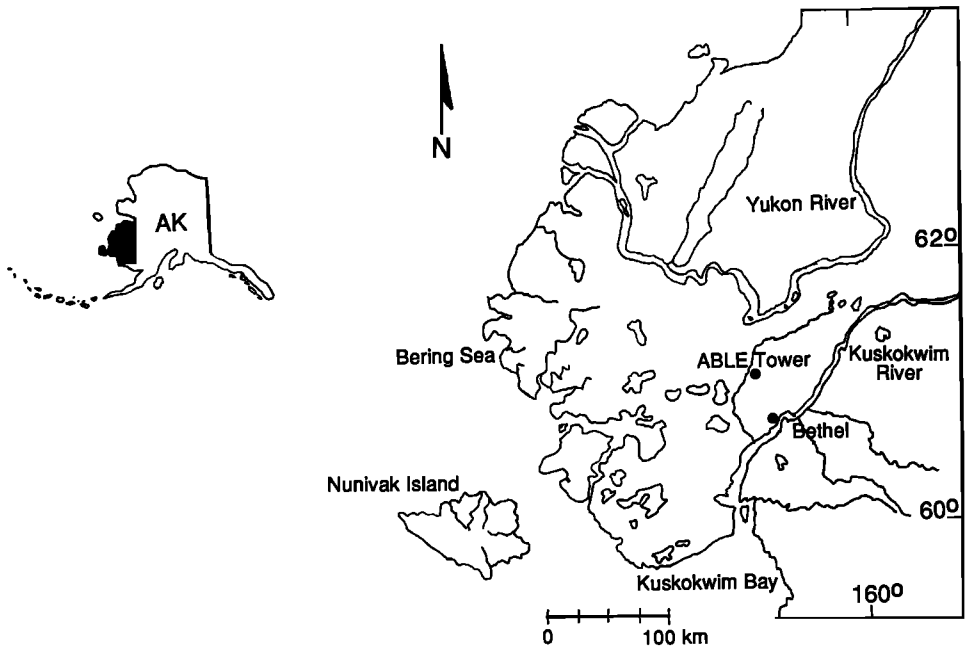
Paper number 91JD02885.
0148-0227/92/91JD-02885$05.00



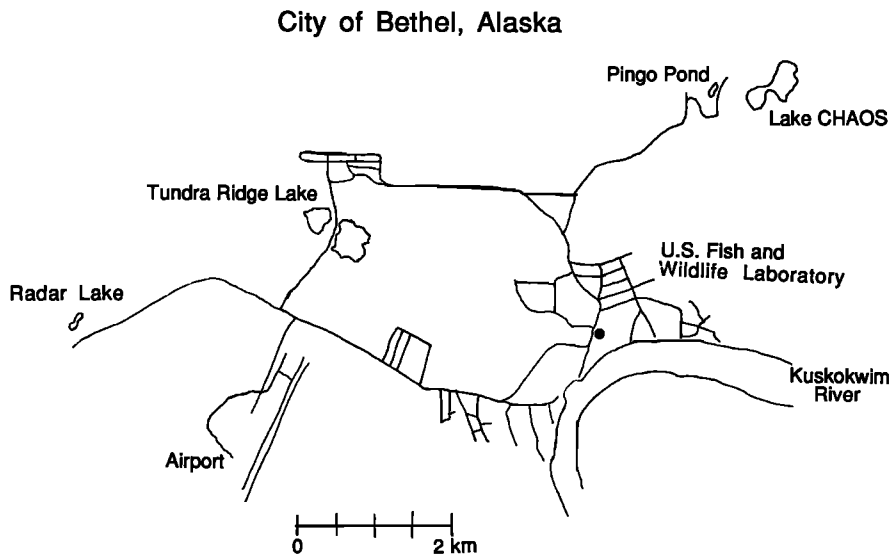


Fig. 1. The locations of the GTE/ABLE 3A tower and lakes on the Yukon-Kuskokwim Delta near Bethel, western Alaska.

ratio and that of the Peedee belemnite standard in parts per mil (‰) [*Craig*, 1953]. When corrected for fractionations resulting from removal by OH radicals in the troposphere and nonsteady-state variations in concentration and isotopic composition, the average $\delta^{13}C$ value of summed methane sources is considerably lighter than the measured atmospheric value. Average values for atmospheric methane sources of -55.5 and -55.4‰ were calculated by *Stevens and Engelkemeir* [1988] and *Craig et al.* [1988], respectively, using *Davidson et al.*'s [1987] kinetic isotope fractionation factor for k_{12}/k_{13} of 1.010 ± 0.007 for OH radical fractionation. Recently, *Cantrell et al.* [1990] have redetermined this fractionation factor to be 1.0054 ± 0.0009, suggesting that total methane sources to the atmosphere may have an average value significantly heavier than -55‰.

In general, natural wetlands appear to produce methane with a lighter, more negative $\delta^{13}C$ value, whereas methane from abiogenic sources and biomass burning has a heavier, more positive $\delta^{13}C$ value (see reviews by *Cicerone and Oremland*, 1988; *Tyler*, 1989]). However, isotopic values of methane from individual wetland environments should reflect the balance of processes controlling its production, transport, and consumption (oxidation) and thus net fluxes to the atmosphere. Isotopic fractionation of carbon during methane production [*Rosenfeld and Silverman*, 1959] and consumption [*Silverman and Oyama*, 1968; *Coleman et al.*, 1981; *Alperin et al.*, 1988] as well as isotopic differences in organic carbon sources will control the isotopic value of the net flux from a specific site. Complications result from observations that seasonal variations which occur in all of these processes can

