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Methane Dynamics of a Northern Boreal Beaver Pond

A thesis submitted to the Faculty of Graduate Studies and Research
in partial fulfillment of the requirements for the degree of
Master of Science by

Department of Geography
McGill University
Montreal, Quebec

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ISBN 0-612-12183-6

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Abstract

Most global and regional "greenhouse gas" budgets have neglected beaver ponds, but they have been found to be relatively high emitters of methane (CH_4) (Roulet et al., 1992). Static chambers, bubble traps, benthic chambers, piezometers, and water column and sediment profiles were used to determine the dynamics of CH_4 production, oxidation, storage, and emissions from a northern boreal beaver pond, as part of the Boreal Forest Ecosystem-Atmosphere Study (BOREAS) from May 1 to September 15, 1994. Samples were analysed by gas chromatography, and isotopic analyses were performed by mass spectrometry.

The mean flux of CH_4 from the beaver pond (155 and 320 mg CH_4 m^{-2} d^{-1} for vegetated and open water sites, respectively) was greater than the flux from most other northern boreal wetlands (Bubier et al., 1995). CH_4 availability was primarily controlled by sediment temperature, and CH_4 transport was controlled by windspeed (diffusion) and atmospheric pressure (bubbles). Bubbles comprised 20 to 52% of the net annual flux (18.2 g CH_4 m^{-2} yr^{-1}), with diffusion comprising the remainder. A large difference in bubble flux was observed between open water (15.7 g CH_4 m^{-2} yr^{-1}) and vegetated sites (2.9 g CH_4 m^{-2} yr^{-1}), and isotopic analyses indicate that this difference is due, in part, to a difference in CH_4 production pathways between sites. Greater oxidation also reduced the CH_4 flux from shallow, vegetated sites.

A preliminary CH_4 budget for the BOREAS northern study area indicates that beaver ponds contribute significantly (6% to 30%) to the regional CH_4 flux. The areal extent of beaver ponds needs to be determined for inclusion in regional and global CH_4 budgets.

Résumé

La plupart des budgets des „gaz d'effet de serre" n'inclus pas les lacs à castors. Pourtant, ces bassins émettent une quantité de méthane (CH_4) relativement elevée (Roulet et al., 1992). La production, l'oxydation, le stockage, et le flux de CH_4 dans un lac à castors au nord du Manitoba ont été déterminés par des enceintes statiques, des pièges à bulles, des enceintes au fond du bassin, des échantillons de CH_4 dans les eaux interstitielles et des profils d'eau et de sédiments. Cette étude, effectuée du premier mai à la mi-septembre, 1994, a été réalisée dans le cadre du „Boreal Forest Ecosystem-Atmosphere Study" (BOREAS). Les échantillons de CH_4 ont été analysés par la chromatographie des gaz et les analyses isotopiques de CH_4 étaient accomplis par la spectrometrie de mass.

La moyenne des émissions de CH_4 par le lac à castors (155 à 320 mg CH_4 m^{-2} an^{-1}) était plus élevée que la majorité de ceux obtenus à d'autres sites tourbeux (Bubier et al., sous presse). La disponibilité de CH_4 était controllée principalement par la température au fond du bassin, et le transport de CH_4 était controllé par la vitesse du vent (diffusion) et par la pression de l'atmosphère (bouillonnement). Les bulles ont contribué de 20 à 52% des émissions annuelles (18.2 g m^{-2} an^{-1}) et la diffusion fut responsable de la balance. De grandes différences de bouillonnement ont été observées entre des sites végétaux (2.9 g CH_4 m^{-2} an^{-1}), et les sites non-végétaux (15.7 g CH_4 m^{-2} an^{-1}); les analyses isotopiques ayant indiqué que ces différences étaient en partie dû aux différents mécanismes chimique de la production de CH_4. Plus d'oxydation a aussi réduit les emissions des sites peu profonds et végétaux.

Un budget préliminaire indique que les lacs à castors émettent de 6% à 30% de la flux de CH_4 régionale, mais l'aire des bassins doit être mieux déterminé pour améliorer les budgets de CH_4 régionaux et mondiaux.

Acknowledgements

I would primarily like to thank my research supervisor, Prof. Nigel Roulet, for his inspiration and guidance. His patience and supervisory skills made for an exceptional graduate experience. I also thank Prof. Tim Moore for his insight and useful comments.

Jeff Chanton provided invaluable assistance and lab resources for analysis of isotopes of ^{13}C and deuterium (D), which comprised an important component of this research. Sue Trumbore collected and analysed sediment samples for radiocarbon isotopes.

Many assisted in field preparation, and data collection and processing. I particularly thank Carol Robinson (the original "Boreas Woman") and Jose Etcheverry for their assistance in the field, and Natalia Popowych for assisting the laboratory incubations. Many thanks to Rick Bourbonniere for the use of his (superior) rubber boat and for the hydrolab data. Patrick Crill gave much needed guidance in the field and lab, and Dean Moosavi provided field assistance and answered seemingly infinite questions. Jill Bubier competently identified the aquatic macrophytes. Neil Comer assisted with measuring pond bathymetry and diel sampling ("Get up!"), and assured that the pond's micro-meteorological tower and equipment were functioning properly. Shannon Glenn processed and quality-checked the tower data. Additional assistance was received from Mike Dalva, Paula Kestleman and Doug Barr at the Department of Geography, McGill University, and from Sarah Dalle and Mike Waddington in the field. Many thanks also to Lianne Bellisario, Kathleen Savage, and the other BOREAS researchers for companionship and inspiration while in Thompson.

I especially thank Laud Matos, who provided encouragement and insight throughout. Special appreciation also goes to my friends Stephanie Weinstein and Stevie Perlman for keeping me laughing and (in)sane while analysing and writing.

This study was funded in part by the Centre for Climate and Global Change Research (C^2GCR).

I dedicate this work to the memory of my parents, John and Lois Dove. I only wish that they could share in this achievement.

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Chapter 1: Introduction

1.0 Introduction

Beaver ponds are a small but important component of northern wetland ecosystems. They have been found to be relatively high emitters of methane (CH_4), an important greenhouse gas, compared to other types of wetlands (Fig. 1.1), but they have been neglected in most global and regional greenhouse gas budgets. Determining the net CH_4 flux and its variability, combined with knowledge about the areal coverage of beaver ponds, will improve understanding of the boreal CH_4 budget. This study, part of the Boreal Forest Ecosystem-Atmosphere Study (BOREAS), measured and explains the CH_4 flux from a northern boreal beaver pond.

1.1 Atmospheric Methane

Methane is the most abundant organic gas in Earth's atmosphere, playing important roles in both radiative climatology, and tropospheric and stratospheric chemistry (Cicerone and Oremland, 1988). Although CH_4 is 150-times less abundant in the atmosphere than CO_2, on a molar basis it is 21-times more effective at absorbing longwave radiation. Therefore CH_4 is projected to contribute approximately 15 to 19% of total greenhouse warming (Rodhe, 1990; Slanina and Warneck, 1994).

The concentration of atmospheric CH_4 was relatively constant between 3,000 and 200 years ago, but it has doubled in the last 200 years, from 800 ppbv (parts per billion by volume) to over 1700 ppbv (Cicerone and Oremland, 1988). The rate of

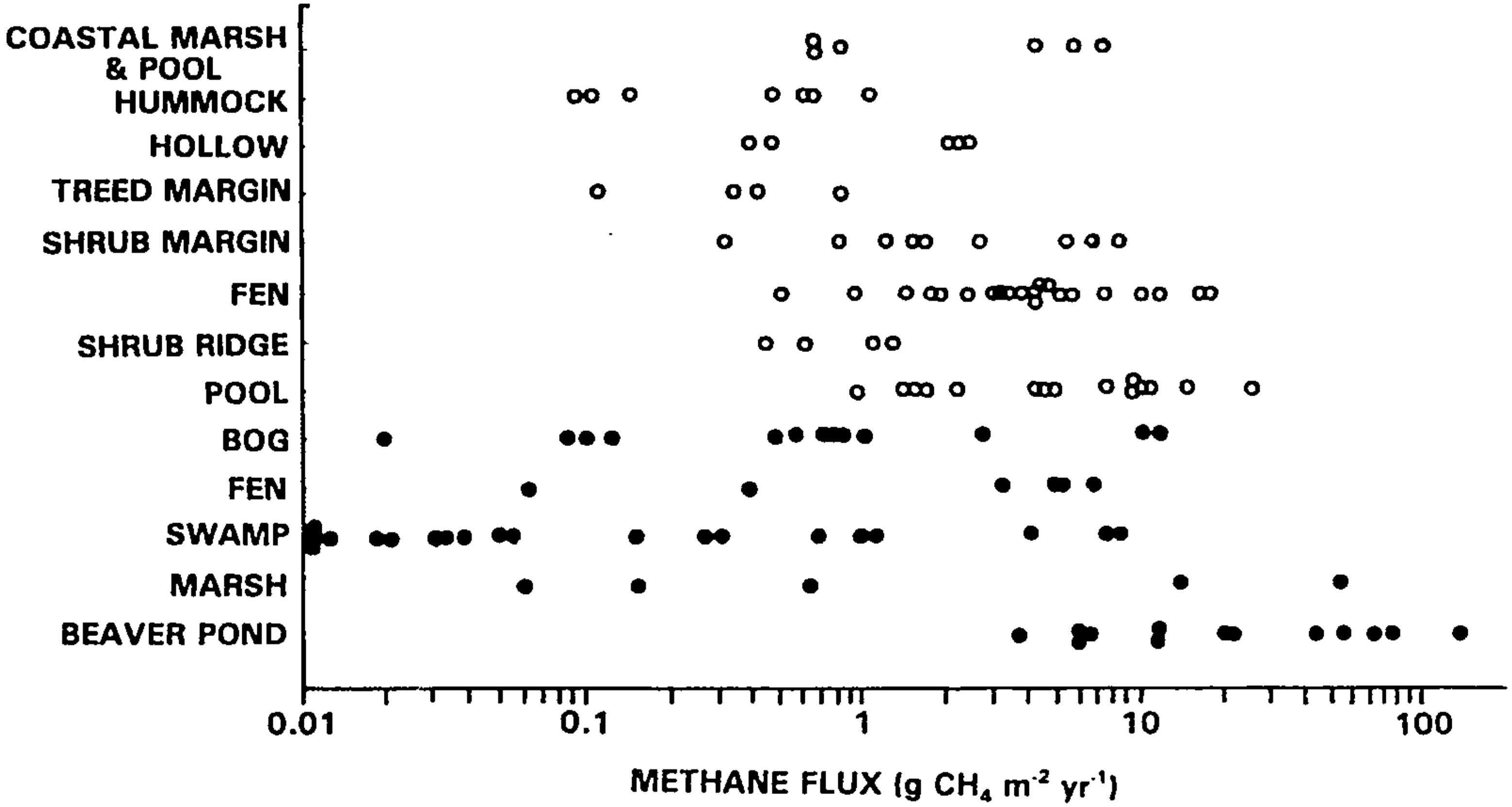


Fig. 1.1: Estimated Annual CH_4 Emission Rates from Wetlands in Canada
based on broad ecological grouping for subarctic (open circle) and boreal-temperate (shaded circle) regions
From Moore and Roulet, 1995

increase peaked at approximately 1% per year over the last decade, but this rate of increase has declined to 0.7% per year (Steele et al., 1992; Matthews, 1994).

The increase in atmospheric CH_4 may be due to an increase in sources, a decrease in sinks, or both (Moore, 1988). Sinks of CH_4 include oxidation by OH radicals in the troposphere (Cicerone and Oremland, 1988) and uptake by soils (Crill, 1991). Atmospheric $\delta^{13}C$ evidence indicates that the largest component of the observed increase has been an increase in CH_4 sources (Cicerone and Oremland, 1988).

1.2 Sources of Methane

The atmospheric CH_4 budget is given in Table 1. The total of CH_4 sources to the atmosphere is estimated to be 500 Tg y^{-1} (1 Tg = 10^{12} g) (Matthews, 1994). Natural wetlands are the largest single contributor to the atmospheric burden.

Seasonal and latitudinal differences in atmospheric CH_4 concentrations indicate a strong source in the northern hemisphere. The world's largest wetland areas are located between 50° and 70° N (Aselmann and Crutzen, 1989; Fung et al., 1991), which is the same region predicted to undergo the greatest climate changes from most general circulation model estimates of doubled atmospheric CO_2 concentrations. In order to predict how wetland CH_4 sources may change in a warmer global climate, recent studies have focused on determining controls of CH_4 emissions from wetlands under present conditions.

Table 1.1: Atmospheric CH_4 Budget (after Matthews, 1994)

	CH_4 (Tg = 10^{12} g)
Atmospheric Burden	4600-4800
Annual Increase	40-45
Annual Sources:	500
1. Fossil fuel:	
Coal mining	35
Natural gas	80
2. Biomass burning	55
3. Natural wetlands	
Northern	35
Tropical	80
4. Rice Cultivation	75
5. Animals (mainly domestic ruminants)	80
6. Termites	20
7. Oceans	10
8. Landfills	25
9. Methane hydrate releases	5
10. Wastewater treatment and animal waste	40
Annual Sinks	
1. OH destruction	450
2. Soil absorption	10

1.3 Processes Affecting Methane Emissions from Freshwater Wetlands

CH_4 flux from wetlands is the result of production, consumption and transport processes. CH_4 is produced by archaeobacteria during decomposition of organic matter under anaerobic conditions. These bacteria (termed methanogens) are dependent on other anaerobic bacteria to supply them with substrates, which include gaseous hydrogen, carbon dioxide, formate, acetic acid, and one-carbon compounds (Svensson and Sundh, 1992; Knowles, 1993). Archaeobacteria can tolerate some oxygen exposure, but require strongly reduced conditions (Eh <-300 mV) for growth

(Knowles, 1993). Methanogens inhabit acid environments typical of most anaerobic soils (pH 6 to 8). Temperature optima have been found to be between 25° and 30°C, with low temperatures (0 to 10 °C) permitting little production activity, even in arctic peat soils (Dunfield et al., 1993) where adaptation to low temperatures might be expected.

The two main pathways for methane production in freshwater ecosystems are acetate fermentation and CO_2 reduction (Whiticar et al., 1986). CH_4 can be derived from a methyl group of any substrate, but since acetate is most common, this pathway is termed acetate fermentation. Acetate fermentation accounts for approximately 70% of all CH_4 produced in freshwater ecosystems (Whiticar et al., 1986). The other major production pathway is CO_2 reduction, in which hydrogen is used as an electron source. These two pathways result in different isotopic compositions of the produced CH_4. Methane produced by acetate fermentation is generally enriched in ^{13}C and depleted in D (deuterium) compared to that produced by CO_2 reduction (Happell et al., 1993).

CH_4 is consumed by methanotrophs which are obligate aerobes. Consumption is dependent on oxygen for the first step of methane oxidation, although some methanotrophs may prefer sub-atmospheric O_2 concentrations (King, 1992). Certain anaerobic methanotrophs have been identified, but their importance in wetland environments has not been studied (Whiticar and Faber, 1985). Optimum temperatures for aerobic CH_4 consumption range from 20 through 25 °C, although substantial activities have been observed at temperatures as low as 0 to 5 °C (Dunfield et al., 1993). Therefore, CH_4 oxidation can occur at lower temperatures than production. During oxidation, methanotrophs preferentially consume the lighter isotopes of both carbon and hydrogen, leaving residual CH_4 enriched in ^{13}C and D (Coleman et al., 1981; Chanton et al., 1992).

CH_4 can be transported from wetland sediments to the atmosphere by three mechanisms: diffusion, gas bubble ebullition, and plant transport. Diffusion is a relatively slow transport mechanism, controlled by the CH_4 concentration gradient and the diffusivity of the medium. Diffusing CH_4 will be subject to oxidation by methanotrophs if it passes through aerobic layers.

Ebullition (bubbling) has been observed in flooded wetlands, and is a much more rapid transport process than diffusion, and more CH_4 bypasses zones of oxidation (Martens and Klump, 1980; Martens et al., 1986). Gas bubbles form as vertical columns in sediments where porewater CH_4 reaches supersaturation. When bubble pressure exceeds pressures exerted by the overlying materials and the atmosphere, bubbles will be released from storage in the sediments to the atmosphere. Ebullition events have been found to be correlated with water table fluctuations (Windsor et al., 1992) and atmospheric pressure fluctuations (Mattson and Likens, 1990), where negative pressure changes stimulate bubble release.

Vascular plants have been identified as being important in the transport of CH_4 but their role is not well understood (Dacey and Klug, 1979; Whiting and Chanton, 1992). Plants may enhance the flux of CH_4 by providing substrate for the production of CH_4 in the root zone, or by acting as conduits for atmospheric exchange (Dacey, 1980). They may attenuate CH_4 flux by transporting atmospheric oxygen to the roots, promoting CH_4 oxidation. The overall effect of plants on CH_4 flux is considered to be positive (Epp and Chanton, 1993).

1.4 Controls of Methane Flux from Wetlands

Several parameters have been identified in laboratory and field experiments as important indicators of CH_4 flux. Formulating strong predictive relationships has largely been unsuccessful, however, since many of these variables are correlated with both production and oxidation processes, but in different ways. Furthermore, many environmental variables affect CH_4 flux from wetlands, and they act at different scales. Factors affecting CH_4 availability may vary over microscales and very short times, while factors controlling CH_4 transport influence larger areas over longer time periods. Field methods measure fluxes over scales that incorporate many scale-dependent processes, therefore fluxes are typically variable, with coefficients of variation (standard deviation:mean) commonly ranging from 30 to 100% within a site (e.g. Moore and Roulet, 1991).

The most successful variables explaining flux are those which integrate environmental factors. Water table position, a surrogate for aerobic/anaerobic status, has been found to be the strongest indicator of CH_4 flux. When the water table is below the wetland surface, an aerobic zone forms, and methanotrophs may deplete the CH_4 reservoir and attenuate flux. When the water table is at or above the surface, anaerobic conditions dominate, and less CH_4 is oxidized. While laboratory experiments have successfully used water table position to predict flux at a single site (Moore and Knowles, 1989; Moore and Roulet, 1993), this variable has been successfully used in the field only to explain differences in fluxes between sites having different water table positions and therefore different degrees of anaerobism (Roulet et al., 1992; Bubier et al., 1993; Dise et al., 1993). The inability to show clear relationships between water table position and flux at a given site is likely due to coincident changes in temperature, plant activities, or pressure causing episodic release of CH_4 stored in porewaters.

Laboratory experiments have revealed the importance of temperature in controlling rates of CH_4 production and consumption (e.g. Svensson, 1984; Dunfield et al., 1993). On a few occasions, significant correlations between CH_4 emissions and temperature have been observed in the field (e.g. Crill et al., 1988; Bubier et al., 1995a). Other studies have found that temperature only explains fluxes once the primary variable of sustained water table position is satisfied (Roulet et al., 1992; Dise et al., 1993), or that it does little to improve the predictive capability of the water table position vs. flux relationship (Moore et al., 1990; Dise et al., 1993). While CH_4 fluxes are often positively correlated with temperature and water table position, these relationships are generally weak and do not hold across ecosystem types.

A strong predictive relationship between temperature at the mean position of the water table and CH_4 flux has recently been demonstrated for northern boreal wetlands (Bubier et al., 1995a). This variable integrates information about moisture and temperature, and may therefore be a useful indicator of flux in other regions. Macrophyte and bryophyte communities have also been used successfully to predict CH_4 flux across wetland types since plants respond to a host of factors and therefore represent good environmental integrators (Bubier et al., 1995a, 1995b).

In addition, plant communities can be mapped more easily than water table or soil temperature, and therefore hold promise as tools for extrapolation of CH_4 fluxes.

Substrate characteristics (such as pH and nutritional status) have been found to control methane production and consumption rates in some laboratory experiments (Knowles, 1993). Field studies indicate that emissions are lowest from nutrient-poor bogs, and increase in order to fens, swamps and marshes (Aselmann and Crutzen, 1989). These wetlands categories have been used to extrapolate regional and global wetland CH_4 emissions using representative CH_4 fluxes and areal coverage estimates (Bartlett and Harriss, 1993; Matthews, 1994).

1.5 Beaver Ponds as a Source of Atmospheric Methane

Very few studies of CH_4 emissions from wetlands have included beaver ponds. Of these, only one investigated diffusive and bubble fluxes separately (Weyhenmeyer, 1992). Boreal wetland CH_4 emissions have ranged from 0.1 to 65.7 g CH_4 m^{-2} y^{-1}, with most <10 g CH_4 m^{-2} y^{-1} (Matthews, 1994), while CH_4 emissions from beaver ponds have ranged from 5.9 (Ford and Naiman, 1988) to 76.2 (Vitt et al., 1990) g CH_4 m^{-2} y^{-1}. Roulet et al. (1992) found that even though beaver ponds comprised 7% of a low boreal wetland area, they contributed approximately 32% of the annual CH_4 flux. However, beaver ponds have not been used in the global CH_4 emission estimates (Matthews, 1994).

Beaver ponds may contribute significantly to the wetland CH_4 budget for three reasons: (1) beavers alter stream ecosystems in a manner that promotes conditions for CH_4 production; (2) these ecosystems receive inputs of carbon-rich materials, increasing the availability of substrate for methanogenesis; and (3) the areal extent of beaver ponds appears to be increasing in response to declining population pressure from humans and other predators.

Beavers (*Castor canadensis*) dam rivers and streams to increase the area of aquatic habitat in order to provide protection from predators and to increase their food supply (Naiman et al., 1988). Impoundment reduces flow velocity, hence suspended sediments and organic matter tend to settle in ponds. The combination of low flow and a high oxygen demand of the decomposing organic sediments results in the formation of anaerobic conditions. In addition to organic matter inputs from upstream and riparian zones, individual beavers can import up to 1 tonne of organic matter into a pond each year (Naiman et al., 1986). When previous wetland or peatland ecosystems are flooded by beavers, the peat profiles can themselves contribute to the supply of organic matter for methanogenesis. Beaver ponds have been found to have greater standing stocks and greater inputs and outputs of carbon per unit length of stream, compared to streams without beavers (Naiman et al., 1986, 1988). However, little of this material is transported downstream; carbon outputs occur instead as respiration and methane evasion (Naiman et al., 1988).

The beaver was made nearly extinct by the turn of the last century, when hunting and trapping removed large numbers of beaver every year (Naiman et al., 1988). Since that time, demand for pelts has decreased, laws have been imposed to regulate trapping, and beaver populations have made a strong recovery in North America. Significant, but poorly quantified, populations inhabit Eurasia and the former Soviet Union, although populations are still low in Europe (Nisbet, 1989). Estimates of current beaver populations in North America are in the range of 6 to 12 million (Naiman et al., 1988), which is about 10% of the pre-European settlement population. Population densities in favourable habitats are 0.4 to 0.8 colonies km^{-2} (1 colony generally consisting of 4 to 8 individuals) but have been found to be as great as 3 colonies km^{-2} (Naiman et al., 1986).

Beaver ponds are typically inhabited for 5 to 20 years (Nisbet, 1989), but changes to the biogeochemistry of stream ecosystems may persist for decades to centuries after occupation (Naiman et al., 1988). Beavers tend to select optimal sites for ponds first, then impound marginal areas as resources become depleted. Ponds that are impounded first have greater longevity than ponds built on less ideal sites (Naiman et al., 1988).

1.6 Conceptual Model of Methane Dynamics in Beaver Ponds

As indicated above, the few studies that have examined the flux of CH_4 from beaver ponds have found them to be relatively high emitters compared to other wetland types. The reasons for these high fluxes are poorly understood. In general, high organic inputs to ponds combined with sustained anaerobism caused by inundation are believed to explain the high emissions.

A conceptual model of a beaver pond and the factors that relate to the flux of CH_4 are shown in Fig. 1.2. A beaver pond can viewed as a system, with CH_4 traveling across several interfaces. Controls of the flux operate at two levels: controls on CH_4 production and consumption processes in the sediments, and controls on the transport processes which in turn may influence further oxidation.

CH_4 is produced in the sediments of a beaver pond at rates controlled by substrate availability and temperature. Since the sediments are always saturated, production is likely to be more closely related to temperature variations than in other wetland ecosystems with variable moisture conditions. Greater sediment heat fluxes and higher maximum temperatures have been observed in beaver ponds compared to other wetland types (Roulet et al., 1992; Naiman et al., 1994), therefore the CH_4 production zone may extend deeper in pond sediments than in other wetlands.

Once produced, CH_4 is either stored in the sediments, oxidized by methanotrophs, or transported to the atmosphere via ebullition, diffusion, and/or plants. Sedimentary CH_4 oxidation may only be a small component of the budget, because the sediments are consistently inundated and because decomposition processes compete with methanotrophs for available oxygen. The zone of greatest activity for methanotrophs will be close to the anaerobic-aerobic interface, where both CH_4 and O_2 are available in significant quantities (Knowles, 1993). Algal or cyanobacterial mats inhabiting the surface of the pond sediments may provide O_2 for CH_4 oxidation during daylight hours (King, 1990).

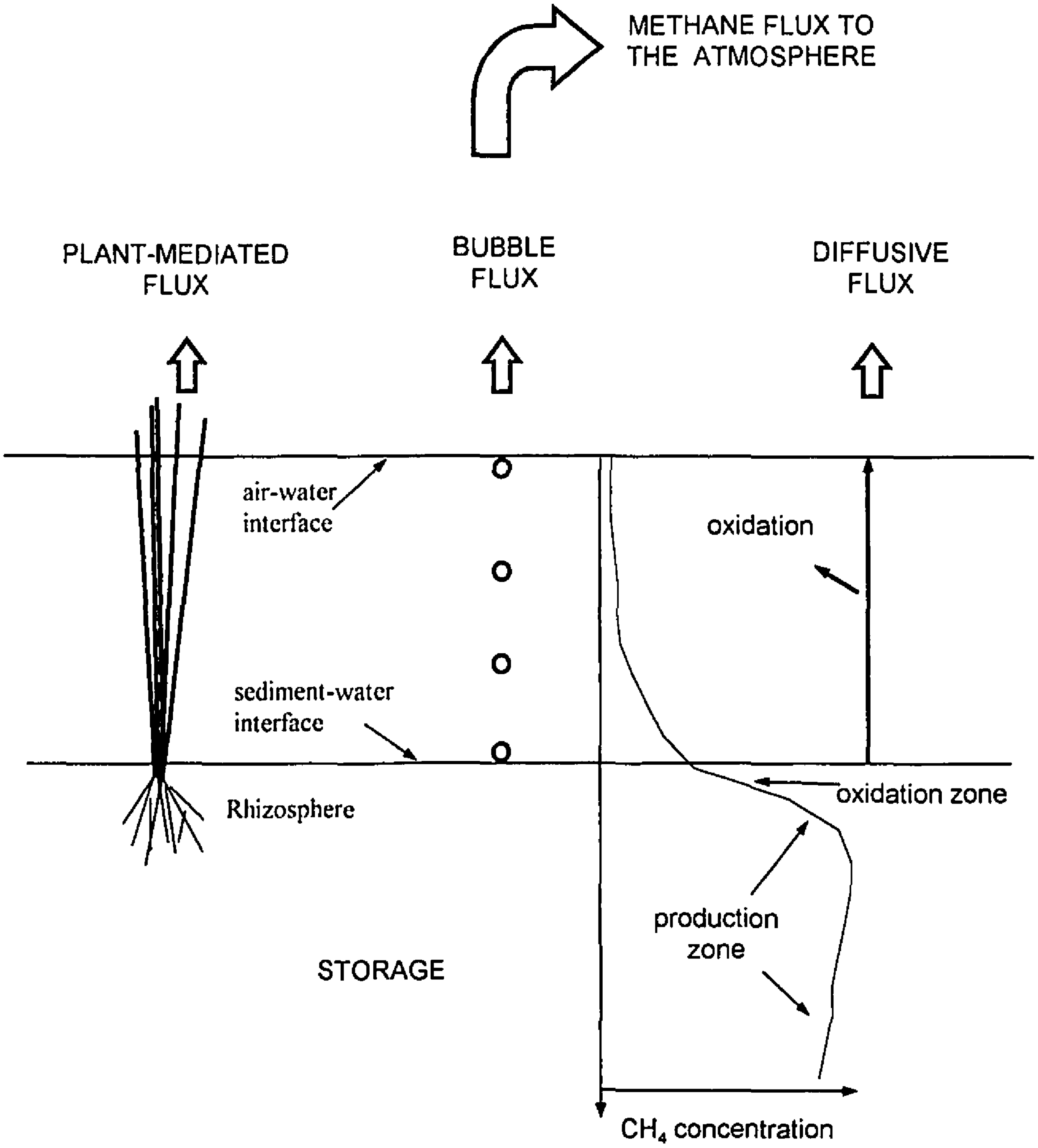


Fig. 1.2: Conceptual Model of Methane Dynamics in a Beaver Pond
Curved line is a theoretical profile of CH$_4$ in the sediments and in the water column

If rates of CH_4 production in ponds are greater than removal rates by diffusion, large amounts of gaseous and dissolved CH_4 can potentially be stored in the sediments. The CH_4 storage reservoir in beaver ponds is likely large, because the sediments consist of high-porosity flocculent organics deposited in a slow-flowing hydrological environment. Bubble fluxes will occur at a rate controlled by the excess of CH_4 production over oxidation, storage, and the other transport mechanisms. The magnitude of these fluxes may be related to changes in pressure (water table position and atmospheric pressure) and the current size of the sediment CH_4 reservoir.

Emissions from vascular plants are likely greater than diffuse emissions from equivalent open water areas because plants may provide a conduit that bypasses the oxidation layer. Certain plant species may actively ventilate the sediments surrounding their roots, resulting in lower porewater CH_4 concentrations and therefore lower bubble emissions. Higher production rates may be associated with root exudates and therefore enhance CH_4 fluxes, or conversely, oxidation associated with O_2 diffusion across the root-sediment interface may fuel higher rates of CH_4 consumption and result in lower CH_4 emissions from vegetated areas.

1.7 Study Objectives

The specific objectives of the research presented in this thesis are to determine: (1) the relative contributions of CH_4 production, consumption and transport processes to the flux of CH_4 from a boreal forest beaver pond; (2) how these processes vary within the pond and over an emission season; and (3) the relationship among these processes and environmental variables.

Specifically, four hypotheses were tested from May through mid-September, 1994, at a single beaver pond near Thompson, Manitoba:

1. The annual flux of CH_4 from the beaver pond to the atmosphere is relatively high compared to values reported in the literature for other wetlands because the hydrological and thermal regimes in beaver ponds maximize CH_4 production and minimize CH_4 oxidation.
2. Oxidation of CH_4 reduces the overall flux little, because:
    - 2.1 ebullition and plant transport mechanisms dominate and bypass the main zone of oxidation
    - 2.2 oxidation of CH_4 at the sediment-water interface is small because the thickness of the zone for potential oxidation is small, and
    - 2.3 little oxidation occurs in open water.
3. As a consequence of hypothesis 2.1, the loss of CH_4 from the sediments relates to negative changes in atmospheric pressure and water table position
4. The flux from plants is greater than the flux from open water areas since plant transport bypasses CH_4 oxidation and CH_4 production is greater in vegetated areas.

The results from this thesis represent a significant advancement in the process-level understanding of CH_4 emissions from beaver ponds. The following chapters describe the field programme, BOREAS and the methods and materials (Chapter 2), and the results obtained (Chapter 3). The results encompass information about CH_4

processes, storage and fluxes over all interfaces and from different areas of the pond. They indicate that the flux of CH_4 from the beaver pond is high and variable, but that these variations relate to environmental factors and site differences.

