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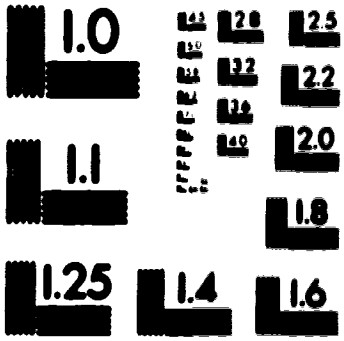

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METHANE FLUXES FROM WETLANDS OF CENTRAL ALBERTA

BY

TAI-LONG JIN 

A THESIS

SUBMITTED TO THE FACULTY OF GRADUATE STUDIES AND RESEARCH IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE OF MASTER OF SCIENCE.

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The undersigned certify that they have read, and recommend to the Faculty of Graduate Studies and Research for acceptance, a thesis entitled METHANE FLUXES FROM WETLANDS OF CENTRAL ALBERTA submitted by Tai-Long Jin in partial fulfillment of the requirements for the degree of MASTER OF SCIENCE in PEATLAND ECOLOGY.

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ABSTRACT

Seasonal and spatial variation in methane fluxes were studied in 6 boreal wetland ecosystems in central Alberta, representing ombrotrophic bog, poor fen, forested rich fen, open rich fen, marsh and beaver pond, during the ice-free seasons of 1989 and 1990 using a static chamber technique.

The seasonal variations in methane fluxes were similar among the six wetlands. Emission rates were generally lower during spring, reaching peak values in late summer and lower in autumn. The gradient in CH_4 fluxes from the six sites is : beaver pond > marsh > open rich fen > forested rich fen > poor fen > ombrotrophic bog. The mean daily fluxes of the 2 year's measurements were 322.8 mg CH_4 m^{-2} d^{-1} in the beaver pond, 87.8 mg CH_4 m^{-2} d^{-1} in the marsh, 77.2 mg CH_4 m^{-2} d^{-1} in the open rich fen, 17.8 mg CH_4 m^{-2} d^{-1} in the forested rich fen, 0.8 mg CH_4 m^{-2} d^{-1} in the poor fen, and zero or negative in the bog. There are significant differences (p<0.0001) in methane fluxes among the sites. Significant variation is also present among sampling dates within each site. Methane concentrations in subsurface waters were generally higher than those in surface water and increase with depth. There was no correlation between net methane flux and methane concentration in pore waters. The methane fluxes were very significantly correlated to water temperature (p<0.01) and significantly correlated with water table position (p<0.05).

Estimated annual emission rates of CH_4 for the wetlands ranged from 0 to 7.6 x 10^4 mg m^{-2} yr^{-1}, with mean of 1.9 x 10^4 mg m^{-2} yr^{-1} in 1989 and from -151 to 1.5 x 10^4 mg m^{-2} yr^{-1}, with mean of 5.1 x 10^3 mg m^{-2} yr^{-1} in 1990, respectively. About 0.91 Tg CH_4 yr^{-1} of CH_4 was emitted to the atmosphere from wetlands in Alberta. Fens (sum of the poor fen, forested rich fen and open rich fen) emitted 0.26-0.35 Tg CH_4 yr^{-1} to the atmosphere.

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TABLE OF CONTENTS

Chapter Page

I. METHANE FLUXES FROM NATURAL WETLAND ECOSYSTEMS-A GENERAL REVIEW 1

INTRODUCTION 1

MECHANISMS CONTROLLING METHANE PRODUCTION AND OXIDATION 3

Methane Production 3

Oxidation of Methane 6

FACTORS CONTROLLING METHANE PRODUCTION AND EMISSION 8

Effects of Substrate 8

Effects of Temperature 9

Effects of Moisture 10

Effects of Geochemical Conditions 11

TECHNIQUES USED FOR METHANE FLUX MEASUREMENTS 12

Closed (Static) Chamber 13

Open and Dynamic Chambers 13

METHANE FLUXES FROM VARIOUS WETLANDS 14

SUMMARY 16

LITERATURE CITED 17

II. METHANE FLUXES FROM BOREAL WETLAND ECOSYSTEMS IN CENTRAL ALBERTA, CANADA 27

INTRODUCTION 27

MATERIALS AND METHODS 28

Study Area 28
Sampling Sites 29
Sampling Methods 30
Analysis 32
Statistical Analysis 33
RESULTS 34
Temporal Patterns of Methane Fluxes 34
Site Differences of Methane Fluxes 34
Annual Methane Fluxes 35
Methane in Wetland Waters 36
Contributions of Alberta Wetlands 36
Relations of Methane Fluxes With Environmental Variables 37
Water Temperature 37
Water Table Position 37
Microtopography 38
DISCUSSION 38
Temporal Pattern of Methane Flux 38
Comparison of Alberta Methane Fluxes With Fluxes in Eastern Canada 39
Relations Between Methane Fluxes and Methane Concentrations in Waters 39
Correlation With Environmental Variables 41
Variability of Methane Flux 43
Estimates of Methane Emissions From Natural Wetlands 44
Contributions of Alberta Wetlands to Global Methane Budget 45
LITERATURE CITED 63
III. CONCLUDING DISCUSSIONS 70

LITERATURE CITED **75**

LIST OF TABLES

Table Page

II-1. Locality and Some Characteristics of Six Sampling Sites in Central Alberta..... 47

II-2. Seasonal and Yearly Mean, Standard Deviation, Dates and Amounts of Maximum and Minimum Methane Fluxes From Wetlands of Central Alberta..... 48

II-3. Results of ANOVAs For Methane Fluxes From Six Wetland Sites of Central Alberta..... 49

Table II-4. Correlation Coefficients Between Logrimethic Methane Flux and Some Environmental Factors in Wetlands of Central Alberta..... 50

II-5. Annual Methane Fluxes From Wetlands of Central Alberta..... 51

Table II-6. Estimated Global Methane Contribution From Wetlands in Alberta Based on Area Data of Each Wetland Type..... 52

Table II-7. Comparisons of Methane Emission Estimates Under the Different Estimates of the Wetland Area in Alberta..... 53

LIST OF FIGURES

Figure Page

II-1. The Location of the Study Area and Sampling Sites····· 54

II-2. Seasonal Patterns of Methane Fluxes in Wetlands of Central Alberta····· 55

II-3. The Comparision of Methane Fluxes in Wetlands of Central Alberta During 1989 and 1990····· 56

II-4. Display of Results of Studentized Newman-Keuls Test on Methane Flux Data in 1989 and 1990····· 57

II-5. Seasonal Variations of Methane Concentrations in the Surface Waters of Six Wetlands in Central Alberta During1989 and 1990····· 58

II-6. Methane Profiles and Seasonal Variation in Pore Waters of Six Wetlands in Central Alberta····· 59

II-7. Seasonal Variation of Water Temperature From Wetland Waters of Central Alberta····· 60

II-8. Seasonal Variation of Water Table Positions in Wetlands of Central Alberta····· 61

II-9. Comparision of Methane Fluxes From Hummocks and Hollows in a Forested Rich Fen of Central Alberta During August 2-3, 1990····· 62

I. METHANE FLUXES FROM NATURAL WETLAND ECOSYSTEMS-A GENERAL REVIEW

INTRODUCTION

Methane (CH_4) is a radiatively active trace gas that plays an important role in numerous chemical reactions in the atmosphere. Atmospheric methane exerts direct and indirect influences over the Earth's climate in several ways. The most important direct influence is that methane acts as a strong greenhouse effect gas absorbing outgoing infrared radiation within the troposphere 20 times more effectively per molecule than CO_2 (Mooney *et al.* 1987). The presence of 1.5 ppm of CH_4 in the atmosphere causes the globally averaged surface temperature of the earth to be about 1.3 °K (271.7 °C) higher than it would be with zero methane, with larger temperature effects at polar latitudes (Donner & Ramanathan 1980).

There are also several potentially important indirect ways that methane can affect climate. One that has received less attention is that methane strongly reacts with the atmospheric hydroxyl radical (OH) and can be involved in the production of tropospheric carbon monoxide (CO) which is further converted to CO_2 (Cicerone & Oremland 1988). The atmospheric production of CO_2 from atmospheric CH_4 is about 6% of the direct annual release of CO_2 from anthropogenic sources (Cicerone & Oremland 1988).

Other indirect effects of increasing atmospheric CH_4 are the chemical production of tropospheric ozone (O_3) and increases in tropospheric water vapor. Increases of the tropospheric O_3 may result from CH_4 increases in the presence of NO_x and also have effects on climate. This is especially so if O_3 concentrations increase in

the upper troposphere where O_3 is a particularly effective greenhouse gas (Cicerone & Oremland 1988).

It is well documented that atmospheric CH_4 is increasing at a rate of approximately 1% per year (Mooney 1987, Crill *et al.* 1988, Blake & Rowland 1988). This increase is most probably due to an increasing global source strength for atmospheric methane (Seiler 1984). As a consequence, studies on the atmospheric CH_4 cycle have focused on determination of the magnitude of CH_4 fluxes from a variety of potentially important CH_4 sources.

Recent estimates indicate that CH_4 is predominantly produced biogenically in anoxic soils of natural wetlands, rice paddies, and in the digestive tract of ruminants (Schütz & Seiler 1989). Methane is also produced by biomass burning, decomposition in land fills, and fossil fuel exploration, transport and combustion (Matthews & Fung 1987).

A recent estimate, based on an improved global data base for the spatial extent of wetlands and CH_4 flux data from published literature, suggests that global wetland areas range from 2.0-6.7 x 10^{12} m^2 and the global CH_4 emissions from wetlands range from 11-300 Tg yr^{-1} (1 Tg=1 x 10^{12} g). About 66% of the total global CH_4 emissions from natural wetlands come from northern (>40° N) regions (Matthews & Fung 1987). Sebacher *et al.* (1986) have also suggested an area of 4.5-9.0 x 10^{12} m^2 for northern peatlands and estimated an annual CH_4 emission from them of 45-106 Tg. Accordingly, the study of CH_4 fluxes from wetland ecosystems, especially from boreal wetlands, is of great importance to better understand the global carbon cycle and the potential effects of global climatic change.

This chapter gives an overview of the parameters and processes that may be important in the control of production and emission of methane from wetland ecosystems into the atmosphere, and also generally reviews methods and results of methane flux measurements from various wetlands.

MECHANISMS CONTROLLING CH_4 PRODUCTION AND OXIDATION

Methane emissions from a particular ecosystem are basically controlled by two different microbial processes: CH_4 production and CH_4 oxidation (Rudd & Taylor 1980).

Methane Production

Biogenic CH_4 production is exclusively accomplished by CH_4-producing bacteria (methanogens) that are able to metabolize and live only in the absence of oxygen and need redox potentials of less than -200 millivolt (mV) (Conrad 1989), or even -300 mV (Cicerone & Oremland 1988). This means that CH_4 production and emission can be expected only in those anoxic ecosystems which have sufficiently reduced conditions.

Thus, methanogenic ecosystems are usually wetland and aquatic environments (such as bogs, fens, marshes, swamps, paddies, shallow lakes, and river banks) where oxygen-deficient zones develop due to O_2 consumption by organic matter decomposition and to limitation of O_2 diffusion from the atmosphere. Under anaerobic conditions, organic matter containing cellulose, hexose, and lignin is generally degraded to the gaseous end products CO_2 and CH_4:

$$C_6H_{12}O_6 \rightarrow 3CO_2+3CH_4 \qquad (1)$$

No single microbial species is able to accomplish this complicated process on its own. Methanogens, in particular, can only use a limited number of very simple compounds (Vogels *et al.* 1988, Whitman 1985). Therefore, many different microbial species contribute to the anaerobic reactions by consecutively degrading complex organic molecules to simpler compounds. This is done in a substrate food chain, whereby the fermentation end products excreted by one bacterium are utilized by

another one until the organic matter is finally broken down to substrates that are utilized by methanogens to form CH_4 as an end product (Zehnder 1978, Zeikus 1983).

The microbial communities and the pathways of electron and carbon flow through the substrate food chain that occur in the process of methane production can be different in different ecosystems. Each type of organic matter has different metabolic capabilities for degradation and is a determining factor for the microbial communities and the pathways of electron and carbon flow (Frea 1984).

Despite the differences in the organic matter and the microbes involved, there seems to be a general scheme of anaerobic methanogenic degradation which requires participation from four types of bacteria within a substrate food chain : (a) hydrolytic and fermenting bacteria, (b) H^+--reducing bacteria, (c) homoacetogenic bacteria, and (d) methanogenic bacteria.

Hydrolytic microorganisms hydrolyze polymeric material and ferment the hydrolysis products to intermediary fermentation products such as fatty acids and alcohols. The H^+-reducing microorganisms further metabolize these intermediary fermentation products to produce mainly acetate, H_2, and CO_2. The homoacetogenic bacteria involved in the terminal steps of organic carbon mineralization are very versatile bacteria that can use sugars, alcohols, fatty acids, purines, and aromatic compounds as well as H_2, CO, formate, and methanol as substrates and produce acetate as the sole fermentation product (Dolfing 1988). The methanogenic microbes that are able to convert the acetate and other organic matters to methane, are called methanogens, and the process termed methanogenesis. Methanogenesis is largely a process mediated by autotrophic microbes that oxidize H_2 with concomitant reduction of CO_2 to CH_4.

In most environments where methane production occurs, acetate (CH_3COOH) is a key product of the decomposition of organic matter (Frea 1984). About two-thirds of the CH_4 produced is estimated to be produced from acetate (Kenealy *et al.* 1982). From a kinetic point of view, where two microbes compete for the same substrate, one will

generally dominate, and this dominance may lead to the near exclusion of the activity of the second. For example, sulfate-reducers and methanogens compete for both hydrogen and acetate. The microbe that has the higher affinity for a given commonly utilizable substrate should out compete others that have a lower affinity. Experiments (Strayer *et al.* 1978b, Lovley *et al.* 1982) have shown that the affinity of methanogens for H_2 is less than that of the sulfate-reducers. On the basis of kinetics alone then, it would be reasonable to expect that in the presence of adequate sulfate, the sulfate-reducers would lower the hydrogen concentration sufficiently to inhibit the methanogens (Frea 1984).

In the process of methane production, the flow of electrons is an indication of microbial activity and products of decomposition. Frea (1984) summarized that under aerobic conditions, oxygen depletion through consumption by aerobic microbes leads to a series of changes including a decrease in Eh (redox potential), a decrease in oxidized species, an increase in reduced species of compounds, and a concurrent change in the nature of the metabolic activity of the microbes. As a consequence of the activity of aerobic bacteria, the O_2 level decreases and oxygen finally disappears, with the redox potential falling to about +350 mV. Nitrate is the next to disappear, and by the time Eh reaches +100 mV, it is essentially gone and denitrifers are rendered inactive. The decrease of Eh to about +100 mV results from the combined activity of denitrifers and facultative anaerobes (fermenters). As the redox potential decreases further, the activity of sulfate-reducers increase and the redox potential drops below -150 mV as sulfide production increases. Methane producers (methanogens) begin to be active as the redox potential falls to below -200 mV and in the absence of sulfate become the dominant microbes below -150 mV.