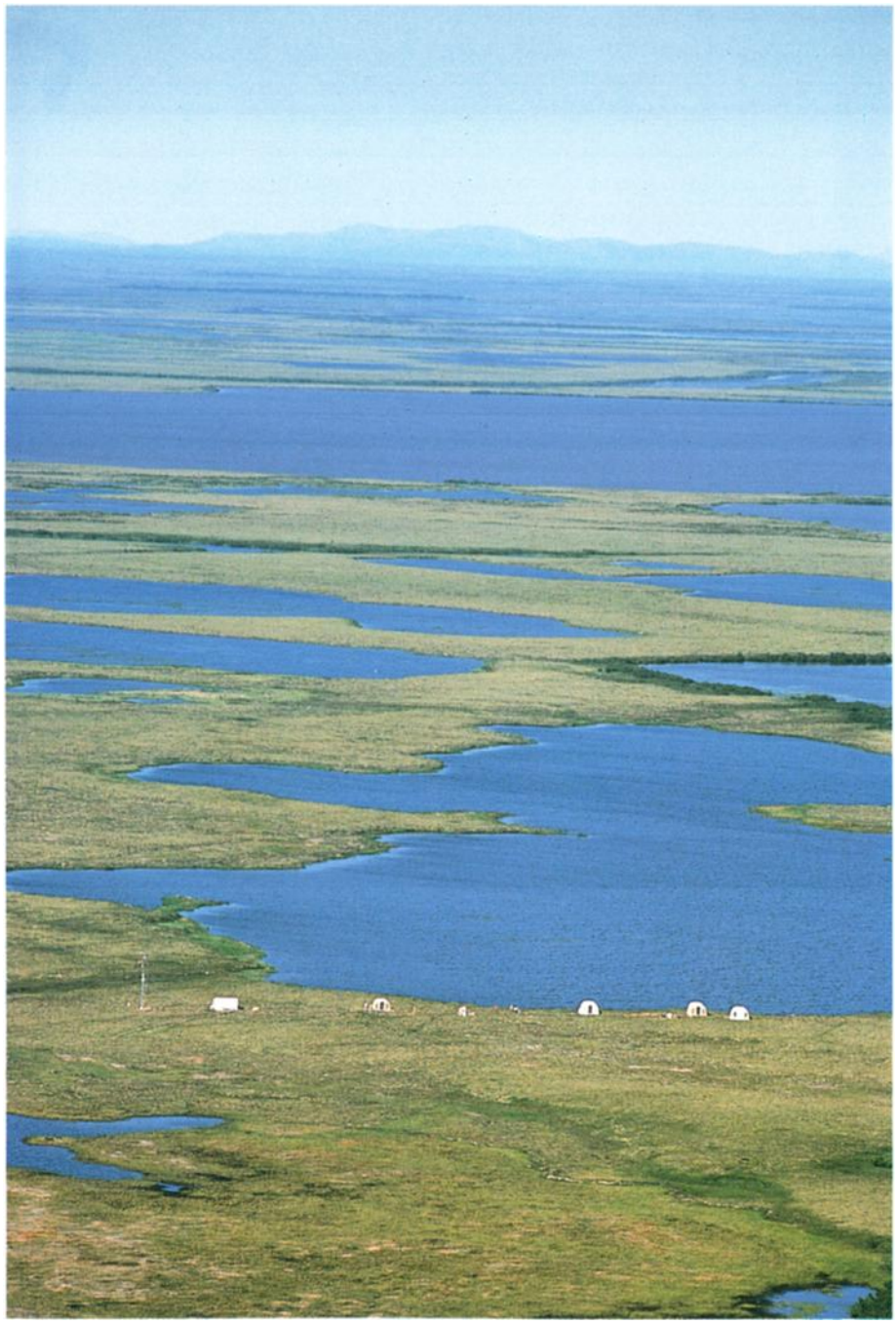


Plate 1. Aerial photograph of Yukon-Kuskokwim Delta surrounding the GTE/ABLE 3A tower site. Lake ABLE is immediately behind tower boardwalk.

apparently lead to relatively large seasonal variations in the $\delta^{13}C$ value of emitted methane [*Martens et al.*, 1986; *Chanton and Martens*, 1988; *Kelley et al.*, 1992]. Seasonal observations may be required to adequately characterize the isotopic composition of methane fluxes from sites where such variations occur. These observations may also require weighting to account for seasonal methane flux variation itself [*Martens et al.*, 1986].

The central objective of our work was to isotopically characterize methane emitted from tundra environments supporting relatively high fluxes to the atmosphere. During initial field reconnaissance, we found large quantities of methane-rich gas bubbles in the sediments of lakes and expanded our objectives to include (1) characterizing both lake and tundra methane releases, (2) examining factors controlling bubble composition in lakes, (3) assessing spatial and temporal variability in gas bubble major gas and isotopic composition, (4) determining the importance of lake gas bubble ebullition to the regional methane flux, and finally, (5) making preliminary measurements of the age of methane carbon in lake gas bubbles using radiocarbon dating.

STUDY AREA

All study sites were located within 40 km of the town of Bethel (60° 45' N, 161° 45' W) on the Yukon-Kuskokwim Delta near the southwestern coast of Alaska (Figure 1). The

Delta consists of flat, poorly drained tundra truncated by the Yukon and Kuskokwim Rivers and numerous shallow lakes (Plate 1). Much of the Delta is a wildlife refuge which has been extensively surveyed [*U.S. Fish and Wildlife Service*, 1988]. A detailed summary of terrain, vegetation, soil types, water coverage and temperature variation is presented in *Bartlett et al.* [this issue].

The isotope measurements we report here were performed on methane collected from static chamber flux experiments and on methane in gas bubbles found in organic-rich tundra lake environments including those in the Bethel area and surrounding the GTE micrometeorological tower site approximately 34 km to the NW of Bethel. In addition, eight accelerator mass spectrometry (AMS) radiocarbon measurements were obtained for methane in gas bubbles from two tundra lakes near Bethel.

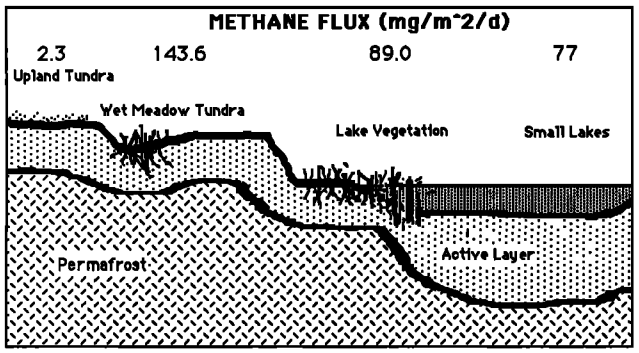


Fig. 2. Methane fluxes from tundra environments of the Yukon-Kuskokwim Delta measured during the 1988 ABLE 3A mission [data from *Bartlett et al.*, this issue].

METHODS

Site Selection

On the basis of the previous methane flux measurements of *Sebacher et al.* [1986] and those conducted during the field experiments by *Bartlett et al.* [this issue] using static chamber techniques, we have focused our isotopic characterization of methane fluxes on herbaceous or "wet meadow" tundra which comprises approximately 25% of the Delta area but contributes approximately 75% of the total regional methane flux. Wet meadow tundra is dominated by grasses and sedges as compared with the drier dwarf scrub or "upland" tundra which includes raised bogs, tussock tundra, and heaths. Upland tundra accounts for approximately 42% of the Delta area.

Wet meadow vegetation on moist to saturated soils grades into aquatic vegetation on flooded and nonflooded margins of lakes and ponds. We measured the isotopic composition of methane emitted from flooded "lake edge" vegetation as part of our characterization of the total wet meadow flux.

Open water comprises approximately 15% of the total Delta area, the small lakes contributing approximately 20% of the annual flux from the Delta [*Bartlett et al.*, this issue]; see below. The remaining 18% of Delta area consists of small areas of forest along the major rivers and scrub thickets. Dominant plant species found in each type of environment are summarized by *Bartlett et al.* [this issue].

Average methane fluxes measured by static chamber techniques from upland tundra, wet meadow tundra and lake edge vegetation, and open lake waters by *Bartlett et al.* [this issue] are schematically presented in Figure 2.

Preliminary observational surveys revealed the presence of large quantities of methane-rich gas bubbles, particularly along lake edge environments and in smaller lakes rich in organic detritus. We systematically collected gas bubble samples from five lakes in order to characterize spatial and temporal variations in concentrations of methane and other gases as well as methane isotopic composition. Other lakes were sampled in order to provide information concerning ranges in composition in the Bethel and tower site areas.

Isotope Flux Measurements

Flux measurements utilized to characterize the $\delta^{13}C$ value of methane emitted from wet meadow tundra were all made over 0.4 m^2 aluminum flux collars installed at the beginning of the study period. The three wet meadow sites were located on the Bethel transect described by *Bartlett et al.* [this issue]. No collars were used to obtain measurements from the nonpermanent lake edge sites. Box-shaped aluminum chambers of 82 or 144 L volume used to capture emitted gases were covered with insulating, solar-reflecting blankets during gas sample collection. Generally, the isotope flux experiments were carried out following the methane flux measurements of *Bartlett et al.* [this issue] and utilized the same chambers left in place to continue collecting emitted gases. We attempted to reach chamber air concentrations of 20 to 100 ppm methane which required total sample collection times averaging four hours. At the end of each experiment, chamber air was pumped into a 4 L evacuated Scotty IV Extra-Life cylinder (Scott Specialty Gases, Plumsteadville, PA) and pressurized to approximately 35 psi using a battery-driven stainless steel bellows pump. During sample pumping, a stopper at the opposite end of the chamber was opened slightly to avoid effects of chamber depressurization. Corrections were made for inclusion of outside air containing low methane concentrations.

