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Methane flux from wetlands areas

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ABSTRACT

Ebullient gases from Michigan wetlands have been collected and analyzed to deduce in situ methane fluxes. Methane flux has been found to be a function of mean air temperature. This relationship has been utilized to extrapolate observed methane fluxes to estimates of fluxes from the Pripet marshes, Sudd, Everglades, and Ugandan swamps. These four wetlands together provide a yearly source of 6.8×10^{13} g of methane to the atmosphere.

1. Introduction

Of the 4.5×10^{15} g of methane in the atmosphere, over 80% is presumed to be produced by microbial activity in anaerobic systems (Ehhalt, 1974). It is well known that ruminants are a significant source of methane to the atmosphere, supplying 7.3×10^{13} g annually (Singer, 1971). Koyama (1963) postulated that 1.9×10^{14} g were produced in rice paddy fields annually. Robinson & Robbins (1972) suggest that methane flux from swamps totals 5.1×10^{14} g yearly. None of these estimates is based on a study of in situ methane flux, although Koyama (1963) based his estimate on the results of laboratory incubation of paddy field soils. Conger (1943) presents four analyses of marsh gas collected in situ, with methane concentrations ranging between 58% and 82%. Ehhalt (1974) interprets Conger's (1943) data to reach an estimate of annual methane flux of 0.12 g/cm^2 from marshes. This paper will discuss the contribution of methane from wetlands areas based on in situ studies conducted in Michigan ponds and swamps during the summer of 1975.

The major sink for atmospheric methane is reaction with hydroxyl (OH) radical. Ehhalt (1974) concludes that a tropospheric destruction of between 5×10^{14} g and 9×10^{14} g of methane would maintain an atmospheric steady state. This would allow for a turnover time between 4 and 7 years for atmospheric methane.

2. Physiochemical influences of methane bacteria

The three genera of known methane-producing bacteria are *Methanobacterium*, *Methanococcus*, and *Methanosarcina*. Koyama (1963) discovered that methane production by these microorganisms increased with increasing temperature. Using data recorded by Koyama (1963) on the production of methane from 100 g of paddy soil incubated at temperatures between 5° and 40 °C, it is possible to generate the following equation using a least-squares multiple regression:

$$\text{flux} = 6.3 \times 10^{-5} - 1.9 \times 10^{-4} T + 1.7 \times 10^{-6} T^2 \qquad (1)$$

where flux is in grams per day and T is the incubator temperature in °C. The multiple correlation coefficient for dependency is 0.99.

Methane bacteria are sensitive to the hydrogen ion activity of the substrate environment, being most active in the range from 6.4 to 7.2 pH units (Barker, 1956). Bell (1969) indicates that methane will not be produced in substrates unless the Eh (redox potential) is −250 mV or less, corresponding to an electron activity ($p\epsilon$) of −4.24. Inhibition of methane production has been observed with the introduction of nitrate (NO_3^-) anion (Lee et al., 1975), or sulfate ($SO_4^=$) anion (Martens & Berner, 1974) to sediment systems. This inhibition of methane production may simply be a function of the relative electron activity of the environment, since the reduction of $SO_4^=$ to hydrogen sulfide gas requires a $p\epsilon^\circ$ of −3.5, compared with the reduction of carbon dioxide to methane, which requires a $p\epsilon^\circ$ of −4.13. Denitrification of NO_3^- to nitrogen gas requires strongly oxidizing conditions, with a $p\epsilon^\circ$ of 12.65 ($p\epsilon^\circ$ values from Stumm & Morgan, 1970).

Under natural conditions, the correct physio-chemical conditions for methane production can be found in the rumen of various animals (e.g. cows, camels, and sheep), in peat bogs, in swamp, marsh, and pond sediment and in rice paddies. Secondary sewage treatment by anaerobic digestion is based on methane fermentation of the waste material.