In conclusion, aerobic conditions inhibit methanogens and the products of aerobic metabolism generally are not significant substrates for methane production. Under anaerobic conditions, if nitrate is available, denitrifers metabolize much as they do aerobically; thus, their products are not useful to the methanogens, and the methanogens

are generally inactive. Where oxygen, nitrate, and sulfate are limiting, methanogens play a dominant role. They are able to capitalize on an energy-producing reaction for which there is little competition, *i.e.*, the oxidation of H_2 coupled to the reduction of CO_2 to produce CH_4. When sulfate reduction is the dominant terminal process, acetate and H_2 are preferentially utilized by sulfate reducing bacteria, and CH_4 production is inhibited. Under conditions of limited sulfate availability, CH_4 production becomes the terminal process of carbon mineralization, producing equimolar amount of CO_2 and CH_4 (Yavitt *et al.* 1987).

Oxidation Of Methane

Methane is oxidized photochemically in the atmosphere. However, almost nothing is known about biological sinks of atmospheric methane. It is believed that the major biological sink of atmospheric methane is microbial activity in soils (Galchenko *et al* 1989).

Biogenically produced CH_4 can be oxidized by CH_4-oxidizing bacteria (methanotrophs) which require oxygen for metabolism. All the methanotrophs so far described need O_2 and are unable to use other electron acceptors, such as nitrate, ferric iron, or sulfate. Many scientists have attempted to isolate bacteria that would be able to oxidize CH_4 without O_2, so far without success (Conrad 1989). Methane oxidation is most likely to occur in the uppermost layers of water-saturated peat, although anaerobic CH_4 oxidation is also known to occur (Alperin and Reeburgh 1984; Alperin *et al.* 1988; Cicerone and Oremland 1988). Therefore, it can be concluded that methane oxidation is controlled by the availability of oxygen in terrestrial ecosystems.

The major factors controlling the availability of O_2 and oxidation of CH_4 are the structure of a particular wetland ecosystem and the transport pathway by which the produced CH_4 reaches the atmosphere (Conrad 1989). When CH_4 production rates are low and /or diffusion paths are long, there is a great opportunity for most of the produced CH_4 to be oxidized on its way to the atmosphere. Yavitt *et al.* (1988) found

that CH_4 oxidation occurred at a rate of 0.2 to 3.3 nmol m^{-2} hr^{-1} in peat cores taken from a *Sphagnum* peatland in West Virginia and the oxidation diminished CH_4 flux by 11 to 53%. King (1990) measured CH_4 oxidation rates of approximately 0.24 nmol m^{-2} hr^{-1} in peat cores from a Danish wetland. Fechner and Hemond (1992) also provided evidence for this that a large fraction of the CH_4 flux was oxidized before it reached the atmosphere and most CH_4 oxidation occurred between the water table, located 12 to 15 cm below the bog surface, and about 6 cm below the bog surface in a *Sphagnum* bog in Massachusetts. Thus, methane oxidation may be an important reason for some bog sites having low CH_4 emissions. However, when CH_4 production rates are high and /or diffusion paths are short, a substantial amount of the produced CH_4 may reach the atmosphere. For example, highly productive sediments often produce so much CH_4 that it can no longer escape by diffusion alone; instead gas bubbles are formed and pass through the overlying oxygenic sediment surface and water so rapidly that there is little chance for CH_4 to be reoxidized by methanotrophs. On the other hand, if CH_4 production rates are too low for bubble formation or if the ebullition is hindered by high hydrostatic pressure, there is a higher probability that the upward-diffusing CH_4 is completely oxidized at the anoxic-oxygenic interfaces (Conrad 1989). Methanotrophic bacteria and CH_4 oxidation activity are usually concentrated in the oxygenic sediment surface layers or in the oxycline of stratified lakes (Rudd & Taylor 1980).

Conrad (1989) concluded that generally CH_4 emission from shallow aquatic ecosystems is more important than that from deep aquatic ecosystems. Wetland ecosystems (*e.g.*, littoral zones, shallow lakes, paddy fields, marshes, rich fens, and swamps) are especially important environments. There, the plant roots (in the rhizosphere) may build a network that traps gas bubbles at least temporarily. The root surface constitutes an additional anoxic-oxygenic interface within the CH_4 production zone of the sediment (Conrad 1989). The ability of aquatic plants to control oxidation of

CH_4 depends largely on the vascular plant gas transport system which allows the diffusion of O_2 into the roots and from there eventually into the sediment. The same vascular system likewise allows the diffusion of CH_4 from the sediment into the atmosphere (Sebacher *et al.* 1985).

Schütz *et al.* (1989) reported the importance of aquatic plants and their influence on gas transport for oxidation of CH_4 in an Italian paddy field. They observed that there was a close relationship between seasonal variation of CH_4 emission and rice plant growth.

Although this result may be a good example of relations between methane emission and vegetation, other vegetated wetland ecosystems may behave differently. The amount of oxygen diffused into sediments from the atmosphere may be different, the extension of roots into the soil matrix may be different, and the microflora of the rhizosphere may be affected by the vascular plant species.

FACTORS CONTROLLING METHANE PRODUCTION AND EMISSION

Numerous physical, chemical, and biological factors can influence the physiology of methanogenic bacteria and the ecology of anaerobic ecosystems. The rate of methane production in a given habitat will reflect these factors (Cicerone & Oremland 1988).

Effects of Substrate

In general, organic matter stimulates CH_4 production. This stimulation is due to enhanced fermentative production of CH_4 precursors. Hence, sediments with high organic load are more active in CH_4 production than low organic sediments. In principle, CH_4 production is expected to be more or less proportional to the input of organic carbon (Conrad 1989). However, in ecosystems containing sulfate, part of the organic

carbon will be used for sulfate reduction and will result in production of CO_2 rather than CH_4 (Ward & Winfrey 1985, Conrad & Schütz 1988).

Electron acceptors such as nitrate or sulfate generally inhibit CH_4 production by competition, as reviewed above. Any input of oxidized compounds (*e.g.*, sulfate- or nitrate-containing fertilizers and atmospheric deposits of N and S) that may serve as electron acceptors will have a strong effect on CH_4 production (Conrad 1989).

Effects of Temperature

Methane production in natural environments is influenced by temperature. If the supply of organic matter is not limiting, as in most wetlands, increasing temperatures generally stimulate CH_4 production. Several studies have provided some evidence for the above conclusion. Crill *et al.* (1988) reported that CH_4 flux increased in response to increasing soil temperature. They found that an open bog in the Marcell Forest of Minnesota with the highest CH_4 flux exhibited a 74-fold increase in flux over a 3-fold increase in temperature. Williams & Crawford (1984) also reported that CH_4 production was temperature dependent, increasing with the increase of temperature (4 to 30 °C), except in peat from deep layers. Methanogens have been found to occur at temperatures as low as 4 °C and as high as 70 °C. Most have temperature optima between 30 and 45 °C (Frea 1984).

Svensson (1984) presented evidence for the occurrence of two populations of methanogens with different temperature optima; one population seemed to utilize acetate as a source for CH_4 formation and had its temperature optimum at about 20 °C ; the other utilized hydrogen and had an optimum between 24 and 28 °C . He stated that an increase in temperature from 2 to 12 °C resulted in an increase in CH_4 formation by a factor of 6.7. He suggested that the small changes in temperature occurring at the depths where CH_4 formation took place might give rise to large changes in CH_4 fluxes. However, this evidence was only obtained from a wet mire site. He surprisingly found that there was no correlation between CH_4 release and seasonal changes in temperature

for a drier site. He suggested that microaerophilic CH_4 oxidizers might be present , as was reported for other acid peats by Williams (1980). If the CH_4 oxidizers have high affinity for CH_4 and a similar temperature response as the methanogens, an increase in CH_4 formation may thus be followed by rapid CH_4 oxidation. The temperature relation for CH_4 formation may not be observed in the emission rates to the atmosphere (Svensson & Rosswall 1984). Moreover, since the majority of CH_4 production occurred between 10 and 24 cm below the peat surface (Svensson & Rosswall 1984), the low heat conductivity of peat would probably also result in low correlations between CH_4 emissions and soil temperature. It is for these reasons that the relations between CH_4 flux and soil temperature are usually complex. For instance, linear (Svensson and Rosswall 1984), polynomial (Baker-Blocker *et al.* 1977), log-linear (Holzapfel-Pschorn and Seiler 1986; Crill *et al.* 1988; Moore and Knowles 1990; Dise *et al.* 1992), and exponential (Moore *et al.* 1990) relationships between CH_4 flux and soil or air temperature have been reported. Experimental work is required in order to understand the mechanism of temperature on CH_4 fluxes in wetlands.

Effects of Moisture

Moisture is another important controlling factor for methane production and subsequent release of methane. The dependency of methane flux on moisture has been previously noted in wetlands (Harriss *et al.* 1982; Svensson & Rosswall 1984; Sebacher *et al.* 1986). According to Svensson & Rosswall (1984), CH_4 production is positively correlated with moisture, but the corresponding release of CO_2 seems unrelated to moisture. They suggested that 80-90% of the variation obtained between the different sites of wetlands may be due to moisture conditions.

Significant correlations between CH_4 and water table position have been reported by some investigators (Moore *et al.* 1990; Moore and Roulet 1992; Roulet *et al.* 1992; Moore and Roulet 1993; Dise 1993). Moreover, the dependence of the thermal regime on moisture conditions of peatlands was also observed by Roulet *et al.* (1992).

They concluded that the temperature of peat (or sediment) and moisture were not independent variables, and that moisture regime controlled both the thermal conductivity and the heat capacity of the peat and sediment.

Effects of Geochemical Conditions

Geochemical and nutritional conditions of wetlands are also important factors affecting CH_4 production. Generally, most methanogens are neutrophilic, growing optimally in a narrow range around pH 7 and tolerating pH values between 6 and 8. A few have their optimum pH between 8 and 10 (Conrad 1989). Most methanogens are sensitive to acidic environments (Frea 1984, Williams & Crawford 1984). No acidophilic methanogens have so far been isolated, although one isolate was shown to be acid-tolerant and tolerated pH values of about pH 3 (but optimum at pH 6-7) (Williams & Crawford 1985). Low rates of methanogenesis have been observed at pH 5.8 (Wolfe & Higgins 1979). The optimum pH for methanogens from the alkaline Big Soda Lake was found to be 9.7. Methane production from the lake decreased by a factor of more than 100 at pH 7.7 (Oremland *et al.* 1982). If the pH is permanently and generally too low or too high, it may exert an important control on CH_4 production similar to temperature (Conrad 1989).

Typical methanogens fulfill their nitrogen requirements through the assimilation of ammonium, although at high concentrations, ammonium ion may slow the conversion of acetic acid to methane at high concentrations (Wolfe & Higgins 1979).

Methanogens fulfill their sulfur requirements from sulfate, sulfide, cysteine, and methionine. Sulfate is a constituent of media recommended for the growth of methanogens. Growth and methane production can usually be optimized only if sulfides are present in the medium; the soluble inorganic sulfides seem to be the most effective (Frea 1984). However, high sulfide concentrations have been shown to inhibit methanogenesis (Williams & Crawford 1984).

Phosphate also has been found to inhibit methanogenesis in lake sediments (William & Crawford 1984), as has nitrate in salt marsh sediments (Balderston & Payne 1976).

Nickel, cobalt, molybdenum, and selenium are required by some methanogens, but concentrations in the nanomolar (ppb) range generally suffice. Patel *et al.* (1978) found that methanogens have a requirement for ferrous iron, with the optimum concentration in the 0.3-0.9 mM range. So far, nothing is known about the effects of electrical conductivity on CH_4 production (Conrad 1989).

The effects of nutrients on CH_4 production are difficult to predict, although it is known that nutrients such as nitrogen (nitrate and ammonium) or phosphorus (soluble inorganic forms) greatly influence biomass formation (primary organic substrates for CH_4 production). The vegetation of wetland ecosystems usually adapt to nutrient limitation and a change of nutrient supply will change the species composition (Conrad 1989). Moreover, it is not very clear whether or how the bacterial species of methanogenic microbial communities adapt to limitation and changes of nutrient content.

TECHNIQUES USED FOR METHANE FLUX MEASUREMENTS

Methane produced in wetland soils and sediments may enter the water column or the atmosphere via different pathways, including molecular diffusion or pressurized ventilation, through the aerenchyma of aquatic plants, ebullition of gas bubbles, and molecular diffusion of dissolved CH_4 across the water/atmosphere boundary layer. Because of these different pathways, separate techniques must be employed for determination of CH_4 fluxes.

During recent years, measurements of CH_4 fluxes from wetland ecosystems employing chamber techniques have been intensified. The most common method for the

determination of the CH_4 fluxes from wetland soils and water surfaces into the atmosphere is the closed or static chamber technique.

Closed (Static) Chamber

This method is applicable in view of the long lifetime of CH_4 in the atmosphere (about 10 years), the low solubility of CH_4 in water (appr. 24 mg L^{-1} at 20 °C and ambient pressure), and the low interaction of CH_4 with common chamber materials. Materials often used for building the chambers are aluminum, glass, and plastics.

The method employs an open bottom chamber that is placed over the measuring site; changes in the methane concentration are monitored. Disadvantages of the chamber technique include the exclusion of natural air turbulence, which may have a significant influence on the exchange of air between wetland surface and atmosphere (Schütz and Seiler 1989), and alterations of photosynthetic reactions, temperature, and humidity due to the enclosure, which may also have influences on CH_4 production, emission and consumption or oxidation at the area covered by the chamber.

To remove these influences, open and dynamic chambers or controlling the environment of closed chambers (*e.g.* shading of the chambers) are often used. In the latter cases, it is possible to reduce heating of the chamber air. However, the effect of shading on soil temperatures must be considered, and the measuring site must be reexposed to natural conditions at regular intervals.

Open and Dynamic Chambers

Chambers used in this technique are flushed with ambient air at a constant flow rate during the measuring period, and methane fluxes are determined from the difference in CH_4 concentration between chamber outlet and chamber inlet. In contrast to static chambers, the continuous air flow in an open and dynamic chamber prevent temperature and humidity increase within the chamber. If high flow rates are applied and the design of the chamber is appropriate, uniform mixing of the chamber air and short residence times for gas molecules in the chamber (<1 min.) are achieved. Relative humidity and

mixing ratios are kept near ambient conditions, and the relatively short measuring periods are advantageous for undisturbed soil conditions (Conrad 1989).

Comparison of methane emission measurements from subarctic fens using static and dynamic chambers has shown that static chambers may underestimate emission rates by about 20% compared to dynamic chambers with a wind speed of about 2 m s^{-1} (Moore *et al.* 1990).