Gas Bubble Sampling Sites

In order to examine factors controlling lake bubble composition including spatial and temporal variability, we established fixed sites at four lakes with widely varying vegetation densities and other lake edge characteristics. These lakes included Lake ABLE adjoining the GTE/ABLE tower site (Plate 1), three Bethel area lakes (Figure 1) named Radar Lake, because of its immediate proximity to the abandoned DEW line radar site known as White Alice; Tundra Ridge Lake, located in the northwestern subdivision of Bethel; and Pingo Pond, located near the wet meadow experimental site just outside the town. A second lake near the wet meadow site, Lake CHAOS, was also sampled extensively at a variety of stations during the expedition. All of the lakes sampled had maximum depths less than 1 to 2 m and were lined along their margins with varying amounts of emergent vegetation. We measured spatial gas bubble composition variations within Lake CHAOS and Lake ABLE through sampling transects between open water sediments and heavily vegetated lake edge sites. In addition, we made single sampling visits to numerous lakes in the tower site area in order to investigate the full range of spatial compositional variation as well as factors controlling it.

Gas Bubble Sampling

Gas bubble samples were collected from flooded lake edge environments utilizing a new invention designed in a leading

Bethel food and department store. The device, nicknamed the "whumper," consists of a 2 m extendable pole, at the end of which a large plastic funnel of rugged construction is mounted. Thick-walled (3.2 mm o.d.) nylon tubing is attached to the inside apex of the funnel such that gas collected while the funnel is under water can be pulled through the tubing into a 60 mL sample syringe at the handle end of the pole. A plastic 3-way stopcock attached to the tubing with tube end fittings provides the interface to which a sample syringe can be attached. When pushed up and down on the surface of gas-rich sediments, the whumper can quickly obtain relatively large gas samples.

Gas bubble samples were collected for measurements of methane, CO_2 and $N_2 + O_2 + Ar$ concentration, $\delta^{13}C$ and δD methane values, and methane radiocarbon concentration. Bubble samples for stable isotope analysis were transferred via water displacement into precleaned 7 or 15 mL glass serum bottles, sealed with thick butyl rubber stoppers and crimp-sealed. Larger volumes of gas needed for radiocarbon measurements were transferred into evacuated stainless steel cylinders.

Gas Bubble Concentration Analyses

The $N_2 + O_2 + Ar$, CO_2 and methane concentrations of gas bubbles from lake edge environments were determined by thermal conductivity detector gas chromatography within hours of sample collection, with the exception of late August and September samples, which were returned to our laboratory at the University of North Carolina for analysis.

Measurements of $\delta^{13}C$ and δD

Methods used for methane $\delta^{13}C$ measurements are described in *Chanton et al.* [this issue]. The preparation of methane in gas bubble samples for δD measurements utilized the same vacuum line employed for $\delta^{13}C$ sample combustion. The δD samples were processed following the zinc preparation technique of *Coleman et al.* [1982] using sealed glass tubes [*Kendall and Coplen*, 1985]. After combustion of methane to CO_2 and H_2O [*Chanton et al.*, this issue], the H_2O was quantitatively trapped with a pentane-liquid nitrogen slush trap (-128°C). The water was then cryogenically transferred to 9 mm o.d. glass tubes containing zinc turnings obtained from John Hayes of Indiana University; the tubes were flame-sealed. Reaction of the water with the zinc to form H_2 was accomplished by heating the tubes in a block heater at 500°C for 30 min. The liberated H_2 gas was then analyzed for H/D content on a Finnigan MAT 251 isotope ratio mass spectrometer at the North Carolina State University Isotope Facility.

Through the courtesy of Susan Trumbore and co-workers at Lawrence Livermore Laboratory's Center for Accelerator Mass

TABLE 1. The $\delta^{13}C$ Values of Methane Emitted from Wet Meadow and Vegetated Lake Edge Environments

Habitat Type	Date in 1988	Chamber Number	Chamber Methane, ppm	Corrected $\delta^{13}CH_4$, ‰
Wet Meadow	July 10	4A	33	-67.69
	July 19	4A	97	-61.06
	July 26	4A	19	-63.85
	Aug. 4	4A	22	-63.72
	Aug. 10	4A	109	-63.64
	July 10	4B	172	-65.95
	July 12	4B	122	-66.02
	July 19	4B	126	-64.78
	*July 19	4B	126	-65.07
	July 26	4B	37	-66.54
	Aug. 4	4B	20	-67.41
	Aug. 10	4B	21	-68.20
	July 10	4C	120	-65.96
	*July 10	4C	120	-66.31
				$\bar{X}$ = -65.43 ± 2.07 (n = 12)
Lake Edge	July 18	A	62	-66.15
	July 18	B	53	-68.55
	July 25	A	94	-65.54
	July 25	B	60	-63.39
	Aug. 2	A	71	-65.70
	Aug. 2	B	64	-70.30
				$\bar{X}$ = -66.61 ± 2.45 (n = 6)
Summed Mean				$\bar{X}$ = -65.82 ± 2.21 (n = 18)

*Duplicate sample processing and analysis ($\bar{X}$ ± 1/2 range); July 19, $\bar{X}$ = -64.92 ± 0.14; July 10, $\bar{X}$ = -66.14 ± 0.18.

Spectrometry (CAMS), we were able to obtain duplicate AMS radiocarbon measurements on methane from four gas bubble samples, two from the fixed temporal sampling site off the dock at Lake ABLE, one from the fixed site in Pingo Pond, and another on the opposite shore of Pingo Pond.

Results and Discussion

The $\delta^{13}C$ Value of Wet Meadow Methane Emissions

The results of 18 wet meadow and vegetated lake edge $\delta^{13}C$ flux measurements are summarized in Table 1. Twelve flux experiments were carried out at the wet meadow sites near Bethel using three different collars numbered 4A, 4B and 4C. The 4A and 4B sites were sampled on a nearly weekly basis from July 10 through August 10, 1988. A mean $\delta^{13}C$ value for emitted methane of -65.43 ± 2.07‰ (±1 sigma) is calculated by summing these fluxes. Six experiments in the flooded lake edge environments at the Lake CHAOS site yielded a mean $\delta^{13}C$ value of -66.61 ± 2.45‰. These sites were sampled on July 18, July 25, and August 2, 1988.

The mean $\delta^{13}C$ value for methane emitted from all wet meadow and vegetated lake edge sites is -65.82 ± 2.21‰. No correlation was observed between fluxes and $\delta^{13}C$ values of emitted methane. Temporal and spatial variations in temperature at wet meadow sites as determined from thermistor probes are presented in *Bartlett et al.*, [this issue]. We observed no correlation between these variations and isotopic values for emitted methane.

Our mean $\delta^{13}C$ value for methane emissions from wet meadow tundra falls within the range of values observed in two previous studies of tundra ecosystems. *Quay et al.* [1988] reported a range of -70 to -59‰ based on 17 chamber flux experiments carried out during August 1987 along a 200 km transect following the Alyeska pipeline from the northern foothills of the Brooks Range to Prudhoe Bay. The mean value for methane emissions was -64 ± 4‰. As in our study, no correlation between methane flux rate and isotopic value was observed.

Wahlen et al. [1989] report a mean $\delta^{13}C$ value of -62.9 ± 1.9‰ (n = 8) for methane emitted from tundra in Manitoba, Canada. This mean value is within the uncertainty of our Alaskan results.