These lines of evidence are pursued in Chapter 4. The magnitude, variability and contributions of the various transport processes to the total CH_4 flux from this beaver pond are described. A detailed error analysis is performed and suggestions are made for future sampling programmes. Comparisons with the flux of CH_4 from other wetlands in the same area indicate that beaver ponds are a significant regional source which should not be neglected in greenhouse gas budgets.

Chapter 2: Study Site and Methodology

2.0 The Boreal Forest Ecosystem-Atmosphere Study

The Boreal Forest Ecosystem-Atmosphere Study (BOREAS) is an international collaborative special project designed to clarify the role of the boreal forest biome in the global climate system and carbon budget. In particular, it is aimed at improving our understanding of the processes which govern the exchanges of energy, water, carbon dioxide, and trace gases between the boreal forest and the atmosphere, and to develop and validate remote sensing algorithms to transfer our understanding of these processes from local to regional scales. Research was undertaken in and between two 600 km^2 study sites in central Canada to represent the north-south ecological gradient of temperature and moisture (Fig. 2.1). The southern study area (SSA), near Prince Albert, Saskatchewan lies along the sourthern edge of the boreal forest biome where ecosystem processes are generally moisture-limited during the summer. The northern study area (NSA), near Thompson, Manitoba, is representative of the northern portion of the boreal forest, where ecosystem processes are generally temperature-limited.

BOREAS includes research from a wide range of scientific fields, i.e. terrestrial ecology, snow hydrology, land surface climatology, boundary layer meteorology, trace gas biogeochemistry and remote sensing science. Over 80 research teams are involved, including 10 teams from Canadian universities. BOREAS is scheduled for a period of four years (1992 - 1996). The first year, 1992-93, was used for planning, site selection, preliminary studies and testing of equipment for the intensive field campaign in 1994.

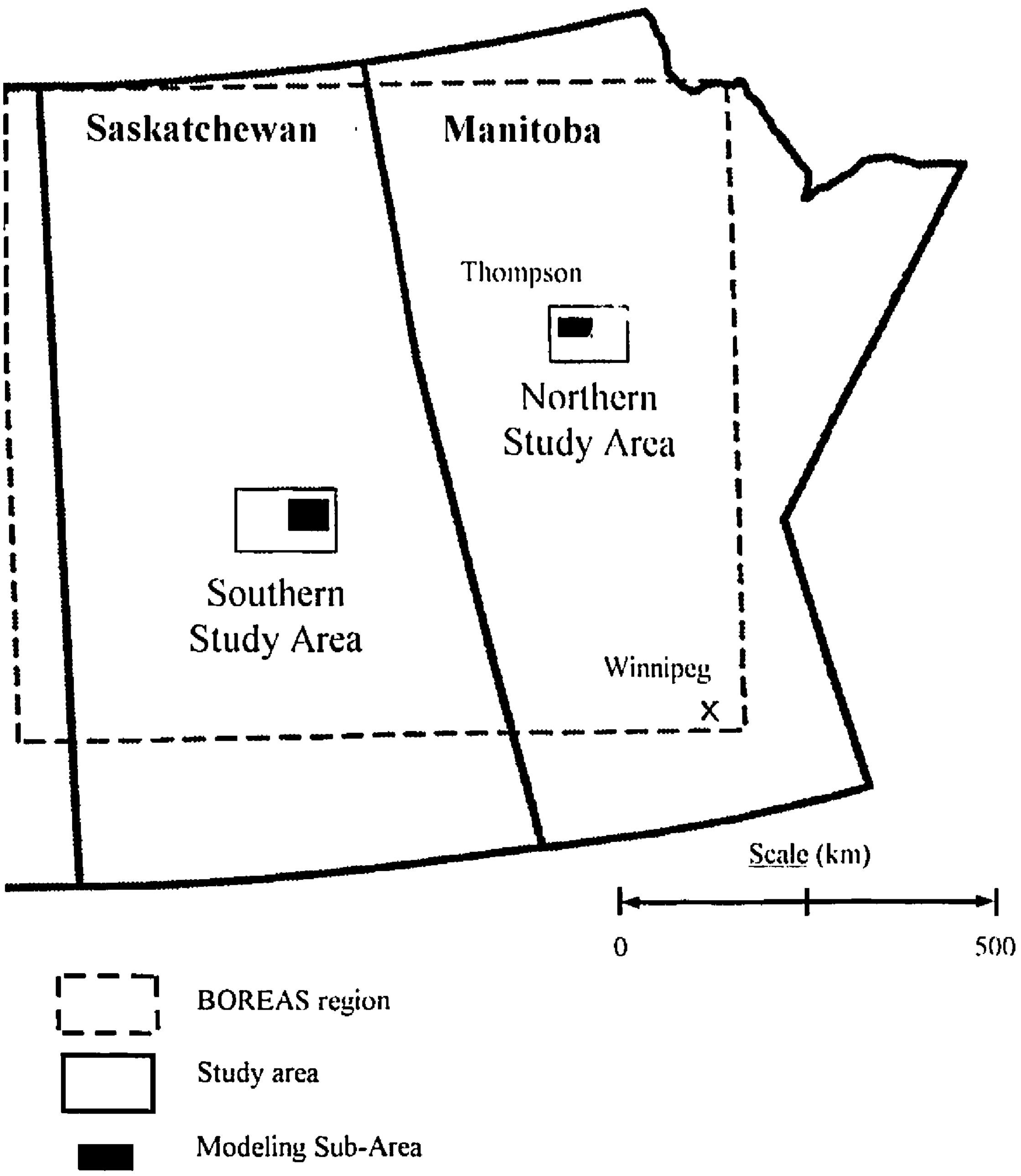


Fig. 2.1: BOREAS Study Areas
Research for this study was undertaken at the Northern Study Area near Thompson, Manitoba

2.1 Study Site

The field work for this study was conducted as part of a BOREAS Trace Gas Biogeochemistry (TGB) investigations at the northern study area (NSA). A single beaver pond, located 13 km west of Thompson, approximately 300 m south of Highway 391 (55° 55' N, 98° 01' W; military grid reference 614887), was selected for study (Fig. 2.2). It is the last, but one, in a series of ponds in a drainage basin that is about 15 km in length and 3 - 5 km in width. The pond covers 5 ha, and has two dams: one on the northern outflow, and one on the eastern outflow. The dam on the primary (east) outflow is approximately 60 m long by 3 m wide. The pond receives waters from many small, seasonal streams at the south end.

The age of the pond is unknown but it is inhabited by a family of 3 or more beavers. It also provided habitat for a family of wood ducks and migratory birds in the spring and fall, 1994. Prior to impoundment by beavers the area was a peatland. The sediments comprise a thick layer (0.05 to 0.2 m) of gyttja, overlying peat sediments (0.1 to 1.0 m) over silt and sands. Clay was observed in one area of the pond at 0.7 to 1.0 m depth.

The maximum pond depth is approximately 2.2 m to the west of the main dam, but most of the pond is 0.5 to 1.0 m deep. About 75% (3.75 ha) of the pond is covered with aquatic emergent vegetation, primarily sedges (*Carex sp.*), some of which grows on mats floating on the pond surface. Submergent aquatic vegetation (primarily *Utricularia sp.*) was present in most areas of the pond. A detailed list of the vegetation is provided in Table 2.1.

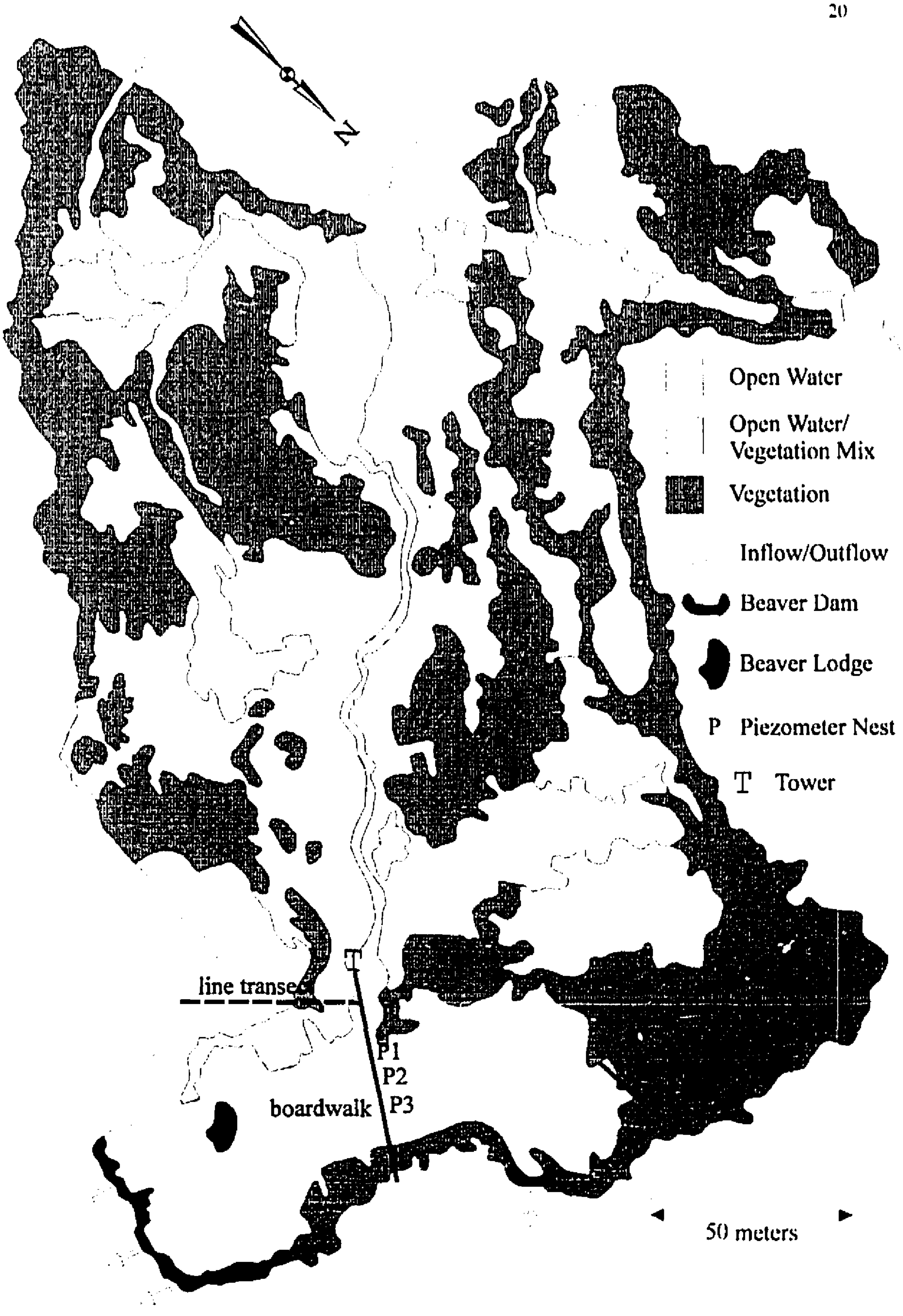


Fig. 2.2: Map of the Beaver Pond with Sampling Locations

Table 2.1 List of Vascular Plant Species at the Beaver Pond
dominant species are marked by an asterisk (*)

Emergent Aquatic Vegetation:
* *Carex aquatilis*
C. limosa
C. diandra
C. rostrata
* *Calamagrostis canadensis*
* *Potentilla palustris*
Salix sp.
Typha latifolia
Potamogetan sp.
Epilobium paslustre
Equisetum fluviatile
Aster sp.
Polyganum nàtans
Sparganium hyperboreum
Nymphaèa tetragona

Submergent Aquatic Vegetation:
Utricularia vulgaris
U. cornata
U. intermedia

2.2 Field Methods

Field work was conducted between May 1 and Sept. 15, 1994. The field measurements comprised determining the flux of CH_4 at the water-air interface as diffusion and ebullition; the flux of CH_4 at the sediment-water interface; the dynamics of CH_4 storage in the sediments and in the open water; and the sampling of bubbles and stored gas for isotopic determination. The beaver pond (Fig. 2.2) was outfitted with a floating boardwalk and a platform on which a 1.5 m tower was erected for measurement of environmental variables and the flux of heat, water, CO_2 and CH_4 by micrometeorological techniques.

2.2.1 Floating Chamber Flux Measurements

Static floating chambers were employed to measure diffusion of CH_4 across the water-air interface approximately every third day during the field season using methods outlined in Moore and Roulet (1991). The chambers were made of 18 L polycarbonate bottles from which the bases had been removed, and were covered with aluminum foil to reduce heating. A styrofoam float was affixed 2 cm above the base of the chamber. The necks were sealed with a rubber stopper containing a glass tube to which 4 m of tygon tubing was attached. Samples were obtained from the end of the tubing through a stopcock after pumping several times with a 60 cc syringe to ensure the air was mixed within the chamber.

Most fluxes were obtained adjacent to the boardwalk. Ten chambers were used on each sampling date; of these, generally 6 measured fluxes from open water sites, 2 from sites colonized by *Carex sp.*, and 2 from other vegetation types. Depth of site, vegetation characteristics and time of day were recorded. Chambers and tubing were flushed with ambient air, then chambers were gently placed on the pond surface. One sample was obtained every five minutes for 20 minutes, so that each flux measurement was based on four data points. The change in CH_4 concentration over time in the chambers was used to determine CH_4 flux (Eq. 1). If the rise in concentration was not linear ($r^2>0.9$ for n=4) then the flux was rejected.

Two diel experiments were performed to determine if fluxes varied systematically with the time of day. On these occasions, 6 fluxes were obtained from various sites every 4 hours for 24 hours.

$$Flux(mg \cdot m^{-2} \cdot d^{-1}) = \frac{(P)(V)}{(R)(T)(A)} \times (MW) \times slope \times \frac{1}{1000}\frac{mg}{g}\frac{L}{ul} \times 1440\frac{\min}{day} \quad \text{[Eq. 1]}$$

where P = pressure (atm)
V = chamber volume (0.019 m^3)
R = ideal gas constant (8.21×10^{-5} atm m^3 $mole^{-1}$ $°K^{-1}$)
T = temperature (°K)
A = area of chamber (0.055 m^2)
MW = molar weight of CH_4 (16 g $mole^{-1}$)
slope = slope of rise in CH_4 concentration over time (ul L^{-1} min^{-1})

2.2.2 Bubble Flux Measurements

Bubble fluxes were measured using inverted funnels along two transects (Fig. 2.2). The line transect comprised 12-14 funnels and extended east from the boardwalk across a vegetated area and deeper open water sites to the pond margin. The beam transect was located west of the boardwalk, extending from a floating mat toward the pond margin, and comprised an additional 14-18 funnels. The beam transect was primarily vegetated by emergent macrophytes such as *Carex sp.* but also crossed several open water channels which flowed between the vegetation.

Thirty-cm diameter inverted funnels were fitted with clear graduated cylinders and a stopper through which bubbles were sampled. Small floats were attached to the funnels to keep them floating at the water-air interface, and the funnels were secured to the line or beam transect by small pieces of rope. Funnel sites were classified as either vegetated or open-water. Vegetated sites contained both emergent and submergent vegetation, and funnels were not placed directly over but rather between the emergent vegetation. Open water sites almost always contained some submergent vegetation.

Bubbles that accumulated in the funnels were sampled by boat, usually within two days. Bubble volume was measured by carefully withdrawing the bubbles into syringes. Flux was calculated (Eq. 3) from the volume of bubbles that had accumulated over the time between measurements, and the concentration of CH_4 in the bubbles.

$$Flux(mg \cdot m^{-2} \cdot d^{-1}) = \frac{(C)(V)}{(A)} \times (SMV) \times (MW) \times \frac{1}{time} \times \frac{1}{1000}\frac{mg}{g}\frac{L}{uL} \qquad [Eq.2]$$

where C = bubble CH_4 concentration (uL L^{-1})
V = volume of accumulated bubbles (L)
A = funnel area (0.073 m^2)
SMV = standard molar volume of gas (1/22.4 mole L^{-1})
MW = molar weight of CH_4 (16 g $mole^{-1}$)

2.2.3 Porewater CH_4 Storage

Porewater CH_4 concentrations were used to calculate storage of CH_4 and changes in storage during the field season. CH_4 concentrations in sediments were determined approximately every third day at 3 sites along the boardwalk from 5 piezometers at each site. The 3 sites comprised one shallow water (≈ 0.2 m) vegetated site, one intermediate site (≈ 0.7 m) with submergent aquatic vegetation, and one deep water site (≈ 2.0 m) with no observable vegetation. The depths of the piezometers at each site were 10, 30, 50, 70, and 100 cm below the sediment-water interface.

Piezometers were constructed from 1.75 cm PVC pipe, were perforated at the desired sampling depth, and fitted with tygon tubing through which samples were drawn. During sampling, the tubing was flushed and 30 ml samples were slowly withdrawn to prevent bubbling and degassing. Storage was calculated by integrating the profiles of dissolved CH_4 concentrations and assuming a constant porosity of 0.8.

2.2.4 Sediment-Water Interface CH_4 Profiles

High resolution profiles of CH_4 concentrations at the sediment surface were determined using peepers (Hesslein, 1976). Peepers comprised 51 chambers at 1 cm intervals which were filled with distilled water in the lab and covered with a semipermeable membrane through which CH_4 can diffuse. Peepers were installed across and below the sediment-water interface 2 weeks prior to sampling to permit equilibration with *in situ* CH_4 concentrations. Profiles were used to identify the zones of CH_4 production and consumption, and to model the Fickian diffusive flux of CH_4 from the sediments (Eq. 3).

$$F_d = \eta D \frac{\Delta C}{\Delta z} \qquad \text{[Eq. 3]}$$

where η = porosity (assumed 0.8)
D = diffusion coefficient ($cm^2\ s^{-1}$) which was determined to vary according to temperature (Lerman, 1979) with r^2=0.99:

$$0.796 + \frac{0.0293 + T}{0.000325 \times T^2}$$ where T = sediment temperature

and $\frac{\Delta C}{\Delta z}$ = maximum CH_4 concentration gradient below the sediment-water interface

2.2.5 Water Column CH_4 Profiles

Profiles of CH_4 in the water column were determined approximately bi-weekly using a pole secured to stationary posts along the boardwalk. Tygon tubes were attached to the pole to sample water at 0, 2, 4, 6, 8, 10, 20, 40, 60, 80, 100, and 120 cm above the sediment-water interface. Samples were drawn slowly through the tubing by syringe.

2.2.6 Surface-Water CH_4 Concentrations

Concentrations of CH_4 in surface water were determined concurrently with about 50% of the floating chamber fluxes, to be used in a thin-film boundary layer model to calculate the diffusive flux of CH_4 from the pond. However, the fluxes derived by this model were an order of magnitude lower than the tower CH_4 fluxes (P. Crill and N. Roulet, unpubl. data) and chamber fluxes; therefore the data were not incorporated into the analysis.

2.2.7 Flux of CH_4 across the Sediment-Water Interface

Benthic chambers were designed to measure the flux of CH_4 across the sediment-water interface. Chambers were built from inverted 12 L tupperware containers (base 26 cm × 38.5 cm) and equipped with a pump and hose with which to slowly circulate water within the chambers. Chambers were lowered to the bottom of the pond adjacent to the boardwalk and gently held in place by foot. The pump was started and water was circulated at 1 L min^{-1}. Samples were taken through the sampling port by syringe every 2 minutes for 10 minutes. CH_4 flux was calculated using Eq. 1 modified for the area and volume of these chambers.

Fluxes measured using methyl fluoride (MF) as a CH_4 oxidation inhibitor followed the same procedure. Flux was first measured without MF, the chamber was flushed and then replaced. MF was injected into the chamber to a concentration of 1% MF by volume, and samples were taken as described above. Oxidation was calculated as the difference between the flux measured with MF and those without MF inhibition.

2.2.8 Environmental Variables

Environmental variables used in the analysis were measured on the micrometeorological tower at the platform at the end of the boardwalk. Table 2.2 lists these variables and the equipment used.

Table 2.2 Measurement of Environmental Variables

Variable	Equipment	Location
Air temperature	thermocouples	1.5 m above pond surface
Pond temperature	thermocouples	1, 10, 20, and 30 cm below pond surface
Sediment temperature	thermocouples	0, 5, 10, 20, 40, 75, and 150 cm below the sediment-water interface
Precipitation	tipping bucket rain gauge	beaver pond and NSA fen
Pond stage	float and sensor	
PAR (photosynthetically-active radiation)	PAR sensor	1.5 m above pond surface
Underwater PAR	PAR sensor	50 to 70 cm below pond surface
Atmospheric pressure	barometer	
Windspeed	anemometer	1 m above pond surface

Half-hourly or hourly averages of the variables were stored in a datalogger located at the base of the tower, and daily means were later calculated for each variable. Daily mean PAR and underwater PAR were calculated using only positive (daytime) values.

2.3 Laboratory Methods

The laboratory methods comprised the analysis of CH_4 samples, incubation experiments to examine the CH_4 production and oxidation potentials of the pond sediments, and analysis for the isotopic composition of carbon and hydrogen in CH_4 stored and emitted from the pond.

2.3.1 CH_4 Analysis

Analysis for CH_4 was determined by gas chromatography within 8 hours of sampling. CH_4 in bubbles was determined using a Shimadzu-8A thermal conductivity detector (TCD) equipped with a HeyeSep column and 5A molecular sieve, using ultra-high purity (UHP) He as carrier gas flowing at 30 ml min^{-1}. The column and detector temperatures were 50 °C and 130 °C, respectively, and the detector bridge current was 160 mA. All other samples were analysed with a Shimadzu Mini-2 equipped with a flame ionization detector (FID) and a 1.8 m Poropak-Q column (50/80 mesh), using UHP N_2 as carrier gas flowing at 40 ml min^{-1}. The column and detector temperatures were 45 °C and 125 °C, respectively. Both machines were also equipped with 1 or 3 ml sample loops to standardize injections.

CH_4 standards of 2.349 and 10 200 ppm were run with samples to calibrate concentrations. The FID responded linearly to CH_4 concentrations between 0.9 ppm and 10 200 ppm. The precision of the FID was 0.4% at both 2.349 ppm and 10 200 ppm, and the precision of the TCD was 1.5% at 10 200 ppm.

CH_4 concentrations in water samples were determined by headspace equilibration technique. An equivalent volume of UHP N_2 was added to the sample then shaken for a minimum of 2 minutes, and the CH_4 concentration in the headspace was determined in duplicate by FID.

2.3.2 Sediment Sample Incubations

Sediment samples were collected in mid-September from 3 sites in the beaver pond. Cores were collected from two open water sites using plastic pipe, and the ends of the pipe were sealed immediately after removal to prevent contamination. Samples of a floating mat were obtained using a knife to cut out mat layers which were transferred into mason jars under water to prevent disturbance of the samples. Sediments were stored at 4 °C until the incubation experiment in the fall of 1994.

Laboratory incubations of the sediment samples were performed to determine potential rates of CH_4 production and consumption under anaerobic and aerobic conditions, respectively. Cores were divided into 10 cm depth intervals, and triplicate (anaerobic incubations) or duplicate (aerobic incubations) samples of approximately 5 g of wet peat from each layer and 5 ml of pond water were transferred into 60 mL Erlenmeyer flasks which were fitted with SubaSeals. Aerobic CH_4 consumption potentials were determined by injecting 50 µl of pure CH_4 into the flasks, which were shaken on a gyrotory shaker at 250 rpm to prevent the formation of anaerobic pockets in the sediments, and observing the decrease in CH_4 concentration over time. Anaerobic production potentials were determined by twice evacuating the flasks and backflushing with N_2 so that little initial CH_4 remained, and the increase in CH_4 concentration in the flask headspace was determined by sampling daily for 5 days. Between sampling, the flasks were incubated in the dark at room temperature.

After the incubations were completed, the samples were oven dried at 60 °C. A regression of the change in CH_4 concentration over time was then expressed as mass of CH_4 produced or consumed per mass of oven-dry sediment. The samples were then combusted in a 450 °C muffle furnace to determine organic matter content.

2.3.3 Isotopic Analysis

Bubble and porewater samples were collected for isotopic analysis in late-August and September. Samples were transferred to 160 ml vials using an inverted vial technique (Jeff Chanton, personal communication) to prevent piercing the vial stopper. The samples were stored upside-down and frozen to prevent leakage. In February, 1995, the samples were analysed at Florida State University. Samples were prepared for carbon isotope analysis by combusting the CH_4 to CO_2 in a helium gas stream passing over 800 °C copper oxide, cryogenically purifying the CO_2 and sealing the sample in a glass tube (Chanton et al., 1992). Hydrogen isotopes (Coleman et al., 1981) were determined by combusting the samples, trapping the released water and liberating the H_2 by heating the tubes at 500 °C for 30 minutes in the presence of Zn.

^{13}C and D (deuterium) were analyzed on a mass spectrometer. Results were corrected for line blanks and expressed in delta notation (Eq. 4).

$$\delta = \left(\frac{R_{sample}}{R_{standard}} - 1\right) \times 1000‰ \qquad [Eq. 4]$$

where R in the respective isotope ratio ($^{13}C/^{12}C$ or D/H)
and the standard is Peedee belemnite (PDB) for carbon and
standard mean ocean water (SMOW) for hydrogen

2.4 Data Analysis

All fluxes and storage were calculated as described above, then flux data were divided according to site vegetation characteristics, and mean daily flux was calculated for each category. Cumulative emissions were calculated by interpolating the daily means for days with missing data and summing all daily means for the season. Total emissions were calculated by adding bubble and chamber flux measurements.

Statistical analyses included regression, Mann-Whitney U-tests and Spearman correlations. A list of data available through BORIS (BOREAS Information Systems) appears in Appendix I.

Chapter 3: Results

3.1 Environmental Variables

The 1994 field season was warm and dry, with total precipitation of 359 mm (Fig. 3.1a) from May 20 (Julian day 140) to September 17 (J.d. 260) (see Appendix II for conversions from Julian days to calendar days). Pond water level (Fig. 3.1b) rose during snowmelt, but declined sharply after a dam failure on June 22 (J.d. 173). Once the beavers repaired the dam it was observed to remain intact for the remainder of the field season. Water level peaked (136.2 cm at the staff gauge, relative to an arbitrary datum) on July 20 (J.d. 201), and then declined gradually through the end of the field season.

Mean daily air temperature (Fig. 3.2a) ranged from 4.2 °C to 21.4 °C. Temperatures in the pond reflected ambient air temperatures (Fig. 3.2b), but fluctuated less due to the higher heat capacity of water. Pond water temperatures often exceeded mean daily air temperature and never fell below 10 °C. Pond sediment temperatures also followed air temperature (Fig. 3.3), but exhibited a lag (4 days at 20 cm and 5 days at 40 cm depth) with smaller fluctuations. At 1.5 m depth, the sediment temperature increased linearly from 2.7 to 7.0 °C throughout the season.

Photosynthetically active radiation (PAR) fluctuated greatly (Fig. 3.4). From July 1 - 6 (J.d. 182 through 187), smoke from forest fires dramatically reduced PAR. Underwater PAR, measured 50 to 70 cm below the water surface (Fig. 3.4), was typically 10% of that incident at the surface.