METHANE FLUXES FROM VARIOUS WETLANDS

A considerable number of field measurements of CH_4 flux from various wetlands (including rice paddies) have been made over the past decade. In boreal peatlands, the average flux of CH_4 reported up to 1988 was 207 mg CH_4 m^{-2} d^{-1} (Crill *et al.* 1988). Among Minnesota peatlands, CH_4 flux was about 77 mg CH_4 m^{-2} d^{-1} from forested bogs, and 142 mg CH_4 m^{-2} d^{-1} from forested fens, whereas CH_4 flux from open bogs was 294 mg CH_4 m^{-2} d^{-1} (Crill *et al.* 1988). Dise (1993) continued to measure CH_4 fluxes at the same wetlands in Minnesota from September 1988 through September 1990 and reported that CH_4 fluxes from poor fen and open bog were 180 mg CH_4 m^{-2} d^{-1} and 118 mg CH_4 m^{-2} d^{-1}, respectively. She also reported that there were differences in CH_4 fluxes within a forested bog site, with 38 mg CH_4 m^{-2} d^{-1} in a hollow, 35 mg CH_4 m^{-2} d^{-1} in a fen lagg, and 10 mg CH_4 m^{-2} d^{-1} in a hummock. Mean CH_4 fluxes measured by Moore and Knowles (1990) from fen, bog and swamp peatlands in Quebec were <200 mg CH_4 m^{-2} d^{-1}, <5 mg CH_4 m^{-2} d^{-1} and <20 mg CH_4 m^{-2} d^{-1}, respectively.

Mean CH_4 flux from Alaskan fens was 39 mg CH_4 m^{-2} d^{-1} (Whalen & Reeburgh 1988, 1990), and the mean CH_4 fluxes from subarctic fens along a transect from fen margin to central and flooded sites were 65, 125, and 36 mg CH_4 m^{-2} d^{-1} (Moore *et al.* 1990). Svensson & Rosswall (1984) also measured the mean CH_4 flux

from a fen in northern Sweden at 95 mg CH_4 m^{-2} d^{-1} (range, 26-350).

Measurements by Sebacher *et al.* (1986) showed that average CH_4 flux varied from 4.9 mg CH_4 m^{-2} d^{-1} on moist tundra to 119 mg CH_4 m^{-2} d^{-1} on waterlogged tundra, and that fluxes averaged 40 mg CH_4 m^{-2} d^{-1} from wet tussock meadows and 289 mg CH_4 m^{-2} d^{-1} from an alpine fen. They measured an average CH_4 flux of 100 mg CH_4 m^{-2} d^{-1} from a boreal marsh.

Cicerone & Shetter (1981) obtained the first field measurements of CH_4 flux from a southern California rice paddy. They reported the average CH_4 flux was 180 mg CH_4 m^{-2} d^{-1}. However, meaningful comparison of the results is difficult, because of differences in the number of flux measurements made per sampling sites, the number of sites per wetland, and the number of wetlands used to develop a wetland type average (Moore *et al.* 1990). As a consequence, great variation is often reported for CH_4 fluxes from wetlands which seem uniform in other respects. Measurements even within the same habitat also showed a striking individuality. For example, values of salt marshes from different authors showed remarkable variation (Svensson 1984). King & Wiebe (1978) also obtained standard deviations of the mean at least 90% in their study of CH_4 flux from a salt marsh. Measurements from the Great Dismal Swamp (Virginia) also showed large variation, with rates varying by more than two orders of magnitude (Harriss *et al.* 1982).

These variations are results of the complex suite of environmental factors that affect the production of CH_4 *via* aerobic or anaerobic decomposition of organic matter in wetland soils and factors that affect the emission of CH_4 from the wetlands into the atmosphere. Fluxes measured at field sites and from soil samples have been independently correlated with local environmental and ecological factors. The factors, including differences in temperature, moisture, nutrient input, organic matter accumulation, composition and structure of organic matter, geochemical condition,

vegetation characteristics and differences in measurement techniques, could contribute to the observed variation in methane fluxes.

SUMMARY

The recent increase of CH_4 in the atmosphere, coupled with global warming, has stimulated considerable interest in the study of CH_4 increase and the process of production and emission. Studies show that CH_4 is a very efficient gas causing a "greenhouse effect". It has been estimated that wetlands are one of the most important sources of CH_4 production and emission to the atmosphere. Measurements of CH_4 fluxes from various wetlands show wide variation, which may result from local environmental and ecological conditions that largely control imbalances between production and oxidation. In the process of CH_4 production in wetlands, the acetate concentration is the most important intermediary product. It is generally held that methanogenesis is the terminal process in anaerobic decomposition of organic matter and becomes significant only if nitrate and sulfate are absent or are depleted through denitrification and sulfate reduction.

Methane production is the final step in a complex chain of anaerobic biogeochemical processes which may be influenced by soil (sediments) conditions and vegetation. In other words, methane production is greatly dependent on methanogenesis and on environmental factors that affect growth and activity of methanogens. Methane oxidation may be as important as CH_4 production in defining the source strength of a wetland ecosystem. For a better understanding of reasons for recent rapid increases and of terrestrial sources for atmospheric CH_4, the following areas of research should be emphasized:

1) The methane flux measurement in the field and extrapolation of measured data to large scale.

2) The role of CH_4 oxidation processes that act as a biofilter for CH_4 diffusing into the atmosphere (Galchenko *et al.* 1989).

3) The influence on CH_4 production and oxidation in wetland ecosystems by diurnal and seasonal rhythms, by acidification, and by fertilizer inputs (N, P, S) from the atmosphere or by human activity.

4) The structure and dynamics of methanogenic bacterial communities in different natural and artificial wetlands by using kinetic, tracer, and enrichment techniques (Conrad & Schütz 1988).

5) Development of mechanistic models of the biogeochemistry and the microbial population dynamics involved in CH_4 production and oxidation in various wetland ecosystems.

The purpose of my study is to investigate number one; the following chapter deals with this important area of research.

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II. METHANE FLUXES FROM BOREAL WETLAND ECOSYSTEMS IN CENTRAL ALBERTA, CANADA

INTRODUCTION

Atmospheric concentrations of methane (CH_4) have increased at a rate of about 1% y^{-1} over the past 15 years (Rasmussen and Khalil 1981; Ehhalt 1985; Blake *et al.* 1982, 1988; Ramanathan *et al.* 1985; Ramanathan 1988). The rapid increase of CH_4 in the atmosphere, coupled with its strong impact on global warming, has stimulated considerable interest in the study of methane production and emission. Natural wetlands are considered to be one of the major biogenic CH_4 sources, because they provide a large area of suitable anaerobic habitat for CH_4 production. Several studies have attempted to quantify the global CH_4 emissions from natural wetlands (*e.g.*, Ehhalt and Schmidt 1978; Khalil and Rasmussen 1983; Seiler 1984; Sebacher *et al.* 1986; Matthew and Fung 1987; Cicerone and Oremland 1988). In one of the more comprehensive studies, Matthew and Fung (1987) suggest that global wetland areas range from 2.0 x 10^{12} m^2 to 6.7 x 10^{12} m^2, and that global CH_4 emissions from wetlands range from 11 Tg yr^{-1} to 300 Tg yr^{-1}.

About 66% of the total global CH_4 emissions from natural wetlands come from north of 40° N regions (Matthew and Fung 1987). Reliable estimates of the contribution of northern wetlands are limited by a paucity of field measurements of CH_4 emissions (Moore and Knowles 1990) and by our knowledge of wetland extent.

Methane fluxes from a variety of wetland types have been measured (Baker-Blocker *et al.* 1977; Svensson and Rosswall 1984; Harriss and Sebacher 1981; Harriss *et al.* 1982, 1985; Sebacher *et al.*, 1986; Crill *et al.* 1988; Devol *et al.* 1988; Wilson *et al.* 1989; Moore and Knowles 1987, 1990; Whalen and Reeburgh 1988, 1990; Moore *et al.*

1990); Holland *et al.* 1992; Roulet *et al.* 1992; Bubier *et al.* 1993; Dise 1993; Dise *et al.* 1993). These studies generally show a wide range of flux rates, often with a strong component of seasonal and spatial variability, suggesting that uncertainties still exist in estimating methane source strength from natural wetlands. Moreover, few seasonal measurements across the gradient from ombrotrophic bog through fen, marsh and beaver pond have been reported in boreal wetland ecosystems, particularly from rich fens which account for a high percentage of areal coverage in wetlands of western Canada (Vitt unpublished data).

The main objectives of this study are: 1) to examine seasonal variation of methane fluxes over a two year period (1989-90) along a wetland gradient from bog, through rich fen to beaver pond; 2) to estimate annual methane contributions of Alberta wetlands to the global methane budget; and 3) to determine correlations between water level and water temperature on methane fluxes from these wetlands.

MATERIALS AND METHODS

Study Area

This study was conducted in six boreal wetland ecosystems in central Alberta in 1989 and 1990. Each wetland possesses different vegetation, hydrology, and chemistry. The vegetation and water chemistry of the sites are described in Vitt *et al.* (1993).

The climate of the area is boreal cold temperate, with cold winters and cool summers. Mean annual precipitation is 493.1 mm, of which 71.5 % is rain. Precipitation is highest in June and July. Mean annual temperature is 1.4 °C. In comparison to the 30 year record for 1951-1980, 1989 was warmer and wetter and 1990 was warmer and drier than the mean. Average monthly temperature and precipitation for May-Oct., 1989 were 12.1 °C and 369.2 mm, and 12.1 °C and 250.8 mm in 1990, whereas average monthly temperature and precipitation for May-Oct., 1951-1980 were 11.6 °C and

349.6 mm, respectively (Athabasca Weather Station 2 data). In an average year, the growing season (days with air temperature mean above 10 °C) is about 164 days in duration (April 25th through October 6th). The frost free period averages about 75-85 days.

The study area is located within the mixedwood section of the Boreal Forest Region. The upland watersheds in this ecoregion are dominated by aspen poplar (*Populus tremuloides*), paper birch (*Betula papyrifera*), and white spruce (*Picea glauca*), with balsam poplar (*Populus balsamifera*) in locations of poorer drainage.

Sampling Sites

Six wetland types (ombrotrophic bog, poor fen, forested and open moderate-rich fens, marsh, and beaver pond) with different vegetation, hydrology and chemical regimes were selected and platforms were built to limit sampling disturbance at each site.

The ombrotrophic bog and poor fen are located at 54° 41' N, 113° 28' W, north of Bleak Lake, Alberta. The bog has developed as an island, with 4-5 m of peat accumulation. The water table was consistently 40-50 cm below the peat hollow surface during the sampling seasons of 1989 and 1990. The vegetation of the site is dominated by *Sphagnum fuscum*, *Ledum groenlandicum*, *Picea mariana*, *Smilicina trifolia*, *Polytrichum strictum*, *Vaccinium vitis-idaea*, and *Vaccinium oxycoccos* with scattered occurrence of *Cladina mitis*.

The poor fen occupies a water track at the edge of the bog island. The peat layer of the poor fen site is 3-4 m thick and the surface is marked by a hummock and hollow microtopography with differences of 30-40 cm in height. The vegetation of the poor fen is dominated by *Sphagnum teres*, *S. angustifolium*, *Carex lasiocarpa*, *Aulacomnium palustre*, *Betula glandulosa*, *Salix discolor*, and *Andromeda polifolia*.

Two moderate-rich fen sites, one forested and the other lacking trees, are located at 54° 28' N, 113° 17' W. The moderate open rich fen surrounds a small pond and is covered by *Carex lasiocarpa*, *Drepanocladus vernicosus*, *Calliergonella cuspidata*,

Menyanthes trifoliata, and *Calliergon giganteum*. The thickness of the floating mat is about 1-1.5 m.

The forested rich fen is covered with *Tomenthypnum nitens*, *Aulacomnium palustre*, *Betula glandulosa*, *Salix pedicellaris*, *Carex lasiocarpa*, *Andromeda polifolia* and *Larix laricina*. About 4.5 m of peat has accumulated at this site. The water table of the site is 15-20 cm below the peat surface and closely related to pond water fluctuations.

The boreal marsh site is located at 54° 28' N, 113° 20' W, and dominated by *Carex lasiocarpa*, *Drepanocladus aduncus*, *Aulacomnium palustre*, *Carex chordorrhiza*, and *Salix pedicellaris*. Shrubs appear to be invading this site and may indicate some change in hydrological regime. Water levels at the site were consistently high during the summer season.

Two different beaver pond sites (54° 34' N, 113° 28' W) were used, one in 1989 and another in 1990. The 1989 site was in a recent (1-2 year old) beaver pond with considerable decomposing vegetation and the littoral zone of the site contained abundant macrophytic vegetation. The 1990 site, although within a kilometer of the 1989 site, was a much older, deeper, and stable beaver pond without littoral macrophytic vegetation and visible signs of disturbance. The ponds both contained about 1500 m^2 of open water, with the sediment covered by a thin layer of organic deposits. The surrounding area was dominated by *Populus tremuloides*

Sampling Methods

Methane fluxes were measured weekly (in 1989) and biweekly (in 1990) from early May to late August, and triweekly (in both years) in September and October. Static sampling chambers were used, similar to those of Ciceron and Shetter (1981), Moore and Knowles (1986) and Whalen and Reeburgh (1988). White plastic chambers with a volume of 13.75 L and a basal area of 0.064 m^2 were painted black inside and silver outside to minimize internal temperature increases and photosynthetic effects. A

sampling port (glass tube) was sealed into the top of the gas chamber with silicon and covered with a rubber septum.

Gas samples were collected from five chambers at each of the six sites during each sampling period. Initial samples were collected from each chamber immediately after placing the chamber on the wetland to establish initial concentrations of CH_4 and to account for any ebullition that might have occurred from chamber placement. The chambers were sampled again after 24 hours. A 24 hour period was chosen to permit measurement of CH_4 in sites with low fluxes and to account for diel methane fluctuations.

Sampling chambers were randomly placed over the wetland surface within each 5 m segment along a 25 m transect using a restricted random sampling design. The direction of the transect was consecutively rotated (about 25°) at each sampling period.

Each chamber was placed onto peat or water, ensuring that the edge of the chamber was sealed with water or wet peat. Major compression and disturbances of the wetland soils were minimized by carefully cutting the peat around the perimeter of the sampling chambers with a circular cutter. At the beaver pond sites, gas chambers were mounted on Styrofoam floats and tied to a sampling dock.

Samples were collected as follows: a 10 ml vacutainer was aerated to eliminate residual CH_4 and then evacuated with a 50 ml syringe 6-7 times, the septa on the chamber and vacutainer were punctured at the same time with a double-ended needle, allowing the pressure in the vacutainer to equilibrate with that of the chamber (about 1 minute).

At each of the sampling periods, duplicate surface water samples (162 ml glass vials) were collected from a shallow pit at each site for determination of methane concentrations in wetland waters. Subsurface water samples were collected in spring (May), summer (August), and fall (October) by withdrawing water from 5 cm (diameter) PVC pipes, perforated at the base and positioned at 0.5, 1.0, and 1.5 m depth, by using a

hand pump after discarding stagnant or air-contacted water. Methane concentrations in the waters were then analyzed as described below.

To evaluate the influence of microtopography on methane emission, methane fluxes from hummocks and hollows within one sampling site were compared. Seven hummocks and seven hollows were selected and sampling chambers placed in the forested rich fen site on August 2-3, 1990. The water tables were similar within the seven hummocks and seven hollows: the hummocks' water table was -25 cm while that of the hollows averaged 5 cm below the surface.