3. Observation of methane flux from wetlands

(a) *In situ gas collection*

Gas samplers of the type shown in Fig. 1 were submerged in a 2-year-old farm pond of 25 m^2 area, a 30-year farm pond of 150 m^2 area, and a swamp known to be at least 100 years old of 88,000 m^2 area during the period May–September 1975. The location of the first two wetlands is about 42°15′N, 84°03′W, while the swamp is situated about 42°30′N, 84°00′W. These locations are in southeastern Michigan, U.S.A. Despite the great differences in size, all three environments contain alkaline (~pH 8) water, with an average depth of 1 m. Rooted aquatic vegetation includes *Chara*, *Ceratophyllum demersum*, and *Elodea canadensis*. Samples of ebullient gases were taken at intervals of 3 days to 2 weeks. Care was taken in obtaining samples not to disturb the sediment.

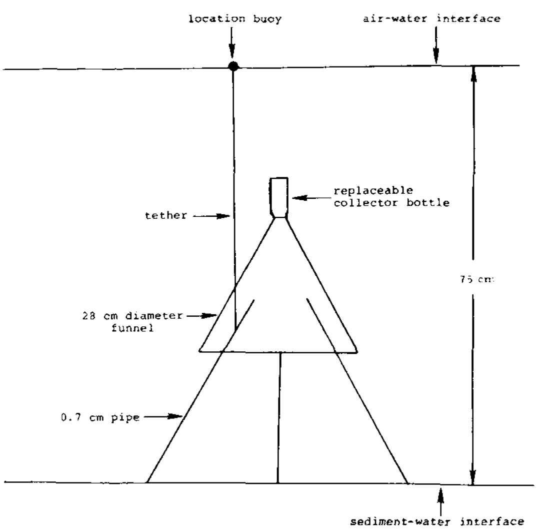

Fig. 1. Schematic diagram for the ebullient gas collector deployed in wetlands. The collector bottle and funnel were made of translucent white polyethylene.

While it is possible that methane in the collection bottle could have been degraded by bacteria, the byproduct of such activity, carbon dioxide, was detected only in a small fraction of samples analyzed. Since the methane in the collection bottles was in the gaseous phase, it would be less readily available to microorganisms than dissolved methane or other organic materials in the water. It appears that microbial destruction of methane in the sample bottles was not important in changing the composition of collected gases in situ.

Chemical analyses were performed on gas samples using a Fisher gas partitioner equipped with a thermal conductivity detector. Some selected results are shown in Table 1. Although gas samples were collected continually, ebullient gases often filled up the collecting bottles before samples were retrieved. The results shown in Table 1 represent samples for which the gas volume did not exceed the size of the collecting bottle. In addition to methane, the major constituents of ebullient gases in these three environments were nitrogen, oxygen, and carbon dioxide. Nitrogen concentrations ranged from not detectable to 80%, while oxygen concentrations ranged from not detectable to 44.5%. Small amounts of carbon dioxide were occasionally observed in gas samples collected from the swamp. All of these gases, including methane, enter into biological cycling in the wetlands areas. Hartman & Brown (1966) postulate that methane produced in sediment enters the rhizome of vascular plants and is flushed into the aqueous environment during photosynthesis. If this is indeed the case, the observation of large amounts of oxygen and methane in the same gas sample is not surprising.

(b) *Methane flux as a function of air temperature*

Development of an empirical model to predict the flux of methane from wetlands under various physical and chemical conditions is dependent upon the availability of pH, Eh, and temperature