Mean daily atmospheric pressure (Fig. 3.5) fluctuated between 98.5 and 101.5 kPa throughout the field season, but the majority of the many fluctuations were less

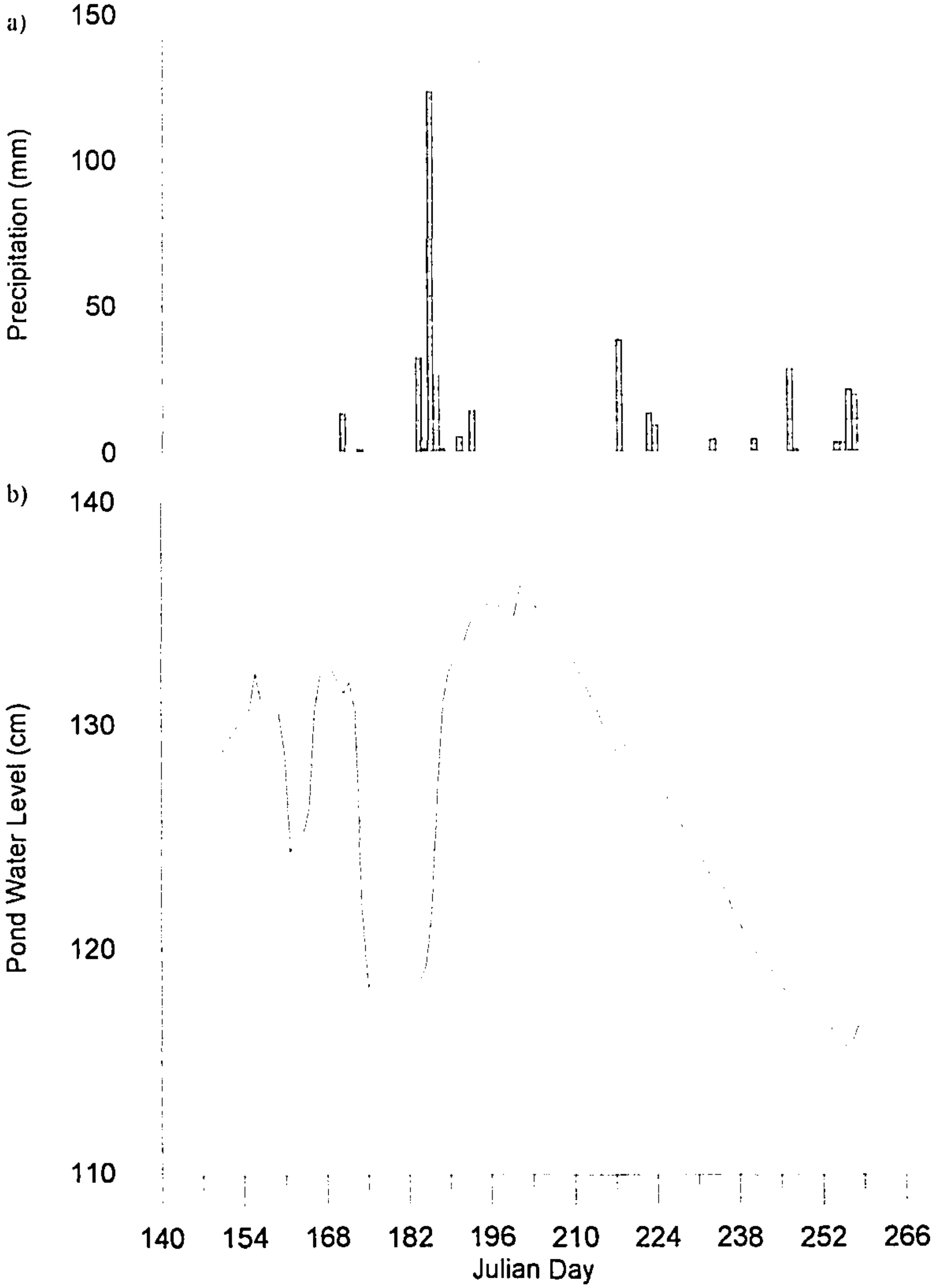
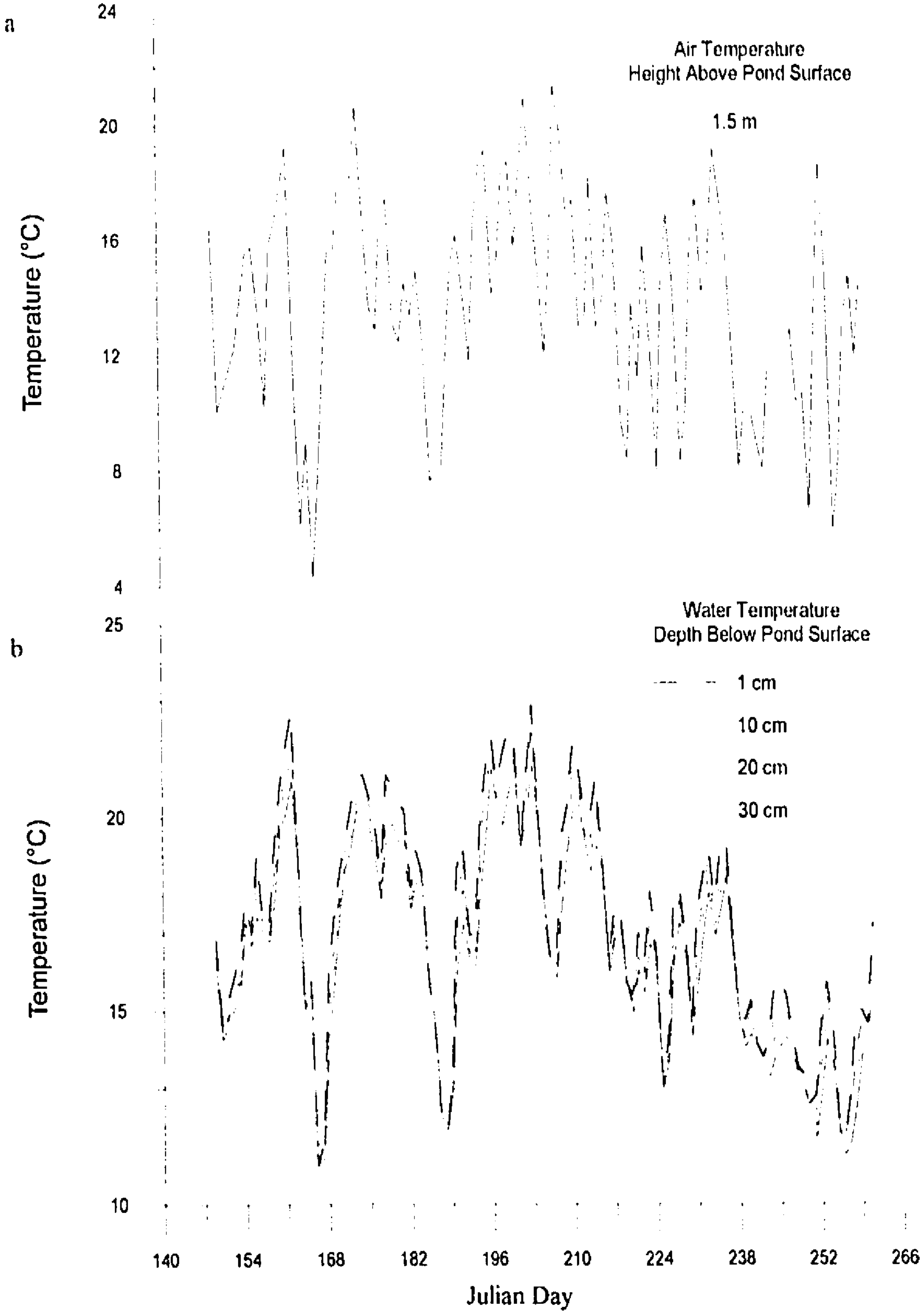


Fig. 3.1 a) Total Daily Precipitation
and b) Beaver Pond Water Level



<u>Fig. 3.2 a) Mean Daily Air Temperature</u>
<u>and b) Mean Daily Pond Water Temperature</u>

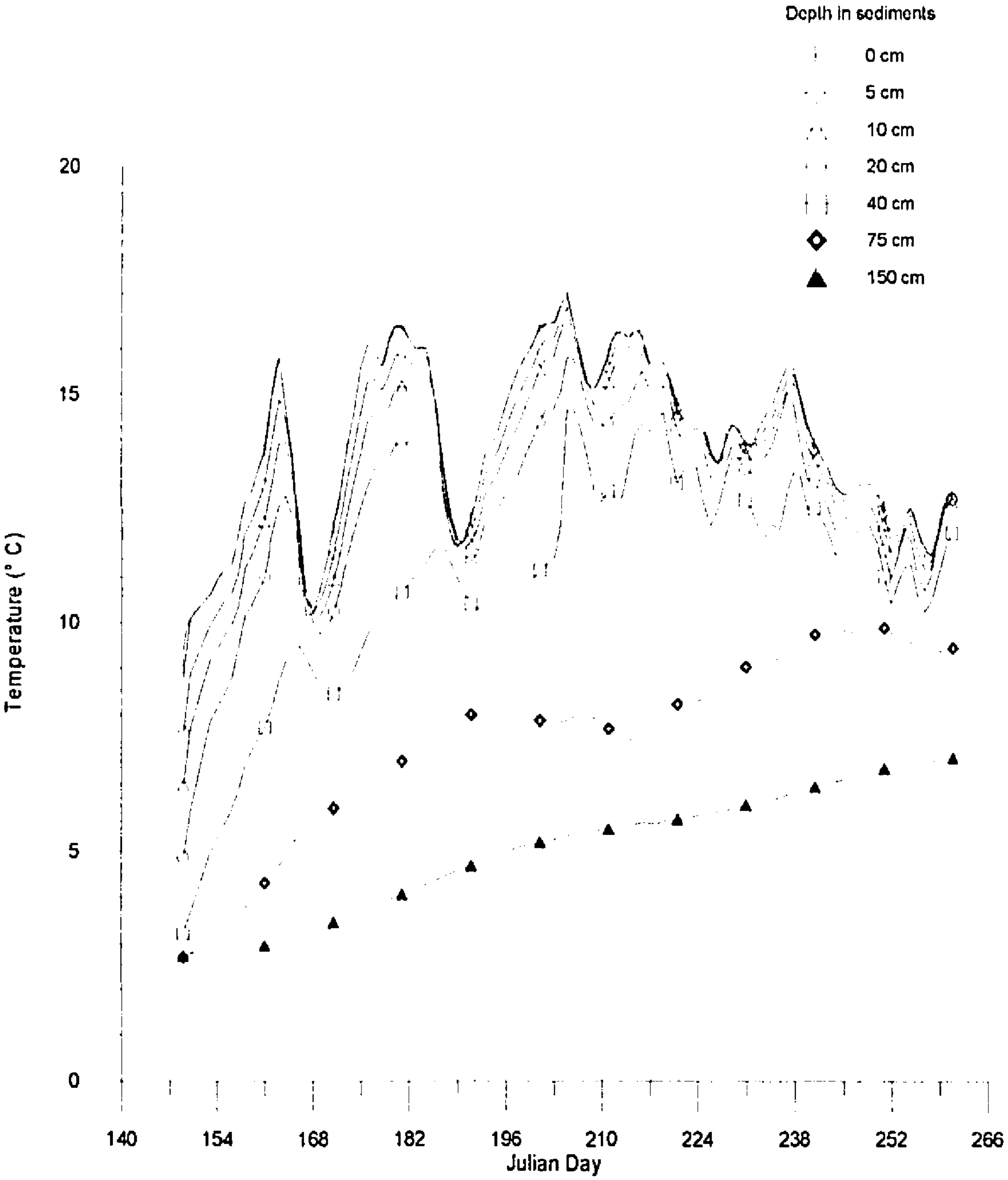


Fig. 3.3 Mean Daily Pond Sediment Temperature

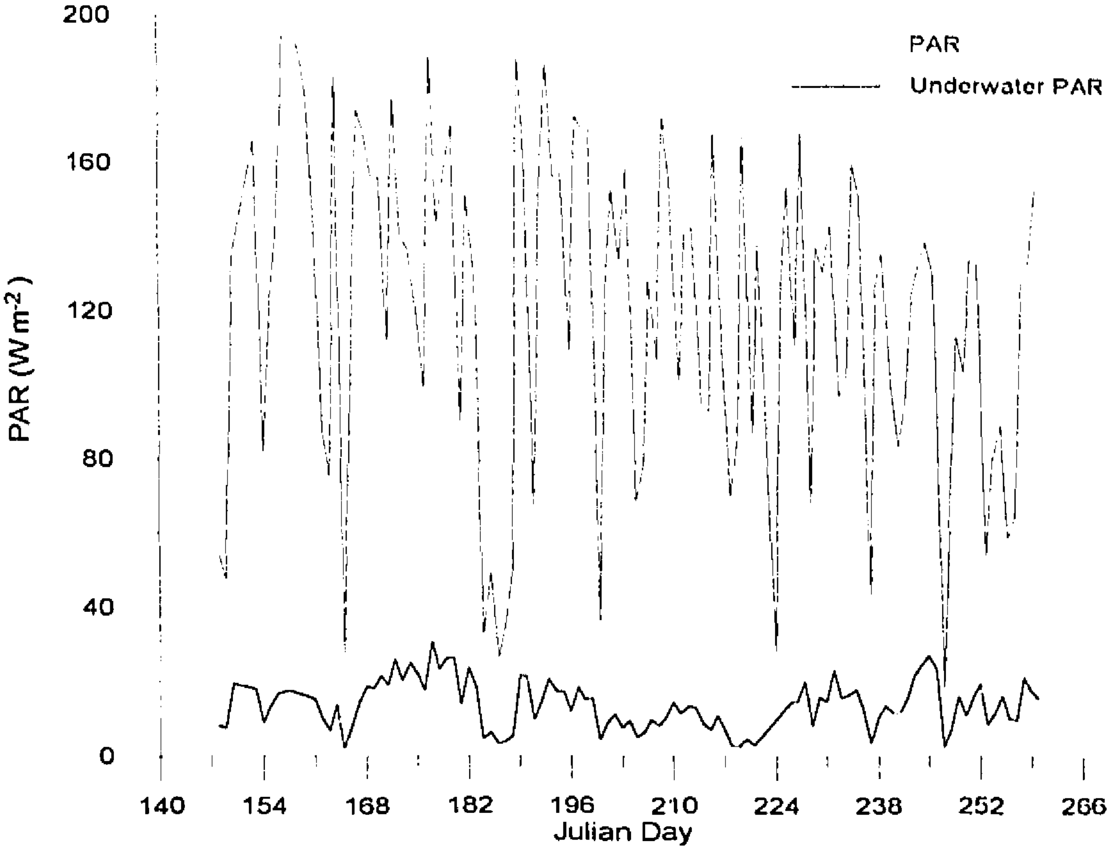


Fig. 3.4 Mean Daily Daytime PAR and Underwater PAR

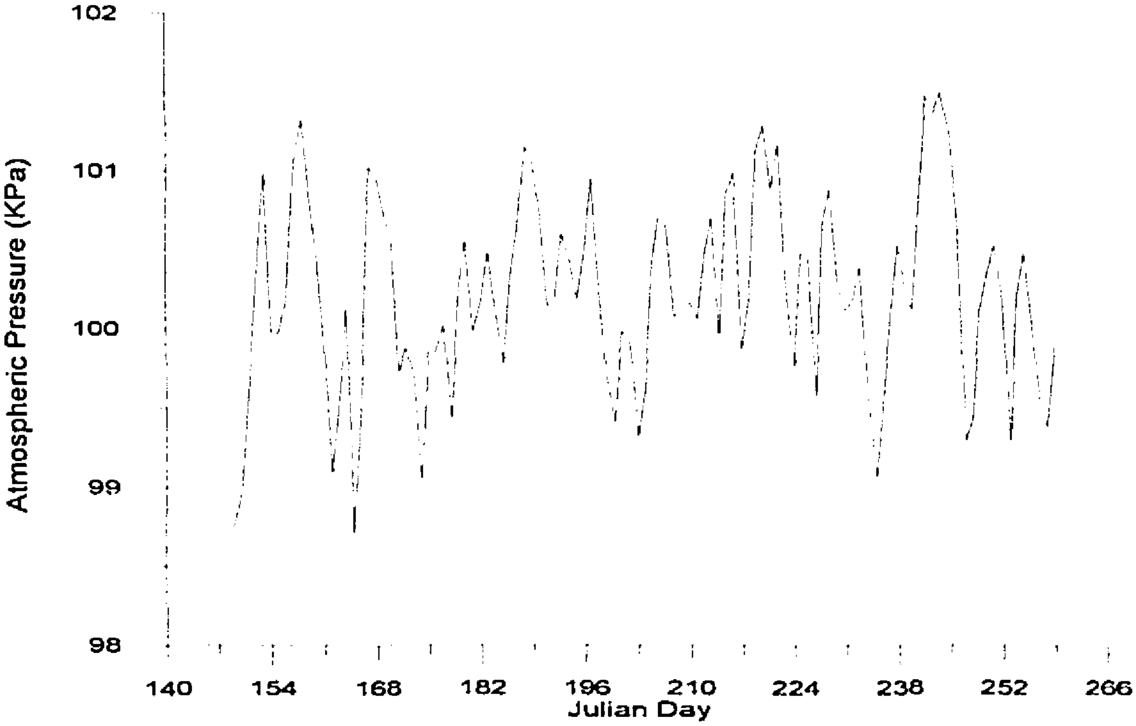


Fig. 3.5 Mean Daily Atmospheric Pressure

than 1 kPa. The maximum 24-hour change was an increase of 2.1 kPa. Mean daily windspeed ranged from 0.46 to 3.65 m s^{-1}, and maximum half-hour windspeeds ranged from 1.69 to 5.98 m s^{-1}. Winds were calm at night and in the early morning and there were usually several hours each day when it was also calm.

3.2 Chamber Fluxes

A total of 260 chamber fluxes were obtained on 42 days from May 20 (J.d. 140) to September 13 (J.d. 256). An additional 53 flux measurements were made during two 24-hour periods in June and July to examine diel trends in diffusive fluxes from the beaver pond. Fluxes ranged from -7.2 to 1080 mg CH_4 m^{-2} d^{-1}, and the distribution was positively skewed (skewness = 2.3; Fig. 3.6). Approximately 75% of all fluxes were below 157 mg CH_4 m^{-2} d^{-1}. The mean flux was 139.2 ± 194 mg CH_4 m^{-2} d^{-1}, and the median was 60.3 mg CH_4 m^{-2} d^{-1}. Geometric means were not calculated because several fluxes were ≤ 0.

3.2.1 Vegetation and Site Differences

The chamber flux measurements were divided into 7 different vegetation categories (Fig. 3.7 and Table 3.1): open water; *Carex sp.* (sedges); *Nymphaea sp.* (waterlilies); *Salix sp.* (willows); *Equisetum sp.* (horsetails); *Calamagrostis canadensis* (grasses); and *Typha sp.* (cattails). Fluxes were lowest over *Calamagrostis* (9.9 ± 9.6 mg CH_4 m^{-2} d^{-1}, n=2), *Equisetum* (50.8 ± 53.4 mg CH_4 m^{-2} d^{-1}, n=6), *Nymphaea* (50.7 ± 65 mg CH_4 m^{-2} d^{-1}, n=17), and *Salix* (35.3 ± 29.5 mg CH_4 m^{-2} d^{-1}, n=5). Fluxes

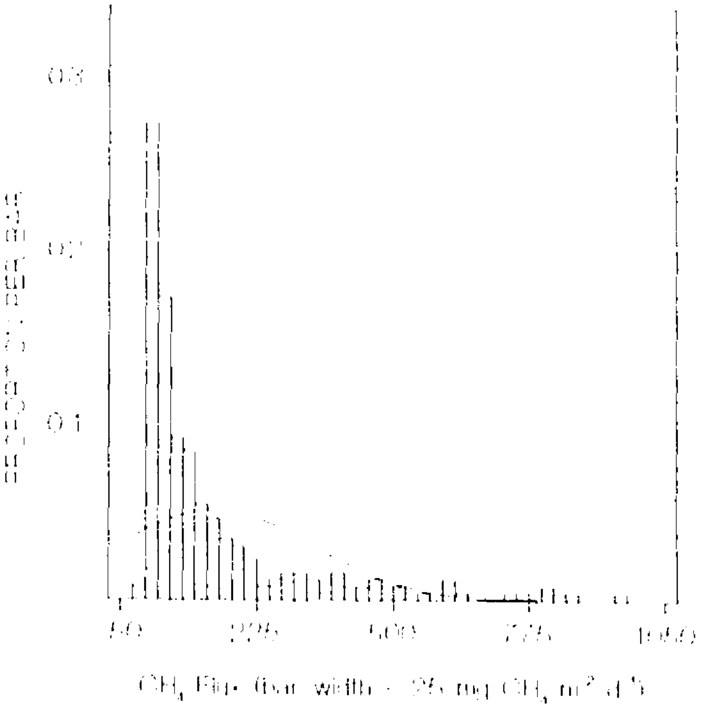


Fig. 3.6 Distribution of All Chamber Fluxes

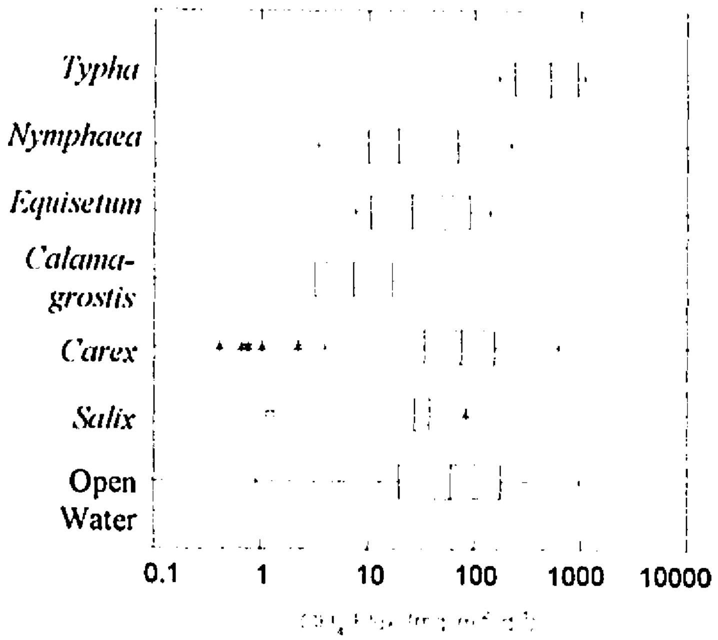


Fig. 3.7 Chamber Fluxes by Vegetation Type

Table 3.1: Chamber Flux Data by Vegetation Type
(Fluxes in mg CH_4 m^{-2} d^{-1})

Open Water:
N = 121
min = -3.9
max = 957.3
mean = 161.2
SD = 223.5
CV = 1.39
median = 57.7

Carex:
N = 105
min = -7.2
max = 621.0
mean = 123.5
SD = 138.2
CV = 1.12
median = 76.5

Salix:
N = 5
median = 27.7
SD = 29.5

Calamagrostis:
N=2
median = 9.9
SD = 9.6

Equisetum:
N = 6
median = 28.7
SD = 53.4

Nymphaea:
N = 17
median = 19.1
SD = 65

Typha:
N = 4
median = 563.4
SD = 418.5

from sites containing *Carex* (123.5 ± 138.2 mg CH_4 m^{-2} d^{-1}, n=105) and open water (161.2 ± 223.6 mg CH_4 m^{-2} d^{-1}, n=121) were higher. *Typha* had the highest fluxes (594.3 ± 418.5 mg CH_4 m^{-2} d^{-1}, n=4). The highest measured flux (1080 mg CH_4 m^{-2} d^{-1}) was obtained from a chamber enclosing a *Typha* plant. There were no statistically significant differences between fluxes from any two vegetation groups (Mann Whitney U tests, $p>0.05$). In several cases this may have been due to small sample sizes.

A further category comprised fluxes measured from a stagnant pool near the north pond outflow. These fluxes were high (432.9 ± 229 mg CH_4 m^{-2} d^{-1}, n=6), likely due to a buildup of CH_4 in surface waters from the lack of water flow, sheltered location, and high organic content of the sediments, but these associations were not tested.

3.2.2 Seasonal Trends and Spatial Variability

Mean daily fluxes from open water and from *Carex* sites are shown in Fig. 3.8. Fluxes were initially very small, but an emission 'pulse' was observed from June 12 to 14 (J.d. 163 - 165), during which the flux from open water sites reached 856 mg CH_4 m^{-2} d^{-1}. This pulse occurred well after ice-off, and may be related to a concurrent rise in sediment temperature and a drop in atmospheric pressure and water table (see Figs. 3.1b, 3.3, and 3.5). For the remainder of the season, the emission patterns from open water and *Carex* sites were similar, with peaks and troughs generally occurring on or about the same days.

Coefficients of variation (standard deviation:mean) indicated that fluxes can be extremely variable over short distances. The average coefficient of variation was 0.62

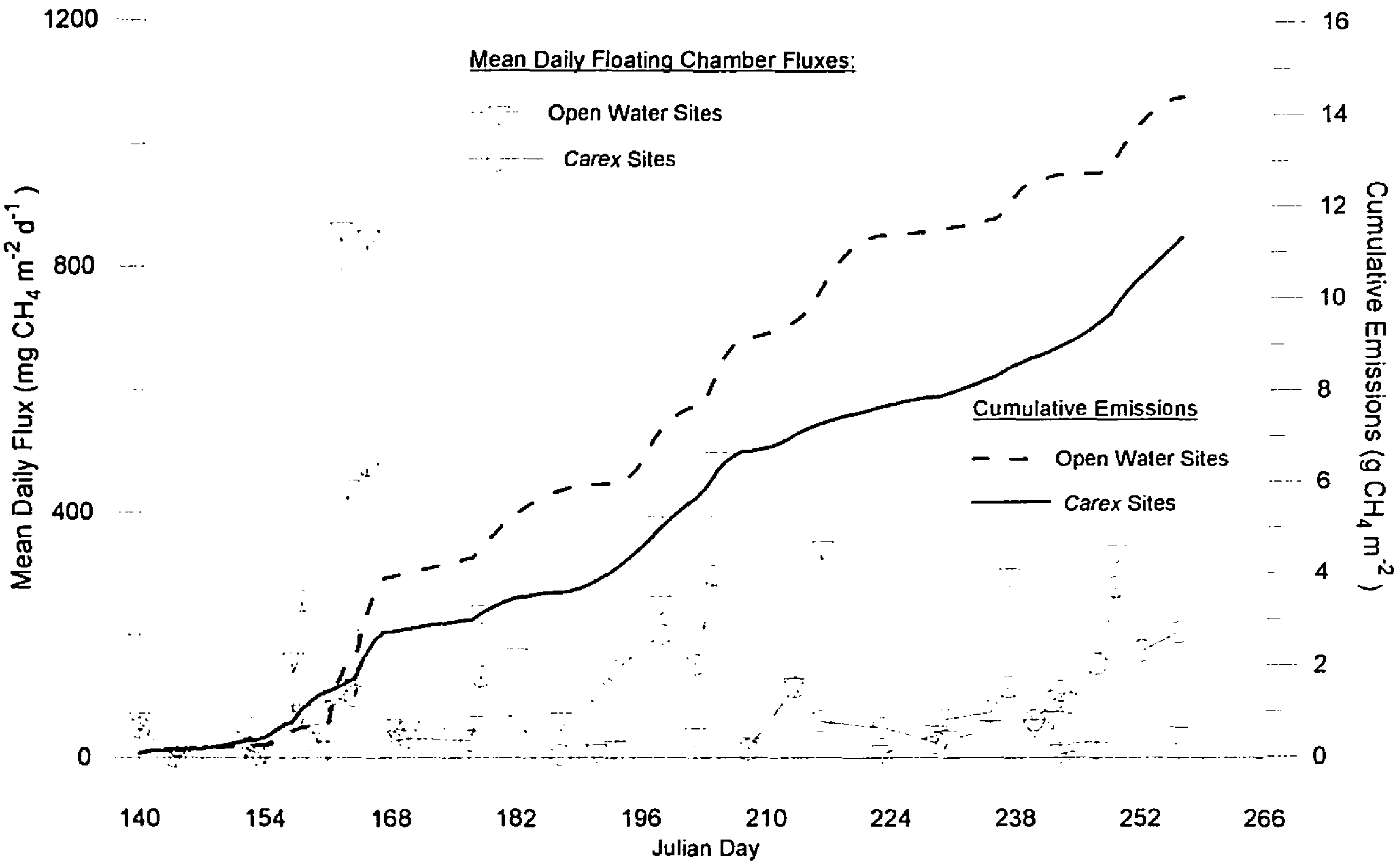


Fig. 3.8 Mean Daily CH_4 Flux from Floating Chambers and Cumulative Emissions

(range 0.06 - 1.8) for *Carex* sites, and 0.64 (range 0.02 - 1.4) for open water sites.

No significant difference was observed between mean daily fluxes from open water and *Carex* sites ($U = 1.62$, $p>0.05$). Cumulative emissions for the season, calculated by integrating the area under the mean daily emissions curves, were 14.4 g CH_4 m^{-2} (10.8 g CH_4-C m^{-2}) from open water sites, and 11.3 g CH_4 m^{-2} (8.5 g CH_4-C m^{-2}) from *Carex* sites.

Measurements from an independent study of CH_4 flux at the beaver pond, using a flux-gradient approach from a 1.5 m micrometeorological tower, showed that the flux of CH_4 was greatest when the wind was blowing from the vegetated areas of the beaver pond (P. Crill and N. Roulet, unpubl. data; see Section 4.2.4). Chamber flux measurements in this study, however, indicated similar flux between *Carex* sites and open water areas. For several reasons, the chamber measurements may not have detected actual enhanced flux through sedges. Most chamber fluxes were measured from the boardwalk, where the measurements were easier to obtain compared to sampling by boat, but where the density of sedges was low compared to other pond areas. In general, floating chamber sedge sites comprised only 1 to 3 *Carex*. By the end of the field season, these plants had become damaged by repeated sampling.

For these reasons, the *Carex* sites along the boardwalk may not represent *Carex* sites elsewhere in the pond. At the beginning of the season, floating chamber measurements were taken from both the boardwalk and other sites, but no difference between the sites was observed as fluxes were uniformly low at the time. Sampling was subsequently restricted to the boardwalk. Toward the end of the season, when it was recognized that the tower measurements showed flux differences between open water and vegetated areas, subsequent chamber fluxes were measured using a boat to access areas with more dense vegetation (4 to 12 *Carex* per chamber) (Fig. 3.9). On these 6 dates, the flux from *Carex* was observed to be significantly greater than flux from open water (Mann Whitney U = 156, $p<0.0001$). Therefore, it is likely that the *Carex* chamber flux measurements reported in this study underestimate the CH_4 flux from these plants.

3.2.3 Relationships between Chamber Fluxes and Environmental Variables

Several analyses were performed to reveal factors that might explain variations in observed fluxes. Since fluxes and other variables were not normally distributed, Spearman correlation coefficients (r for non-normal distributions) were calculated to determine the direction and strength of relationships (Table 3.2). No significance level is available for Spearman correlations. Scatter plots of these relationships are shown in Fig. 3.10. Since daily means of variables are most likely to describe flux variations on a similar time scale, mean daily fluxes from open water and *Carex* sites were used for these analyses.

In general, open water fluxes were more strongly correlated with environmental variables than fluxes measured from *Carex* sites. Open water fluxes related negatively to mean daily atmospheric pressure for the day prior to measurement, while *Carex* fluxes related less strongly with pressure and exhibited no lag in response. Open water fluxes were most strongly (and positively) related to near-surface sediment temperatures, while *Carex* fluxes were only weakly related to deeper sediment

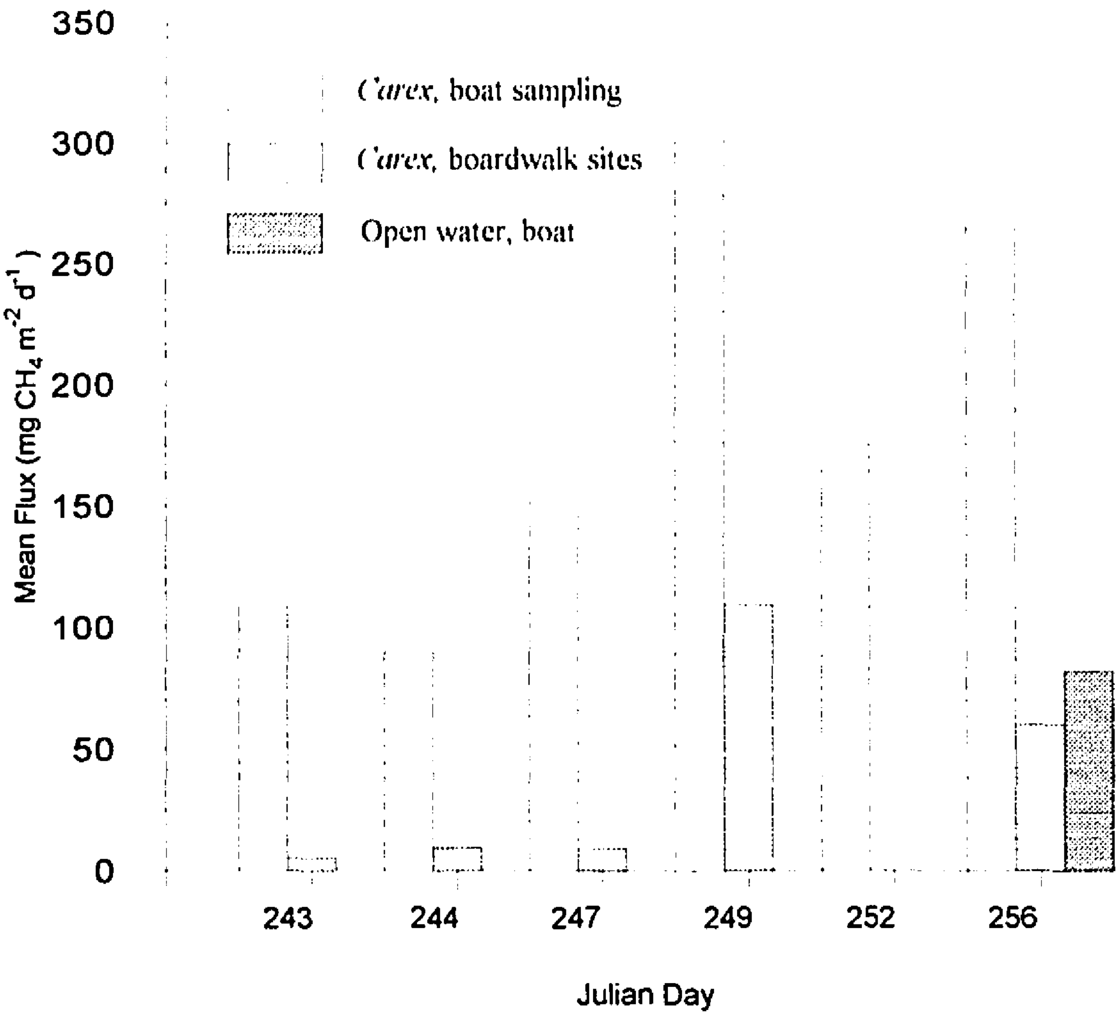
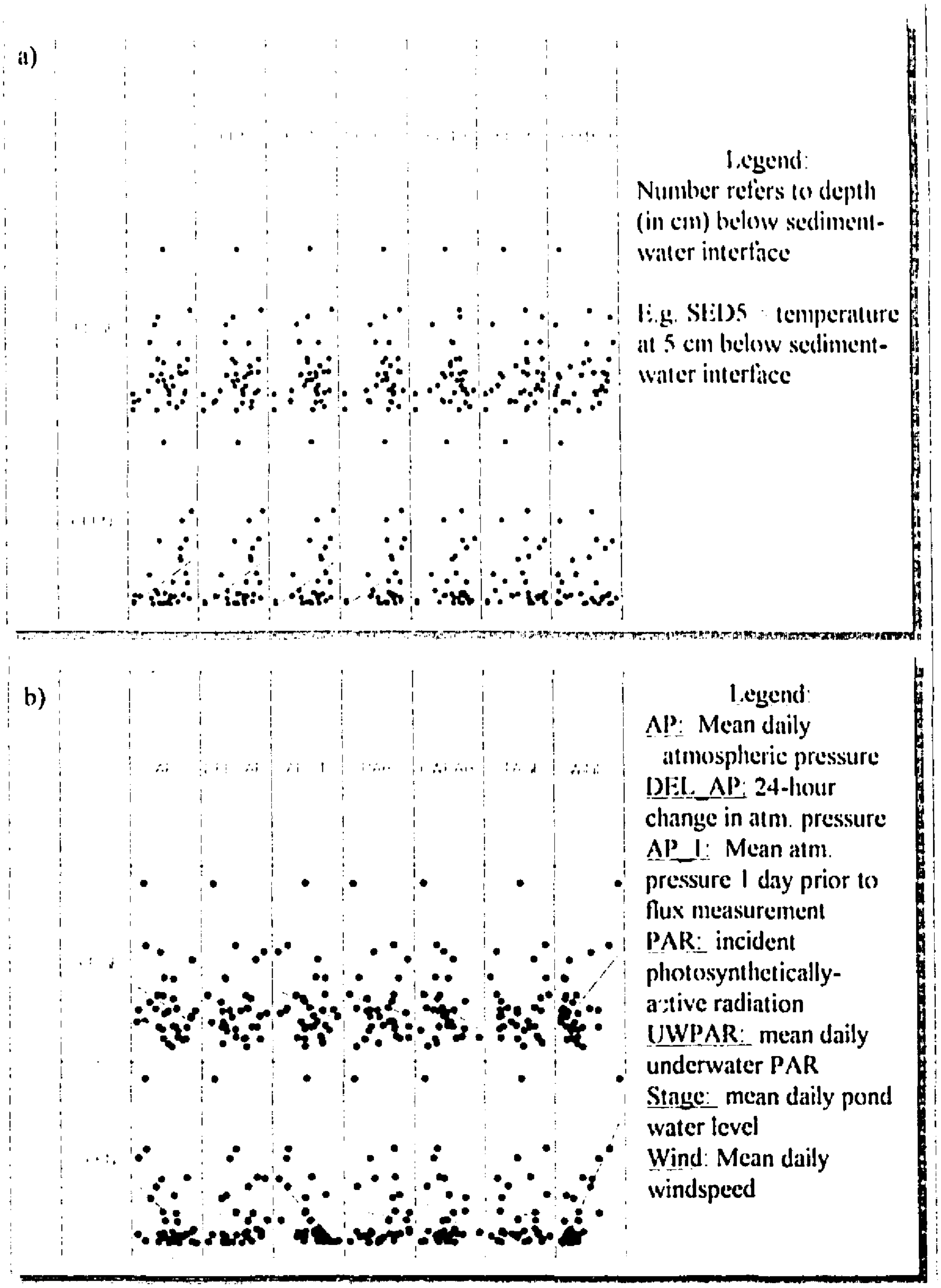


Fig. 3.9: Late-Season Evidence for Enhancement of CH_4 Flux by *Carex* plants
Dense *Carex* stands (boat sampling) produced higher fluxes than adjacent open water sites or sparse *Carex* stands along the boardwalk



Legend:
Number refers to depth (in cm) below sediment-water interface

E.g. SED5 = temperature at 5 cm below sediment-water interface

Legend:
AP: Mean daily atmospheric pressure
DEL_AP: 24-hour change in atm. pressure
AP_1: Mean atm. pressure 1 day prior to flux measurement
PAR: incident photosynthetically-active radiation
UWPAR: mean daily underwater PAR
Stage: mean daily pond water level
Wind: Mean daily windspeed

Fig. 3.10: Scatter Plot Matrices of Mean Daily Chamber Fluxes from Sedge (*Carex*) and Open Water Sites vs Mean Daily a) Sediment Temperatures and b) Atmospheric Pressure, PAR , Pond Stage and Windspeed

temperatures. Fluxes were occasionally negatively related to deeper sediment temperature which may be due to the time lag of sediment temperature at depth.