Analysis

Initial gas samples and samples after 24 hours (post) were refrigerated and usually analyzed within 48 hours. Samples in 1989 were analyzed for CH_4 using a thermal conductivity gas chromatography (Varian 700 areograph system) with a propack column. The minimum detectable methane concentration was 0.05-0.07% in the Varian 700 System and repeatability was approximately 96%. The detection limit was too high to detect CH_4 fluxes in the bog.

In 1990 samples were analyzed using a Hewlett Packard 5890 Series II Gas Chromatography with a 200 cm Poropak-N column held at 70 °C under a Flame Ionization Detector (FID). The detector was maintained at 220 °C, and H_2-Hi_2-O_2 (1:4:2) carrier gas flow rate was 30 ml min^{-1}. The detection limit of the CH_4 analyzing system was 0.0001% and the repeatability was >90%. A certified commercial standard of methane (100% methane gas from LINDE) was used as a standard.

Water samples were injected with 20 ml of N_2 to allow for methane evolution and then methane concentration in the head space of sample vials were analyzed.

The analysis was occasionally delayed for up to 2 weeks (in 1990). Vacutainers filled with methane standards were used to check for gas leakage and results showed that the vacutainer tubes could hold CH_4 for over 30 days with less than 0.001 % loss if they were refrigerated and well sealed.

The methane peaks were quantified with a HP 5890 Series II recording integrator. Mean daily flux values and standard deviations were calculated for CH_4 at each site for each sampling period. These mean daily values were used to calculate annual flux values for each wetland type. Annual CH_4 fluxes were determined by integrating the area under a curve. The curves used were produced by an unclamped cubic spline technique that uses a different third order polynomial to join each of the points, and extrapolates the slope and curvature using the previous and following points.

The methane flux was calculated by 1) determination of CH_4 concentration in pre- and post- samples; 2) subtraction of the concentration in the pre-samples from the post-samples; 3) standardization of this volume to a constant temperature and pressure (273 °K and 760 mm Hg); 4) conversion of the volume produced to moles using the standard molar volume of an ideal gas, and then converting to milligrams using the molecular weight of the gas; and 5) calculation of the flux by dividing the amount produced by the basal area of the air chamber and the period of sampling time.

Total annual methane emission for each of the wetland types in Alberta was estimated by multiplying the annual calculated mean flux of each wetland type by an estimate of the total provincial area of each wetland type. Total wetland areas were estimated from Turchenek and Pigot (1988) and 1:1,000,000 (Vitt 1992) and 1:250,000 (unpublished) scale maps of the peatlands of Alberta.

Statistical Analysis

A split-block design for analysis of variance (ANOVA), where sampling sites are treated as blocks with sampling dates as subunits within blocks, was used to determine if there were significant variations in methane fluxes between sampling sites (Steel and Torrie 1980; Sokal and Rolf 1981; Prepas 1982). Studentized Newman-Keuls (SNK) method was used to determine differences between individual sampling sites. The ANOVA and SNK were computed with the Statistical Analysis System (SAS) package on VM at the University of Alberta Computer System.

The methane flux measurements in 1989 and 1990 were considered as two different experiments, because different instruments (gas chromatography) were used in each year. Thus, the ANOVA and the SNK test were performed separately for each year's data.

The methane flux data were log-transformed to provide a near-normal distribution and to decrease variance heteroscedasticity (Sokal and Rohlf 1981; Prepas 1982).

A t-test was conducted in order to determine whether hummocks and hollows differed in methane emissions using of Systat program on a Macintosh computer.

RESULTS

Temporal Patterns of Methane Fluxes

A seasonal pattern in methane fluxes was observed with emission rates generally lower during the spring, and reaching peak values in late summer and lower in autumn (Fig. II-2; II-3). Seasonal patterns of methane fluxes were similar in the six wetlands, although the methane fluxes were highly variable both in space and time. The highest daily fluxes in 1989 occurred in August at all wetland sites, although the dates of peak value were not synchronous (Table II-2). The highest daily fluxes in 1990 occurred in July, August, or October (Fig. II-2; II-3).

The mean daily fluxes at the six sites were generally higher in 1989 than in 1990 (Fig. II-3; Table II-2). Methane fluxes from the six wetlands showed high seasonal variability in both years (Fig. II-2; II-3). The coefficient of variance (C.V.=standard deviation/mean) was between 85% to 365%. The C.V. of the methane fluxes in 1989 were in general higher than those in 1990 (Table II-2).

Site Differences of Methane Fluxes

There were great differences in the magnitude of CH_4 flux in the six wetlands (Table II-2; Fig. II-2, II-3). The highest mean daily fluxes were observed at the beaver pond site in both 1989 and 1990, with 547.1 mg CH_4 m^{-2} d^{-1} and 98.5 mg CH_4 m^{-2} d^{-1}, respectively. The daily methane fluxes at the beaver pond sites ranged from 8.7 mg CH_4 m^{-2} d^{-1} to 4,748.7 mg CH_4 m^{-2} d^{-1} in 1989 and from 0.3 mg CH_4 m^{-2} d^{-1} to 211.5 mg CH_4 m^{-2} d^{-1} in 1990. The lowest mean daily methane fluxes were found at the bog site in both 1989 and 1990, with 0.0 mg CH_4 m^{-2} d^{-1} and -1.23 mg CH_4 m^{-2} d^{-1}, respectively (Table II-2). Methane flux at the bog site in 1990 was generally <0.2 mg CH_4 m^{-2} d^{-1} or negative and in 1989 was generally below the detection limit, because of the low sensitivity of the gas chromatography used in that year.

The analysis of variance for each of the two year's data indicates that there are significant differences (p<0.0001) in methane fluxes among sampling sites in both years. Significant variation is also present among sampling date within each site (Table II-3). However, the Studentized Newman-Keuls test indicates that among six sampling sites there is no significant difference in methane flux between the ombrotrophic bog, the poor fen and the forested rich fen sites and no significant difference between the marsh and the open rich fen sites in 1989. In 1990, there is no significant difference between the ombrotrophic bog, the poor fen and the forested rich fen sites and no significant difference between the open rich fen and the beaver pond sites (Fig. II-4).

Annual Methane Fluxes

Estimated annual emission rates of CH_4 for in the six wetlands in central Alberta ranged from 0 to 7.6 x 10^4 mg m^{-2} yr^{-1}, with a mean of 1.9 x 10^4 mg m^{-2} yr^{-1} in 1989 and from -151 to 1.5 x 10^4 mg m^{-2} yr^{-1}, with a mean of 5.1 x 10^3 mg m^{-2} yr^{-1} in 1990 (Table II-4).

There was a strong gradient in annual CH_4 fluxes in the six sites in both years with the beaver pond > marsh > open rich fen > forested rich fen > poor fen > ombrotrophic bog. The annual CH_4 flux in the beaver pond was about 300 times greater

than that in poor fen, let alone in bog site where the annual methane emission was zero or negative (see Table II-4).

Methane in wetland waters

Seasonal variations of CH_4 concentration in surface water are not as great as seasonal variation of CH_4 emissions from these wetlands (Fig. II-5). The coefficient of variance of the methane concentrations in surface waters ranged from 129% to 227% in 1989 and 65% to 192% in 1990. There is no clear pattern of seasonal variation of CH_4 in the surface waters. Methane emission rates are not correlated to CH_4 concentrations of surface waters in most of the sites (r=0.001, n=157). Only in the forested rich fen site was the methane flux and methane concentration in the surface water significantly correlated (r=0.70, n=27, p<0.0001).

The lowest CH_4 concentration in surface waters of the wetlands occurred in the beaver pond and the highest in the open rich fen (Fig. II-5). Methane profiles in water columns of the wetlands showed that CH_4 concentrations in subsurface waters were generally much higher than that in surface water and generally increased with depth (Fig. II-6).

Contributions of Alberta Wetlands

Based on area estimates of each wetland type, with a total area of wetlands: 1.46×10^5 Km^2 (Vitt *et al.* 1990) and the annual methane fluxes above, the wetlands in Alberta would yield 0.91 Tg CH_4 yr^{-1} to the atmosphere (Table II-5). Others have compared fen and bog (*i.e.* Bubier *et al.* 1993), when this is done, fens (sum of the poor fen, forested rich fen and open rich fen) would emit 0.26 Tg CH_4 yr^{-1} to the atmosphere (Table II-6). However, from the statistical results shown in (Fig. II-4), bog, poor fen, and forested rich fen have similar methane emissions and are quite dissimilar from open rich fen, marsh, and beaver pond. Comparisons of bogs to fens should only be done after careful consideration of the regional data set. Based on more recent estimates of wetland area in Alberta (Vitt unpublished data), the methane emissions to the

atmosphere from the Alberta fens would be 0.35 Tg CH_4 Yr^{-1} (Table II-6). Thus , differences in area estimates alone produced a difference of 30% in methane emissions.

Relations of Methane Fluxes with Environmental Variables

Water Temperature

Temperatures of the surface waters increased over the season, peaking in mid summer (Fig. II-7). Temperatures of subsurface waters decreased with depth in the peat profile, particularly between the surface and 0.5 m depth. The bog site consistently had lower temperatures at all depths when compared to the fens. The insulating abilities of the bog is clearly evident when compared to the poor fen: bog water temperature was always lower than that of poor fen, and at depth the bog temperatures remained lower (*e.g.*, at 1.0 m maximum bog temperature was about 5 °C, compared to between 7 and 12 °C for other wetland types-Fig. II-7).

Generally, there was a very significant correlations ($p<0.01$) between methane flux and water temperature (surface and -0.5 m subsurface) for overall sites. For individual site, a very significant correlations ($p<0.01$) were found between surface water temperatures and methane emissions at the open rich fen ($r=0.60$, n=27) and marsh sites ($r=0.65$, n=27), while significant correlations ($p<0.05$) were found at the forested rich fen ($r=0.35$, n=27) and beaver pond sites ($r=0.38$, n=27). No correlation was found between water temperatures and methane emissions in the bog and poor fen sites (Table II-7).

Water Table Position

The highest mean water table position among the wetland types was found in the marsh in 1989 and in the open rich fen in 1990, while the lowest water table was always in the bog in both years (Fig. II-8). The beaver pond was excluded from this analysis, since the site was not really a wetland but was a pond.

The water table generally responded quickly to precipitation events over 60 mm, whereas weekly precipitation amounts of less than 25 mm elicited little movement in the

water table. When periods of little or no precipitation lasted longer than one week, water tables fell noticeably. During 1989, the single large precipitation event during week 137-143 filled the basins and they remained relatively full for the summer season. In 1990, water tables gradually fell throughout the growing season in all wetland types (Fig. II-8).

A less significant correlation (r=0.31, n=130, p<0.05) between methane flux and water table position for overall sites than water temperature was observed and there was no significant correlation at individual sites except at the marsh site where the correlation between methane flux and water table position was very significant (r=0.53, n=27, p<0.01) (Table II-7).

Microtopography

A higher rate of methane emission in hollows compared to hummock was observed, with hollows having 60 % higher emissions on average than hummocks (Fig. II-9). There is a significant difference in methane fluxes (p<0.001) between these two microtopographic levels.

DISCUSSION

Temporal Pattern of Methane Flux

The temporal patterns of CH_4 fluxes from wetlands of central Alberta are similar to results reported by Svensson and Rosswall (1984), where they observed the highest methane flux in July and a high emission in the autumn. The seasonal pattern from this study is slightly different from studies reported by other investigators (Wilson *et al.* 1989; Moore *et al.* 1990), in which the CH_4 fluxes increased in spring (thaw peak), declined in early summer, then increased again in late summer. The differences may be due to different climate patterns (different date of thaw), different wetland type, or length

of sampling period. Rates of methane production and emission during the winter months from our sites are not known.

The general increase of methane fluxes during summer are probably associated with the gradual warming of the subsurface layers of the wetlands; the major site of methanogenesis (Moore and Knowles 1987). The statistically significant overall correlation between methane flux and pore water temperature at 0.5 m depth suggests that temperature is an important environmental variable influencing methane fluxes.

Comparison of Alberta Methane Fluxes With fluxes in Eastern Canada

The methane fluxes measured in Alberta wetlands are comparable to those measured in eastern Canada by Moore *et al.* (1990), Holland *et al.* (1992), Roulet *et al.* (1992), and Bubier *et al.* (1993). The daily mean methane fluxes in the bog and marsh sites were lower and fens higher than the rates in comparable boreal wetlands in northern Ontario (Bubier *et al.* 1993). The daily mean flux in the beaver pond was similar to the emission rate in a beaver pond from eastern Canada (Bubier *et al.* 1993). However, from this study and others (Swain 1973; Baker-Blocker *et al.* 1977; King *et al.* 1978, 1981; Harriss *et al.* 1981, 1982; Svensson and Rosswall 1984; Sebacher *et al.* 1986; Crill, *et al.* 1988; Whalen and Reeburgh 1988; Moore *et al.* 1990; Holland *et al.* 1992; Roulet *et al.* 1992; Bubier *et al.* 1993; Dise 1993; Dise *et al.* 1993), meaningful comparison of the emission rate is difficult, due to differences in the experimental design, number of flux measurements made per sampling site, the number of sites per wetland, and the number of wetlands used to develop a wetland type average (Moore *et al.* 1990). Furthermore, using limited individual site measurements to represent an entire wetland type to estimate annual fluxes may result in great error, since a high spatial variability of methane flux from wetlands has often been reported, even at sites which appear to be homogeneous.

Relations Between Methane Fluxes and Methane Concentrations in Waters

In wetlands, methane flux to the atmosphere is ultimately dependent on production and emission of methane from anoxic sediments to the overlying peat or pore water. Methane concentrations in profiles of wetland waters suggest that significant quantities of methane might be produced in subsurface peat layers and super-saturated in pore waters. Increases of methane concentrations with depth also suggest that super-saturated methane is emitted at the surface or near the surface. In other words, pore water methane profiles may reflect the balance of production and emission of methane (Dise 1993). However, in this study generally (except in forested rich fen site) no significant correlations are observed between net methane fluxes and methane concentrations in pore waters, although the concentration gradient of methane between the sediment and water has been shown to be a factor controlling rates of diffusive methane flux (Bartlett *et al.* 1985). The reason for the exception in the forested rich fen site is not known. Wilson *et al.* (1989) also reported similar results in which methane concentration in pore waters were not correlated with methane fluxes. They explained that a poor correlation resulted from other mechanisms of methane emissions into the atmosphere such as ebullition and diffusive transport through plants. They emphasized the complexity of the processes controlling emissions.

Moore and Knowles (1990) reported very low rates of methane production and emission from a laboratory study of bog peat, and stated that the low methane producing capacity of their two bog sites may be related to the microbiological and chemical properties of the acid, fibric peat. However, other investigators have obtained different results (*e.g.* Clymo & Reddaway 1971; Svensson 1976; Harriss *et al.* 1985; Crill *et al.* 1988). These authors reported that there were substantial productions emissions of methane from the bog peats they studied, though summer emission rates tended to be low. The contradictory results may be due to different quality of substrate, *i.e.* the status of decomposition and mineralization of organic matter, and the constituents of the

organic deposits. The relations between methane fluxes and the quality of substrate in wetlands of central Alberta still remains unclear and deserves further study.