Variation in Gas Bubble Composition

The concentrations of methane, $N_2 + O_2 + Ar$ and CO_2 observed in gas bubbles sampled from July through September at the fixed sites in the three lakes near Bethel plus Lake ABLE at the tower site are presented in Table 2. The vegetation at these sites ranged from low density in Lake ABLE and Pingo Pond to high density at Radar Lake and Tundra Ridge Lake. Compositional differences at these sites (Figure 3) appear to reflect observed variations in the density of both living vegetation, primarily *Carex rostrata*, and macrophyte plus tundra

TABLE 2. Temporal Variations in Bubble Composition From Four Alaskan Lakes

Lake	Date in 1988	Methane, %	N_2+O_2+Ar, %	CO_2, %
Radar Lake	July 13	16.0 (2, 4.4)*	82.8 (2, 4.8)	1.07 (2, 0.48)
	July 22	19.9 (3, 0.6)	78.9 (3, 0.7)	1.24 (3, 0.27)
	July 31	20.5 (3, 3.3)	77.5 (3, 3.8)	1.97 (3, 0.45)
	Aug. 5	18.7 (3, 1.0)	79.3 (3, 0.9)	1.96 (3, 0.14)
	Aug. 28	29.6 (2, 0.6)	67.8 (2, 1.8)	1.48 (1)
	Sept. 25	42.2 (2, 1.2)	55.2 (2, 0.2)	1.66 (1)
	Mean	23.5 (15, 8.8)	74.6 (15, 9.3)	1.60 (13, 0.48)
Tundra Ridge Lake	July 13	34.8 (3, 5.3)	64.4 (3, 5.4)	0.78 (3, 0.37)
	July 22	43.6 (3, 3.6)	54.6 (3, 3.6)	1.85 (3, 0.09)
	July 31	18.1 (3, 0.3)	79.8 (3, 0.3)	2.11 (3, 0.02)
	Aug. 5	20.4 (3, 0.5)	77.7 (3, 0.6)	1.98 (3, 0.15)
	Aug. 28	29.7 (2, 5.3)	66.8 (2, 7.0)	5.11 (1)
	Sept. 25	35.0 (2, 17.4)	64.1 (2, 17.6)	1.18 (1)
	Mean	30.0 (16, 11.9)	68.2 (16, 11.9)	1.89 (14, 1.08)
Pingo Pond	July 13	61.2 (2, 3.2)	32.8 (2, 3.0)	6.06 (2, 0.16)
	July 22	60.6 (3, 5.6)	30.1 (3, 7.1)	9.26 (3, 1.50)
	July 31	44.2 (3, 0.5)	50.0 (3, 0.5)	5.71 (3, 0.11)
	Aug. 1	37.2 (1)	57.7 (1)	5.15 (1)
	Aug. 5	39.9 (3, 2.6)	53.4 (3, 3.8)	6.70 (3, 1.66)
	Aug. 28	45.0 (2, 9.4)	52.1 (2, 11.9)	5.49 (1)
	Sept. 25	55.6 (1)	41.4 (1)	n.d.
	Mean	49.3 (15, 10.4)	44.6 (15, 11.8)	6.75 (13, 1.76)
Lake ABLE	July 14	47.0 (2, 4.8)	51.5 (2, 4.8)	1.53 (2, 0.15)
	July 21	62.4 (3, 8.8)	32.4 (3, 11.7)	5.24 (3, 3.11)
	July 25	66.5 (6, 3.8)	27.8 (6, 3.3)	5.73 (6, 1.62)
	Aug. 8	62.2 (6, 11.9)	34.7 (6, 13.1)	3.08 (6, 1.16)
	Mean	62.0 (17, 9.9)	33.8 (17, 11.4)	4.21 (17, 2.21)

*Data include number of analyses plus standard deviation or 1/2 range if n = 2 (n, S.D.); n.d., not determined.

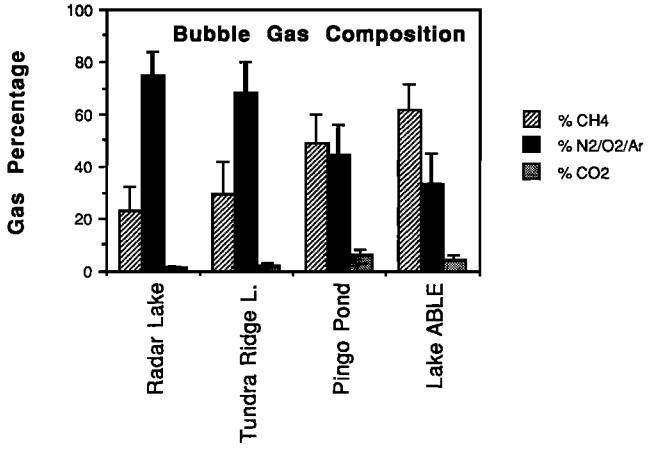


Fig. 3. Variations in mean bubble gas concentrations from fixed temporal sampling sites in four Delta lakes (error bars = 1 σ).

detritus; no systematic temporal changes are apparent. Gas bubbles from gently sloping, shallow (< 50 cm deep) lake edge sites dominated by *Carex* plants such as Radar Lake, Tundra Ridge Lake, and Lake CHAOS (Table 3) have low methane concentrations and correspondingly high $N_2 + O_2 + Ar$ concentrations. Gas bubbles from the deeper edges of relatively steep-sided lakes such as Pingo Pond and Lake ABLE with less dense and patchy stands of *Carex* and evidence for ongoing or recent slumps of tundra detritus have methane concentrations as high as 79% with much lower $N_2 + O_2 + Ar$ content. Mean methane content at the Lake ABLE fixed site is 62.0 ± 9.9% (n = 17). Similar gas bubble compositional differences between vegetated and nonvegetated sites have been previously observed by *Chanton et al.* [1989] and *Chanton and Dacey* [1991].

Mean gas composition values from the four fixed sites (Table 2) plus spatial variation data from within-lake and multiple-lake surveys are summarized in Table 3. These data further amplify the differences seen between the fixed sites.

TABLE 3. Spatial Variations in Bubble Composition of Lakes on the Yukon-Kuskokwim Delta Near Bethel, Alaska

Lake	Date in 1988	Methane, %	N_2+O_2+Ar, %	CO_2, %	Comments
Table 2 Means					
Radar Lake	–	23.5 (15, 8.8)*	74.6 (15, 9.3)	1.60 (13, 0.48)	July 13 to Sept. 25
Tundra Ridge	–	30.0 (16, 11.9)	68.2 (16, 11.9)	1.89 (14, 1.08)	July 13 to Sept. 25
Pingo Pond	–	49.3 (15, 10.4)	44.6 (15, 11.8)	6.75 (13, 1.76)	July 13 to Sept. 25
Lake ABLE	–	62.0 (17, 9.9)	33.4 (17, 11.4)	4.21 (17, 2.21)	July 13 to Sept. 25
Lake CHAOS Survey					
Lake CHAOS	July 12	28.0 (2, 1.4)	70.4 (2, 1.8)	1.60 (2, 0.36)	*Arctophila* bed
Lake CHAOS	July 12	20.4 (1)	78.0 (1)	1.57 (1)	*Carex* bed
Lake CHAOS	July 12	42.2 (2, 0.4)	54.4 (2, 0.4)	3.42 (2, 0.12)	muddy sediment
Lake CHAOS	July 22	18.1 (1)	80.6 (1)	1.27 (1)	muddy sediment
Lake CHAOS	July 31	24.9 (3, 3.2)	71.5 (3, 4.2)	3.57 (3, 1.14)	*Arctophila* bed
Lake CHAOS	Aug. 5	11.2 (2, 3.2)	86.6 (2, 2.8)	2.20 (2, 0.44)	*Arctophila* bed
Lake CHAOS	Aug. 10	15.4 (1)	82.6 (1)	2.04 (1)	*Carex* bed
Lake ABLE Edge Surveys					
Lake ABLE	July 14	65.1 (2, 2.5)	28.7 (2, 3.1)	6.22 (2, 0.62)	slumping tundra detritus
Lake ABLE	July 14	42.6 (2, 5.4)	55.6 (2, 5.4)	1.75 (2, 0.09)	*Carex* bed
Lake ABLE	July 14	12.3 (2, 1.3)	84.4 (2, 0.2)	2.26 (2, 0.44)	*Carex* bed
Lake ABLE	July 14	61.6 (2, 2.4)	35.2 (2, 2.6)	3.26 (2, 0.16)	7 m into lake
Lake ABLE	July 25	69.0 (6, 4.6)	22.7 (6, 7.7)	8.26 (6, 3.13)	slumping tundra detritus
Lake ABLE	Aug. 8	72.9 (6, 2.7)	18.3 (6, 3.8)	8.80 (6, 2.33)	slumping tundra detritus
Lake ABLE Cross Lake Transect					
Lake ABLE	July 18	44 5 (2, 5.0)	51.6 (2, 6.2)	3.74 (2, 1.80)	~100 m into lake; *Equisetum* bed; muddy
Lake ABLE	July 18	54.2 (2, 1.1)	41.2 (2, 2.0)	4.54 (2, 0.96)	~90 m into lake; muddy detritus
Lake ABLE	July 18	57.2 (2, 0.1)	38.2 (2, 0.6)	4.62 (2, 0.49)	~70 m into lake; muddy detritus
Lake ABLE	July 18	62.4 (1)	32.2 (1)	5.46 (1)	~40 m into lake; muddy detritus
Lake ABLE	July 18	59.6 (2, 1.8)	33.0 (2, 3.6)	7.30 (2, 1.88)	~15 m into lake; muddy detritus
Tower Site Area Lake Survey					
Lake BREW	July 19	16.6 (4, 5.3)	82.7 (4, 5.6)	0.73 (4, 0.33)	detritus-rich
Lake BREW	Aug. 8	21.3 (3, 1.5)	76.7 (3, 2.2)	2.12 (3, 0.75)	detritus-rich
Lake Peter	Aug. 8	31.8 (1)	59.3 (1)	8.84 (1)	
Lake Karen	Aug. 8	69.6 (1)	26.9 (1)	3.49 (1)	
Shirley Slough	Aug. 8	63.4 (1)	31.2 (1)	5.39 (1)	
Lake Turn the Corner	Aug. 8	36.9 (1)	62.0 (1)	1.04 (1)	
Lake Drewry	Aug. 8	26.5 (1)	71.7 (1)	1.76 (1)	
Lake Crill	Aug. 8	48.8 (1)	47.2 (1)	3.99 (1)	
Lake Kathy	Aug. 8	29.6 (1)	66.6 (1)	3.78 (1)	
Lake Song-Miao	Aug. 8	13.1 (1)	82.1 (1)	4.78 (1)	