Table 3.2 Spearman Pairwise Correlation Coefficients (r)
Between Mean Daily Chamber Fluxes and Environmental Variables

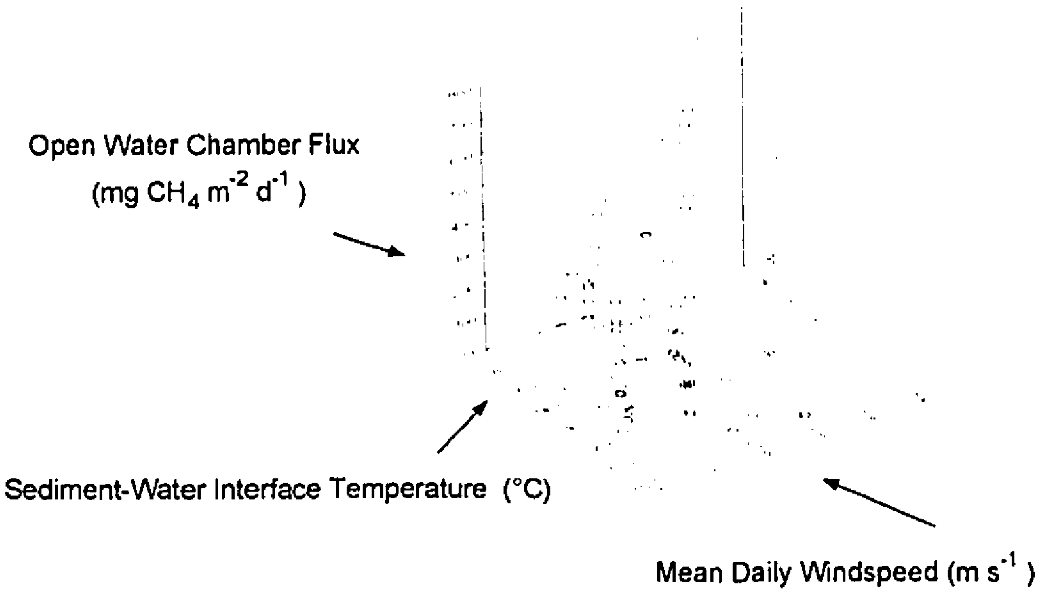
Variable	z	Mean Daily Open Water Fluxes	N	Mean Daily *Carex* Site Fluxes	N
Mean Daily Sediment Temperatures	0	0.50	39	0.16	35
	5	0.50		0.11	
	10	0.45		0.09	
	20	0.35		0.02	
	40	0.08		-0.04	
	75	-0.12		0.25	
	150	-0.04		0.28	
PAR		0.15	38	-0.21	34
Underwater PAR		0.02		-0.20	
Pond Stage		-0.01		-0.11	
Atmospheric Pressure		-0.36	39	-0.34	35
Atm. Pressure Lag = 1 day		-0.62	37	-0.15	33
Atm. Pressure Lag = 2 days		-0.43	37	-0.15	34
24-hr change in mean daily pressure		0.21	38	-0.17	34
Windspeed		0.48	38	-0.03	34

z- depth below sediment-water interface

Forwards and backwards stepwise multiple linear regressions were modelled to determine the best predictive relationships for chamber fluxes (Fig. 3.11). Most relationships were weak; the best explained only 44% of the variance in flux. For the regression model of mean daily open water flux, mean daily windspeed explained 35% of the variance in fluxes ($p<0.001$), and mean daily temperature at the sediment-water interface explained a further 9% of variance ($p<0.05$). Mean daily windspeed was the only significant predictor of flux from *Carex* sites, but relationships were much weaker than those for open water sites.

Individual Open Water Chamber Flux = -481.4 + 121.48 Mean Windspeed + 32.6 Sediment-Water Interface Temperature

$F = 36.5$ $p<0.0001$ $r^2 = 0.42$ $N = 80$ $SEE = 137.7$



Mean Daily Open Water Chamber Flux = -570.3 + 158.7 Mean Windspeed + 36.7 Sediment-Water Interface Temperature

$F = 13.96$ $p<0.0001$ $r^2 = 0.44$ $N = 38$ $SEE = 164$

Individual Sedge Site Chamber Flux = 58.5 + 53.3 Mean Windspeed

$F = 11.7$ $p<0.005$ $r^2 = 0.11$ $N = 95$ $SEE = 133$

Mean Daily Sedge Site Chamber Flux = 31.4 + 60.9 Mean Windspeed

$F = 9.6$ $p<0.005$ $r^2 = 0.23$ $N = 34$ $SEE = 88.3$

Fig. 3.11: Multiple Linear Regression Equations for Chamber Fluxes

To further examine the relationships between pond sediment temperatures and chamber fluxes, the flux data were divided into specific intervals of increasing or decreasing temperature (Table 3.3). Between May 20 through June 14 (J.d. 140 - 165), during which sediment temperatures continuously increased, the correlation between open water chamber fluxes and sediment temperatures was strong and positive (Spearman r>0.6) (Table 3.3a). Over the same period, *Carex*-site chamber

Table 3.3 Spearman Pairwise Correlation Coefficients (r)
Between Chamber Fluxes and Sediment Temperatures

a) Julian Days 140-165: Increasing Sediment Temperatures

Variable	z	Open Water Fluxes	N	*Carex* Site Fluxes	N
Sediment Temperature	0	0.62	40	0.20	26
	5	0.64		0.24	
	10	0.61		0.34	
	20	0.61		0.34	
	40	0.65		0.57	
	75	0.66		0.56	
	150	0.65		0.57	

b) Julian Days 190-205: Increasing Sediment Temperatures

Variable	z	Open Water Fluxes	N	*Carex* Site Fluxes	N
Sediment Temperature	0	0.75	14	0.24	12
	5	0.73		0.20	
	10	0.73		0.20	
	20	0.73		0.22	
	40	0.71		0.21	
	75	-0.73		-0.21	
	150	0.75		0.23	

c) Julian Days 214-231: Decreasing Sediment Temperatures (with fluctuations)

Variable	z	Open Water Fluxes	N	*Carex* Site Fluxes	N
Sediment Temperature	0	0.19	8	0.58	6
	5	0.29		0.64	
	10	0.58		0.46	
	20	0.68		0.46	
	40	0.31		0.58	
	75	-0.17		-0.58	
	150	-0.31		-0.58	

z- depth in sediments below sediment-water interface (cm) fluxes were most positively correlated with deep sediment temperatures (Spearman r>0.56). As temperatures warmed further (July 9 through 24; J.d. 190 - 205) open water chamber fluxes again correlated with all sediment temperatures, but fluxes from *Carex*-colonized sites did not (Table 3.3b). Toward the end of the season open water fluxes correlated best with declining sediment temperature at 10 to 20 cm depth, but *Carex* fluxes correlated best with near-surface sediment temperatures (Table 3.3c). Despite poor statistical relationships between chamber flux and temperature, the graphical trend in both is strikingly similar (Fig. 3.12).

3.2.4 Diel Chamber Fluxes

The diel experiment on June 20-21 (Fig. 3.13a), yielded no consistent change in flux with time of day. The July diel experiment (July 10-11) showed a pattern of increased flux from *Carex* during daylight hours (8:00 to 20:00) (Fig. 3.13b). These data are inconclusive, however, due to the small sample sizes (each bar in Fig. 3.13 represents a single flux measurement) and because the spatial variability observed is greater than any detectable change in flux due to time of day. It is interesting to note that no significant relationships were found between chamber fluxes from *Carex* sites and PAR or underwater PAR (above).

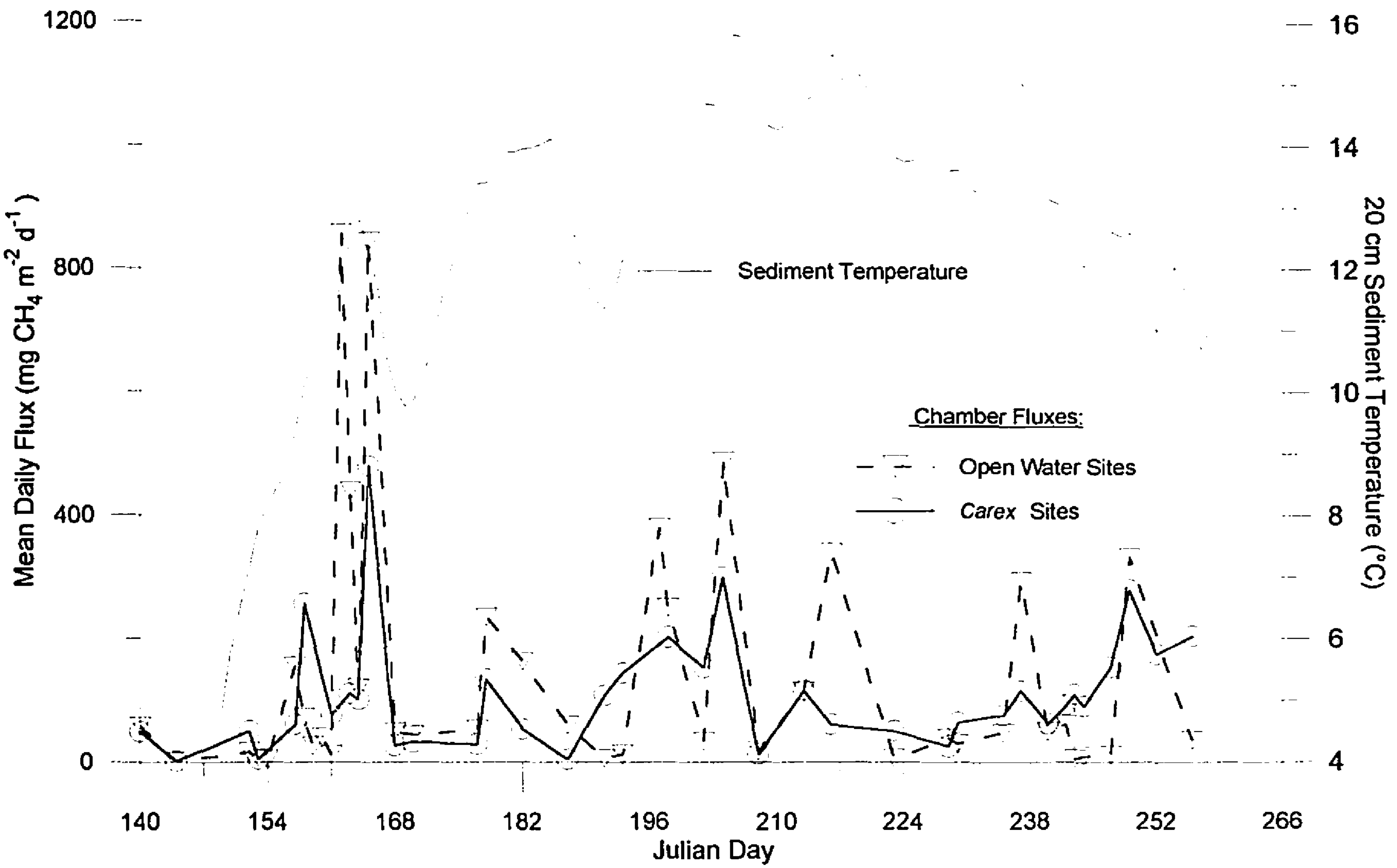


Fig. 3.12: Mean Daily Chamber Flux and 20 cm Sediment Temperature

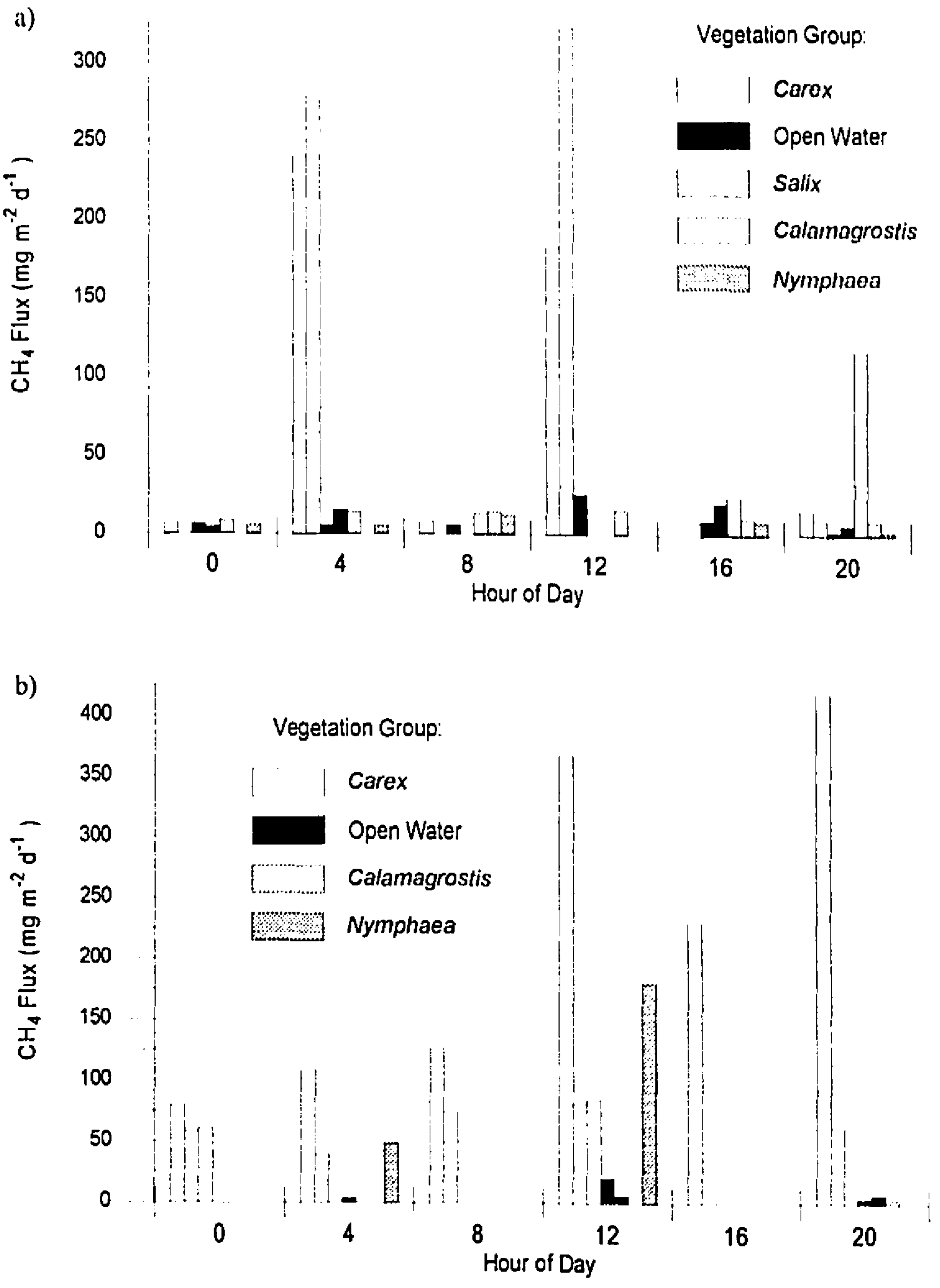


Fig. 3.13: Histogram of Diel Chamber Fluxes from a) June 20-21, 1994 and b) July 8-9, 1994 each bar represents one chamber flux

3.3 Bubble Fluxes

A total of 771 bubble fluxes were measured from June 6 (J.d. 157) to September 14 (J.d. 257). The minimum flux was 0 and the maximum 1849.3 mg CH_4 m^{-2} d^{-1}. The distribution was positively skewed (skewness = 4.6; Fig. 3.14). The mean flux was 83.8 ± 141 mg CH_4 m^{-2} d^{-1} and the median was 32.3 mg CH_4 m^{-2} d^{-1}. Since many fluxes were zero, geometric means could not be calculated.

3.3.1 Vegetation and Site Differences

Bubble flux measurements were divided into open water sites and vegetated sites, which contained emergent macrophytes, notably *Carex* (Table 3.4). Bubble fluxes were significantly greater (U = 37230, $p<0.0005$) from open water sites (159.5 ± 192.3 mg CH_4 m^{-2} d^{-1}) than from vegetated sites (30.6 ± 33.2 mg CH_4 m^{-2} d^{-1}) (Fig. 3.15a), and this difference was observed at both the line (U = 9366.5, $p<0.0005$) and beam (U = 7433.5, $p<0.0005$) transects. The difference in fluxes was due both to greater bubbling rates (U = 38426.5, $p<0.0005$) (Fig. 3.15b) and higher CH_4 concentrations in the bubbles (U = 14911, $p<0.0005$) (Fig. 3.15c) from open water sites. The mean open water bubbling rate and CH_4 concentration were 542.8 ± 1683 ml m^{-2} d^{-1} and 471,885 ± 207,562 ppm, respectively. The mean rate of bubbling and average bubble CH_4 concentration for vegetated sites were 165.3 ± 285 ml m^{-2} d^{-1} and 265,951 ± 124,300 ppm, respectively.

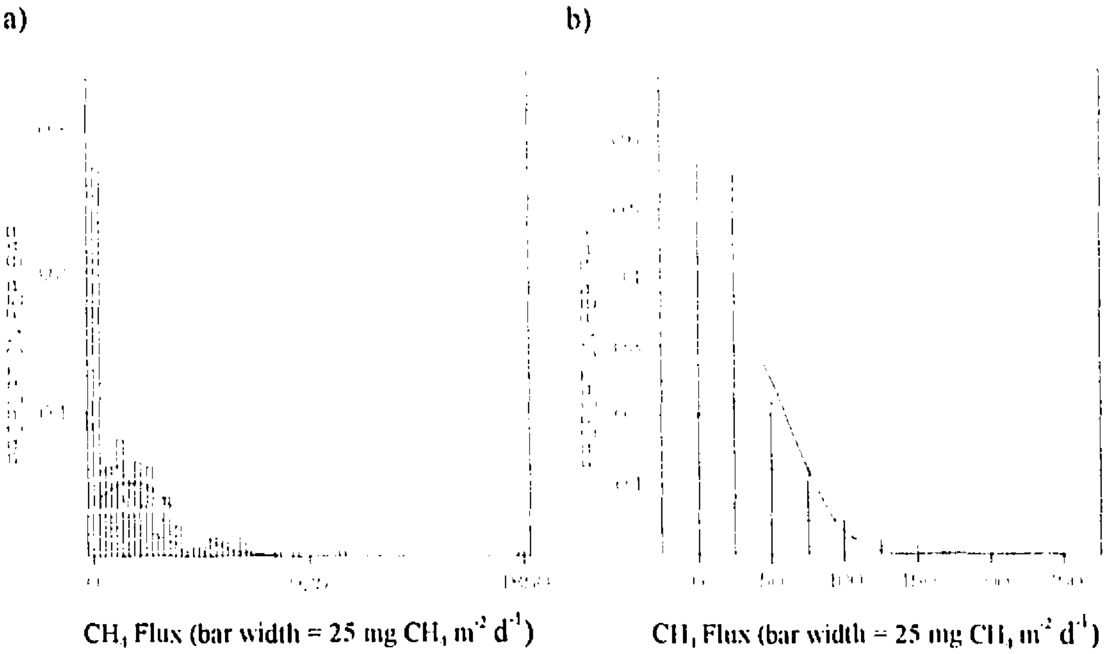


Fig. 3.14: Distributions of a) Open Water Bubble Fluxes and b) Vegetated Site Bubble Fluxes

Table 3.4 Summary of Bubble Flux Data
Fluxes in mg CH$_4$ m^{-2} d^{-1}

	Open Water Sites	Vegetated Sites
N	318	453
min	0	0
max	1849.3	342.2
mean	159.5	31.2
SD	192.3	36.2
skewness	3.25	3.06
CV	1.21	1.16
median	112.5	19.3

a)

Average Open Water Bubble Flux:
159.5 ± 192 mg CH_4 m^{-2} d^{-1}

Average Vegetated Site Bubble Flux:
30.6 ± 33 mg CH_4 m^{-2} d^{-1}

b)

Average Open Water Bubbling Rate:
542.8 ± 1683 ml m^{-2} d^{-1}

Average Vegetated Site Bubbling Rate:
165.3 ± 285 ml m^{-2} d^{-1}

c)

Average Open Water Bubble CH_4 Concentration:
47.2 ± 21%

Average Vegetated Site Bubble CH_4 Concentration:
26.6 ± 12%

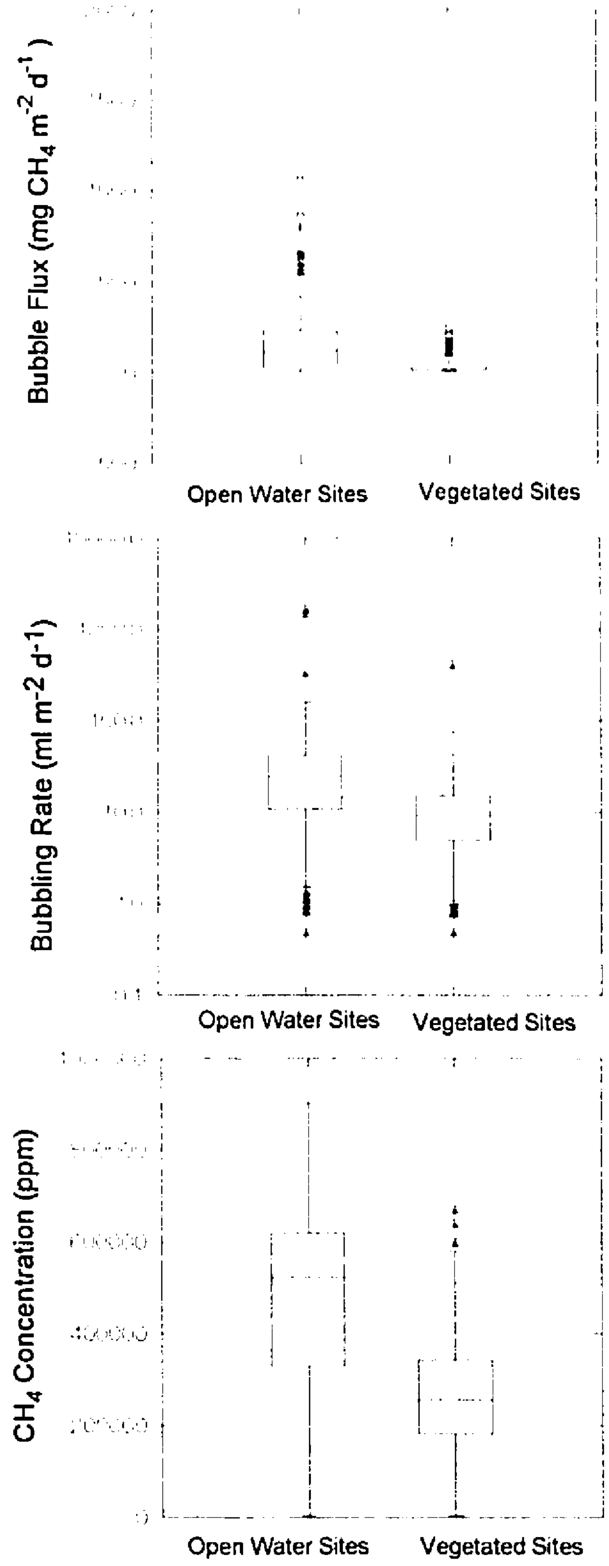


Fig. 3.15: a) Differences between bubble fluxes from open water and vegetated sites are due both to b) differences in bubbling rates and c) differences in concentration of CH_4 in bubbles
Centre line of box plots are medians; edges are 25 and 75th percentiles; asterisks are outliers; open circles are far outliers

3.3.2 Seasonal Trends and Flux Variability

Mean daily and cumulative bubble fluxes for open water and vegetated sites are shown in Fig. 3.16. Bubble fluxes from vegetated sites were consistently lower but followed the same pattern as the open water bubble fluxes. Cumulative CH_4 bubble emissions, calculated by integrating mean daily bubble fluxes over the field season, were 2.9 g CH_4 m^{-2} (2.2 g CH_4-C m^{-2}) from vegetated sites and 15.7 g CH_4 m^{-2} (11.8 g CH_4-C m^{-2}) from open water sites.

Daily coefficients of variation indicated a large spatial variability, ranging from 0.31 through 1.80 for vegetated sites and from 0.23 through 2.33 for open water sites. Coefficients of variation at a single site indicated high temporal variability, ranging from 0.40 through 1.21 for vegetated sites and 0.35 through 2.28 for open water sites.

3.3.3 Relationships between Bubble Fluxes and Environmental Variables

Spearman correlation coefficients were computed to test for relationships between bubble fluxes and environmental variables (Table 3.5). Mean daily open water bubble fluxes were strongly correlated with sediment temperatures to a depth of 20 cm ($r \geq 0.68$). Correlations between mean daily vegetated site bubble fluxes and sediment temperature were strongest at 20 cm depth.

Bubble fluxes were negatively correlated with atmospheric pressure, but not to the extent that was originally hypothesized. The strength of these correlations was not improved by using relative change in pressure from the previous day (vs. relative change in bubble flux per day), nor by using time lags for response of bubble fluxes to pressure changes. Although the correlations between bubble fluxes and atmospheric

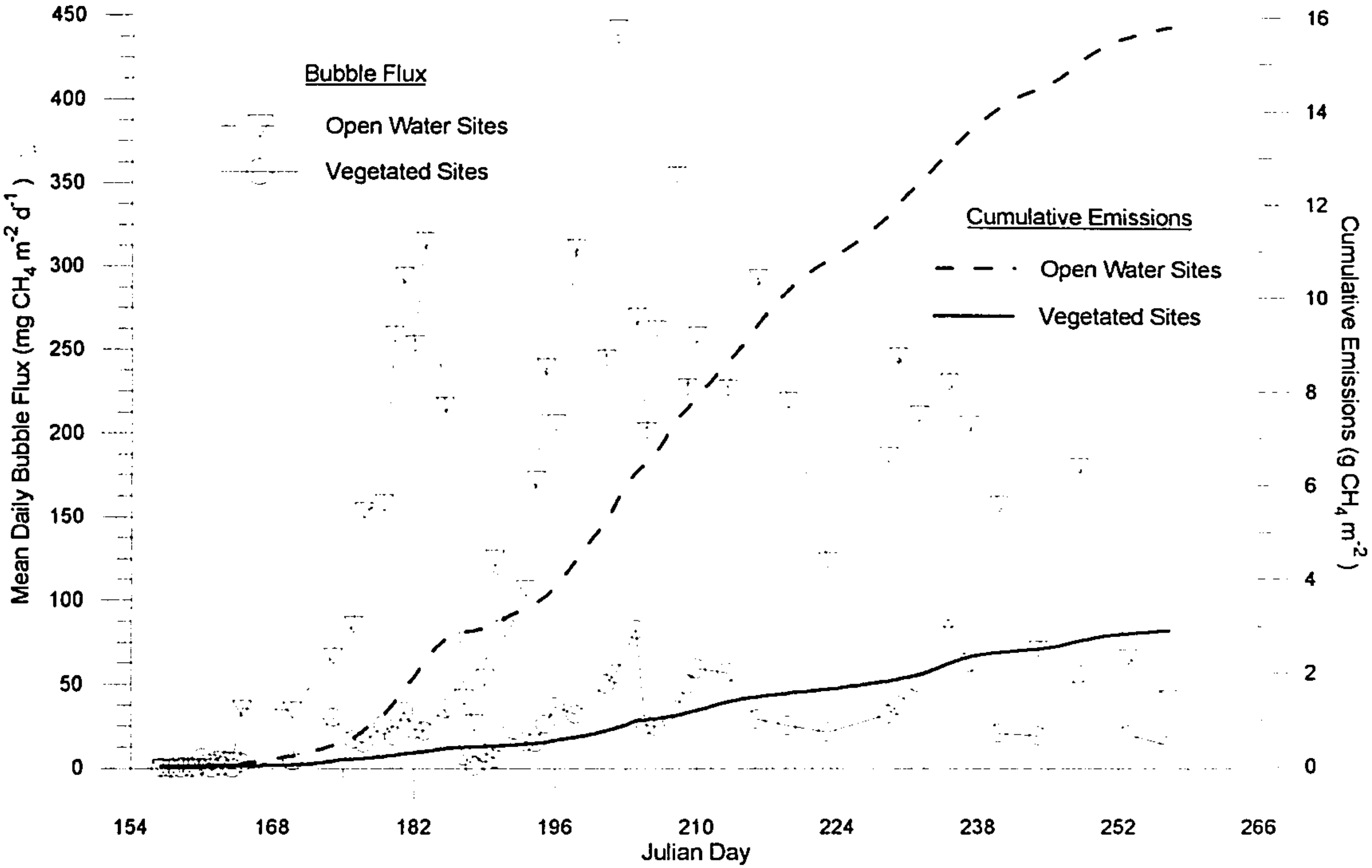


Fig. 3.16: Mean Daily Bubble CH$_4$ Flux and Cumulative Emissions

pressure were poor, their temporal trends display a high degree of synchronicity (Fig. 3.17). Atmospheric pressure was also found to be a significant component of flux regression equations (see below).