Correlation With Environmental Variables

The importance of peat temperature on methane flux has been previously noted in wetlands. Crill *et al.* (1988) reported that CH_4 flux increased with increasing soil temperature. They found that an open bog in the Marcell Forest of Minnesota with a high CH_4 flux exhibited a 74-fold increase in flux with a 3-fold increase in temperature.

Williams and Crawford (1984) also reported that CH_4 production was temperature dependent, increasing with the increase of temperature (4 to 30 °C), except in peat from deep layers.

Svensson (1984) also presented evidence that an increase in temperature from 2 to 12 °C resulted in an increase in CH_4 formation by a factor of 6.7. However, he found that there was no correlation between CH_4 emission and seasonal changes in temperature for a dry site. In this study, there was no significant correlation between methane flux and surface water temperature (r=0.34, n=27, $p < 0.1$) in the ombrotrophic bog site where water table position was about 40-50 cm below the peat surface throughout the year. A possible explanation for the poor correlation given by Svensson (1984) was the occurrence of microaerophilic CH_4 oxidizers, as reported for other acid peats by Williams (1980). If the CH_4 oxidizers have high affinity for CH_4 and a similar temperature response as the methanogens, an increase in CH_4 formation may thus be followed by rapid CH_4 oxidation. The temperature relation for CH_4 production may then not be observed in the emission rates to the atmosphere (Svensson and Rosswall 1984). Moreover, the low heat conductivity of peat in drier wetlands (e.g. ombrotrophic bog) would result in more stable temperature at the subsurface and would probably also result in low correlation between CH_4 emissions and temperature. Dependence of the thermal regime on the moisture condition of peatlands was observed by Roulet *et al.* (1992). They concluded that the temperature of peat (or sediment) and moisture were

not independent variables, and that moisture regime controlled both the thermal conductivity and the heat capacity of the peat and sediment.

The effect of temperature on CH_4 flux may be attributed to the effect of temperature on the physiological activity of methanogens. Methanogens have been found to grow at temperatures as low as 4 °C and as high as 70 °C. Most have temperature optima between 30 and 45 °C (Frea, 1984). Wilson *et al.* (1988) found that CH_4 flux appeared to be relatively constant at temperatures below 10 °C and above 16 °C, with major changes in CH_4 flux occurring between 10-16 °C. Svensson (1984) presented evidence for the occurrence of two populations of methanogens with different temperature optima; one population, seemed to utilize acetate as a source for CH_4 formation and had its temperature optimum at about 20 °C; the other utilized hydrogen with an optimum between 24 and 28 °C. It is for these reasons that the relations between CH_4 flux and soil temperature are usually complex. For instance, linear (Svensson and Rosswall 1984; Holzapfel-Pschorn and Seiler 1986; Crill *et al.* 1988; Moore and Knowles 1990), polynomial (Baker-Blocker *et al.* 1977), and exponential (Moore *et al.* 1990) relationships between CH_4 flux and soil or air temperature have been reported.

Moisture is important controlling factor for methane production and subsequent release of methane. The dependency of methane flux on moisture (and water table position) has been previously noted in wetlands (Harriss *et al.* 1982; Svensson and Rosswall 1984; Sebacher *et al.* 1986; Moore *et al.* 1990; Moore and Roulet 1992; Roulet *et al.* 1992; Dise 1993; Bubier *et al.* 1993). According to Svensson and Rosswall (1984), CH_4 production was positively correlated with moisture. They suggested that 80-90% of the variation in methane flux obtained between different sites may be due to moisture variation.

Although other investigators have reported strong correlation between CH_4 and water table position, limited success had been achieved in this study. The less significant correlation between methane flux and water table position in this study may partially be

due to the great variation of the methane fluxes, since the methane flux value used for computing the correlationship was the mean of five values from randomly placed positions within a site and thus the methane flux value was largely dependent on the probability of sampling position in hummock or hollow.

The less significant correlation with water table position also implies that methane emission was controlled by a variety of factors affecting methanogenesis or methane consumption. Even if a significant correlation between methane flux and water table position had been found, it would have provided only an approximation of the true dynamics of methane emission, since methane flux is a function of a variety of processes and emission mechanisms which may vary differently in seasons and between sites.

Variability of Methane Flux

The methane fluxes from wetlands in central Alberta varied widely over the course of this study. Similar variability of CH_4 flux has been reported from a variety of wetlands (Swain 1973; Baker-Blocker *et al.* 1977; King *et al.* 1978, 1981; Harriss and Sebacher 1981; Harriss *et al.* 1982, 1985; Svensson and Rosswall 1984; Sebacher *et al.*, 1986; Crill *et al.* 1988; Devol *et al.* 1988; Wilson *et al.* 1989; Moore and Knowles 1987, 1990; Whalen and Reeburgh 1988, 1990; Moore *et al.* 1990; Holland *et al.* 1992; Roulet *et al.* 1992; Bubier *et al.* 1993; Dise 1993; Dise *et al.* 1993).

This variability presumably results from the complexity and heterogeneity of processes controlling the production, consumption, and emission of CH_4 from soils, including seasonal temperature, water level fluctuation, spatial heterogeneity of microhabitats and bacterial distribution in peat, and differences in substrate quality and quantity. Methane flux is the result of the combined activity of several different emission processes. The observed flux includes diffusive emissions from the peat profile to the water column to the atmosphere, episodic emission of methane through

ebullition when methane concentrations in the peat (or sediments) reach saturation, and transport of methane through the stems of emergent aquatic plants.

From this study, the large variation of CH_4 flux partially resulted from variation within sites. One possible source of this variation may be the difference of microtopography at which the sampling chambers were placed, since methane fluxes from hummocks and hollows were significantly different ($p<0.001$). The daily methane fluxes from hollows were about 60 % higher than that from hummocks.

To reduce error in the estimation of methane fluxes from site measurements to large areas of wetlands, a random placement of sampling chamber was done in this study. The random sampling method may provide more practical and more accurate methane flux data than the fixed chamber method. This is especially true in those wetlands that have high variability in microtopography, for example, fens with complexity of hummocks and hollows. In addition, the static chamber method itself may involve several errors. For instance, gaseous fluxes may be underestimated because the chamber creates turbulence at the peat surface, and on the other hand, the fluxes may be overestimated because the temperature within the chamber may be higher than the surrounding atmosphere. One further problem is that gaseous fluxes from wetlands may involve ebullition (bubble release) due to the placement of the chambers. The high methane flux from the beaver pond in 1989 is likely due to ebullition during sampling.

Estimates of Methane Emissions From Natural Wetlands

Estimates of methane contributions from natural wetlands to the atmosphere often show a wide range of methane fluxes. This may be due, in part, to differing assumptions about area estimates of the wetlands, the magnitude and annual duration of methane fluxes from wetlands, and from the wide variability in measured flux rates themselves (Wilson *et al.* 1989). The great difference of methane flux in different wetland types in this study implies that variability of methane flux reported by some

investigators may be partially due to the different wetland classification systems being used in their studies.

Spatial variability of methane fluxes from this study and others suggest that an estimate of global methane emission from natural wetlands is dependent on distinguishing different wetland types and calculating each wetland area precisely. For example, different wetland types may differ considerably in CH_4 emissions, and these differences could have a significant effect on the estimate of the global role of northern wetland ecosystems as a source of atmospheric CH_4 (Moore *et al.* 1990). In Vitt *et al.* (1990), fens (poor fen, forested rich fen and open rich fen) and bogs account for 61% and 12% of the areal coverage of peatlands in Alberta. These areas multiplied by the methane fluxes in this study suggest that fens and bogs contribute 59% and -0.2% of the annual CH_4 emissions in Alberta wetlands, respectively.

Area estimates are important in estimating of methane contribution from wetlands to atmospheric methane. For example, based on the component wetland areas in Vitt *et al.* 1990, the area of fens in Alberta wetlands is 89,033 Km^2 and may emit 0.26 Tg CH_4 yr^{-1}. More recent estimates of wetland area components (Vitt unpublished data) indicate that there are 90,585 Km^2 of fens in Alberta, resulting in an annual emission of 0.35 Tg of CH_4. This shows that the uncertainty in estimating the areal coverage of fen types alone results in a range of 30% in annual CH_4 emission estimates in the wetlands of Alberta.

In conclusion, data from a few individual site measurements and area estimates of wetlands without consideration of wetland type can produce large errors in calculating methane emissions over large areas. To improve the accuracy in estimating of methane emissions from large areas, methane emissions of different wetland types should be estimated separately and different microtopographies within each wetland type should be distinguished.

Contributions of Alberta Wetlands to Global Methane Budget

Natural wetlands are an important source of atmospheric methane and because of the large area they cover in northern latitudes, wetlands may make a significant contribution as a global source of methane, and this may partially account for the large increase in atmospheric methane in northern latitudes during the fall season (Khalil and Rasmussen 1983).

Based on the study, the estimated total annual methane emissions indicate that boreal wetlands in Alberta are significant source of biogenic CH_4 to the atmosphere. This estimate is about 0.3-0.5% of Ehhalt and Schmit's (1978) estimates of total wetland CH_4 contributions, 190-303 Tg CH_4 yr^{-1}, and about 1.5% of Matthews and Fung's (1987) estimate of 62 Tg CH_4 yr^{-1} from peatlands between 50° and 70° N.

Table II-1. Locality and Some Characteristics of Six Sampling Sites in Central Alberta

Wetland Types	Locality	Latitude; Longitude; Elevation	Physiography	Dominant Vegetation
Ombrotrophic bog	Bleak Lake	54°41' N; 113°28' W; 610m	Forested Hummocks	*Picea mariana; Sphagnum fuscum*
Poor fen	Bleak Lake	54°41' N; 113°28' W; 610m	Non-forested Water track	*Carex tenuiflora; Sphagnum teres*
Forested rich fen	Colinton Creek	54°28'N; 113°17'.W; 678m	Forested Hummocks	*Larix lariciana; Tomenthypnum nitens*
Open rich fen	Colinton Creek	54°28' N; 113°17' W; 678m	Floating Mat	*Carex lasiocarpa; Drepanocladus vernicosus*
Marsh	Perryvale	54°28',N; 113°20'W; 663m	Non-forested Carpet	*Carex lasiocarpa Drepanocladus sp.*
Beaver pond	Muskeg Creek	54°34' N; 113°28'W; 640m	Open water	

Table II-2. Mean Daily Methane Flux and Max.+Min. Fluxes From Six Wetlands in Central Alberta.

Sites	Year	Mean±(S.D)[1]	C.V.(%)[2]	Max.(date)[3]	Min.(date)[3]
Ombrotrophic bog	1989	0.0(0.0)	0.0	0.0(----)	0.0(----)
	1990	-1.2(1.8)	150	0.3(Oct. 3)	-6.0(Aug. 9)
Poor fen	1989	0.4(1.1)	275	4.4(Aug. 30)	0.0(May 17)
	1990	1.2(2.0)	167	4.7(July 25)	-1.3(June 27)
Forested rich fen	1989	23.9(87.2)	365	372.4(Aug. 16)	0.0(May 17)
	1990	11.7(37.2)	318	123.8(July 11)	1.6(June 27)
Open rich fen	1989	109.1(239.8)	220	1031.7(Aug. 23)	0.0(May 17)
	1990	45.3(94.8)	209	327.1(July 11)	1.6(Sept. 5)
Marsh	1989	125.7(296.1)	236	1220.8(Aug. 16)	0.0(May 17)
	1990	49.8(50.2)	101	156.2(Aug. 9)	-0.8(May 17)
Beaver pond	1989	547.1(1087.2)	199	4748.7(Aug. 16)	8.7(May 17)
	1990	98.5(83.6)	85	211.5(July 11)	0.3(May 17)

1) Data in CH_4 mg m^{-2} d^{-1}±(standard deviation).
2) Coefficient of variance.
3) Data in CH_4 mg m^{-2} d^{-1}. Date in the bracket is the occurred date.

Table II-3. Results of ANOVAs for methane fluxes from wetlands of central Alberta.

Source of variation	*df*	*F* value	*p* -value
1989 CH_4 flux data			
Among sites	5	183.53	0.0001
Among dates within sites	90	9.22	0.0001
Within dates	384		
Total	479		
1990 CH_4 flux data			
Among sites	5	34.09	0.0001
Among dates within sites	52	3.27	0.0001
Within dates	232		
Total	289		

Table II-4. The Annual Methane Fluxes From Wetlands of Central Alberta.

SITE	YEAR	MEAN DAILY FLUX (mg CH_4 m^{-2} d^{-1})	ANNUAL FLUX (mg CH_4 m^{-2} yr^{-1})
BOG	1989	0.0	0.0
	1990	-1.23	-151
POOR FEN	1989	0.37	129
	1990	1.23	185
FORESTED RICH FEN	1989	23.9	3,432
	1990	11.7	1,755
OPEN RICH FEN	1989	109.1	9,534
	1990	45.3	6,714
MARSH	1989	125.7	21,746
	1990	49.8	7,082
BEAVER POND	1989	547.1	76,159
	1990	98.5	14,656

Table II-5. Estimated global methane contribution from wetlands in Alberta based on area data of each wetland type. The mean methane flux when all areas are considered together is 11,770 Kg CH_4 Km^{-2} Yr^{-1}.

WETLAND TYPE	AREA OF WETLANDS* (Km^2)	COVERAGE (%)	MEAN CH_4 FLUX (Kg CH_4 Km^{-2} Yr^{-1}) (1989 and 1990)	TOTAL CH_4 EMISSION (Tg CH_4 Yr^{-1})
Bog	17,987	12.3	-151**	-2.72×10^{-2}**
Poor fen	20,984	14.4	157	3.30×10^{-2}
Forested rich fen	58,956	40.4	2,594	1.53×10^{-1}
Open rich fen	9,093	6.3	8,124	7.39×10^{-2}
Marsh	35,973	24.7	14,414	5.19×10^{-1}
Beaver pond	2,798	1.9	45,408	1.27×10^{-1}
Total	145,791	100	--------	0.91

* Based on Vitt *et al.* 1990.
** Based on 1990 data of this study only.

Table II-6. Comparisons of methane emission estimates under the different estimates of the wetland area in Alberta.

WETLAND TYPES	ESTIMATE BASED ON VITT *ET AL.* (1990)	ESTIMATE BASED ON VITT (UNPUBLISHED)
FENS		
Area (Km^2)	89,033	90,585
CH_4 emission ($Tg\ CH_4\ Yr^{-1}$)	0.26 *	0.35 **
BOGS		
Area (Km^2)	17,987	16,160
CH_4 emission ($Tg\ CH_4\ Yr^{-1}$)	-2.7×10^{-2} *	-2.4×10^{-2} **

* Calculated from Table II-5. Fens are the sum of the poor fen, forested rich fen, and open rich fen.