Table 1. *Observed flux of methane from Michigan wetlands*

Site	Collection period	% of CH_4 in sample	Flux (g/cm^2 day)	Average temperature °C
New pond	June 20–27, 1975	23.6	9.2×10^{-6}	23.3
	June 27–July 3, 1975	46.6	4.3×10^{-5}	23.7
	July 25–31, 1975	45.4	4.6×10^{-5}	22.9
	July 31–Aug. 4, 1975	40.7	5.2×10^{-5}	25.8
	Aug. 4–8, 1975	25.4	2.7×10^{-5}	19.5
	Aug. 12–18, 1975	61.1	6.5×10^{-5}	21.8
	Aug. 18–25, 1975	82.5	4.7×10^{-5}	21.3
	Sept. 2–14, 1975	45.6	1.8×10^{-5}	14.7
	Sept. 14–26, 1975	42.3	1.1×10^{-5}	12.3
Old pond	June 2–12, 1975	23.5	9.3×10^{-6}	16.8
	June 12–20, 1975	50.0	2.6×10^{-5}	22.1
	June 20–27, 1975	73.7	4.2×10^{-5}	23.3
	June 27–July 3, 1975	75.0	4.9×10^{-5}	23.7
	July 3–11, 1975	74.5	5.9×10^{-5}	21.7
	July 11–21, 1975	75.4	4.8×10^{-5}	21.6
	July 21–25, 1975	69.2	4.5×10^{-5}	23.2
	July 25–31, 1975	92.3	8.3×10^{-5}	22.9
	July 31–Aug. 4, 1975	94.4	1.1×10^{-4}	25.8
	Aug. 4–8, 1975	55.3	3.0×10^{-5}	19.5
	Aug. 8–12, 1975	87.7	6.9×10^{-5}	24.1
	Aug. 12–18, 1975	77.8	4.2×10^{-5}	21.8
	Aug. 18–25, 1975	97.0	6.3×10^{-5}	21.3
	Aug. 25–Sept. 2, 1975	78.5	6.5×10^{-5}	21.3
	Sept. 2–14, 1975	79.8	2.6×10^{-5}	14.7
	Sept. 14–26, 1975	86.0	2.8×10^{-5}	12.3
Swamp	July 9–15, 1975	76.3	2.8×10^{-5}	18.2
	July 24–30, 1975	84.2	5.7×10^{-5}	22.5
	Aug. 4–7, 1975	70.0	3.8×10^{-5}	18.2
	Aug. 7–11, 1975	91.6	6.1×10^{-5}	22.7
	Aug. 11–19, 1975	75.0	3.9×10^{-5}	22.2
	Sept. 6–12, 1975	59.1	1.4×10^{-5}	15.3
	Sept. 12–19, 1975	75.6	1.2×10^{-5}	13.3

data. To gain some measure of general applicability, an investigation of the use of mean air temperature as an independent variable in a predictor equation was conducted. Mean air temperatures for the periods during which gas samples were collected were computed by averaging the daily maximum and minimum air temperatures observed at Ann Arbor (42°17′28″N, 83°45′32″W). These mean temperatures are given in Table 1.

A scatter plot of methane flux versus mean air temperature is shown in Fig. 2. Although this scatter plot suggests a second-order relationship between methane flux and mean air temperature, the multiple correlation coefficient is 0.70, while the linear correlation coefficient is 0.69. The corresponding regression equations computed by least squares are:

$$\text{flux} = 4.6 \times 10^{-5} - 5.6 \times 10^{-6} T + 2.6 \times 10^{-7} T^2 \tag{2}$$

and

$$\text{flux} = -4.2 \times 10^{-5} + 4.1 \times 10^{-6} T \tag{3}$$

where flux is in g/cm^2 day and T is in °C. These two equations have been plotted along with the data in Fig. 2. Since the dependency of flux on temperature is known to be second order (data of Koyama, 1963), the use of the second-order relationship is justified (Draper & Smith, 1966). Using eq. (2), the total methane source strength

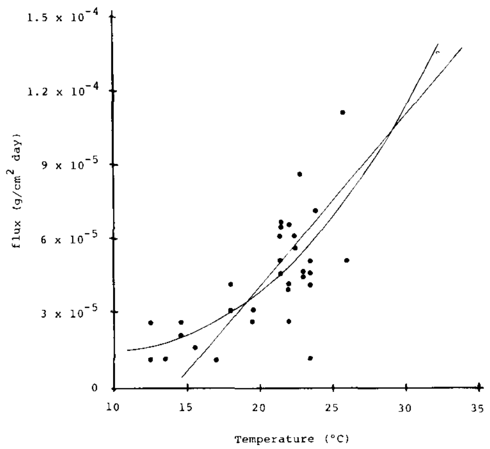

Fig. 2. Scatter plot of methane flux data versus mean air temperature for the three wetlands studied. The straight line is the plot for a linear regression based on the data, while the curved line is the plot for the polynomial regression of degree 2.

from the small pond was 1.5×10^3 g, while it was 7.6×10^3 g from the large pond, and 5.4×10^6 g from the swamp during the period May 1 to September 26, 1975. If the linear equation had been used, the methane source strengths would have been 7% less.