*Data include number of analyses plus standard deviation or 1/2 range if n = 2 (n, S.D.).

The spatial variation in methane concentration is large, ranging from 11% to 79% (Table 3), the lowest concentrations generally found in heavily vegetated lake edge sites and highest concentrations in detritus-laden open water sites. For example, the mean methane content of all Lake ABLE samples (data from Tables 2 and 3) is 60.0 ± 14.3% (n = 46), which includes samples from patches of lake edges with dense stands of emergent macrophytes. This mean value rises to 63.1 ± 9.3% (n = 42) when samples from these latter, heavily vegetated edge sites are excluded.

Gas Bubble Composition and Ebullitive Methane Fluxes

It is now thought that gas bubble ebullition is the dominant mode of methane transport from organic-rich sediments and nonvegetated wetlands in tropical and temperate environments [e.g., *Martens and Klump*, 1980; *Chanton et al.*, 1989; *Devol et al.*, 1988; *Crill*, 1992].

Direct observations suggest that the small organic detritus-rich lakes of the Yukon-Kuskokwim Delta can support significant ebullitive fluxes. During the expedition, gas bubbles were frequently sighted breaking the surface of Lake ABLE during calm weather conditions. Even gentle disturbances of the bottom of Lake ABLE and Pingo Pond induced by samplers or swimmers resulted in eruptions of gas bubbles.

Turbid lake waters observed during low-altitude flights (Plate 1) suggest that the shallow lakes are frequently stirred by high winds associated with storm events. Spontaneous release of methane-rich bubbles appears to occur at least into early fall. Local Bethel residents note the practice of flaring gas pockets trapped under ice immediately following lake ice formation in late September or October. Aerobic oxidation of methane trapped under the ice may play a major role in producing anoxic winter lake conditions as previously observed in the Experimental Lakes Area of Canada [*Rudd et al.*, 1976; *Rudd and Hamilton*, 1978] and for a subalpine lake in the Cascades of Washington [*Rau*, 1978].

Recent work has established an empirical relationship (Figure 4) between gas bubble methane (or N_2) concentrations and ebullitive fluxes through a direct comparison of concentration versus flux results from a variety of open water wetland and river-estuarine environments in the southeastern United States [*Chanton et al.*, 1989]. This relationship is based on the fact that the pore waters of sediments experiencing greater rates of bubble production and ebullition are more effectively stripped of dissolved $N_2 + O_2 + Ar$, which generally must be replaced by relatively slow diffusion from overlying waters [*Kipphut and Martens*, 1982]. As a result, gas bubbles from sites with high ebullitive fluxes are depleted in $N_2 + O_2 + Ar$ and enriched in methane.

An estimate of ebullitive transport from the Delta can be made by interpolating a bubble release rate from the ebullitive flux versus composition results (Figure 4). This estimate is likely to be conservative on an aerial basis if we assume that significant ebullition only occurs from small, detritus-rich lakes such as Lake ABLE and Pingo Pond during the warm season (June to September). As observed by *Bartlett et al.* [this issue], diffusive methane fluxes from such small lakes and ponds are nearly 20 times higher than those from larger lakes and are approximately equal to fluxes from wet meadow sites (Figure 2). Such small lakes represent approximately 5% of the total Delta area according to these authors.

Gas bubble composition data for all the small lakes we sampled are included in Tables 2 and 3. Mean gas bubble

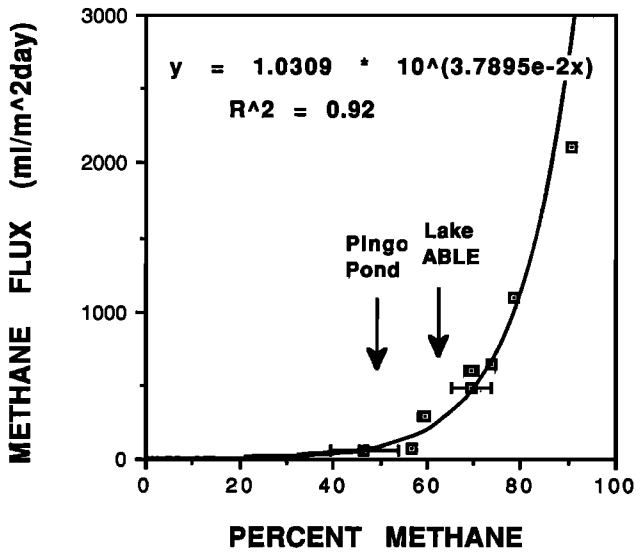


Fig. 4. Relationship between ebullitive methane flux and gas bubble methane concentration for southeastern U.S. wetland and coastal environments. Mean methane concentrations for Lake ABLE and Pingo Pond samples are indicated.

methane concentration data from the four frequently sampled small lakes are listed in Table 2. Methane content ranges from 23.5% in Radar Lake to 62.0% in Lake ABLE. Using this range of values, we interpolate the Figure 4 curve fit to obtain methane ebullition rates ranging from 8.0 to 231 mL CH_4 m^{-2} d^{-1}, or 5.4 to 155 mg CH_4 m^{-2} d^{-1}. If ebullition occurs for approximately 130 days during frost-free conditions [*Bartlett et al.*, this issue], then the small lakes of the Delta comprising approximately 4800 km^2 area can emit approximately 0.34 to 9.7 x 10^{10} g CH_4 yr^{-1} to the atmosphere. This range of values is approximately 0.8% to 22% of the wet meadow flux of 45 x 10^{10} g CH_4 yr^{-1} or 0.6% to 17% of the total emission calculated for the Delta by *Bartlett et al.* [this issue]. The calculated bubble ebullition rates indicate that nonvegetated areas of detritus-rich lakes such as Lake ABLE and Pingo Pond will support much higher ebullitive fluxes than heavily vegetated areas. Further work will obviously be required to establish what fraction of the total lake area actually supports ebullitive emissions and to directly determine bubble ebullition rates.