Table 3.5 Spearman Pairwise Correlation Coefficients (r)
Between Mean Daily Bubble Fluxes and Environmental Variables

Variable	z	Mean Daily Open Water Flux	Mean Daily *Carex* Site Flux	N
Mean Daily Sediment Temperatures	0	0.69	0.55	51
	5	0.75	0.60	
	10	0.82	0.66	
	20	0.68	0.75	
	40	0.31	0.71	
	75	0.31	0.47	
	150	0.47	0.66	
PAR		-0.02	0.02	51
Underwater PAR		-0.04	-0.11	50
Pond Stage		0.16	0.14	51
Atmospheric Pressure		-0.07	-0.26	51
Atm. Pressure Lag = 1 day		-0.12	-0.26	
Atm. Pressure Lag = 2 days		-0.20	-0.09	
24-hr change in mean daily pressure		0.07	0.03	
24-hr change in mean pressure, lag 1 day		0.11	-0.12	
24-hr change in mean pressure, lag 2 days		-0.07	-0.15	

	24-hr Change in Open Water Flux	24-hr Change in *Carex* Site Flux	N
24-hr change in mean daily pressure	-0.19	-0.23	50
24-hr change in mean pressure, lag 1 day	0.35	-0.36	
24-hr change in mean pressure, lag 2 days	0.15	0.11	

z- depth below sediment-water interface

Fig. 3.18 shows the temporal trend of mean daily bubble flux with mean daily 20 cm sediment temperatures and pond level. The sudden 14 cm drop in pond water level caused by dam failure on June 22 (J.d. 173), and coincident sediment temperature increase, were associated with a large increase in mean daily open water bubble flux from 66 to 315 mg CH_4 m^{-2} d^{-1}. Both open water and vegetated site fluxes then

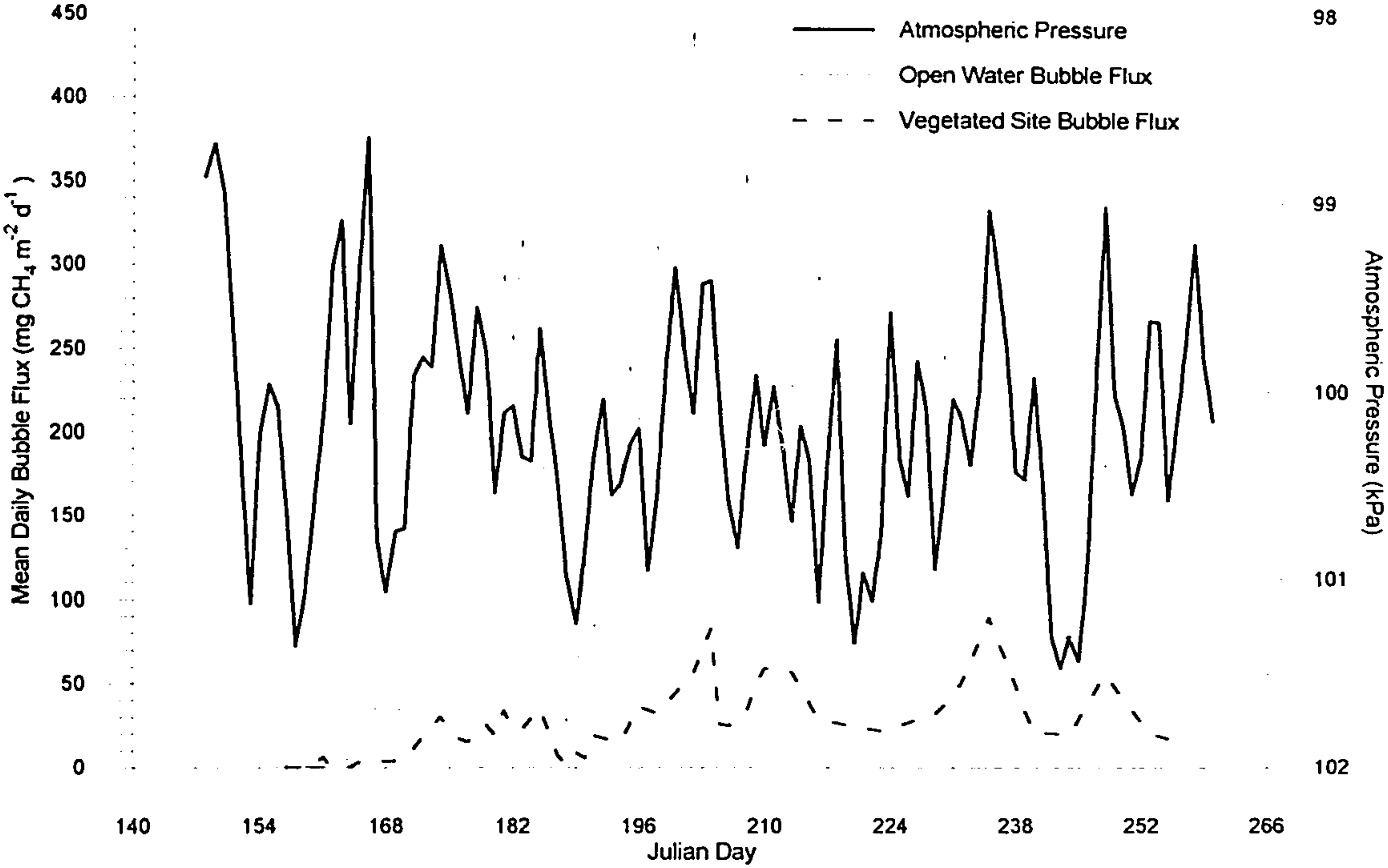


Fig. 3.17 Mean Daily Bubble Flux with Mean Daily Atmospheric Pressure
Note atmospheric pressure axis is inverted

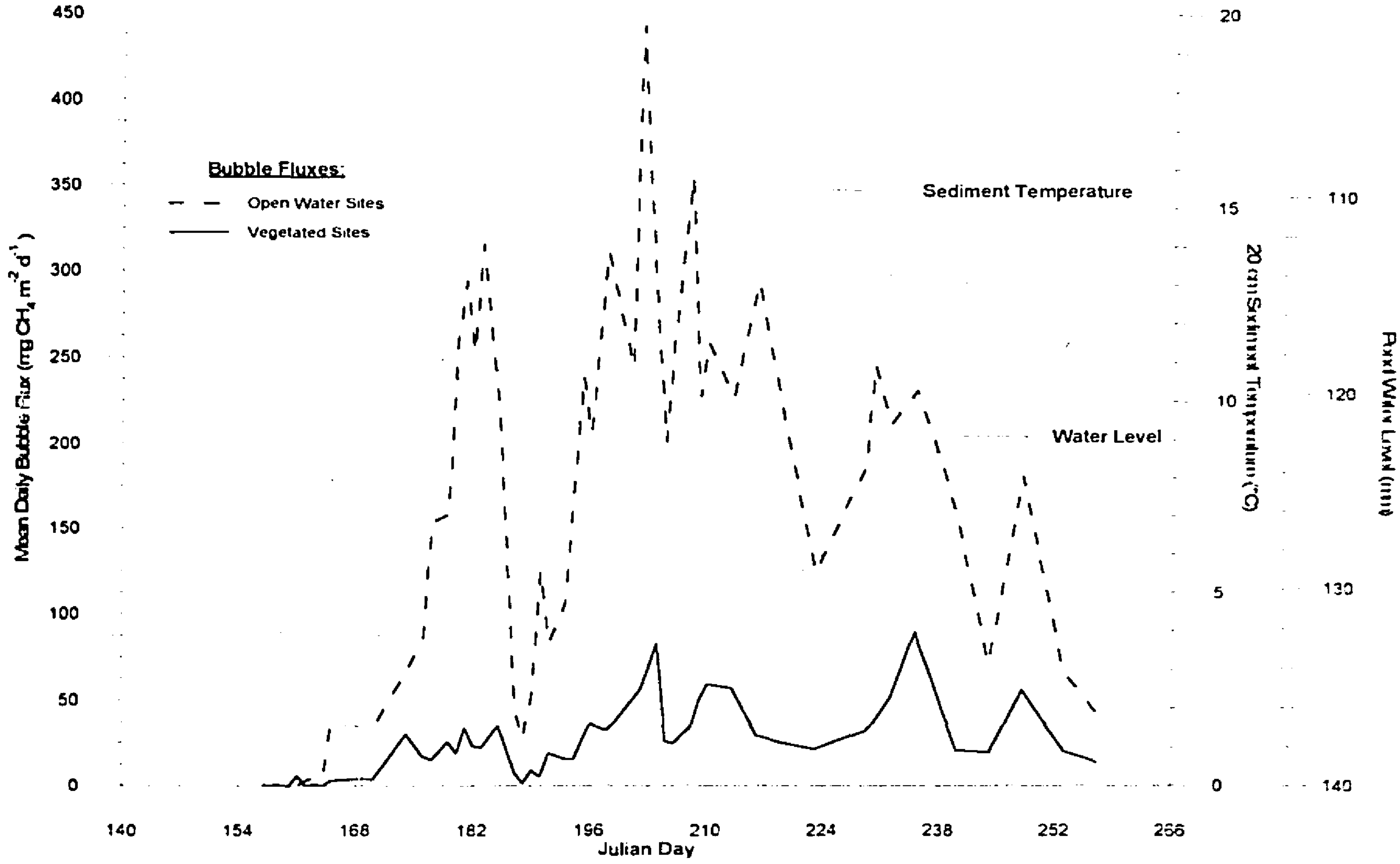


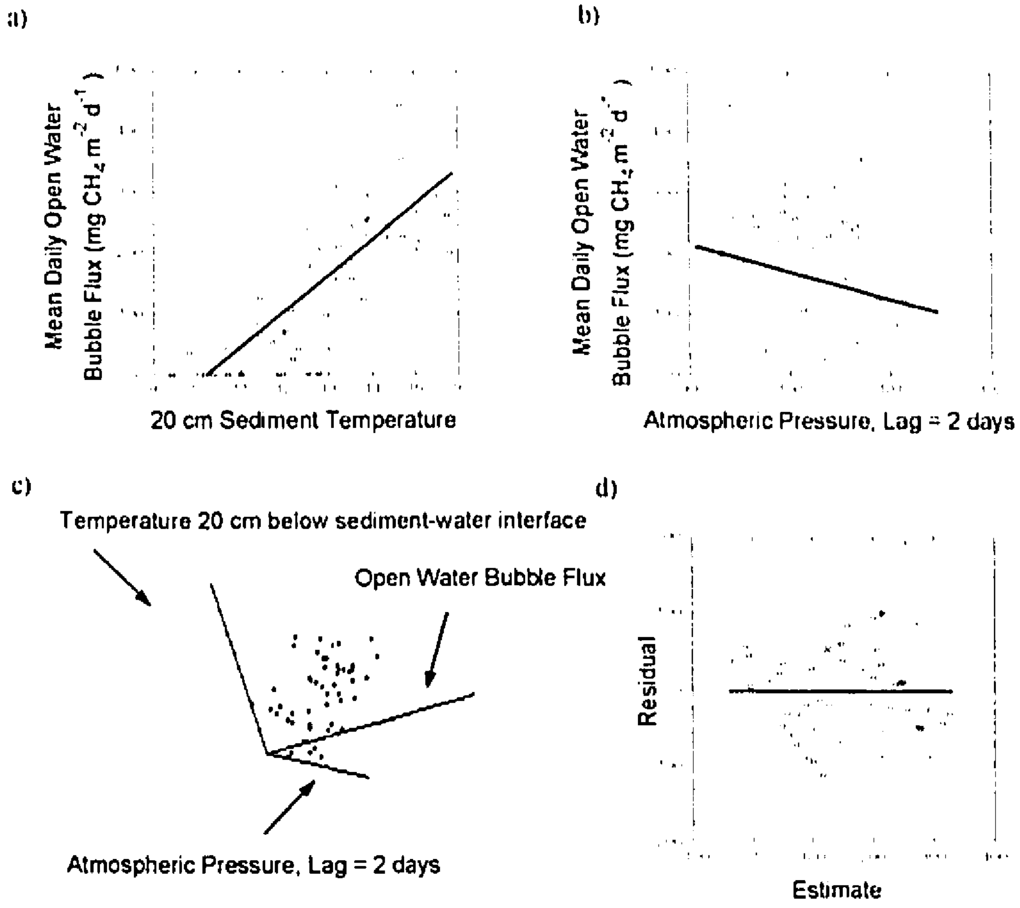
Fig 3.18: Mean Daily Bubble Flux, Sediment Temperature and Pond Water Level
Note water level axis is inverted

declined dramatically on July 4 (J.d. 185). This decline corresponded to the recovery of the pond water level, a reduction in sediment temperatures, and a rise in atmospheric pressure. Subsequent smaller changes in mean daily fluxes were also occasionally synchronous with changes in sediment temperature.

Sediment temperature at 20 cm depth was the strongest predictor of bubble fluxes, explaining 64% and 45% of the variance in mean daily fluxes from open water and vegetated sites, respectively. Atmospheric pressure terms explained a further 4% and 11% of variance in these fluxes. The regression equations, with significance levels, scatter plots of the relationships, and distribution of regression residuals are shown for open water sites in Fig. 3.19, and for vegetated sites in Fig. 3.20. All predictive variables were significant to $p<0.05$.

3.3.4 Bubble Release from Storage

The partitioning of dissolved and gaseous CH_4 stored in sediments depends on temperature and pressure according to Henry's law (e.g. Lerman, 1979). Equilibrium between dissolved and gaseous CH_4 in sediments cannot be demonstrated here because they were not determined concurrently. Using Henry's law, however, the onset of bubbling (J.d. 165-170) was determined to coincide with the saturation of dissolved CH_4 in porewaters at most piezometer sites. Chanton et al. (1989) have shown that dissolved CH_4 in porewaters maintains equilibrium with CH_4 bubbles in wetland sediments over changing pressures and temperatures. Therefore, changes in CH_4



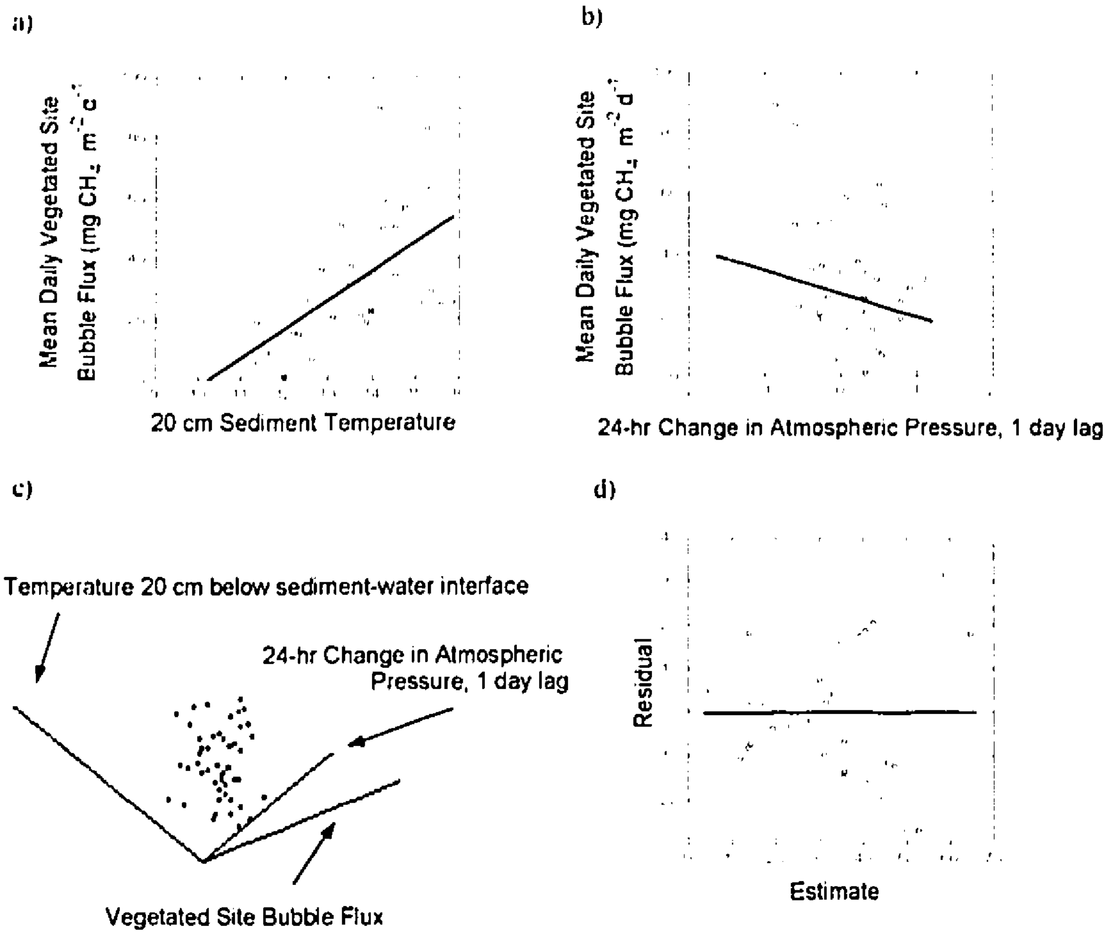
Multiple Linear Regression Equation:

Mean Daily Open Water Bubble Flux = -4448 + 67.7 Temp
+ 36.6 Atm. Press. Lag 2 days + 0.45 PAR

r^2 =0.70 N =51 SEE = 63

F = 37.2 p<0.0005

Fig. 3.19: Regression Analysis of Mean Daily Open Water Bubble Fluxes
a) Sediment Temperature at 20 cm depth
explains 64 % of variance in mean open water bubble fluxes
b) Atmospheric Pressure 2 days prior to measurement
explains a further 4% of variance; PAR explains a further 4% (not shown)
c) 3D plot of most significant predictors with flux
d) Distribution of regression residuals is homogeneous



Multiple Linear Regression Equation:

Mean Daily Vegetated Site Bubble Flux = -104.1 + 10.0 Temp - 13.5 Change in Atm. Press. Lag 1 day

$r^2 = 0.55$ N = 51 SEE = 14.8

F = 29.3 $p < 0.0005$

Fig. 3.20: Regression Analysis of Mean Daily Vegetated Site Bubble Fluxes
a) Sediment temperature at 20 cm depth
explains 45 % of variance in mean vegetated site bubble fluxes
b) 24-hr change in atmospheric pressure 1 day prior to measurement
explains a further 11% of variance
c) 3D plot of predictors with flux
d) Distribution of regression residuals is homogeneous

inventories calculated from dissolved CH_4 concentrations may be used to indicate changes in the total pool of CH_4 in the sediments of the beaver pond.

Bubble fluxes could not be detected by changes in porewater CH_4 storage. Spearman correlation coefficients were computed between interpolated % 24-hour changes in porewater CH_4 storage and bubble fluxes (Table 3.6). Many correlations are negative, indicating that increasing bubble flux is sometimes associated with declining porewater CH_4 concentrations. Regression analysis yielded no significant relationship, however, between changes in porewater CH_4 storage and changes in bubble flux. Bubble fluxes comprised merely 4-6% of stored CH_4, exceeding 10% only on three sampling dates. A significant relationship would not be expected since bubbles comprised a small fraction of potential CH_4 emissions.

Table 3.6 Spearman Pairwise Correlation Coefficients (r) Between 24-hour % Change in Bubble Fluxes and Porewater CH_4 Concentrations

Relative % Change in Porewater CH_4 concentration	Depth of Piezometer	Relative % Change in Mean Daily Vegetated Site Bubble Fluxes	Relative % Change in Mean Daily Open Water Bubble Fluxes	n
Shallow Piezometer Nest (approx. water depth 0.2 m)	1.0 m	0.36	-0.41	10
	0.7 m	0.00	-0.03	10
	0.5 m	-0.52	-0.15	12
	0.3 m	-0.25	0.35	12
	0.1 m	0.06	0.05	12
Intermediate Piezometer Nest (approx. water depth 1.0 m)	1.0 m	-0.21	-0.46	10
	0.7 m	-0.41	-0.27	10
	0.5 m	-0.32	0.22	12
	0.3 m	-0.22	0.19	12
	0.1 m	-0.04	-0.20	12
Deep Piezometer Nest (approx. water depth 1.7 m)	1.0 m	0.00	-0.83	8
	0.7 m	0.26	-0.21	10
	0.5 m	-0.55	0.06	11
	0.3 m	-0.47	0.06	11
	0.1 m	-0.08	0.08	11

3.3.5 Gross Bubble Storage and Production

Estimates of bubble CH_4 reservoirs were obtained on Aug. 27, 1994 (J.d. 239) by prodding sediments to a depth of approximately 1 m, at two previously undisturbed boardwalk sites, until no more bubbles were observed. At a site vegetated with grasses by the pond margin, 5.4 g CH_4 m^{-2} was collected, while 7.1 g CH_4 m^{-2} was collected at a non-vegetated deep water (1.4 m) site. The pond margin released numerous small bubbles, while the deeper site released fewer, but much larger bubbles. Bubble volumes were 15.6 L m^{-2} at the vegetated site, and 16.5 L m^{-2} at the open water site. To my knowledge, these are the largest bubble storage volumes recorded (see Chanton and Dacey, 1991).

The funnels were kept *in situ* and within two weeks (to J.d. 253) the vegetated site had emitted a further 0.8 g CH_4 m^{-2}, and the open water site had emitted 0.11 g CH_4 m^{-2}. Further prodding yielded 4.8 g CH_4 m^{-2} produced at the margin, and 0.8 g CH_4 m^{-2} produced at the deep water site. Total production, calculated as the sum of all bubbles produced since the sites had been initially prodded, was 399 mg CH_4 m^{-2} d^{-1} at the vegetated site, and 68 mg CH_4 m^{-2} d^{-1} at the open water site.

3.3.6 Isotopic Analysis of Bubble CH_4

CH_4 in bubbles (Fig. 3.21) from vegetated sites was significantly heavier in carbon (C) ($\delta^{13}C$ = -55.8 ± 1.8 ‰, n = 17) (t = 4.78, $p<0.05$) and significantly lighter in hydrogen (H) (δD (deuterium) = -378.1 ± 15.6 ‰, n = 17) (t = -2.43, $p<0.05$) than bubbles from open water sites ($\delta^{13}C$= -59.6 ±.2.6 ‰; δD = -362.9 ± 18.7 ‰, n = 13).

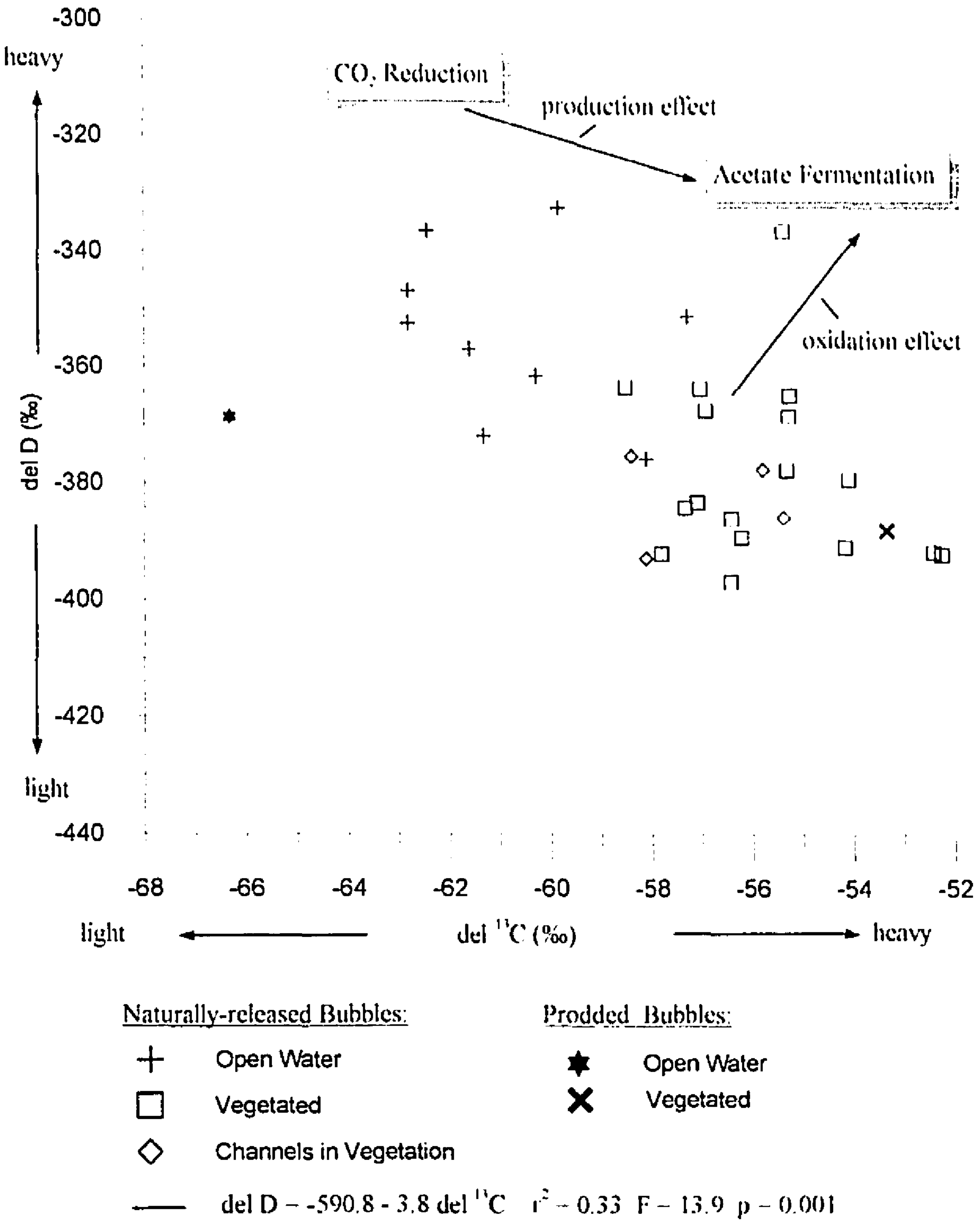


Fig. 3.21: Isotopic Composition of CH_4 in Bubbles
with line of best fit for naturally released bubbles, and slopes for
production (Whiticar et al., 1986) and oxidation (Coleman et al., 1981) effects

Regression analysis of the isotopic composition of all naturally-released bubbles yielded the equation:

$$\delta D(‰) = -590.8 - 3.8\,\delta^{13}C(‰) \qquad r^2 = 0.33 \qquad p<0.05$$

Bubbles obtained by prodding were similar to naturally-released bubbles at a vegetated site, but isotopically lighter compared to naturally-released bubbles at an open water site (Fig. 3.21).

Bubbles collected from open water sites along the beam transect (which comprised small channels between the vegetation) were intermediate in composition, compared to bubbles from open water sites along the line transect and bubbles from all vegetated sites (Fig. 3.21). The isotopic signature of bubbles from these channels was more similar, however, to bubbles from vegetated sites (δD: $t=0.59$, $p>0.05$; $\delta^{13}C$: $t=1.21$, $p>0.05$) than those from open water sites (δD: $t=4.60$, $p<0.005$; $\delta^{13}C$:$t=-3.32$, $p<0.01$).

These results indicate differences in isotopic composition between open water and vegetated sites which are likely due to a difference in production processes. If the differences were due to greater oxidation at vegetated sites, one would expect CH_4 in bubbles emitted from vegetated sites to be isotopically heavier in both carbon and hydrogen compared to open water sites. CH_4 oxidizers preferentially consume the lighter isotopes of C and H (Coleman et al., 1981; see direction of oxidation effect line shown in Fig. 3.21). However, the slope of the regression line through the isotope data in Fig. 3.21 is similar to a slope determined by Whiticar et al. (1986), expressing differences created by different production pathways. This indicates that different substrates are used by methanogens between vegetated and open water sites. At open water sites, CO_2 is the dominant substrate for CH_4 production while in vegetated sites, CH_4 is produced by acetate reduction.

3.4 Sediment-Water Fluxes

Between June 25 through August 20 (J.d. 176 - 232), 39 fluxes of CH_4 across the sediment-water interface were measured using benthic chambers. No fluxes were obtained over emergent macrophytes, although some chambers contained submergent macrophytes. All sites are, therefore, analogous to chamber and bubble flux open water sites. There was no significant difference between fluxes over submergent macrophytes and those with no vegetation ($t=0.80$, $p>0.05$).

Some difficulties arose while using the benthic chambers. The chambers had to be held in place on the pond bottom and some disturbance resulted. CH_4 would also continue to accumulate in the chambers between sampling (despite venting) so that the chambers had to be removed and replaced, exacerbating the disturbance. It is not known if the measurements reflect diffusive fluxes or disturbance of the sediments causing high but linear CH_4 emissions.

Two sediment-water fluxes, measured near the pond margin (1923.1 ± 476 mg CH_4 m^{-2} d^{-1}), were much greater than fluxes obtained elsewhere along the boardwalk (183.9 ± 112 mg CH_4 m^{-2} d^{-1}). Because the reasons for this difference are not understood and because this difference was so pronounced, the fluxes obtained from the pond margin were not included in subsequent analyses.

Sediment-water (benthic) chamber and water-air (floating) chamber fluxes were rarely measured on the same day, so comparisons (Fig. 3.22) were made using all data for the period from June 25 through August 20. Fluxes across the sediment-water interface (183.9 ± 112 mg CH_4 m^{-2} d^{-1}) were significantly greater ($U = 31$, $p<0.005$) than fluxes across the water-air interface from *Carex* sites (96.3 ± 80 mg CH_4 m^{-2} d^{-1}). The sediment-water fluxes were higher but not significantly greater ($U = 64$, $p>0.05$) than chamber fluxes from open water sites (138.6 ± 154 mg CH_4 m^{-2} d^{-1}).

3.4.1 Sediment and Water Column CH_4 Oxidation

The observed difference between mean daily sediment-water fluxes (183.9 mg CH_4 m^{-2} d^{-1}) and mean daily open water-air fluxes (138.6 mg CH_4 m^{-2} d^{-1}) may be due to oxidation in the water column. By difference, the average amount of CH_4 oxidation is 45.3 mg CH_4 m^{-2} d^{-1}, for this time interval.