(c) *Extrapolation to other wetlands environments*

Estimates of methane flux using either the first-order (eq. (3)) or second-order (eq. (2)) equations yield essentially the same results for mean air temperatures between 18° and 24°C. Accordingly, the methane flux and source strength from several large wetlands areas—the Pripet Marshes of the U.S.S.R., the Sudd region of the Sudan, Ugandan swamps, and the Everglades of Florida, U.S.A.—have been estimated by inserting the mean monthly temperatures recorded at nearby cities into eq. (2). If the mean monthly temperature was less than 12°C, a flux of zero was assumed. The results are shown in Table 2.

These estimates of methane source strength assume that the same sort of chemical environment for methane production exists in these wetlands as exists in the Michigan wetlands studied.

The influence of climate on methane flux is brought out by the comparison of the Pripet Marshes with the Everglades. The Pripet Marshes are three times as large, but liberate only one-half the amount of methane that the Everglades liberates. The Sudd is the largest wetland considered, and it is estimated to liberate 6×10^{13} g of methane to the atmosphere annually. This is only slightly less than the methane generated by all ruminants (Singer, 1971) and is about 13% of the total biogenic contribution of methane needed for the atmosphere if a turnover of 7 years is assumed. Even if the concentration of hydroxyl radical is somewhat greater than 5×10^5 cm^{-3} in the ambient atmosphere, and the turnover time is faster than 7 years, the Sudd remains an impressive source of atmospheric methane.

4. Concluding remarks

Wetlands are an important source of atmospheric methane. The flux of methane from a wetland is a function of the mean air temperature. The dependency of flux on mean air temperature can be expressed by:

$$\text{flux} = 4.6 \times 10^{-5} - 5.6 \times 10^{-6} T + 2.6 \times 10^{-7} T^2.$$

The net methane source strength of the Pripet Marches, Sudd, Everglades and Ugandan swamps is estimated to be 6.8×10^{13} g annually. The Sudd alone is estimated to have an annual source strength of 6×10^{13} g.

Baker-Blocker (1975) has roughly estimated that bogs world-wide contribute about 6.5×10^{13} g of methane per year to the atmosphere. A reasonable estimate of total methane liberated from all types of wetlands would be 1.5×10^{14} g annually, slightly greater than the sum of the contribution of the four large wetlands considered here and the contribution from bogs.

Methane flux from rice paddy soils probably resembles the rates computed for methane flux from the Sudd, Everglades, and Ugandan swamps. Using an average flux of 2.6×10^{-2} g/cm^2 year, and Ehhalt's (1974) estimate of 1.35×10^6 km^2 for the area of rice paddies, the corresponding source strength would be 3.5×10^{14} g of methane liberated to the atmosphere annually by paddy soils. This estimate may be high, since rice paddies are usually drained for a portion of each year. Ehhalt (1974) estimates that the source strength of paddy fields is 2.8×10^{14} g of methane yearly. Most probably, the methane flux from rice paddies is between 1.3×10^{-2} and 2.6×10^{-2} g/cm^2 year, and the source strength between 1.7×10^{14} and 3.5×10^{14} g.