Stable Isotope Composition of Gas Bubble Methane

Upon finding significant reservoirs of methane-rich gas bubbles in Delta lakes, we systematically collected samples for isotope analyses at the same sites where the gas bubble composition measurements summarized in Figure 3 were made. In order to investigate the possibility of temporal as well as spatial variations in methane isotopic composition, we resampled the fixed sites from mid-July through September in three of the five lakes. Lake CHAOS was not systematically sampled because of water level fluctuations. We sampled Lake ABLE on five dates between July 11 and August 8, 1988, when the tower experiments were shut down. The results of $\delta^{13}C$ and δD analyses at the fixed stations for temporal studies are summarized in Table 4, while spatial data from all lakes sampled are summarized in Table 5.

Combined stable carbon and hydrogen isotopic analyses were carried out because they can together provide greater insights concerning methane production and oxidation processes

TABLE 4. Temporal Variations in Gas Bubble Methane Stable Isotopic Composition

Lake	Date in 1988	Methane $\delta^{13}C$, ‰	Methane δD, ‰
Radar Lake	July 13	-60.30 (2, 3.12)*	n.d.
	July 22	-56.26 (2, 0.02)	-360.0 (1)
	July 31	-55.48 (3, 0.20)	n.d.
	Aug. 5	-55.18 (2, 0.40)	-360.0 (1)
	Aug. 28	-56.58 (2, 0.24)	-381.3 (1)
	Sept. 25	-57.78 (2, 0.02)	-376.9 (1)
	Mean	-56.82 (13, 2.19)	-369.6 (4, 11.8)
Tundra Ridge Lake	July 13	-62.90 (4, 5.19)	n.d.
	July 22	-57.37 (2, 0.41)	-382.5 (1)
	July 31	-59.57 (2, 0.07)	-361.0 (1)
	Aug. 5	-59.27 (2, 0.46)	-367.4 (1)
	Aug. 28	-57.93 (2, 1.43)	-382.4 (1)
	Sept. 25	-61.67 (1)	-360.5 (1)
	Mean	-60.12 (13, 3.49)	-370.8 (5, 11.0)
Pingo Pond	July 13	-63.26 (3, 0.72)	-340.6 (1)
	July 22	-62.67 (2, 0.03)	-326.4 (1)
	July 31	-62.54 (2, 0.08)	-338.6 (1)
	Aug. 1	-59.96 (1)	n.d.
	Aug. 5	-59.80 (2, 0.38)	-370.8 (1)
	Aug. 28	-63.54 (1)	-361.0 (1)
	Sept. 25	-58.04 (1)	-362.1 (1)
	Mean	-61.78 (12, 1.88)	-349.9 (6, 17.2)
Lake ABLE	July 11	-60.99 (2, 0.01)	-321.5 (1)
	July 14	-58.41 (2, 2.71)	-346.6 (1)
	July 21	-60.51 (3, 0.37)	-342.4 (1)
	July 25	-59.16 (2, 0.16)	-354.4 (3, 2.6)
	Aug. 8	-61.64 (3, 0.40)	-361.1 (1)
	Mean	-60.30 (12, 1.69)	-347.8 (7, 13.2)

*Data includes number of analyses plus standard deviation or 1/2 range if $n = 2$ (n, S.D.); n.d., not determined.

ultimately controlling net fluxes to the atmosphere. In particular, the combination of these stable isotope values has proven useful for differentiating between production and oxidation mechanisms [*Schoell*, 1980; *Coleman et al.*, 1981; *Woltemate et al.*, 1984; *Whiticar et al.*, 1986; *Burke et al.*, 1988]. Heavier $\delta^{13}C$ and lighter δD values are associated with methane production via acetate fermentation as opposed to CO_2 reduction. The oxidation of biogenic methane leads to a shift to heavier values for both $\delta^{13}C$ and δD.

Temporal Variation in Isotopic Values

Seasonal variations in the $\delta^{13}C$ of methane attributed to changes in production pathways or substrates utilized in production have been observed at several sites in North Carolina [*Martens et al.*, 1986; *Burke et al.*, 1988; *Chanton and Martens*, 1988]. Evidence for seasonal variations in the $\delta^{13}C$ of methane at the Alaskan lake sites is summarized in Figure 5.

In all four lakes there appears to be a trend toward heavier $\delta^{13}C$ values during late July or early August, and a drop toward lighter values later in the summer. One exception is the heavy -58‰ value found in Pingo Pond in late September. The midsummer shift toward heavier values ranges from 2‰ to 5‰ among the lakes. As mentioned above, we have observed similar, though generally larger midsummer shifts toward heavier $\delta^{13}C$ values in gas bubble methane from a coastal marine basin, Cape Lookout Bight [*Martens et al.*, 1986], and tidal freshwater sediments of the White Oak River Estuary [*Chanton and Martens*, 1988]. The seasonal range observed at these previously studied sites ranged from 3‰ to 12‰. Combined measurements of seasonal $\delta^{13}C$ and δD variations at the Cape Lookout Bight site [*Burke et al.*, 1988] indicated that production rather than oxidation effects resulted in the observed isotopic variations.

Also included in Figure 5 are δD variations in methane from the Alaskan lake bubble samples. Although there is some tendency for δD values to become lighter as $\delta^{13}C$ values become heavier (see discussion below), it is not possible to discern any clear seasonal trends in the δD values alone.

Spatial Variations in Isotopic Values

Among lakes, there are trends toward lighter $\delta^{13}C$ and heavier δD values (Figure 6) as one progresses from lakes with lowest gas bubble methane concentration (Radar Lake) toward lake sites with the least emergent vegetation and highest gas bubble methane concentrations (Pingo Pond and Lake ABLE). A plot (Figure 7) of all gas bubble $\delta^{13}C$ versus δD values (Tables 4 and 5) from the four frequently sampled lakes,

TABLE 5. Spatial Variations in Gas Bubble Methane Stable Isotopic Composition

Lake	Date in 1988	Methane $\delta^{13}C$, ‰	Methane δD, ‰	Comments
Table 2 Means				
Radar Lake	--	-56.82 (13, 2.19)*	-369.6 (4, 11.8)	July 13 to Sept. 25
Tundra Ridge	--	-60.12 (13, 3.49)	-370.8 (5, 11.0)	July 13 to Sept. 25
Pingo Pond	--	-61.78 (12, 1.88)	-349.9 (6, 17.2)	July 13 to Sept. 25
Lake ABLE	--	-60.30 (12, 1.69)	-347.8 (7, 13.2)	July 11 to Aug. 8
Lake CHAOS Survey				
Lake CHAOS	July 12	-56.70 (5, 3.40)	n.d.	*Arctophila* bed
Lake CHAOS	July 22	-70.86 (2, 0.10)	n.d.	muddy sediment
Lake CHAOS	July 31	-52.53 (2, 0.05)	n.d.	*Arctophila* bed
Lake CHAOS	Aug. 5	-55.23 (1)	n.d.	*Arctophila* bed
Lake CHAOS	Aug. 10	-61.44 (1)	n.d.	*Carex* bed
Lake ABLE Edge Survey				
Lake ABLE	July 14	-56.50 (1)	-371.0 (1)	slumping tundra detritus
Lake ABLE	July 14	-54.08 (2, 0.50)	-364.4 (2, 1.8)	*Carex* bed
Lake ABLE	July 14	-50.04 (2, 1.76)	n.d.	*Carex* bed
Lake ABLE	July 14	-59.47 (3, 5.44)	-337.9 (1)	7 m into lake
Lake ABLE Cross Lake Transect				
Lake ABLE	July 18	-63.65 (2, 1.11)	-312.6 (1)	~100 m into lake; *Equisetum* bed
Lake ABLE	July 18	-63.76 (2, 0.28)	-317.9 (2, 2.8)	~90 m into lake; muddy detritus
Lake ABLE	July 18	-63.47 (2, 0.01)	-327.7 (1)	~70 m into lake; muddy detritus
Lake ABLE	July 18	-62.17 (1)	n.d.	~40 m into lake; muddy detritus
Lake ABLE	July 18	-63.39 (3, 0.02)	-328.9 (2, 6.1)	~15 m into lake; muddy detritus
Tower Site Area Lake Survey				
Lake BREW	July 19	-60.26 (1)	n.d.	detritus-rich
Lake BREW	Aug. 8	n.d.	-369.0 (1)	detritus-rich
Lake Peter	Aug. 8	-54.25 (1)	-351.1 (1)	
Lake Karen	Aug. 8	-64.23 (1)	n.d.	
Shirley Slough	Aug. 8	-63.15 (1)	n.d.	
Lake Tum the Corner	Aug. 8	-53.08 (1)	n.d.	
Lake Drewry	Aug. 8	-53.60 (1)	n.d.	
Lake Crill	Aug. 8	-55.23 (1)	n.d.	
Lake Kathy	Aug. 8	-46.35 (1)	-384.0 (1)	
Lake Song-Miao	Aug. 8	-47.42 (1)	n.d.	