Sediment-water flux measurements using methyl fluoride (MF) to inhibit CH_4 oxidation yielded mean fluxes of 353.5 ± 236 and 435 ± 788 mg CH_4 m^{-2} d^{-1}, on July 1 (J.d. 192) and July 15 (J.d. 196), respectively (Fig. 3.22). The differences between these fluxes and the sediment-water diffusive fluxes without MF on the same dates were 95 and 271 mg CH_4 m^{-2} d^{-1}. These differences may represent oxidation in the upper layers of the sediments and the bottom 25 cm of the water column, but the standard deviations associated with the measured MF-inhibited fluxes are greater than the differences attributed to oxidation so the data should be interpreted with a great deal of caution.

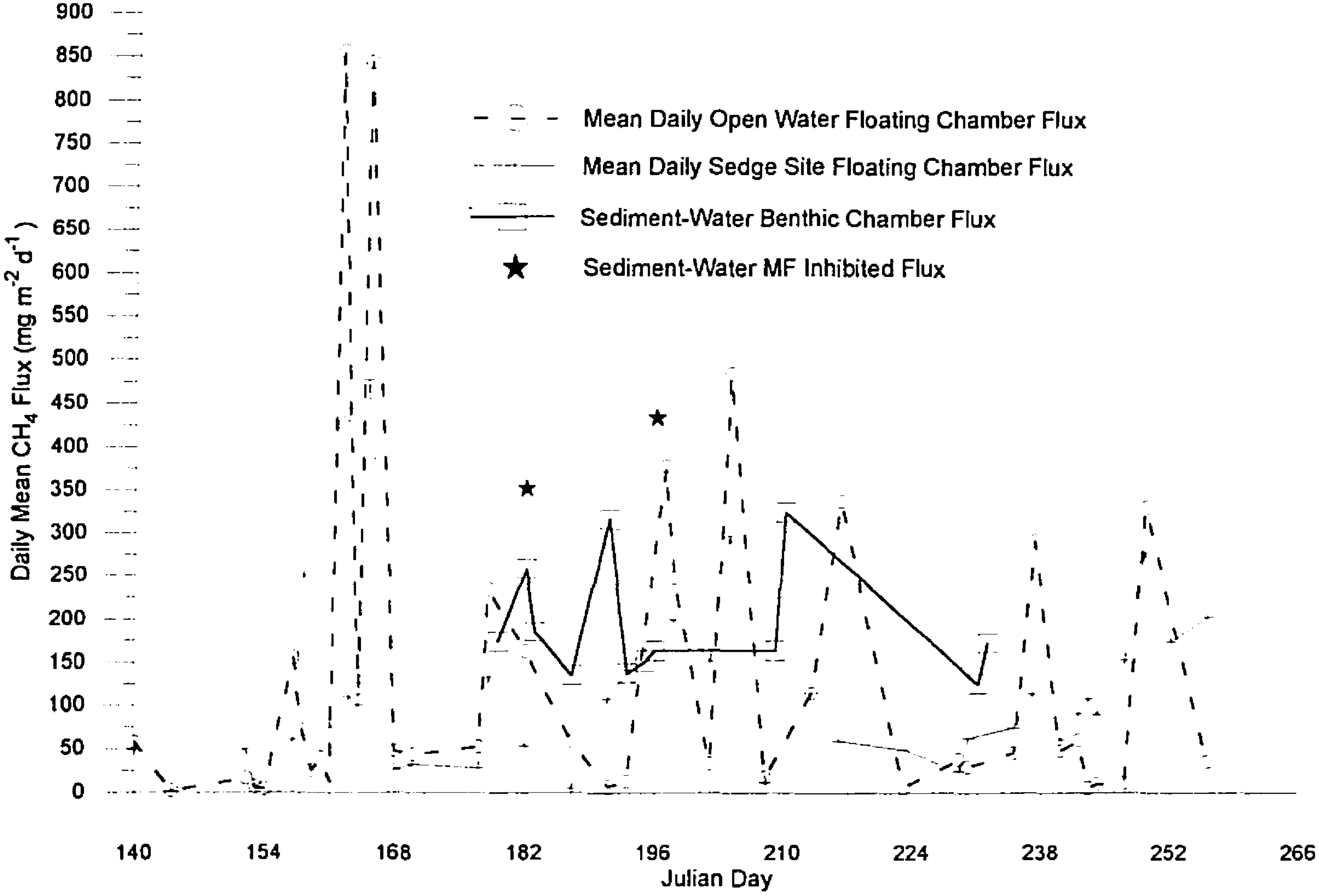


Fig. 3.22: Comparison of Water-Air and Sediment-Water CH_4 Fluxes

3.5 Sediment-Water Interface CH_4 Profiles

Ten profiles of CH_4 concentrations in the sediments were obtained from June 23 to September 11 (J.d. 174 - J.d. 254) (Fig. 3.23). Generally, the profiles showed lowest CH_4 concentrations in the water column, rapidly increasing concentrations across and below the sediment-water interface, and greatest CH_4 concentrations at depth. Only 2 profiles (Fig. 3.23a and f) showed significant decreases in CH_4 at depth. The profile from a floating mat (Fig 3.5.1h) showed a decrease in CH_4 at depth because the peeper penetrated the mat and measured CH_4 in the water column beneath it.

CH_4 concentrations were generally lower in the profiles from shallow water sites (range 0.9 to 1.7% CH_4) than from deeper sites (range 1.7 to 2.5% CH_4). The layer below the sediment water interface, in which the concentrations of CH_4 increased steeply, was also thicker (9 to 16 cm) for shallow water sites (Fig. 3.23 b,c,f and h) than for deep-water sites (3 to 9 cm) (Fig. 3.23 a,d,e and g). Oxidation may be partially responsible for these steep gradients, therefore the oxidation zone may penetrate deeper in shallow water sediments. It is important to note, however, that an algal layer was observed even at the deepest site (Fig. 3.23d), indicating that most areas of the pond receive enough light to support algal populations and may therefore also support populations of methanotrophs.

Fluxes of CH_4 from the sediments were modelled using a Fickian diffusion model, an estimate of porosity (0.8), and the CH_4 gradient between the depth of maximum CH_4 concentration and the sediment water interface (Table 3.7). These fluxes are shown in Fig. 3.24 for comparison with average daily water-air diffusive

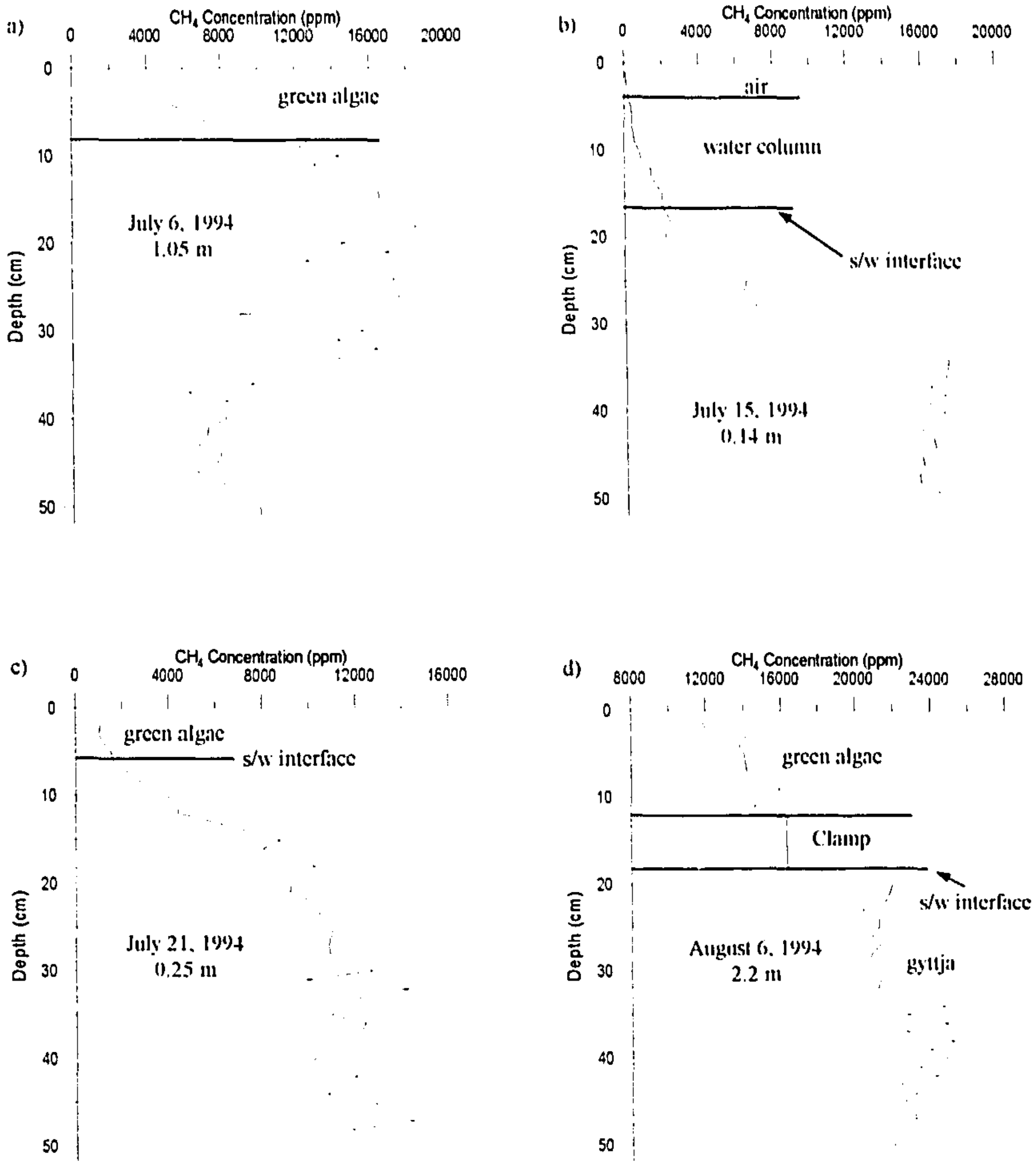


Fig. 3.23: Peeper Porewater CH_4 Profiles
with mid-date between peeper placement and removal, depth of water at site,
and characteristics observed on peeper after removal

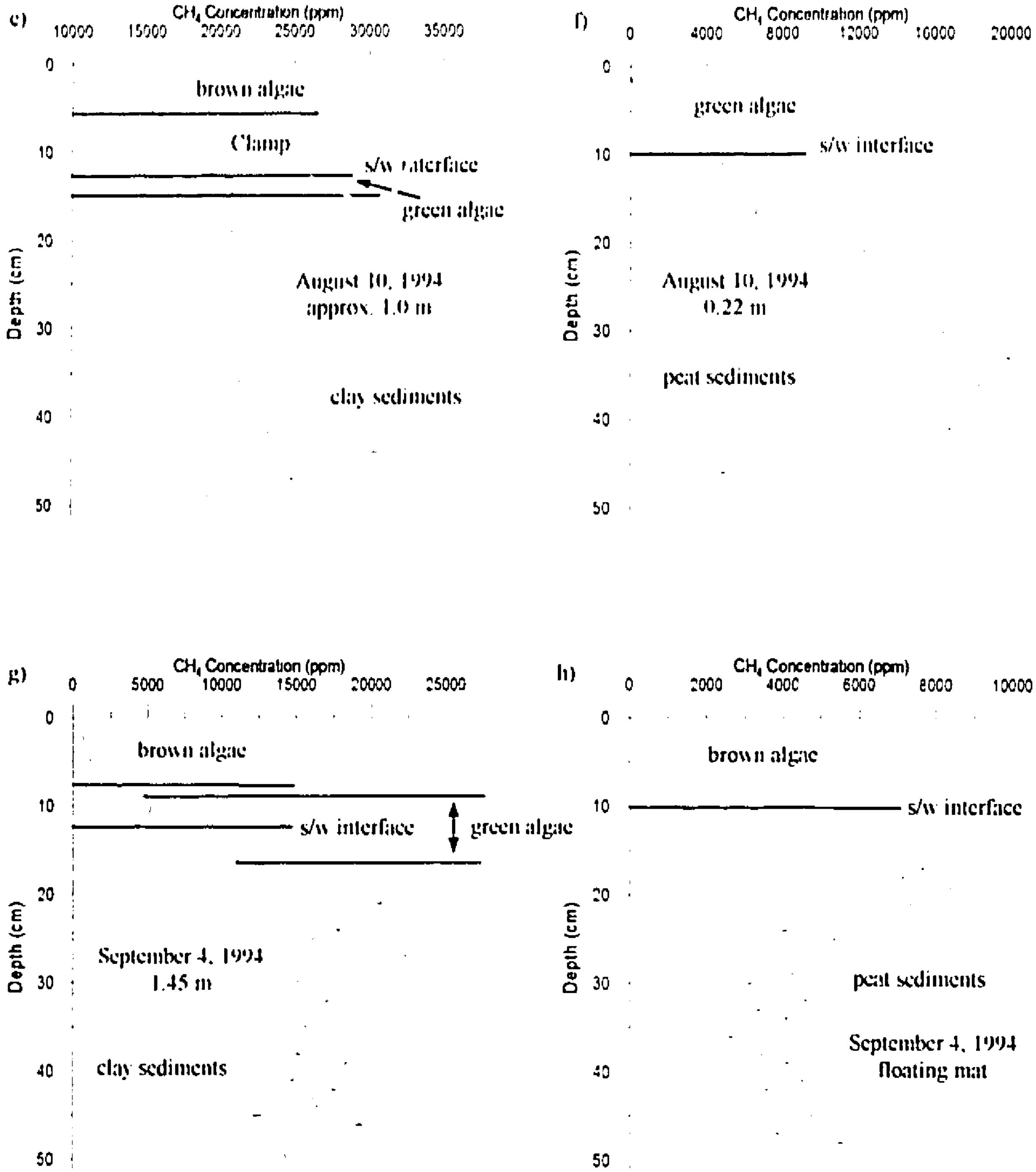


Fig. 3.23: Peeper Porewater CH$_4$ Profiles, cont.

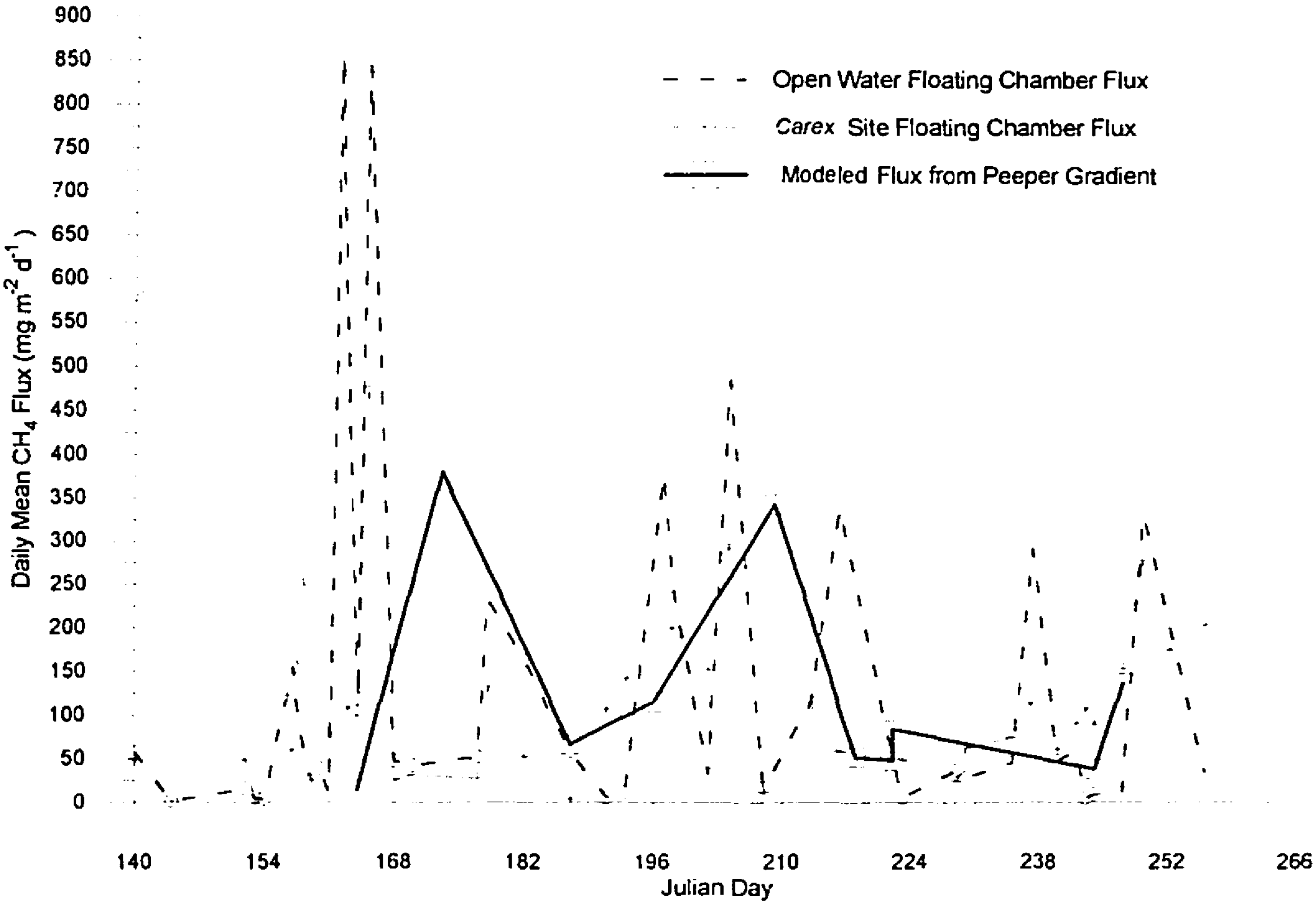


Fig. 3.24. Modeled Sediment-Water Diffusive CH_4 Fluxes from Peeper Profiles and Measured Water-Air Fluxes from Floating Chambers

fluxes. The trends are similar, but the modelled sediment-water fluxes are neither consistently greater nor smaller than the measured mean daily open water-air (floating chamber) fluxes.

Table 3.7 Fickian Sediment-Water Diffusive Fluxes Modelled from Peeper Profiles

Date[1]	Depth of Water (m)	Modelled Flux
June 13 (J.d. 164)	0.7	15.2
June 22 (J.d. 173)	1.1	380.4
July 6 (J.d.187)	1.05	67.0
July 15 (J.d. 196)	0.14	115.3
July 21 (J.d. 209)	0.25	343.2
Aug. 6 (J.d. 218)	2.2	52.4
Aug. 10 (J.d. 222)	1.0	48.2
Aug. 10 (J.d. 222)	0.22	83.8
Sept.1 (J.d. 244)	1.45	136.3
Sept 4 (J.d. 247)	0.02 (floating mat)	38.5

[1] - mid-date between peeper placement and removal

3.6 Water Column CH_4 Profiles

From June 3 through September 11 (J.d. 154 - J.d. 254), a total of 20 profiles of CH_4 concentrations in the water column (Fig. 3.25) were obtained from 3 different sites in the beaver pond. The majority of these (e.g. Fig. 3.25 d-i) were taken from the tower platform at the end of the boardwalk, adjacent to the pond level gauge. The first three water profiles shown (Fig. 3.25 a-c), and two others taken in July (not shown), were sampled from shallower sites.

Most profiles were stratified, with the highest concentrations of CH_4 close to the sediment-water interface, and steeply declining concentrations in the bottom 10 to

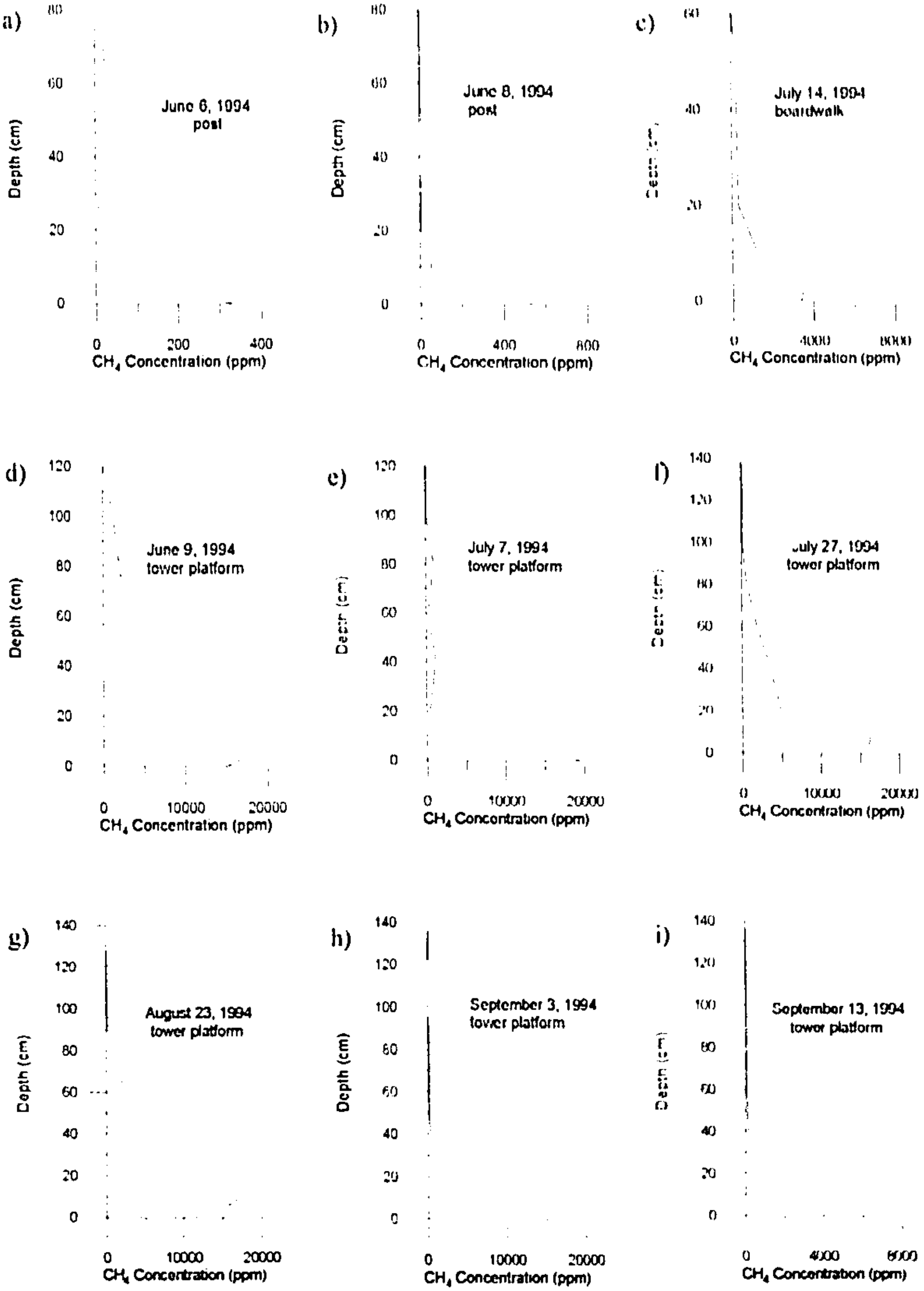


Fig. 3.25 Water Column CH$_4$ Profiles

20 cm. Shallow water sites had lower CH_4 concentrations at the sediment-water interface (1259 ± 1302 ppm) than the deeper platform site (15218 ± 4806 ppm). The sediment-water interface CH_4 concentrations were often greater than those observed in the peeper profiles (see Fig.s 3.23 and 3.25). The peeper profiles and water column profiles were never taken at the same sites, however, and these differences illustrate the high spatial variability in CH_4 concentrations observed in the beaver pond.

Bottom-water CH_4 concentrations were fairly consistent at the platform site from June 9 through Sept. 3 (J.d. 160 - J.d. 246) (16399 ± 3948 ppm), but decreased in mid-September (J.d.252 - 256) (7539 ± 510 ppm). This is consistent with the decrease in porewater CH_4 observed at the same time (see Section 3.7).

3.6.1 Isotopic Composition of CH_4 in the Water Column

Two samples of CH_4 from a profile at the tower platform were analysed for H and C isotopes (see Fig. 3.28). CH_4 from the sediment-water interface was lighter both in C ($\delta^{13}C$ = -63.8 ‰) and H (δD = -365.2 ‰) than CH_4 in water 6 cm above the interface ($\delta^{13}C$ = -62.3 ‰; δD = -363.1 ‰). This difference is not significant, but is consistent with a change due to oxidation as CH_4 diffuses upwards in the water column.

3.7 Porewater CH_4 from Piezometers

From June 2 (J.d. 154) through Sept. 10 (J.d. 253) CH_4 dissolved in porewaters was measured from 15 piezometers in 3 nests. Porewater CH_4 concentrations (Fig. 3.26) were initially low, dramatically increased from June 13 to July 1 (J.d. 164 - 182), then remained consistently high through the season. On the final sampling date, however, CH_4 concentrations decreased by up to 50% since the previous day. There was no consistent trend in concentration with depth between the three sites, but CH_4 concentrations were lowest near the sediment surface at the shallow, vegetated site, while highest concentrations were observed near the surface at the open water sites.

Porewater storage of dissolved CH_4 was calculated using profiles of CH_4 from piezometers, assuming a porosity of 0.8, and a profile depth of 1.5 m (Fig. 3.27). The reservoirs were large, containing up to 30 g CH_4 m^{-2} in early July. The reservoirs were similar between sites, although the piezometer nest at the deep site penetrated clay at 0.7 and 1.0 m and therefore contained less CH_4. The dissolved CH_4 reservoir was very small in the spring, but was still fairly large at the end of the field season.

3.7.1 Isotopic Composition of Porewater CH_4

Samples of porewaters from the 3 piezometer nests were analysed for isotopic composition (Fig. 3.28). Regression analysis of these samples yielded the equation:

$$\boxed{\delta D\ (‰) = -454.6 - 1.9\ \delta^{13}C\ (‰) \qquad r^2 = 0.14 \qquad p = 0.20 \qquad n = 12}$$

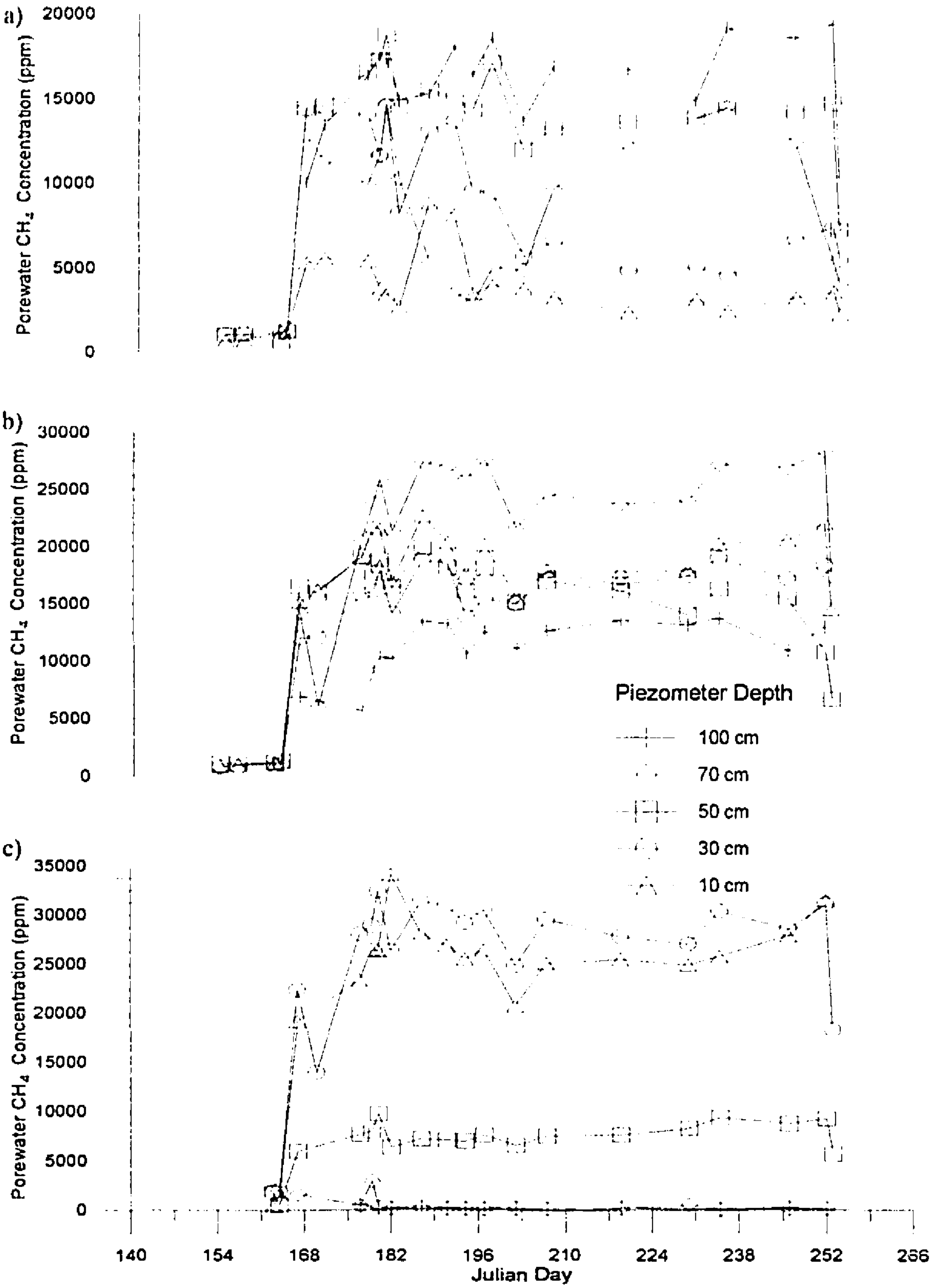


Fig. 3.26 Porewater CH_4 in 3 Piezometer Nests:
a) Shallow (0.4-0.2m) Nest; b) Intermediate (0.7-0.5m) Nest; c) Deep (2.2-2.0m) Nest
Legend applies to all figures