** Flux rates are from Table II-5. Areas of the fens and bogs are based on revised estimate by Vitt (unpublished data). Poor fen, forested rich fen and open rich fen are estimated as 24,203.1 km, 36,092.7 km and 30,289.2 km, respectively.

Table II-7. Correlation coefficients between logrimethic methane flux and some environmental factors in wetlands of central Alberta.

Significant level: ** = very significant ($p<0.01$); * = significant ($p<0.05$); WT.= water temperature, WL.= water level.

Wetlands	Factors	Surface	-0.5 m	-1.0 m	-1.5 m
Ombrotrophic Bog	W.L.	0.21	------	------	------
	W.T.	0.34	0.14	0.0	0.071
Poor Fen	W.L.	0.28	------	------	------
	W.T.	0.078	0.15	0.078	0.0
Forested Rich Fen	W.L.	0.063	------	------	------
	W.T.	0.35*	0.26	0.045	0.045
Open Rich Fen	W.L.	0.0	------	------	------
	W.T.	0.60**	0.52**	0.40*	0.30
Marsh	W.L.	0.35*	------	------	------
	W.T.	0.65**	0.46**	0.50**	0.30
Beaver Pond	W.L.	------	------	------	------
	W.T.	0.382*	------	------	------

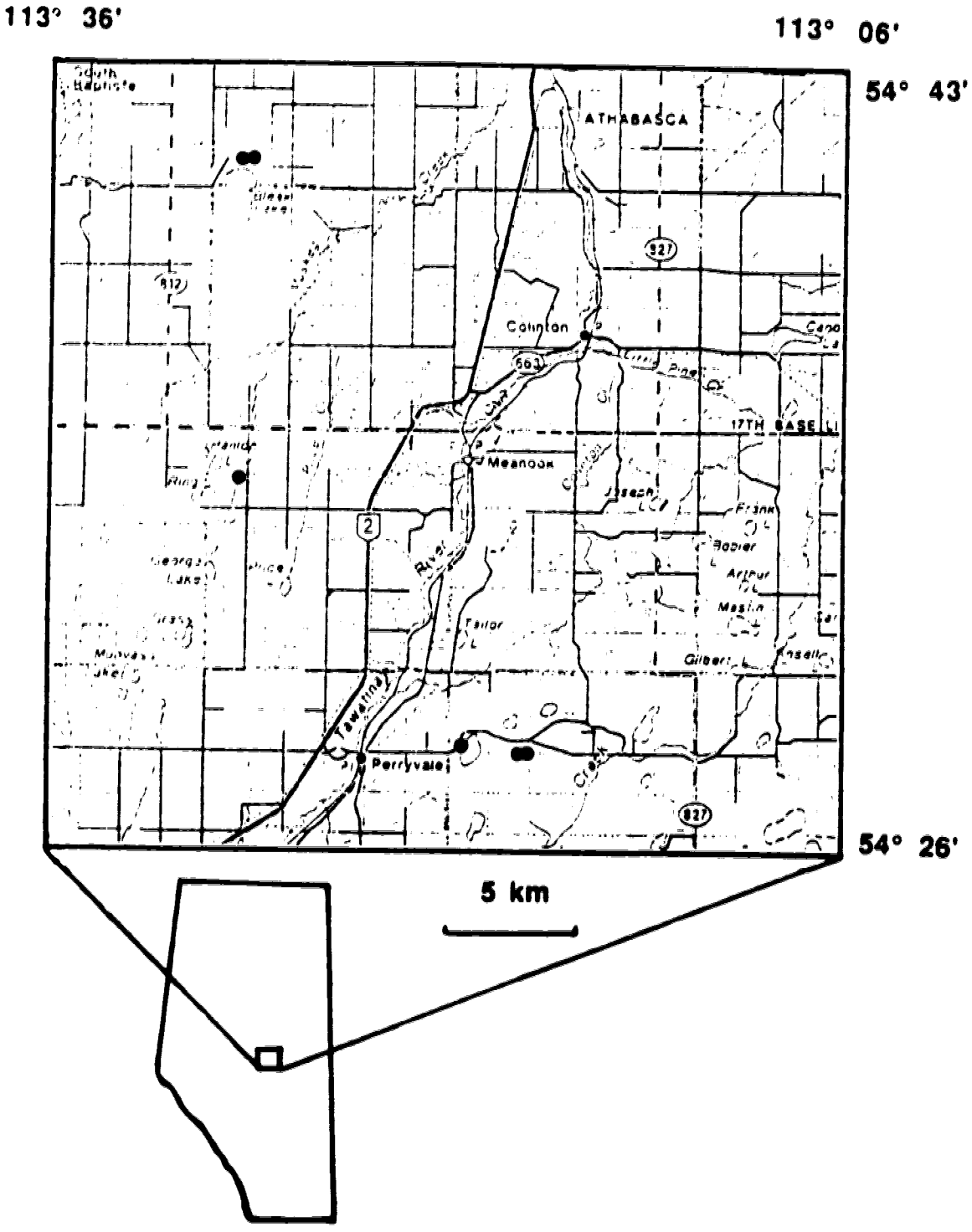

Figure II-1. The Location of the Study Area and Sampling Sites.

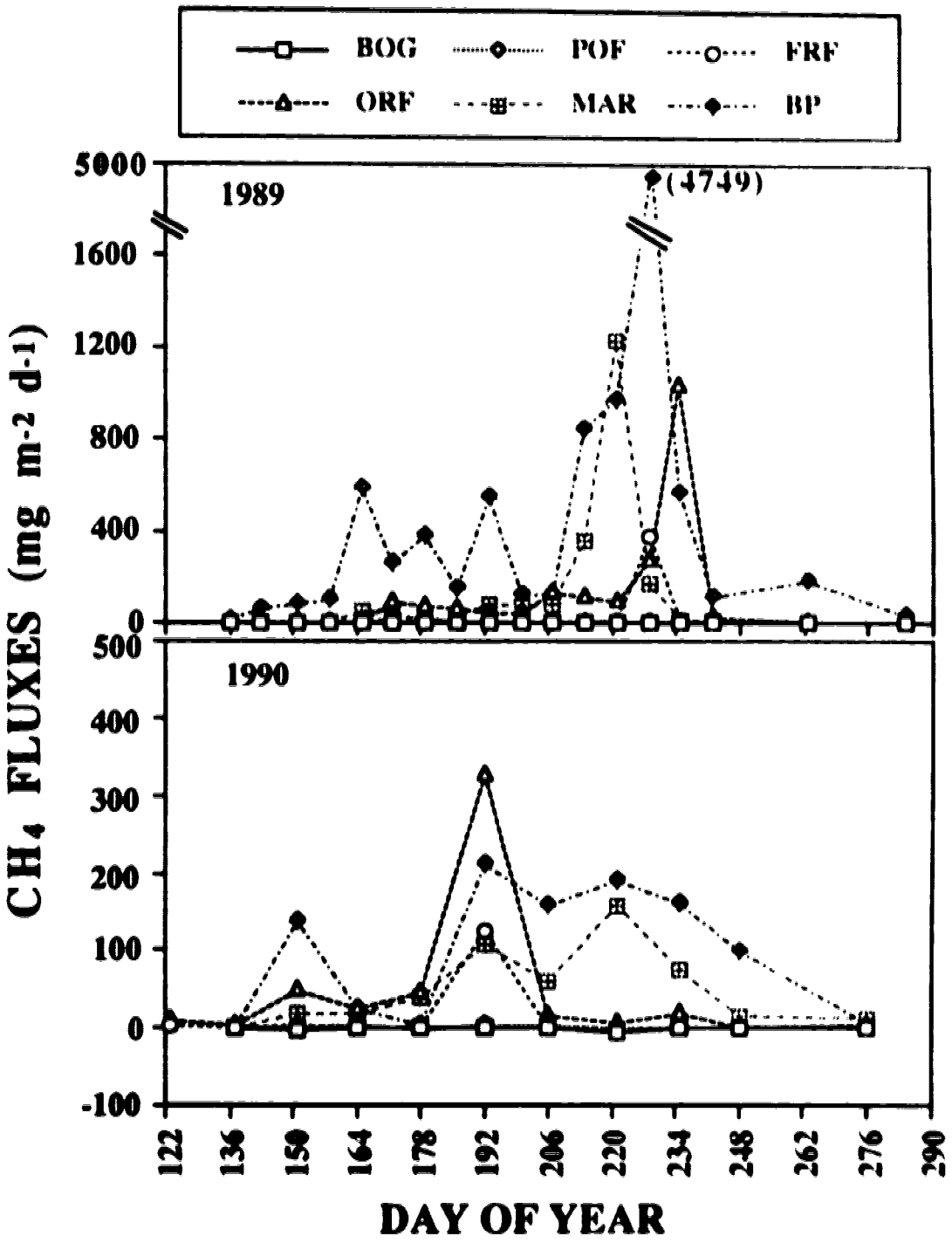

Figure II-2. Seasonal Pattern of Methane Flux in Wetlands of Central Alberta. BOG=Ombrotrophic Bog; POF=Poor Fen; FRF=Forested Rich Fen; ORF=Open Rich Fen; MAR=Marsh BP=Beaver Pond.

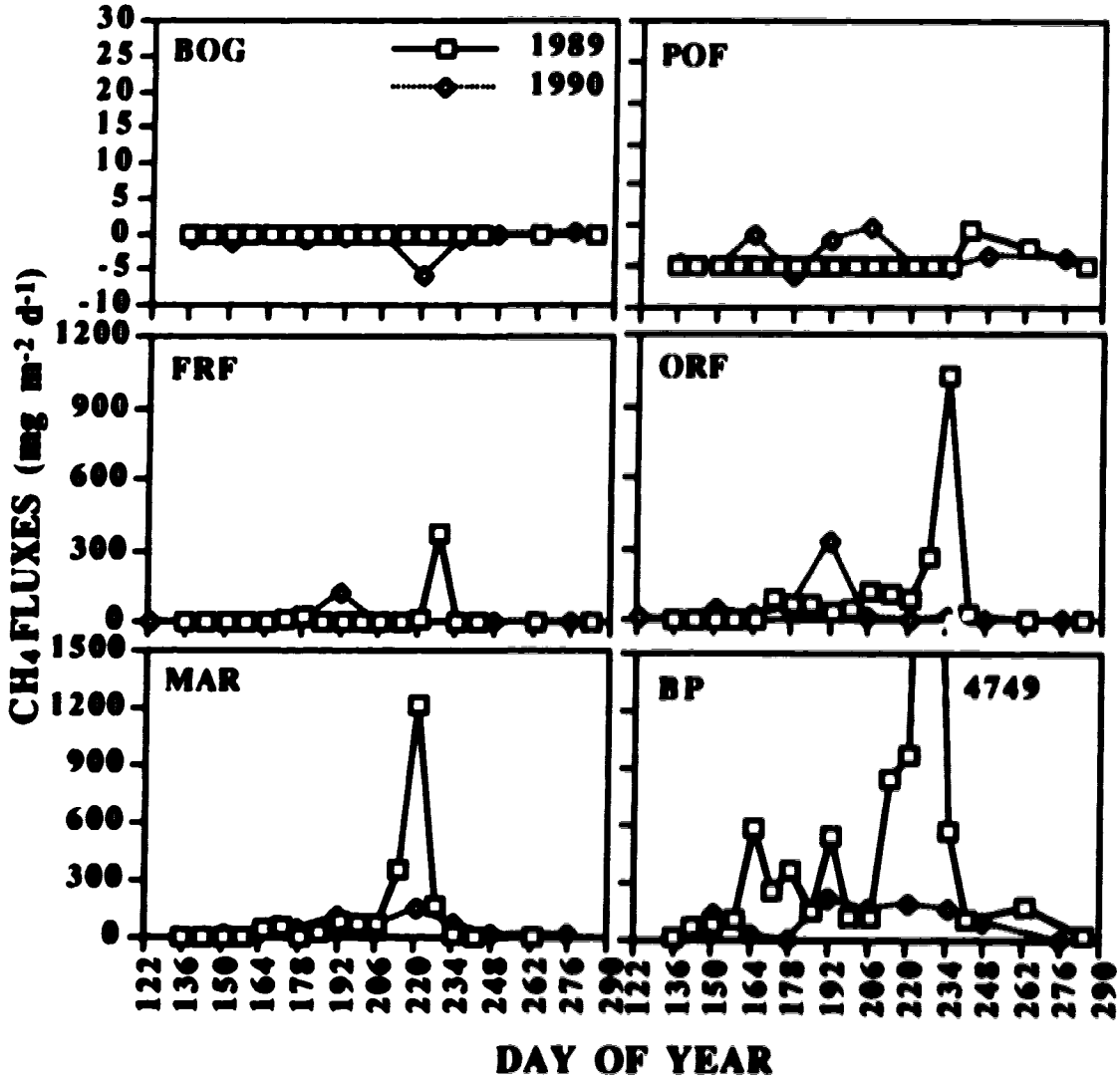

Figure II-3. The Comparison of Methane Fluxes Between years in Six Wetlands in Central Alberta. BOG=Ombrotrophic Bog; POF=Poor Fen; FRF=Forested Rich Fen; ORF=Open Rich Fen; MAR=Marsh; BP=Beaver Pond.