*Data include number of analyses plus standard deviation or 1/2 range if $n = 2$ (n, S.D.); n.d., not determined.

including fixed site and survey stations in Lake ABLE, illustrates this trend.

Within individual lakes these same trends in isotopic values can be discerned. In Lake CHAOS, for which only $\delta^{13}C$ data are available, isotopic values are heavier in samples from lake edge sites heavily populated by *Carex* (July 12, 1988, -56.70‰; July 31, 1988, -52.53‰) as compared with samples from muddy bottom sites (July 22, 1988, -70.86‰) in open water areas.

The cross lake transect and lake edge survey of gas bubble composition within Lake ABLE provide the best evidence for trends associated with emergent macrophytes. The combined $\delta^{13}C$ and δD from these studies are included in Table 5. Ten samples from open water areas of the lake had $\delta^{13}C$ values ranging from -63.76 to -62.17‰; δD values for these same samples ranged from -328.9 to -312.6‰. Four samples collected along the edges of Lake ABLE within 2 m of the shoreline, all in areas of relatively luxuriant emergent plant communities, had $\delta^{13}C$ values ranging from -54.08 to -50.04‰ and δD values averaging -364.4‰.

The spatial isotopic trends observed in our study appear to be caused by variations in production processes and substrates rather than by preferential consumption of ^{12}C-enriched methane during microbially mediated oxidation. Previous work on isotopic shifts caused by methane oxidation [*Coleman et al.*, 1981] indicates that both $\delta^{13}C$ and δD values should become heavier. Our data, instead, suggest that δD values become lighter as $\delta^{13}C$ values become heavier, as seen earlier in the Cape Lookout Bight study [*Burke et al.*, 1988]. The isotopic trends we observe follow those suggested for a shift from methane production via CO_2 reduction to acetate fermentation (to heavier $\delta^{13}C$ and lighter δD values) by *Whiticar et al.* [1986] and others.

The $\delta^{13}C$ and δD Signature of the Ebullitive Methane Flux

The relationship between bubble methane content and ebullition rate illustrated in Figure 4 indicates that the ebullitive methane flux emanates largely from detritus-rich small lakes. The $\delta^{13}C$ and δD values of this flux are therefore best estimated from our Pingo Pond and Lake ABLE data. The mean $\delta^{13}C$ of methane from open-water sites for both lakes (Tables 4 and 5) is -61.41 ± 2.46‰ (n = 38), whereas the corresponding δD value is -341.8 ± 18.2‰ (n = 21).

If a significant ebullitive flux actually occurs from more heavily vegetated lake environments, we would then expect the

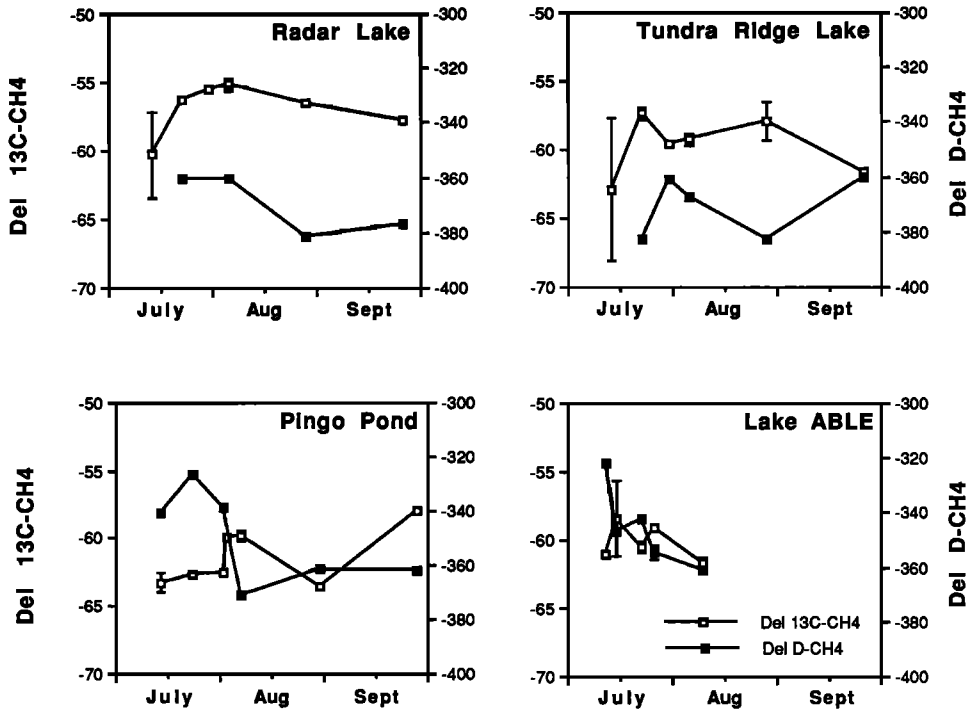


Fig. 5. Temporal variations in gas bubble methane $\delta^{13}C$ and δD values from fixed sampling sites in four Delta lakes.

$\delta^{13}C$ value of the total ebullitive flux to be heavier, and the corresponding δD value to be lighter. This conclusion is based on the combined isotopic results summarized in Figure 7 as well as the individual site data listed in Tables 4 and 5.

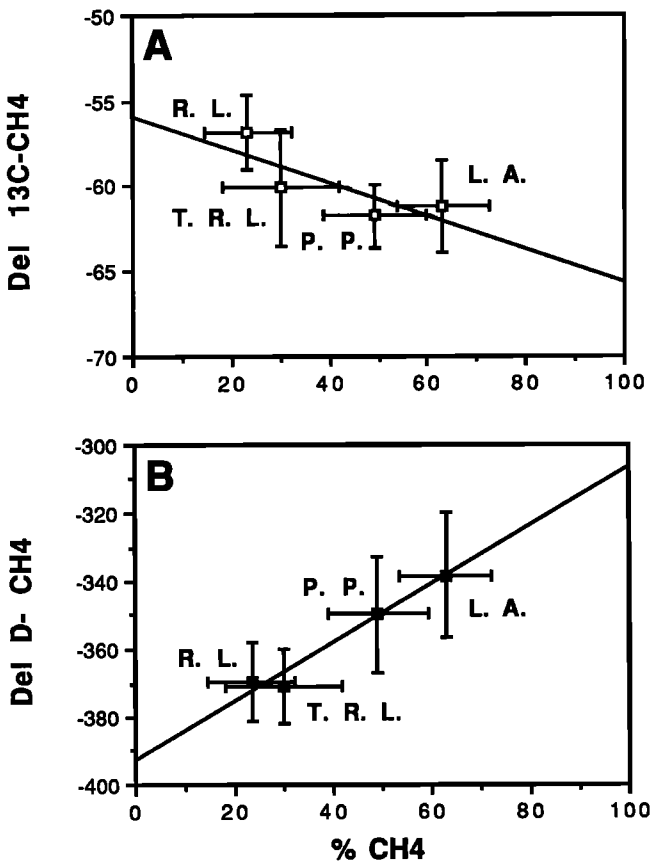


Fig. 6. Relationship between mean gas bubble methane concentrations and methane $\delta^{13}C$ (A) and δD (B) isotopic values in four Delta lakes.