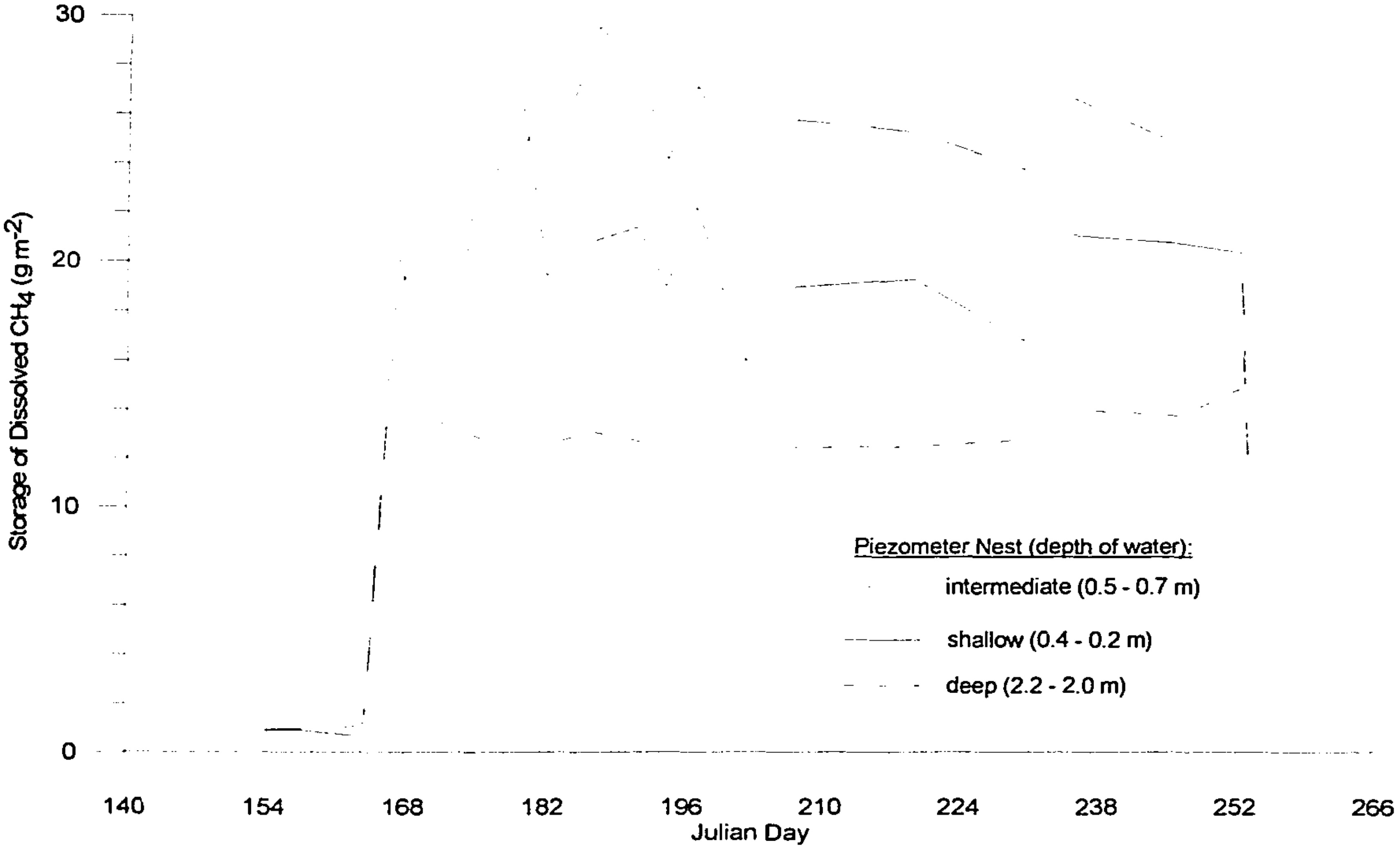


Fig. 3.27: Storage of CH_4 Dissolved in Porewater
(integrated to a depth of 1.5 m in sediments)

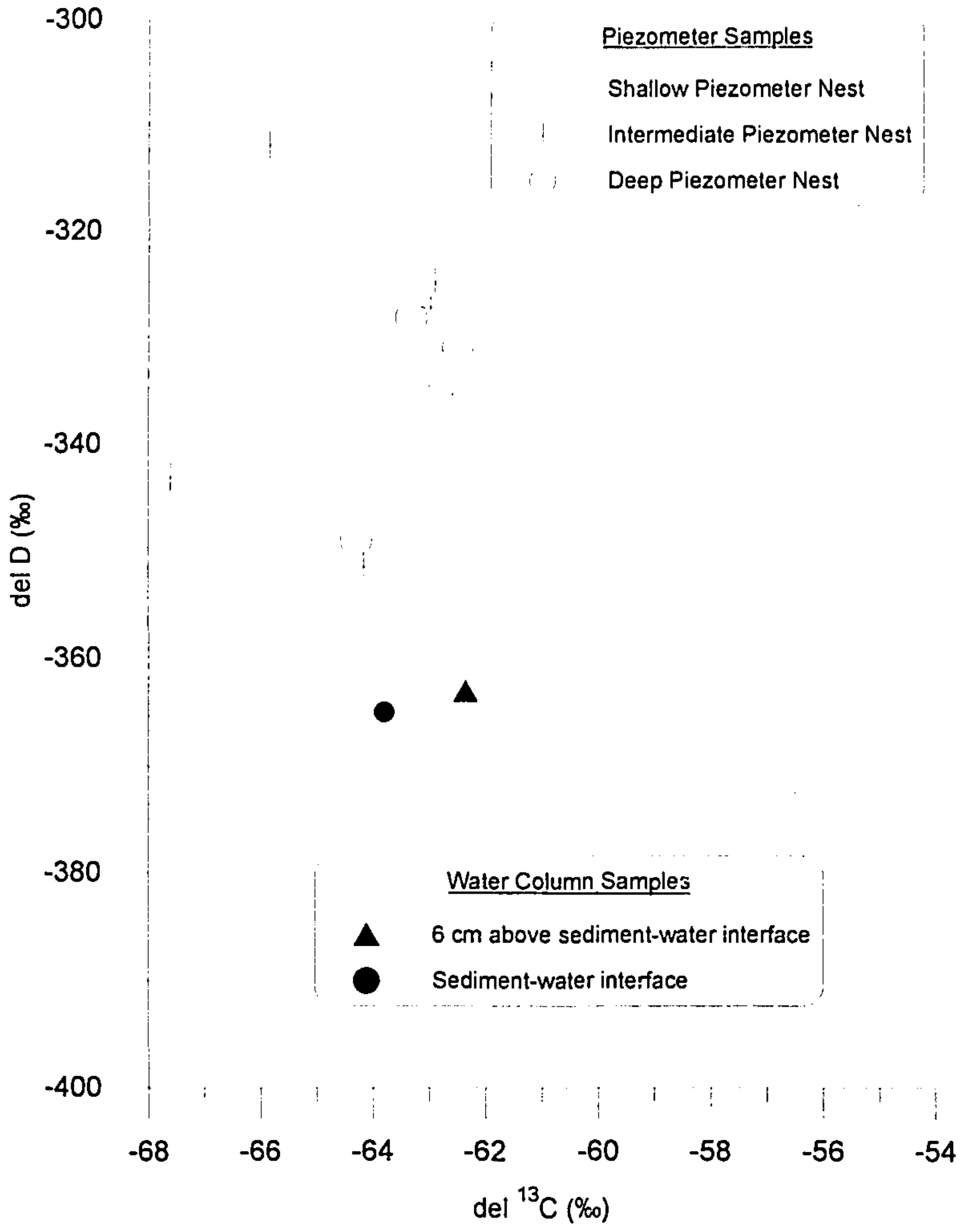


Fig. 3.28 Isotopic Composition of Porewater CH_4 with Line of Best Fit, and Isotopic Composition of CH_4 in the Water Column

There was no consistent trend in isotopic composition with porewater depth, either within a nest or between nests. The compositions of CH_4 were similar between nests, although C was significantly lighter ($U = 25$, $p<0.05$) in the intermediate nest ($\delta^{13}C = -64.7 \pm 2$ ‰) compared to the shallow nest ($\delta^{13}C = -59.6 \pm 3$ ‰).

3.8 Laboratory Incubations

Incubations of pond sediments in the laboratory showed differences in the capacity of vegetated and open water sites to produce and consume CH_4 (Fig. 3.29 and Table 3.8; note that more negative values indicate higher consumption rates). Production potentials, determined under anaerobic conditions, spanned 3 orders of magnitude, and were much greater in sediments from a floating mat than from open water sites. Consumption potentials, determined under aerobic conditions, spanned 2 orders of magnitude, and were also greatest in the floating mat core. Consumption rates were almost invariably greater than production rates. Both production and consumption were greater in a core from a deep open water site where high bubble fluxes were observed (core 2), compared to a core obtained from an open water site adjacent to the boardwalk (core 3).

CH_4 production was greatest at or near the sediment-water interface (Fig. 3.29a). In the floating mat, production was greatest at the surface, and decreased with depth. The cores from open water sites had maximum CH_4 production potentials at depths of 5 to 10 cm below the sediment-water interface, below which production decreased. Consumption potentials were highest in surface sediments (Fig. 3.29b).

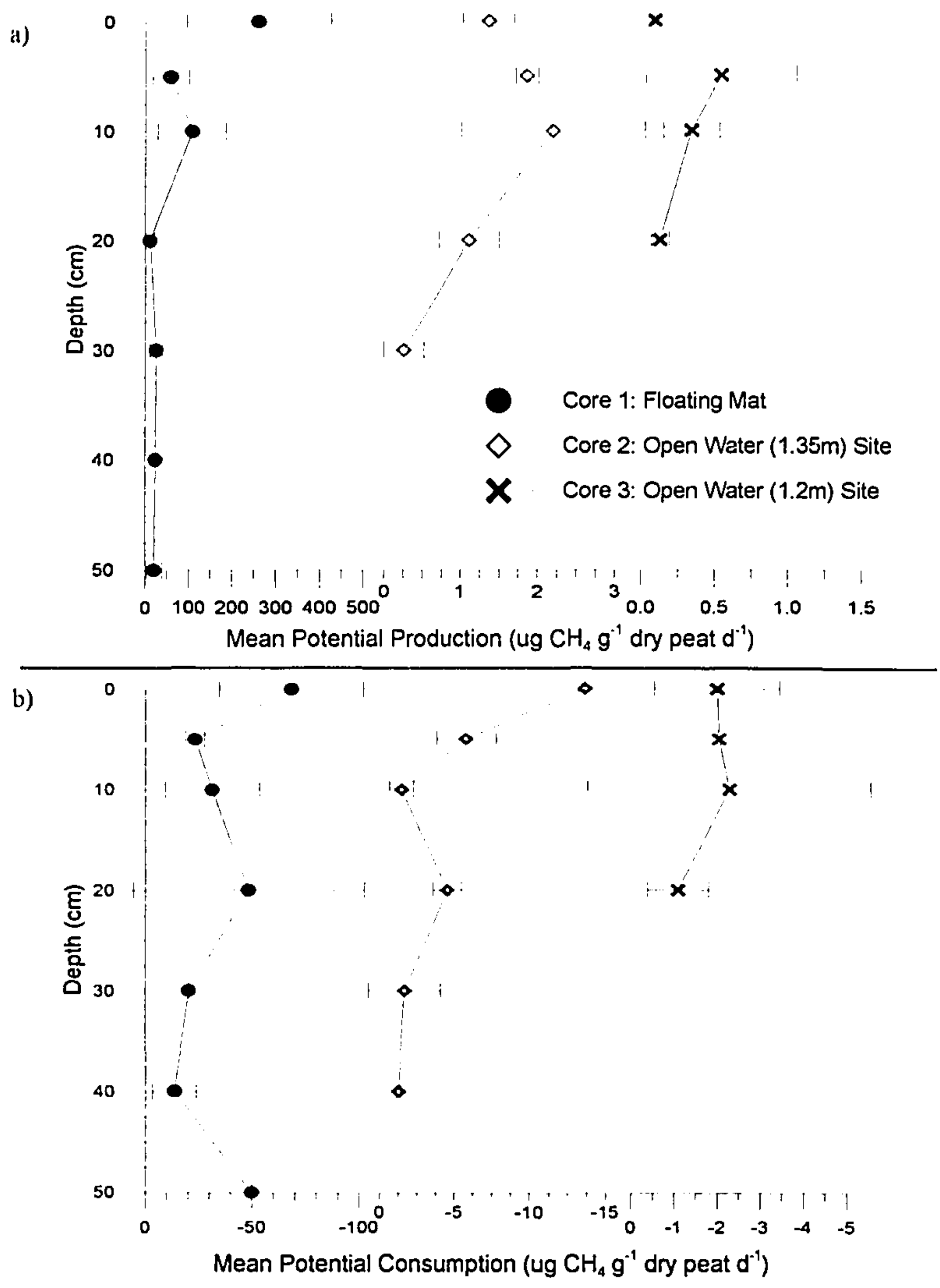


Fig. 3.29 Laboratory Incubations of Sediment Samples
a) Potential CH_4 Production and b) Potential CH_4 Consumption, with depth
Error bars indicate 1 standard deviation from mean for 3 (production) and 2 (consumption) samples. Legend applies to both graphs.

Table 3.8 Potential Anaerobic CH_4 Production and Aerobic CH_4 Consumption of Beaver Pond Sediments Determined in the Laboratory

Values are means of 3 samples (production) and 2 samples (consumption)
SD = standard deviation CV = coefficient of variation (SD:mean)

		Anaerobic CH_4 Production			Aerobic CH_4 Consumption		
Core	Depth	(ug g^{-1} d^{-1})	SD	CV	(ug g^{-1} d^{-1})	SD	CV
Core 1	0	259.6	166.3	0.64	-68.55	33.64	0.51
Floating	5	58.05	41.65	0.72	-23.33	4.50	0.19
Mat	10	107.24	78.48	0.73	-31.54	22.10	0.70
	20	11.35	10.24	0.90	-48.49	54.18	1.12
	30	25.25	14.64	0.58	-20.37	0.16	0.01
	40	23.67	6.36	0.27	-13.57	10.19	0.75
	50	20.53	18.01	0.88	-49.79	0.30	0.01
Core 2	0	1.38	.33	0.24	-13.71	0	-
Deep	5	1.88	.15	0.08	-5.87	1.99	0.34
(1.35 m)	10	2.21	1.19	0.54	-1.52	0.81	0.53
Open	20	1.12	00.39	0.35	-4.58	0.98	0.21
Water	30	0.26	0.27	1.04	-1.70	2.4	1.41
	40	0	0	-	-1.25	0.14	0.11
Core 3	0	0.11	0.01	0.09	-2.03	1.46	0.72
(1.2 m)	5	0.56	0.52	0.93.	-2.07	0.03	0.01
Open	10	0.36	0.19	0.53	-2.31	3.27	1.42
Water	20	0.14	0.06	0.43	-1.13	0.7	0.62

The variability in rates of CH_4 production and consumption were both fairly large. Standard deviations of duplicate samples for each depth ranged from 1 to 142% of the mean for the aerobic CH_4 consumption incubations. Standard deviations of CH_4 production rates ranged from 9 to 104% of the mean of triplicate samples at each depth.

Consumption and production potentials were positively related (Fig. 3.30). Layers with low production generally also had low consumption potentials, and those with higher production potentials were greater consumers of CH_4. This trend was found in all cores (see inset, Fig. 3.30), although some variation in individual samples

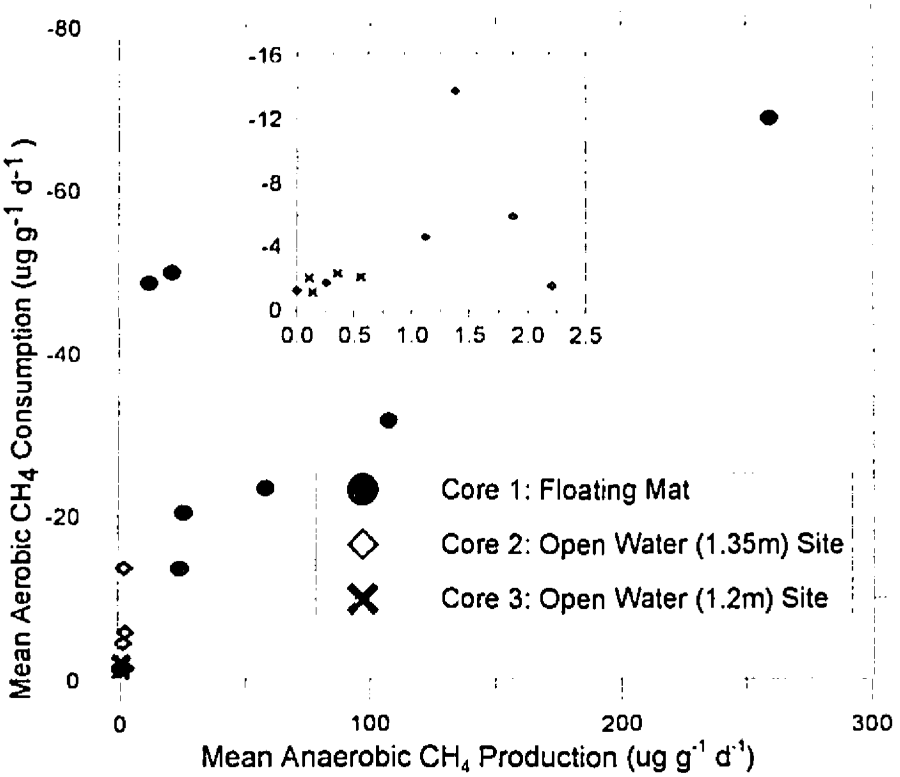


Fig. 3.30 Potential CH_4 Production vs Consumption
inset graph shows open water sites alone

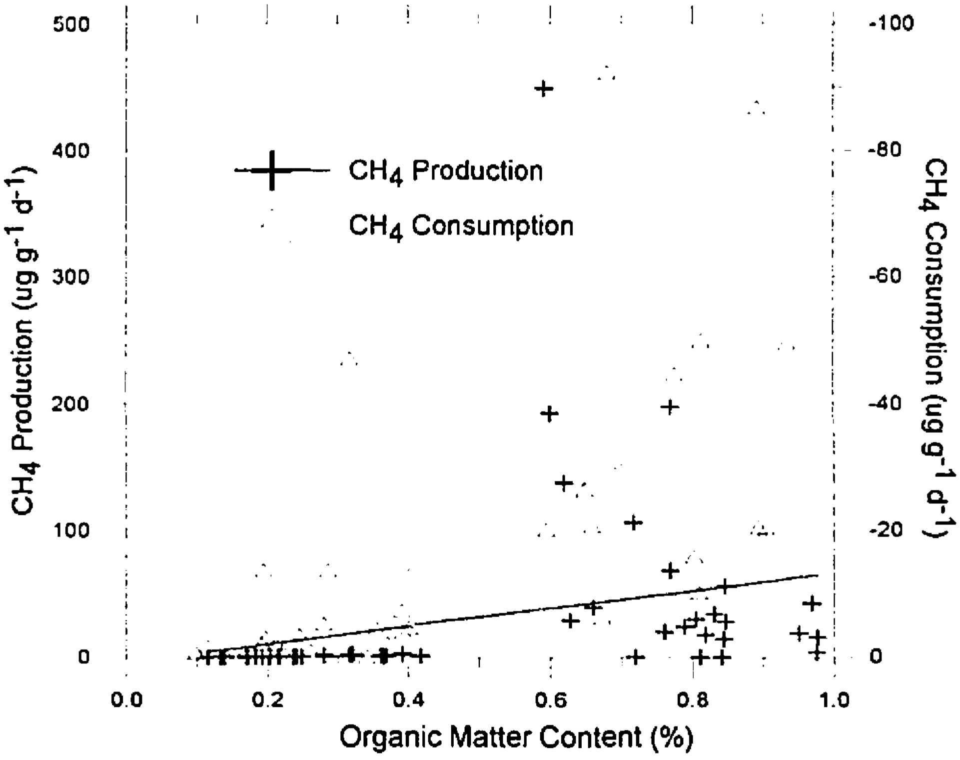


Fig. 3.31 Potential CH_4 Production and Consumption vs. Organic Matter Content

occurred. In general, open water sites had low CH_4 production and consumption potentials, and the floating mat site had much higher potentials. Linear regression of CH_4 consumption vs. production rates yielded the following equation:

Mean potential CH_4 production (ug g^{-1} dry peat d^{-1}) = -9.9 - 2.3 × mean consumption
$F = 18.4$ $r^2 = 0.55$ $SEE = 45.3$ $p < 0.005$ $n = 17$

Rates of potential CH_4 production and consumption were both positively related to the organic matter content of sediments (Fig. 3.31), although the relationship between production and organic matter was not significant.

Potential CH_4 consumption (ug g^{-1} dry peat d^{-1}) = -8.5 - 55.5 × organic content (%)
$F = 20.9$ $r^2 = 0.40$ $SEE = 18.7$ $p < 0.001$

Chapter 4: Discussion

4.0 Introduction

The research objectives and hypotheses outlined in Section 1.7 were tested during a field campaign from May through September, 1994. The contributions of CH_4 production, consumption and transport to the total flux of CH_4 from a beaver pond were determined, and the relationships among these processes and environmental variables were examined.

The following discussion will first examine the total flux of CH_4 from the beaver pond, and compare this flux and its error with the CH_4 flux reported for other boreal wetlands. The significance of beaver ponds in the regional CH_4 budget will be assessed using this comparison and preliminary estimates of the areal coverage of beaver ponds in the region. The relationships between the transport components of the flux (i.e. diffusive, bubble and plant-transported flux) and environmental variables will be examined to determine the probable controls on the transport of CH_4. The relative strengths of the production and consumption processes will be deduced. Finally, the controls of these processes will be discussed in light of evidence of differences in CH_4 dynamics between vegetated and open water areas of the beaver pond.

4.1 Total CH_4 Emissions

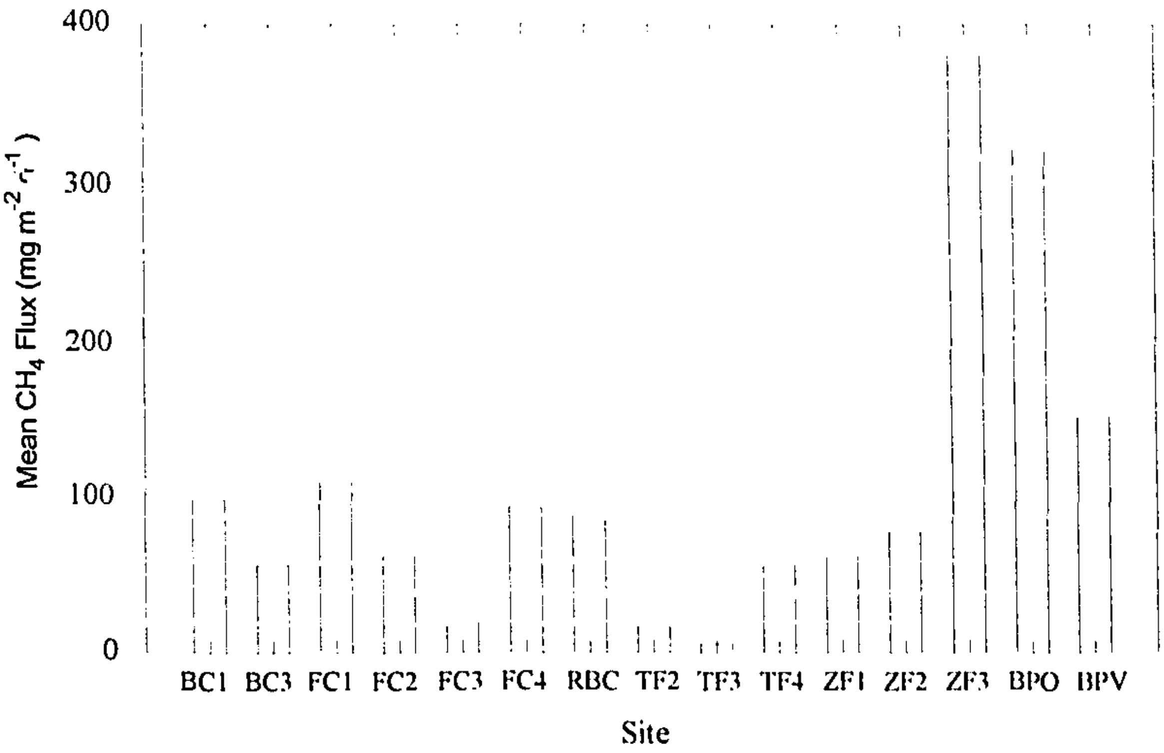
The total flux of CH_4 is the sum of the flux transported by bubbling and by diffusion. By adding the mean bubble flux and the mean diffusive flux, the total flux is calculated to be 320 mg CH_4 m^{-2} d^{-1} for open water sites and 155 mg CH_4 m^{-2} d^{-1} for vegetated sites in the pond. These fluxes are greater than the flux from other wetland types in the BOREAS northern study area (Bubier et al., 1995a), except for the flux from an open graminoid fen (Fig. 4.1). The mean fluxes from other wetlands are commonly less than 50% of the flux from the beaver pond.

Total annual emissions, calculated by interpolating the mean daily flux data to account for missing sampling dates, and integrating the areas under the curves, are summarized in Fig. 4.2. Cumulative diffusive flux (measured by floating chambers) was similar at open water and vegetated sites, but bubble-transported flux was 5-times greater at open water sites. Therefore, the total flux of CH_4 was twice as great at open water sites (30.1 g CH_4 m^{-2} y^{-1}) compared to vegetated sites (14.2 g CH_4 m^{-2} y^{-1}).

Because differences in flux were observed between open water and vegetated sites, it is important to weight the total flux for the pond according to the relative areas covered by vegetation and open water. Using an aerial photograph (Manitoba Ministry of Natural Resources), the pond was determined to be 5 ha, with vegetation covering 75% of the pond area and open water comprising the remaining 25%. An areal-weighted flux was determined by summing the products of the annual total emissions by the percent cover for the two classes:

$$\text{(Open Water Annual Flux} \times \text{\% Cover)} + \text{(Vegetated Annual Flux} \times \text{\% Cover)}$$
$$= \text{Areal-Weighted Annual Flux}$$

$$(30.1 \text{ g } CH_4 \text{ m}^{-2} \text{ yr}^{-1} \times 0.25) + (14.2 \text{ g } CH_4 \text{ m}^{-2} \text{ yr}^{-1} \times 0.75)$$
$$= 18.2 \text{ g } CH_4 \text{ m}^{-2} \text{ yr}^{-1}$$

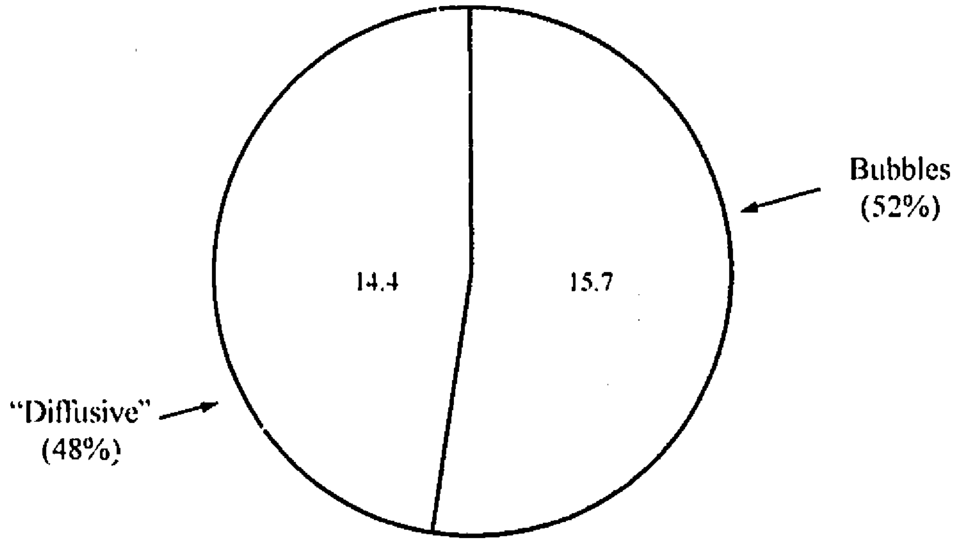


Site Legend:
BC: bog collapse (open low shrub bog);
FC: fen collapse (FC1-2: open graminoid poor fen; FC3: treed low shrub poor fen);
RBC: remote bog collapse (open graminoid bog);
TF: tower fen (TF2: treed lowshrub fen; TF3: treed tallshrub fen; TF4: open lowshrub fen);
ZF: Zoltai fen (ZF1-2: open low shrub fen; ZF3: open graminoid fen);
BP: beaver pond (BPO: open water; BPV: vegetated sites)

All data except beaver pond from Bubier et al., 1995a

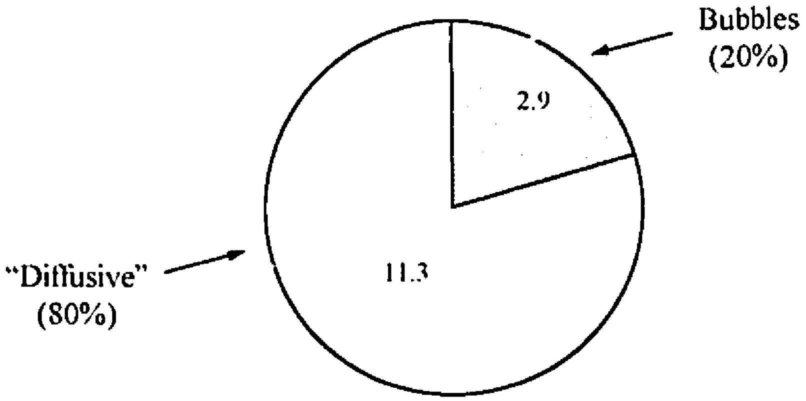
Figure 4.1: Comparison of Mean CH_4 Fluxes from Wetlands in the BOREAS Northern Study Area, for the period from May 15 to September 15, 1994

a) Open Water Sites



Total 30.1 g CH_4 m^{-2} yr^{-1}

b) Vegetated Sites



Total 14.2 g CH_4 m^{-2} yr^{-1}

Fig. 4.2: Total Annual CH_4 Emissions
from a) Open Water Sites and b) Vegetated Sites.
(g CH_4 m^{-2} yr^{-1})

4.1.1 Comparison with Flux Measured from other Beaver Ponds

Annual CH_4 flux from other studies of beaver ponds are presented in Table 4.1. The flux of CH_4 measured here lies within the range measured in these studies.

Table 4.1 Summary of CH_4 Flux from Beaver Ponds

Study	Location	Latitude	Number of Ponds	Mean Daily Flux (mg m^{-2} d^{-1})	Annual Integrated Flux (g m^{-2})
This study	Manitoba	55° 51' N	1	154.7^{a} 320.7^{b}	18.2
Vitt et al., 1990	Alberta	54-55° N	1	518	76.2
Ford and Naiman, 1988	Quebec	50° 15' N	1	21.6 18.7	5.9
Bubier et al., 1993	northern Ontario	49° N	1 4	350 290	52.5^{d} 43.7^{b}
Naiman et al., 1991	Minnesota	48° 34' N	1	n/a	14.4^{c} 11.6^{b}
Weyhenmeyer, 1992	Ontario	45° 23' N	1	38	6.2
Roulet et al., 1992	Ontario	45° 04' N	3	90.6 29.7 47.4	7.6
Windsor, 1993	southern Quebec	45° N	1	396 694	78^{d} 130^{b}
Yavitt et al., 1992	New York	43° 50' N 42° 52' N	2	138 162	34 40

^{a} emergent vegetation sites

^{b} open water sites

^{c} submergent vegetation sites

^{d} shallow margins

This study and the study by Weyhenmeyer (1992) are the only two in which bubbles were measured explicitly. Chamber methods commonly reject bubbles because the fit of the rise in CH_4 concentration over time is poor (e.g. Roulet et al., 1992; Sundh et al., 1995). Bubbles were detected in 5-10% of the floating chamber measurements in this study, and these data were rejected from the final data set.

Bubbles, however, were found to be a significant transporter of CH_4 in this beaver pond, comprising 20% and 52% of the total flux of CH_4 from vegetated and open water sites, respectively. Bubbles have been shown to contribute 65% of the total flux from a low boreal beaver pond (Weyhenmeyer, 1992) and 50% of total CH_4 emissions from a coastal wetland (Chanton et al., 1989). Using floating chambers alone, therefore, underestimates flux, and future studies of CH_4 emissions from flooded wetlands should include separate measurements of bubbles.

The omission of bubble measurement is problematic for open water sites where bubbles comprise more than half of the total CH_4 flux. The beaver pond in this study was mostly vegetated, but may not be representative of other boreal beaver ponds in this respect. In a regional survey of 12 beaver ponds in the BOREAS northern study area, most comprised open water only (C. Robinson and N. Roulet, personal communication). Other boreal beaver ponds also comprised open water with smaller amounts of emergent or floating vegetation (e.g Roulet et al., 1992; Weyhenmeyer, 1992). If beaver ponds generally contain open water, then any regional extrapolation of measurements without measuring bubbles will seriously underestimate the CH_4 flux.