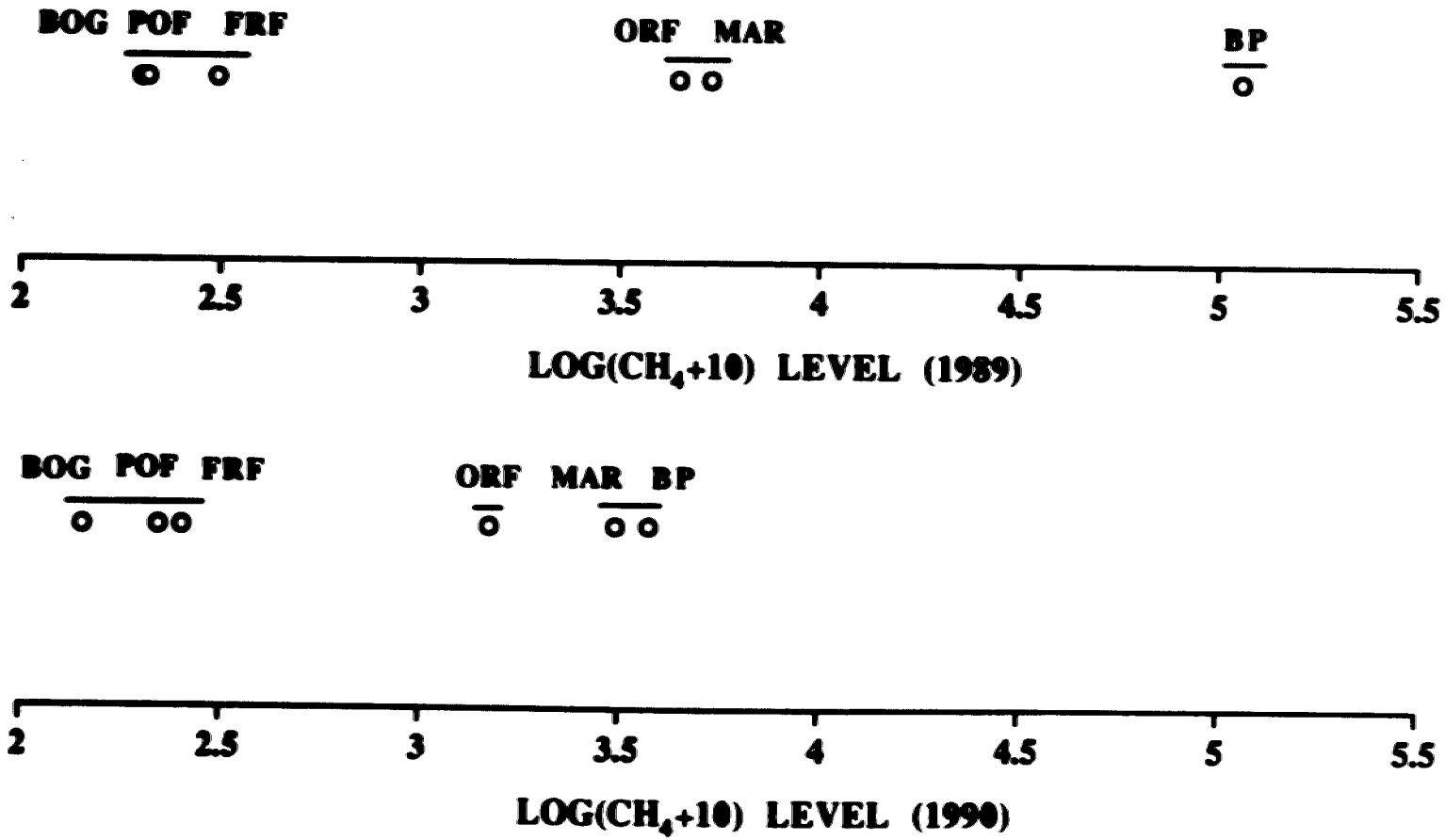

Figure II-4. Display of results of Studentized Newman-Keuls test on methane flux data in 1989 and 1990. BOG=ombrotrophic bog; POF=poor fen; FRF=forested rich fen; ORF=open rich fen; MAR=marsh; BP=beaver pond. There are no significant differences within underlined groups of sites.

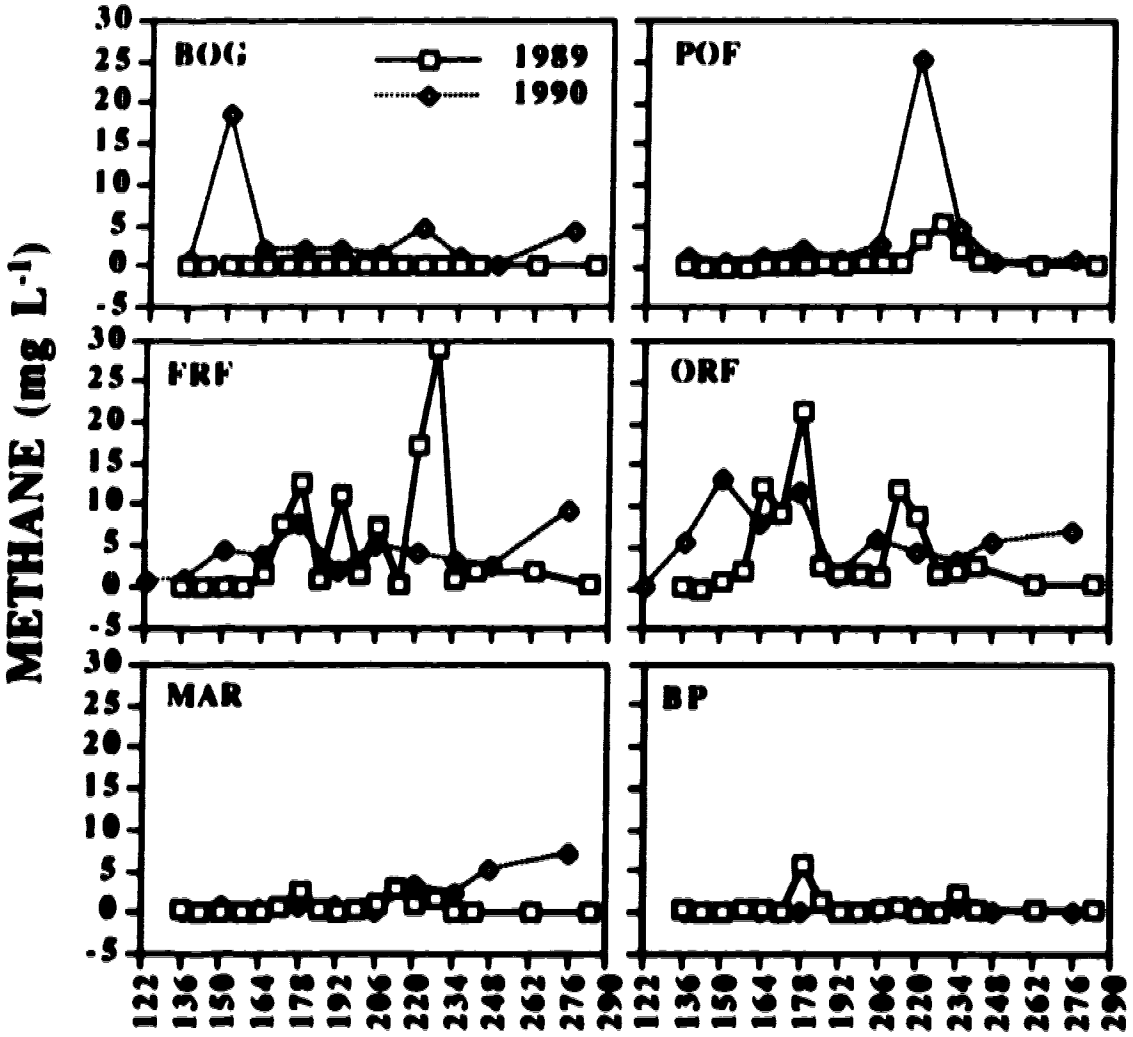

Figure II-5. Seasonal Variations of Methane Concentrations in the Surface Waters of Six Wetlands in Central Alberta During 1989 and 1990. BOG=Ombrotrophic Bog; POF=Poor Fen; FRF=Forested Rich Fen; ORF=Open Rich Fen; MAR=Marsh; BP=Beaver Pond.

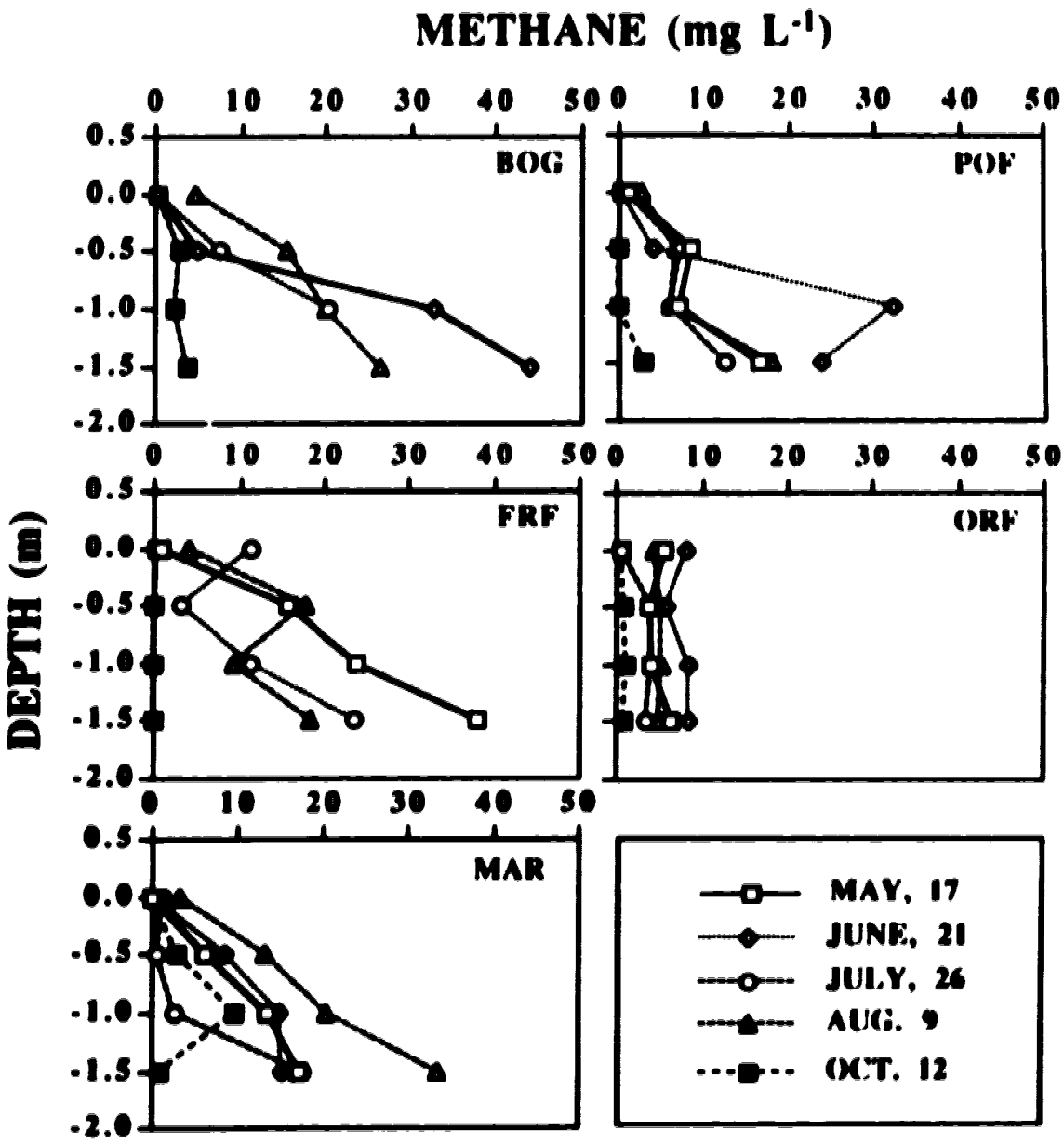

Figure II-6. Methane Profiles and Seasonal Variation in Pore Waters of Wetlands in Central Alberta (only based on data in 1990). BOG=Ombrotrophic Bog; POF=Poor Fen; FRF=Forested Rich Fen; ORF=Open Rich Fen; MAR=Marsh.

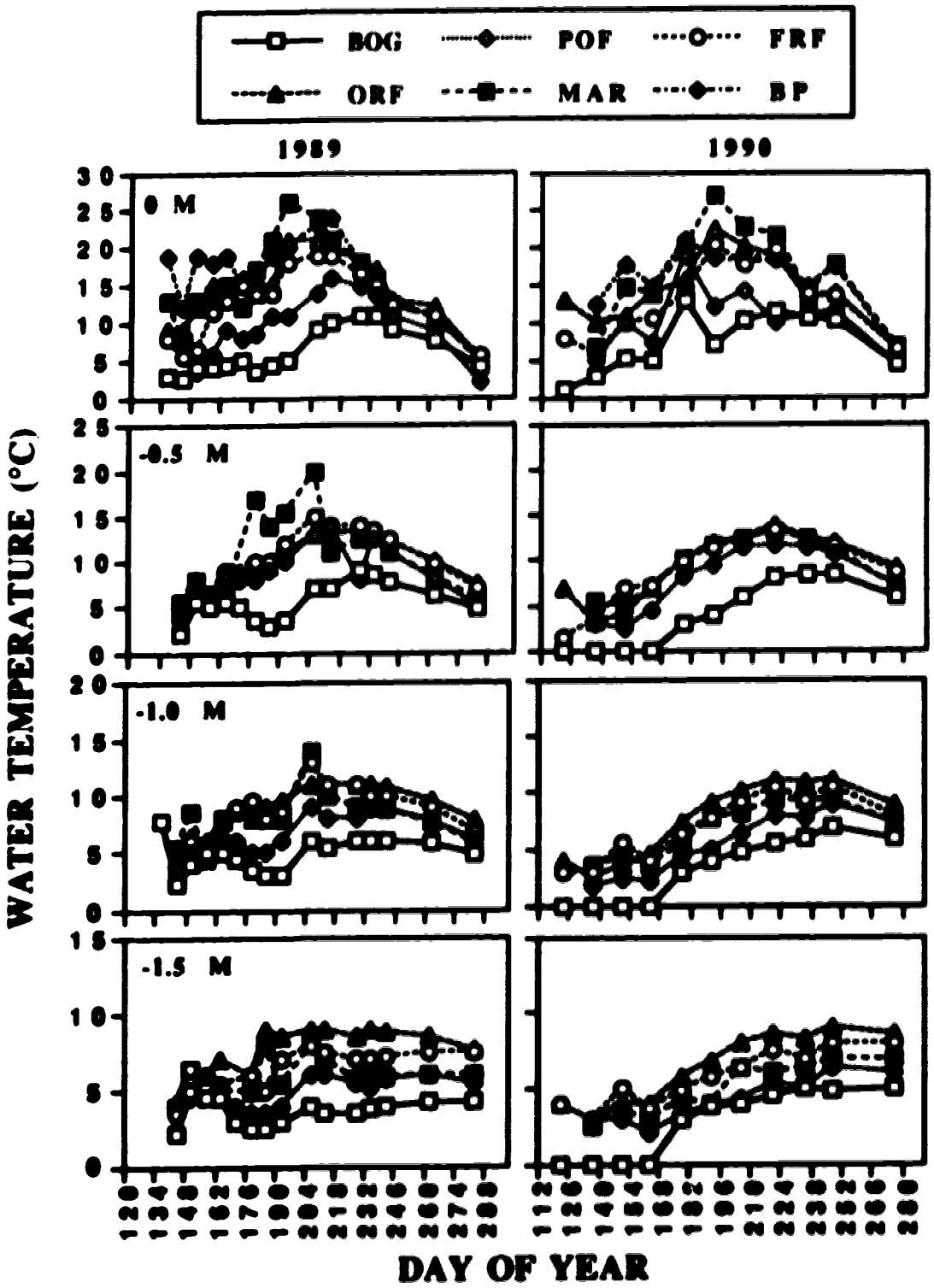

Figure II-7. Seasonal Variation of Water Temperature From Wetlands of Central Alberta. BOG=Ombrotrophic Bog; POF=Poor Fen; FRF=Forested Rich Fen; ORF=Open Rich Fen; MAR=Marsh; BP=Beaver Pond. 0 M, -0.5 M, -1.0 M and -1.5 M are Depthes Below the Wetland Surface.