Radiocarbon Content of Gas Bubble Methane

Our purpose in obtaining radiocarbon measurements was to establish whether the organic carbon source supporting methane fluxes was old or recently produced (modern) organic matter containing bomb radiocarbon. The results are summarized in Table 6. With the exception of one sample from Lake ABLE, for which duplicate runs yield radiocarbon ages of 156 ± 155 and 280 ± 130 years B.P., respectively, the methane sampled is bomb carbon enriched. The relatively large precision errors listed in Table 6 resulted from instabilities in the high voltage accelerator. Variations in the radiocarbon content of the two samples (four AMS analyses) collected sequentially from the same Lake ABLE site as well as differences between Lake ABLE and Pingo Pond samples (Table 6) suggest that further radiocarbon data must be obtained in order to better characterize the mean radiocarbon content of organic materials supporting these methane fluxes. It appears, however, that methane production and fluxes to the atmosphere at our lake sites are supported primarily by the degradation of recently produced organic matter as opposed to older materials slowly degrading over hundreds or thousands of years.

SUMMARY AND CONCLUSIONS

The $\delta^{13}C$ value of diffusive methane emissions from wet meadow tundra of the Yukon-Kuskokwim Delta near Bethel, Alaska, is -65.82 ± 2.21‰ (n = 18). This value is within the uncertainty of previous observations by *Quay et al.* [1988] of -64 ± 4‰, n =17 and *Whalen et al.* [1989] of -62.9 ± 1.9‰, n = 6 in tundra environments.

We have discovered that detritus-rich sediments of tundra lakes are loaded with methane-rich gas bubbles during the warm season. Spatial trends in the major gas concentrations and isotopic values of methane in these gas bubbles appear to reflect processes associated with production rates and mechanisms; high methane concentrations, lightest $\delta^{13}C$ values and heaviest δD values occur in detritus-rich sediments isolated from

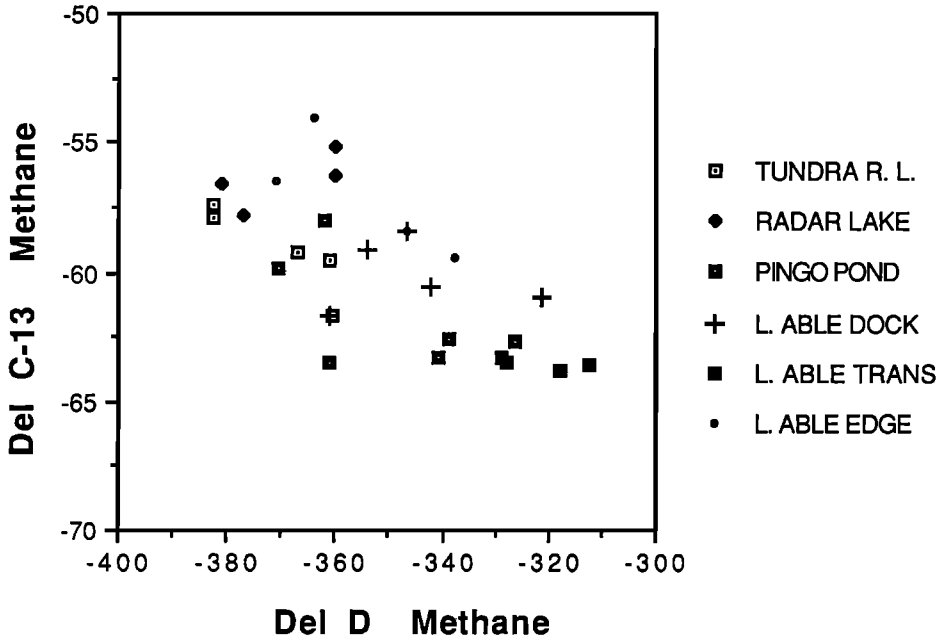


Fig. 7. Relationship between methane $\delta^{13}C$ and δD isotopic values in four Delta lakes.

TABLE 6. Radiocarbon Content of Methane in Four Gas Bubble Samples From Two Lakes on the Yukon-Kuskokwim Delta Near Bethel, Alaska

Lake	Date in 1988	Mean $\delta^{13}C$,* ‰	CAMS Run No.	$\Delta^{14}C$, ‰	Radiocarbon Age†
Pingo Pond	Aug. 1	-61.78	530	150 (68)‡	115 (7) % Modern
Duplicate	Aug. 1	-61.78	531	111 (65)	111 (7) % Modern
Pingo Pond	Aug. 2	-61.78	532	205 (18)	121 (2) % Modern
Duplicate	Aug. 2	-61.78	533	177 (56)	118 (6) % Modern
Lake ABLE	Aug. 6	-60.16	526	-28 (20)	185 (155) Years B.P.
Duplicate	Aug. 6	-60.16	527	-42 (15)	310 (130) Years B.P.
Lake ABLE	Aug. 6	-60.16	528	71 (63)	107 (6) % Modern
Duplicate	Aug. 6	-60.16	529	72 (18)	107 (2) % Modern

*Mean values from Table 4.
†Quoted age in radiocarbon years using Libby half life of 5568 yr and following conventions of *Stuiver and Polach* [1977].
‡Data includes standard deviation (S.D.).

emergent vegetation. Heavier $\delta^{13}C$ and lighter δD values in methane from heavily vegetated lake margins suggest a shift toward a larger role for acetate fermentation in association with aquatic plants and plant detritus. Preliminary radiocarbon dating indicates that gas bubble methane largely originates from modern carbon.

There appears to be a seasonal variation in $\delta^{13}C$ values of gas bubble methane at most sites, the heaviest values occurring at midsummer, as previously observed at other sites. However, no seasonal trends in δD values could be discerned and no seasonal trends in $\delta^{13}C$ values of the wet meadow flux were observed.

Small, organic-rich lakes are potentially significant sources of methane to the atmosphere via bubble ebullition. Based on detailed work on several lakes in the Bethel area from which methane-rich bubbles are released, we estimate that bubble ebullition can account for up to 17% of total Delta emissions. The $\delta^{13}C$ and δD values of ebullitive emissions from open water areas of detritus-rich small lakes are calculated to be -61.41 ± 2.46‰ ($n = 38$) and -341.8 ± 18.2‰ ($n = 21$), respectively. The $\delta^{13}C$ value should be heavier and the δD value lighter if heavily vegetated lakes with less methane-rich gas bubbles contribute significantly to the ebullitive flux.

Acknowledgments. We wish to thank Kelley Cox, Patrick Crill, Bernie Genna, and the rest of the McCorkle family, for assistance in the field and with laboratory analysis. Special thanks to the U.S. Fish and Wildlife Service, Bethel, Alaska, for generously providing laboratory space, and to Rick Ernst for collecting gas bubble samples late in the season. Thanks also go to Bill Ussler for his computer wizardry. This research was supported in part by NASA grants NAGW-1455 and NAGW-834.

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J. P. Chanton, Department of Oceanography, Florida State University, Tallahassee, FL, 32306-3048.

C. A. Kelley and C. S. Martens, Marine Sciences Program, CB# 3300, University of North Carolina, Chapel Hill, NC, 27599-3300.

W. J. Showers, Department of Marine, Earth, and Atmospheric Sciences, Box 8208, North Carolina State University, Raleigh, NC, 27695-8208.

(Received January 2, 1991;
revised November 13, 1991;
accepted November 13, 1991.)