The total amount of methane estimated to be

Table 2. *Methane flux and source strength from four large wetlands areas estimated by a second-order equation using mean air temperature as an independent variable*

Mean air temperatures were obtained from Kendrew (1961); information about the Pripet Marshes and Everglades is from Gresswell & Huxley (1966); information about The Sudd and Ugandan swamps is from Walter (1973)

	Pripet Marshes (4.7×10^{10} m²)		Sudd (1.5×10^{11} m²)		Ugandan swamps (1.3×10^{10} m²)		Everglades (1.7×10^{10} m²)	
Month	Average temperature in Kiev (°C)	Flux of CH_4 (g/cm²)	Average temperature in Khartoum (°C)	Flux of CH_4 (g/cm²)	Average temperature in Entebbe (°C)	Flux of CH_4 (g/cm²)	Average temperature in Miami (°C)	Flux in CH_4 (g/cm²)
January	−6.1	—	23.3	1.7×10^{-3}	22.2	1.5×10^{-3}	20.0	1.1×10^{-3}
February	−4.4	—	25	2.1×10^{-3}	22.2	1.5×10^{-3}	20.0	1.1×10^{-3}
March	0.0	—	28.3	2.9×10^{-3}	22.2	1.5×10^{-3}	21.7	1.4×10^{-3}
April	6.7	—	31.7	3.8×10^{-3}	21.7	1.4×10^{-3}	23.3	1.6×10^{-3}
May	14.4	5.7×10^{-4}	33.3	4.5×10^{-3}	21.7	1.4×10^{-3}	25.0	2.1×10^{-3}
June	18.9	9.5×10^{-4}	33.3	4.3×10^{-3}	21.1	1.3×10^{-3}	26.7	2.4×10^{-3}
July	18.3	9.1×10^{-4}	31.7	3.9×10^{-3}	20.6	1.2×10^{-3}	27.8	2.8×10^{-3}
August	18.9	9.8×10^{-4}	30.6	3.6×10^{-3}	20.6	1.2×10^{-3}	27.8	2.8×10^{-3}
September	13.0	5.4×10^{-4}	32.2	4.0×10^{-3}	21.1	1.3×10^{-3}	27.2	2.5×10^{-3}
October	7.8	—	32.2	4.1×10^{-3}	21.7	1.4×10^{-3}	25.6	2.2×10^{-3}
November	0.6	—	28.3	2.8×10^{-3}	21.7	1.4×10^{-3}	22.8	1.6×10^{-3}
December	−3.9	—	25	2.1×10^{-3}	21.7	1.4×10^{-3}	20.6	1.2×10^{-3}
Total flux during year (g/cm²)		4.0×10^{-3}		4.0×10^{-2}		1.7×10^{-2}		2.3×10^{-2}
Total source strength		1.9×10^{12} g		6.0×10^{13} g		2.2×10^{12}		3.9×10^{12}

liberated by wetlands, rice paddies, and ruminants is in the range of 4.0×10^{14} and 5.8×10^{14} g annually, with fossil sources probably adding an additional 1×10^{14} g. Between 1×10^{14} and 2×10^{14} g of methane are lost to the stratosphere annually by eddy diffusion and Hadley circulation (Ehhalt, 1974). This implies that the hydroxyl radical concentration necessary to maintain a tropospheric steady state is in the neighborhood of 5×10^5 cm^{-3}, and the atmospheric turnover time near the maximum of 7 years suggested by Ehhalt (1974).

Wetlands are estimated to contribute between 22 and 30% of the methane in the atmosphere, about twice the amount emitted by ruminants. Rice paddy soils are estimated to liberate between one to two times the amount of methane as natural wetlands, given the present areas of paddy fields and wetlands.

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ПОТОК МЕТАНА С ВЛАЖНЫХ ПОВЕРХНОСТЕЙ СУШИ

Газы, выделяющиеся из переувлажнённых участков суши в Мичигане, были собраны и проанализированы для получения потоков метана. Найдено, что поток метана является функцией средней температуры воздуха. Это соотношение было использовано для экстраполяции наблюдаемых потоков метана на оценки его потоков с болот Полесья, Сюдд, Эверглэйдз и Уганды. Эти четыре болотистые области образуют источник метана для атмосферы производительностью $6{,}8 \cdot 10^{13}$ г/год.