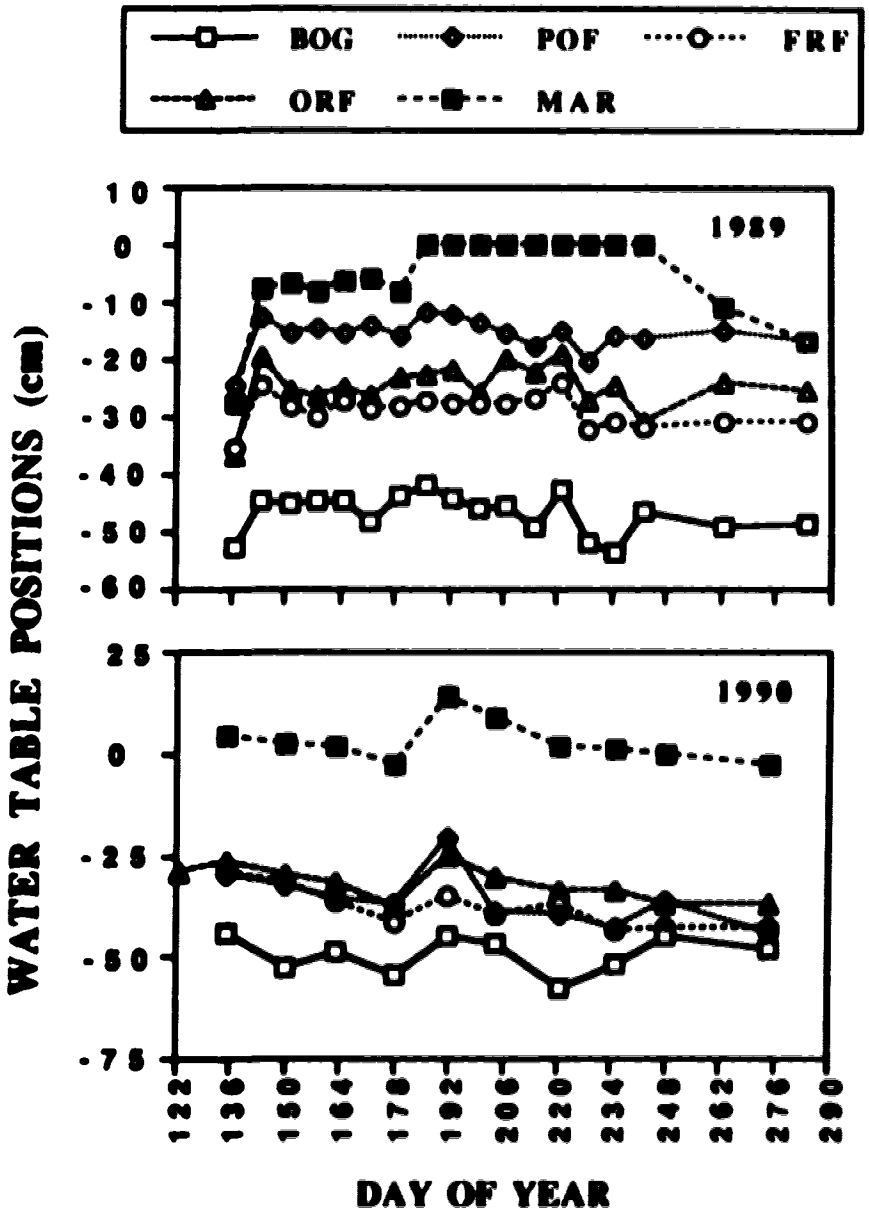

Figure II-8. Seasonal Variation of Water Table Positions in Wetlands of Central Alberta. BOG=Ombrotrophic Bog; POF=Poor Fen; FRF=Forested Rich Fen; ORF=Open Rich Fen; MAR=Marsh. The Negative Numbers are Depths Below the Wetland Surface.

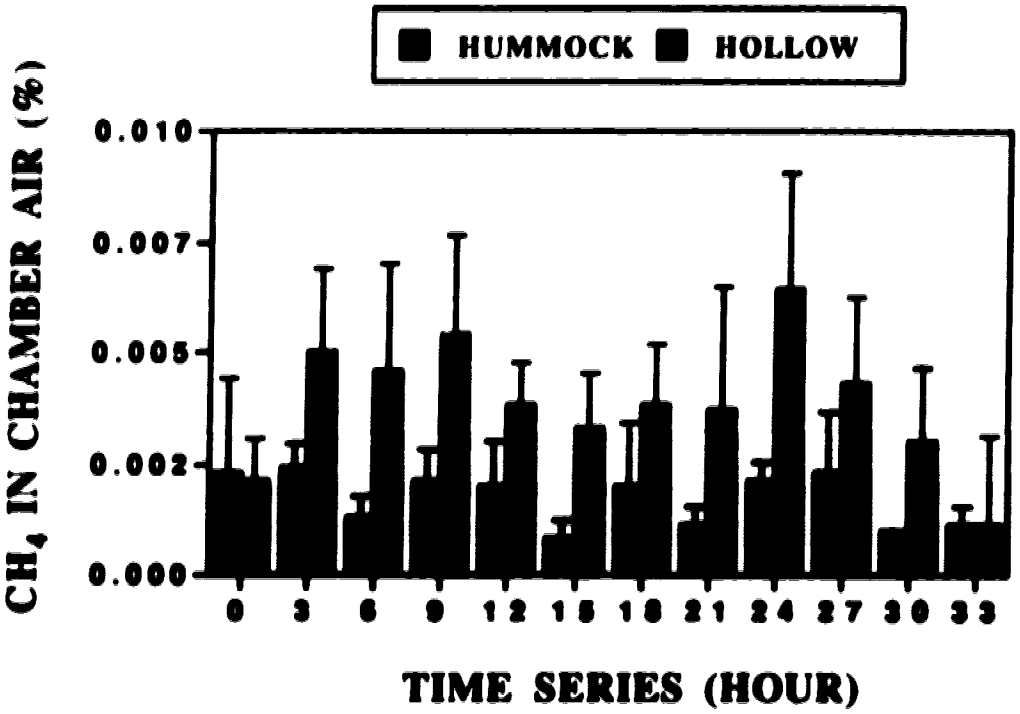

Figure II-9. Comparision of Methane Fluxes From Hummocks and Hollows in a Forested Rich Fen of Central Alberta During August 2-3, 1990. Samples were Taken Each 3 Hours After Chamber Placement. Bars are Standard Deviations.

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III. CONCLUDING DISCUSSION

The study of methane fluxes and related environmental variables from natural wetlands are very important because methane is the most efficient gas in the "greenhouse effect" (Cicerone & Oremland 1988) and atmospheric concentrations of methane have increased at a rate of about 1% yr^{-1} over the past 15 years (Rasmussen and Khalil 1981; Ehhalt 1985; Blake *et al.* 1982, 1988; Ramanathan *et al.* 1985; Ramanathan 1988).

Seasonal patterns of methane fluxes in this study are similar among the six wetlands: emission rates are generally lower during the spring, reaching peak values in late summer and lower in autumn. The seasonal pattern from this study is slightly different from studies reported by other investigators (Wilson *et al.* 1989; Moore *et al.* 1990). The differences may be due to different climate patterns (different date of thaw), different wetland type, or length of sampling period. The general increase of methane fluxes during summer is probably associated with the gradual warming of the subsurface layers of the wetlands; the major site of methanogenesis (Moore and Knowles 1987). Evidence for this is the statistically significant correlation between methane fluxes and 0.5 m subsurface water temperature at all wetland sites (except the beaver pond).

The spatial patterns or gradient of methane fluxes from the study shows that the open water wetlands, *e.g.* beaver pond, marsh, and open rich fen are more important in methane emission to atmosphere than other types of wetlands. Whereas the low concentration, (sometimes negative) amounts of CH_4 in gas samples from the bog site suggests that most of the methane produced from peat profiles may be consumed or oxidized before reaching the atmosphere. Accordingly, the ombrotrophic bog may act seasonally as an atmospheric CH_4 sink instead of source.

The analysis of variance for each of the two year's data indicates that there are significant differences ($p<0.0001$) in methane fluxes among sampling sites in both years. Significant variation is also present among sampling date within each site. However, the Studentized Newman-Keuls test indicates that among six sampling sites there is no significant difference in methane flux within the group consisting the ombrotrophic bog, the poor fen and the forested rich fen sites and no significant difference between the marsh and the open rich fen sites in 1989, while there is no significant difference within the group consisting the ombrotrophic bog, poor fen and forested rich fen sites and no significant difference between open rich fen and beaver pond sites in 1990.

The methane fluxes from each wetland site varied greatly over the course of this study. Similar variability of CH_4 flux has been reported from a variety of wetlands (Swain 1973; Baker-Blocker *et al.* 1977; King *et al.* 1978, 1981; Harriss and Sebacher 1981; Harriss *et al.* 1982, 1985; Svensson and Rosswall 1984; Sebacher *et al.*, 1986; Crill *et al.* 1988; Devol *et al.* 1988; Wilson *et al.* 1989; Moore and Knowles 1987, 1990; Whalen and Reeburgh 1988, 1990; Moore *et al.* 1990; Holland *et al.* 1992; Roulet *et al.* 1992; Bubier *et al.* 1993; Dise 1993; Dise *et al.* 1993). These variabilities presumably result from the complexity and heterogeneity of processes controlling the production, consumption, and emission of CH_4 from wetlands, including seasonal temperature, water level fluctuation, spatial heterogeneity of microhabitats and bacterial distribution in soils, and differences in substrate quality and quantity.

From this study, the large variation partially resulted from variation within individual sampling days, *i.e.* between replicate samples. The possible source of this variation may be the difference of microtopography at which the sampling chambers were placed, since methane fluxes from hummocks and hollows were significantly different ($p<0.001$). The daily methane fluxes from hollows were about 60 % higher than those from hummocks.

To reduce error in the estimation of methane fluxes from site measurements to large areas of wetlands, a random placement of sampling chamber was done in this study. The random sampling method may provide more practical and more accurate methane flux data than the fixed chamber method. This is especially true in those wetlands that have high variability in microtopography, for example, fens with complexity of hummocks and hollows.

Comparing the methane fluxes from wetlands of Alberta (western Canada) with wetlands of northern Ontario (eastern Canada), the daily mean methane fluxes at bog and marsh were lower and at fens higher than that in boreal wetlands of northern Ontario (Bubier *et al.* 1993), and the daily mean flux at beaver pond was similar to the beaver pond in eastern boreal wetlands (Bubier *et al.* 1993). However, from this study and others, meaningful comparison of the results is difficult, because of differences in the number of flux measurements made per sampling site, the number of sites per wetland, and the number of wetlands used to develop a wetland type average (Moore *et al.* 1990). Furthermore, using limited individual site measurements to represent entire wetland types to estimate annual fluxes may result in great error, since a high spatial variability of methane flux from wetlands has often been reported, even at sites which appear to be homogeneous.

Methane concentrations in subsurface waters are generally much higher than those in surface waters and increase with depth. In wetlands, methane flux to the atmosphere is ultimately dependent on production and emission of methane from anoxic sediments (including peat) to the overlying peat or water column. Methane concentrations in profiles of wetland waters suggest that highly decomposed peat has a high capacity for meth ne production, and that significant quantities of methane might be produced in subsurface peat layers and super-saturated in pore waters. Increases of methane concentrations with depth also suggest that super-saturated methane is emitted

at the surface or near the surface. Dise (1993) suggests that pore water methane profiles may reflect the balance of production and emission of methane.

In this study, no correlation was found between net methane fluxes and methane concentration in pore waters. The lack of correlation may be due to some mechanisms of methane emissions into the atmosphere such as ebullition and diffusive transport of CH_4 through plants (Wilson *et al.* 1989).

The strong correlation between methane flux and water temperature of wetlands in this study suggests that methane emission in natural wetlands are influenced by soil temperature, and that if the supply of organic matter is not limiting (as in most wetlands) an increase in temperature may generally stimulate CH_4 production and increase CH_4 emissions. The effect of temperature on CH_4 flux may be attributed to the effect of temperature on the physiological activity of methanogens.

Moisture is an important controlling factor for methane production and subsequent release of methane. The dependency of methane flux on moisture has been previously noted in wetlands (Harriss *et al.* 1982; Svensson and Rosswall 1984; Sebacher *et al.* 1986; Moore *et al.* 1990; Moore and Roulet 1992; Roulet *et al.* 1992; Dise 1993; Bubier *et al.* 1993). Although other investigators have reported strong correlations between CH_4 and water table position (Moore *et al.* 1990; Moore and Roulet 1992; Roulet *et al.* 1992; Dise 1993), limited success was achieved in this study. The weak correlations between water table fluctuations and methane fluxes in this study suggests that impacts of physical conditions on methane fluxes may be different in different wetlands, *i.e.* they are site-specific.

Estimates of methane contributions from natural wetlands to the atmosphere often show a wide range of methane fluxes. This may be due, in part, to differing assumptions about area estimates of wetlands, the magnitude and annual duration of methane fluxes from wetlands, and from the wide variability in measured flux rates themselves (Wilson *et al.* 1989). The great difference of methane flux in different

wetland types in this study implies that variability of methane flux reported by some investigators may be partially due to the different wetland classification systems being used in their studies.

Spatial variability of methane fluxes from this study and others suggest that an estimate of global methane emission from natural wetlands is dependent on distinguishing different wetland types and calculating each wetland area precisely. For example, different wetland types may differ considerably in CH_4 emissions, and these differences could have a significant effect on the estimate of the global role of northern wetland ecosystems as a source of atmospheric CH_4 (Moore *et al.* 1990). In this study, fens (poor fen, forested rich fen and open rich fen) and bogs account for 61% and 12% of the areal coverage of peatlands in Alberta and contribute 59% and -0.2% of the annual CH_4 emissions, respectively.

Area estimates are important in estimating of methane contribution from wetlands to atmospheric methane. For example, based on wetland area of this study (from Vitt *et al.* 1990), the area of fens in Alberta wetlands are 89,033 Km^2 and may emit 0.26 Tg CH_4 yr^{-1}. More recent area estimates (Vitt unpublished data) indicates that there are 90,585 Km^2 of fens in Alberta, and this yields an annual estimate of 0.35 Tg of CH_4 emission. This result shows that uncertainty in estimating areal coverage of fens alone results in about 30% error in annual CH_4 emission estimates for wetlands of Alberta.

In conclusion, data from a few individual site measurements and area estimates of wetlands without consideration of wetland type produce large errors in calculating methane emissions over large areas. Thus, to improve the accuracy in estimating of methane emissions from large areas, methane emissions of different wetland types should be estimated separately and different microtopographies within each wetland type should be distinguished.

The estimated total annual methane emissions from this study indicate that boreal wetlands in Alberta are significant source of biogenic CH_4 to the atmosphere, contributing 0.91 Tg CH_4 yr^{-1}. This estimate is about 0.3-0.5% of Ehhalt and Schmit's (1978) estimates of total wetland CH_4 contributions, 190-303 Tg CH_4 yr^{-1}, and about 1.5% of Matthews and Fung's (1987) estimate of 62 Tg CH_4 yr^{-1} from peatlands between 50° and 70° N.

Natural wetlands are an important source of atmospheric methane. Nevertheless, because of the large areas they cover in northern latitudes, wetlands may make a significant contribution as a global source of methane, and this may partially account for the large increase in atmospheric methane in northern latitudes during the fall season (Khalil and Rasmussen 1983).

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