4.1.2 Regional Significance of CH_4 Emissions from Beaver Ponds

The flux of CH_4 from this beaver pond was greater than the flux from most other northern boreal wetland types, but the regional significance of this source depends also on the areal coverage of all ecosystems in the boreal forest and their respective rates of CH_4 consumption or emission. The contribution of beaver ponds to the CH_4 budget of the 1100 km^2 BOREAS northern study area is estimated assuming the areal coverage of uplands, wetlands, lakes and beaver ponds (Table 4.2). Flux data from upland and wetland ecosystems were determined in studies by other BOREAS researchers. Two scenarios are presented: scenario 1 assumes 5% coverage by beaver ponds, and scenario 2 assumes only 1% coverage by beaver ponds. Within each scenario, maximum and minimum estimates are derived. The maximum net flux would result from minimum upland CH_4 consumption and maximum wetland CH_4 emission rates, and the minimum flux assumes maximum upland consumption and minimum wetland flux of CH_4.

Table 4.2 CH_4 Budget for the BOREAS Northern Study Area

	Measured Flux (g m^{-2} y^{-1})		Area (%)	Scenario 1 Flux (g m^{-2} y^{-1})		Area (%)	Scenario 2 Flux (g m^{-2} y^{-1})	
	Max.	Min.		Max.	Min.		Max.	Min.
Uplands[1]	-0.04	-0.07	50	-0.02	-0.035	50	-0.02	-0.035
Wetlands[2]	10	8.5	25	2.5	2.125	29	2.9	2.465
Lakes	0	0	20	0	0	20	0	0
Beaver Ponds	18.2	18.2	5	0.91	0.91	1	0.182	0.182
Net Flux (g m^{-2} y^{-1}):				3.4	3.0		3.0	2.6
Contribution of beaver ponds to net flux:				27%	30%		6%	7%

[1] Data from K. Savage, unpubl. data
[2] Data from Bubier et al., 1995a

The net flux of CH_4 from the NSA is estimated to lie between 2.6 and 3.4 mg CH_4 m^{-2} y^{-1} (Table 4.2). The flux from beaver ponds is disproportionately large, and comprises a significant portion of the regional budget. If beaver ponds cover only 1%

of the area of the NSA, they may contribute between 6 and 7% of the total emissions from all wetlands. If beaver ponds cover 5% of the NSA, they may contribute up to 30% of all wetland emissions. Any effort to determine the regional flux of CH_4 from northern boreal areas without consideration of the flux from beaver ponds would underestimate the net flux by up to 30%, and this error would increase if the area of beaver ponds is greater than 5%.

4.2 Error Analysis

CH_4 emissions from wetlands commonly display high spatial and temporal variability, even within apparently uniform ecological sites (Bubier et al., 1993). Differences in emissions may result from this inherent variability, or from actual errors in measurement and/or statistical analysis. While the variance of flux measurements is easily determined, the accuracy of measurements is often impossible to assess. Fortunately, independent measurements of the CH_4 flux from the same beaver pond was made concurrently by other BOREAS researchers.

4.2.1 Flux Variability

Emissions of CH_4 showed high spatial variability, with standard deviations that often exceeded the daily mean flux. Due to the large sample sizes, however, this observed variability had little effect on the average flux. Variograms (Fig. 4.3) were produced by randomizing the individual flux measurements, and then observing the change in confidence in the mean flux as the sample size was increased. The ratio of

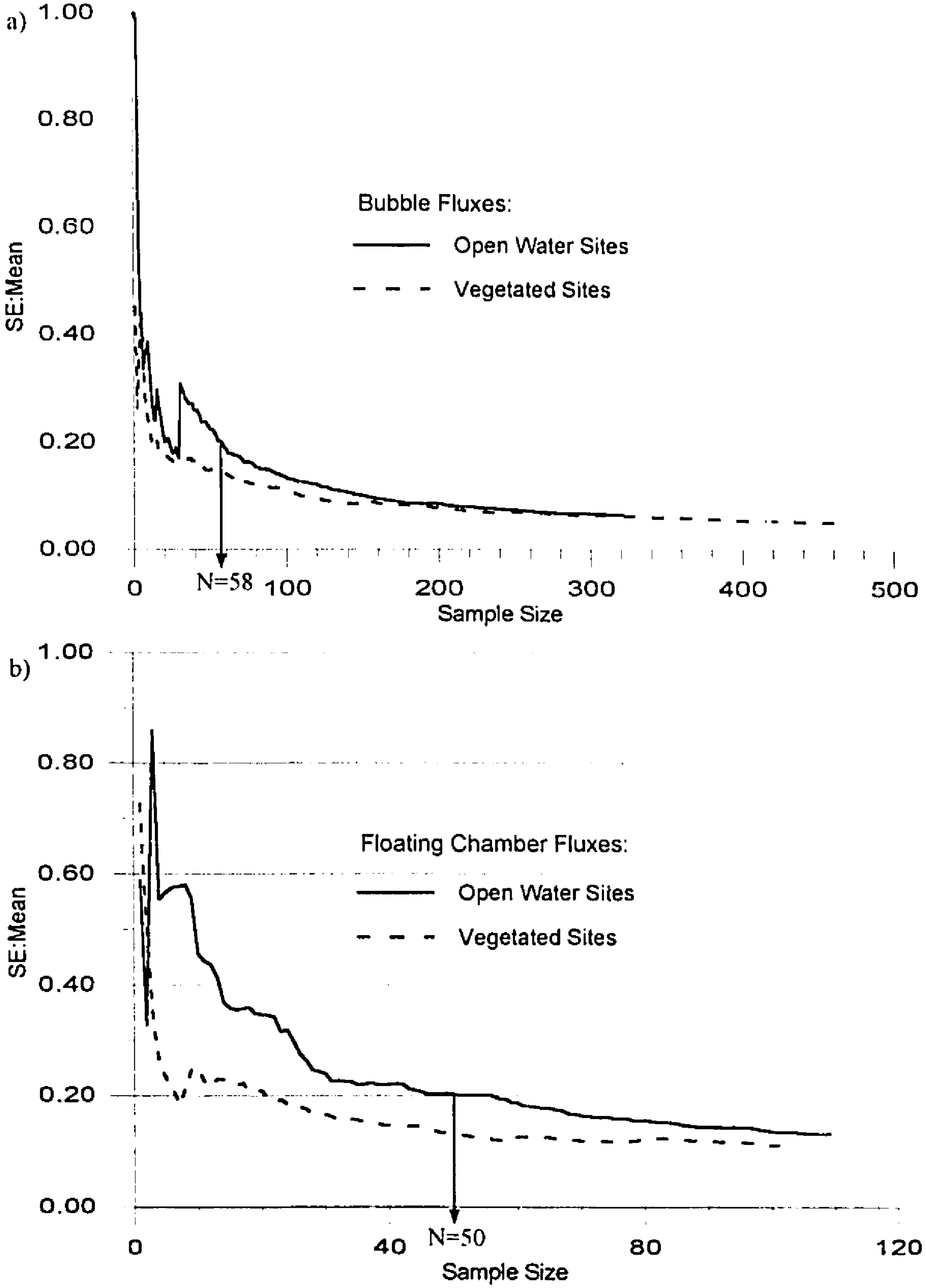


Figure 4.3: Ratio of Standard Error to Mean Flux for different sample sizes of randomly selected a) Bubble Flux and b) Floating Chamber Flux data.

the standard error to the mean flux decreased with increasing sample size, but reasonable confidence in the mean flux (where the standard error is less than 20% of the mean) was obtained when the floating chamber sample size reached 20 to 50, and when the bubble flux sample size reached 10 to 60 measurements, depending on the vegetation characteristics of the sites. With additional samples, the means themselves did not change significantly, but the ratio of standard error to mean flux decreased further due to the continued variability in emissions. Since the mean flux changed little after about 60 flux measurements, and the sample sizes obtained in this study were much larger, the accuracy of the flux determined here is considered to be better than ± 20%.

These results have implications for future measurement programmes. In this study, a large sample size was neccessary because the objectives were to determine the sources and controls of the flux variability. A careful sampling programme, however, using as few as 50 chamber flux and 60 bubble flux measurements over the season, would be sufficient to accurately determine the net flux. Estimating the annual flux by multiplying the measured mean daily flux by the length of the field season would have overestimated the seasonal integrated flux by only 15% (34.7 g CH_4 m^{-2} yr^{-1}) and 22% (17.4 g CH_4 m^{-2} yr^{-1}) for open water and vegetated sites, respectively. Studies to determine the net annual CH_4 flux from beaver ponds need to determine the mean flux and length of the emission season.

4.2.2 Flux Accuracy: Comparison with Continuous Tower CH_4 Flux Measurements

It is rare that an independent measurement of CH_4 flux is available, but CH_4 flux was also measured at the beaver pond using a flux-gradient approach from a 1.5 m micrometeorological tower with a 50-120 m footprint over the pond (P. Crill and N. Roulet, unpubl. data). Mean daily flux measured from the tower ranged from 29 to 282 mg CH_4 m^{-2} d^{-1}, which agrees well with the areal-weighted flux calculated in this study (193 mg CH_4 m^{-2} d^{-1}). The annual flux from the tower (11.1 g CH_4 m^{-2} yr^{-1}, calculated by interpolating and integrating daily mean flux over the season) was lower than that measured here using static chambers and funnels (18.2 g CH_4 m^{-2} yr^{-1}), but the tower may not measure bubble emissions accurately. High concentrations of CH_4 in the air above the pond (presumably resulting from bubble emissions) were often observed in the tower data, but some of these were only observed at the higher sampling inlet. Since the tower flux calculations rely on the gradient of atmospheric CH_4, a downward gradient of CH_4 thus measured results in a calculated uptake rather than efflux, and leads to an underestimate of net emissions from the pond.

In general the CH_4 flux measured from the tower is lower than the net (floating chamber + bubble) flux measured in this study (Fig. 4.4a), but it is similar to the floating chamber flux alone (Fig. 4.4b). Indeed, the annual areal-weighted flux from floating chambers (12.1 g CH_4 m^{-2} yr^{-1}) compares well with the tower flux (11.1 g CH_4 m^{-2} yr^{-1}). Statistical comparisons (Mann-Whitney U tests) indicated that the mean daily flux measured at the tower was greater than the floating chamber flux ($U = 1174$,

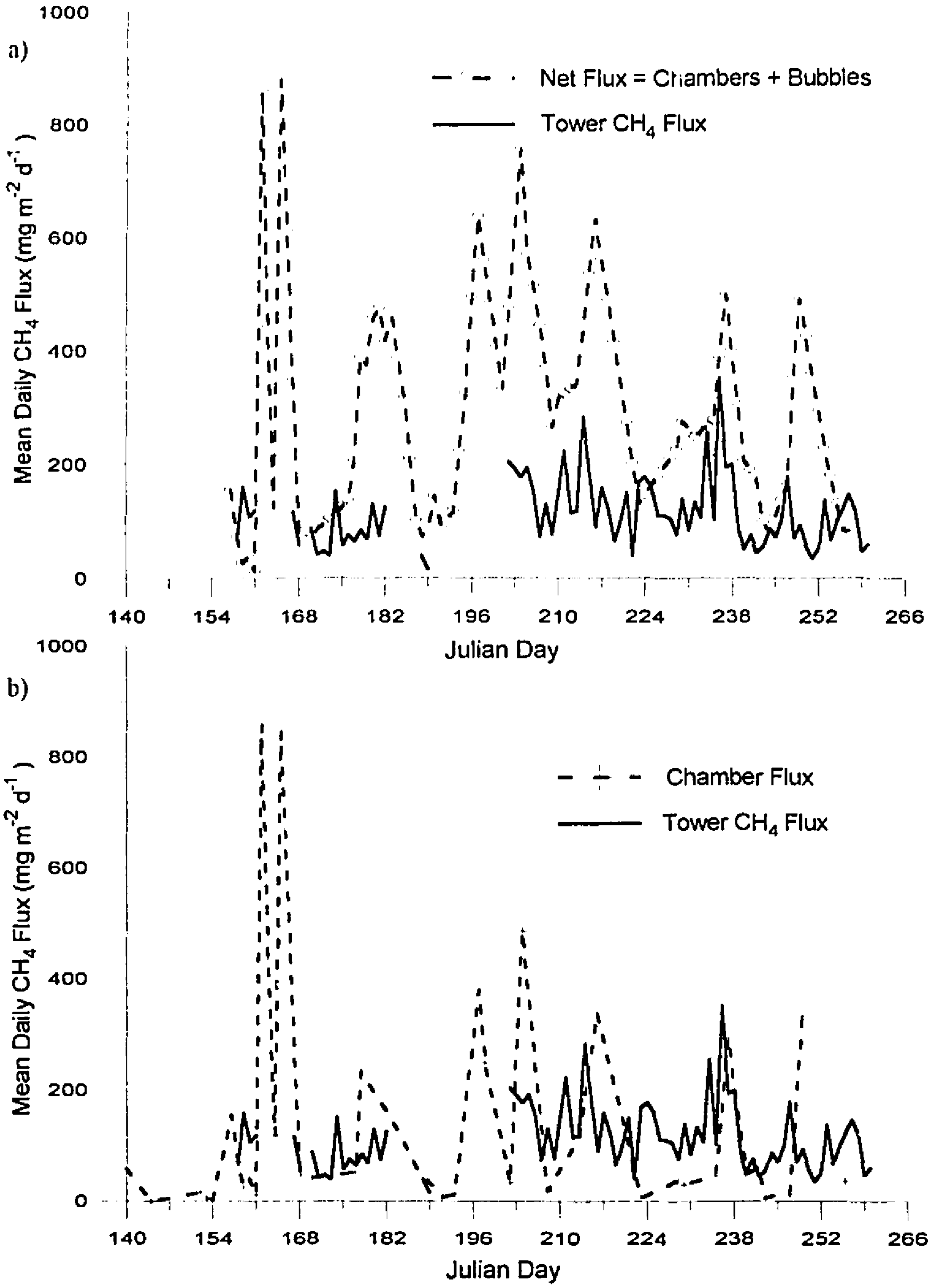


Fig. 4.4: Seasonal CH_4 Flux from Tower vs. a) Net Flux from Bubble Traps and Floating Chambers and b) Floating Chamber Measurements alone
Tower data from P.Crill and N. Roulet (unpubl. data)

$p<0.01$) (Fig. 4.5a), but less than the bubble flux ($U = 1639$, $p<0.05$) (Fig. 4.5b) measured at open water sites. The flux measured from the tower, therefore, lies between the flux from diffusion and bubbles (Table 4.3). Since the tower may not accurately measure bubble emissions, the flux-gradient results independently confirm that the results presented here are a reasonable estimate of spatially-averaged CH_4 emissions from the beaver pond .

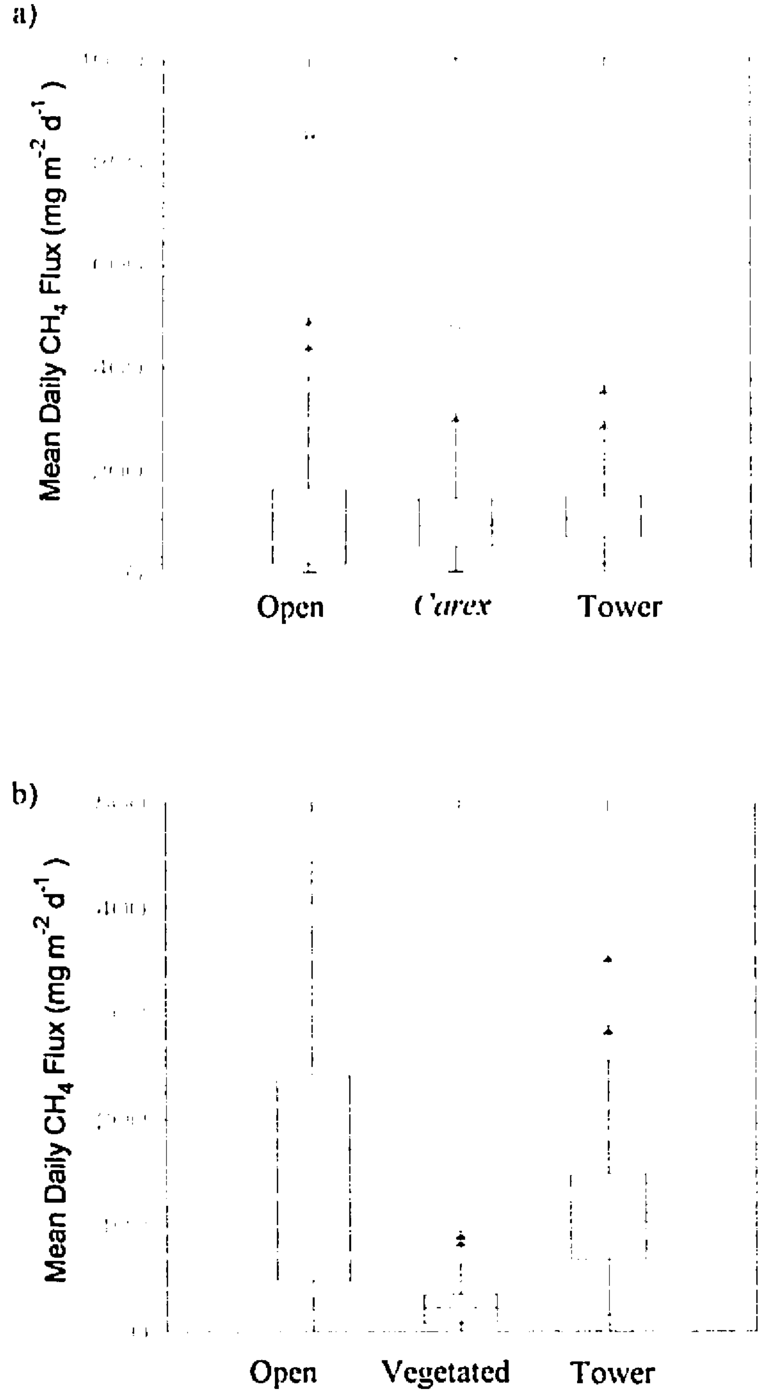
Table 4.3 Comparison of CH_4 Flux Measured Continuously at the Tower with Chamber and Bubble Flux Measurements

Statistic	Open Water Chamber Flux	*Carex* Site Chamber Flux	Tower Flux	Open Water Bubble Flux	Vegetated Site Bubble Flux
N (days)	41	37	82	51	51
Min.	1.2	0.7	15.3	0.02	0.01
Max.	856.4	476.9	351.6	443.2	89.54
Mean	141.4	109.1	112.5	156.7	26.0
SD	208.4	97.8	60.6	112.6	21.6
Median	47.9	89.8	103.8	172.4	22.2

All values are daily mean flux (mg CH_4 m^{-2} d^{-1})

4.2.3 Arithmetic vs. Geometric Means

Other investigators have criticized the use of arithmetic means in CH_4 flux studies (e.g. Wehenmeyer, 1992). Geometric means may be more appropriate than arithmetic means when distributions are positively skewed because high values tend to inflate arithmetic means. Arithmetic means were used here, however, despite the skewed distribution of flux measurements, because several fluxes were zero or negative which caused geometric means to be indefinite. Geometric means were calculated where possible, and cumulative emissions were compared using the two



Mann-Whitney U Tests:

Tower > Open
Tower = *Carex*
Carex = Open

Mann-Whitney U Tests:

Open > Tower >Vegetated

Fig. 4.5 Comparison of Mean Daily CH_4 Flux Measured from the Tower vs. a) Floating Chamber Measurements and b) Bubble Flux Measurements from this study
Tower data from P.Crill and N. Roulet (unpubl. data)

methods (Table 4.4). Annual emissions calculated by integrating geometric mean daily fluxes were roughly 10 to 20% lower than those calculated using arithmetic means, but the contributions of bubbles and floating chamber fluxes to the total flux remained very similar. Correlation coefficients between geometric mean daily flux and environmental factors did not differ significantly from those reported for arithmetic means (Sections 3.2.3 and 3.3.3). Furthermore, the variograms presented above and the agreement with the tower flux measurements indicate that the arithmetic mean provides a reliable estimate of flux.

Table 4.4 Comparison of Annual CH_4 Flux Calculated by Integrating Geometric and Arithmetic Mean Daily Flux

	Chamber Flux ($g\ m^{-2}\ yr^{-1}$)		Bubble Flux ($g\ m^{-2}\ yr^{-1}$)		Total Flux ($g\ m^{-2}\ yr^{-1}$)	
	Vegetated	Open	Vegetated	Open	Vegetated	Open
Arithmetic Mean	11.3	14.4	2.9	15.7	14.2	30.1
Geometric Mean	10.3	12.2	2.4	12.5	12.7	24.7
% Difference[1]	-9	-15	-18	-21	-11	-18

[1] $$\frac{\text{(integrated daily arithmetic mean flux - integrated daily geometric mean flux)}}{\text{integrated daily arithmetic mean flux}} \times 100$$

4.2.4 Possible Errors in Floating Chamber Measurements

As described in the results (Section 3.2.1), the density of *Carex* at the selected sites along the boardwalk may have been too low to detect enhancement of flux by these plants. *Carex* densities were generally only 1 to 3 plants within a chamber, and the annual flux resembled that from unvegetated sites. Enhanced flux through *Carex* has been found in other studies (e.g. Whiting and Chanton, 1992; Bubier et al., 1995a), and is suspected here because higher fluxes were observed in the tower CH_4 flux data (P. Crill and N. Roulet, unpubl. data) when the wind was blowing from densely vegetated areas of the pond (Fig. 4.6). Furthermore, the tower data showed marked diel variation (Fig. 4.7), with daytime enhancement of flux concurrent with photosynthetic activity. Therefore, the reported annual flux from *Carex* sites (11.3 g CH_4 m^{-2} y^{-1}) and the areal-weighted flux (18.2 g CH_4 m^{-2} y^{-1}) are likely underestimates. Since most beaver ponds in the region appear to be largely unvegetated, this error is not considered to affect the regional assessment of the importance of CH_4 emisisons from beaver ponds. At worst, the regional budget may underestimate the role of beaver ponds since the areal-weighted flux for beaver ponds used in the budget may be too low.

Rates of bubbling and CH_4 concentrations in bubbles were high, yielding high bubble fluxes from this pond. It is possible that small bubbles contributed to flux measurements made with floating chambers (cf. Yavitt et al., 1990). Large bubbles that entered floating chambers were easily detected in the time series of CH_4 measurements (they were detected in 5-10% of all floating chamber fluxes), but smaller bubbles may have entered chambers at a linear rate since chamber fluxes were negatively (but poorly) correlated with atmospheric pressure ($r \geq -0.26$; Section 3.3.3). The only way in which atmospheric pressure should correlate negatively with floating chamber measurements is if bubble release is related to atmospheric pressure (or some other co-dependent variable) and if bubbles were measured in chambers. If small bubbles contributed to floating chamber flux measurements, then the total flux

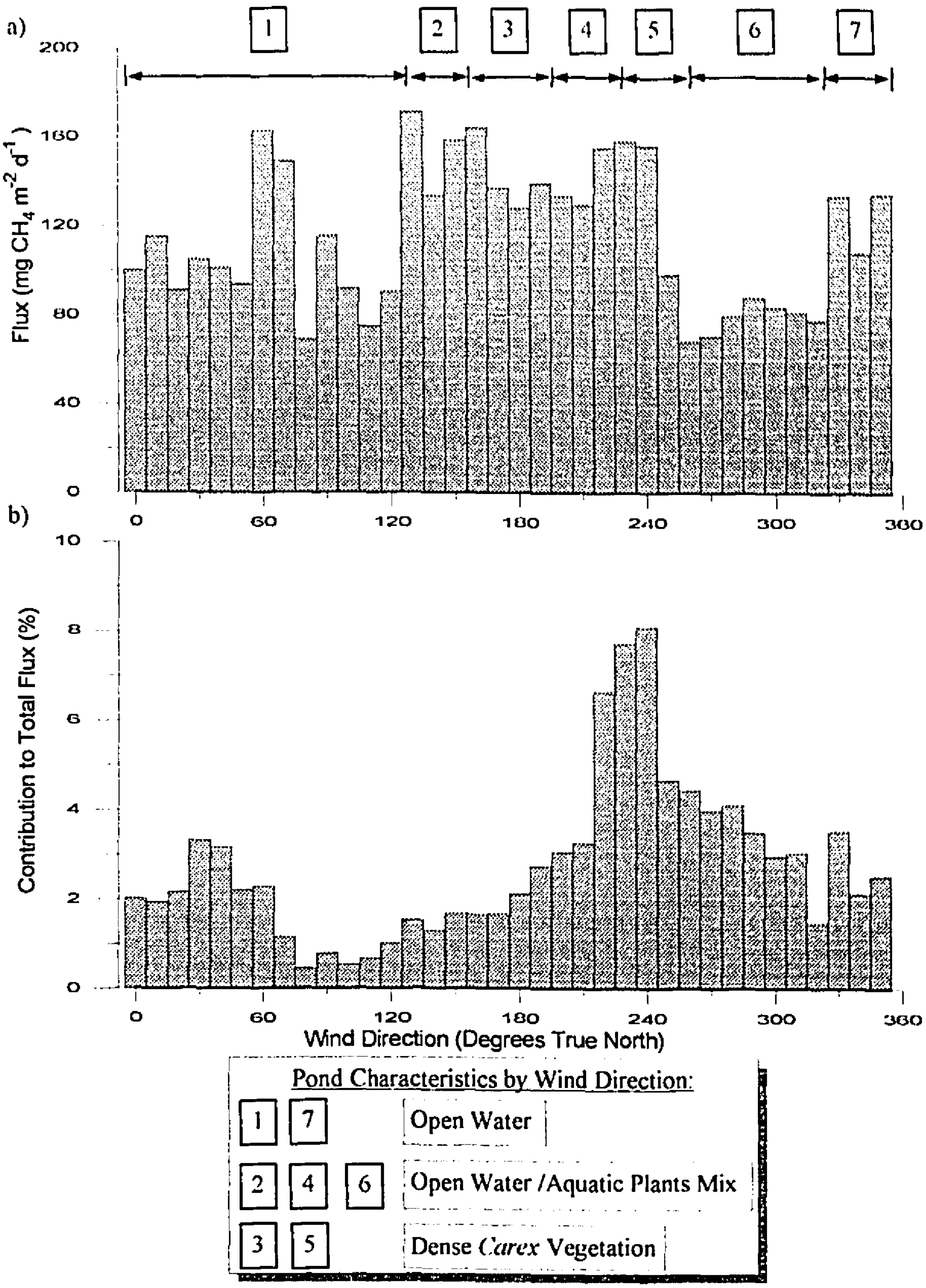


Fig. 4.6: Continuous CH_4 Flux Tower Data by Wind Direction:
a) Flux and b) % Contribution to Total Flux (P. Crill and N. Roulet, unpubl. data)

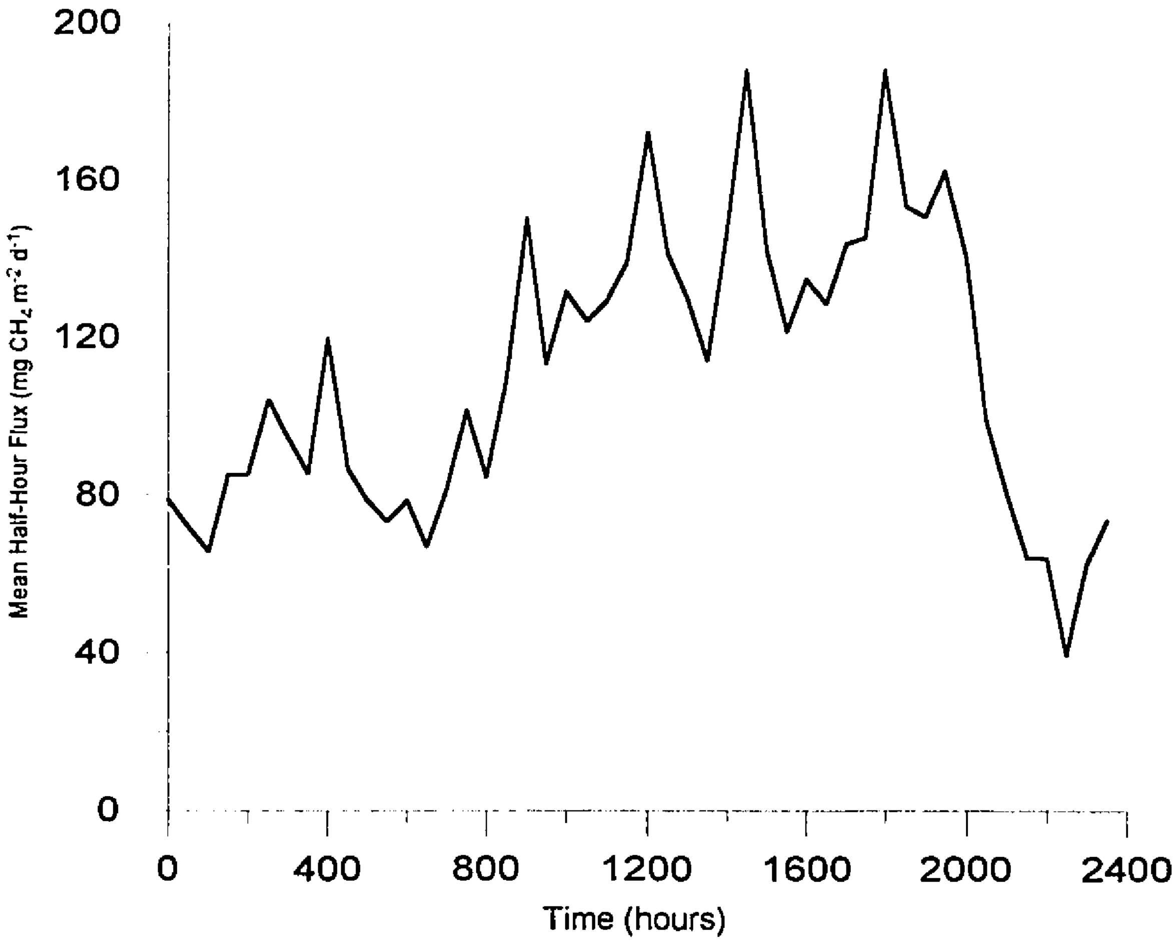


Fig. 4.7: Diel Variation in Continuous Tower CH_4 Flux Data
(P. Crill and N. Roulet, unpubl. data)

calculated by summing floating chamber and bubble fluxes will be overestimated since small bubbles are included in both measurements. Unfortunately, there is no way to identify whether this is the case, although it is unlikely since atmospheric pressure was not a significant predictor of floating chamber flux using multiple regression analysis (Section 3.2.3).

4.2.5 Winter CH_4 Emissions

Studies of CH_4 emissions from wetlands have traditionally assumed that winter fluxes are negligible due to low temperatures and cover by snow and ice. A few studies have recently included measurements over a full annual cycle (Whalen and Reeburgh, 1992; Dise et al., 1993). No measurements of winter CH_4 emissions were made here, but seasonal changes in the CH_4 pool size indicate that CH_4 stored in sediments in the fall is either released and/or oxidized before spring. In the spring, a small sediment CH_4 pool was present, but when sampling was terminated, a large CH_4 pool remained. Assuming no CH_4 is oxidized but CH_4 production ceases, winter CH_4 emissions can be calculated as the difference between fall and spring storage (Table 4.5).

Table 4.5 Winter CH_4 Emissions Calculated as the Difference between Fall and Spring Porewater CH_4 Storage

	Open Water Sites (g m^{-2})	Vegetated Sites (g m^{-2})
Fall Porewater CH_4 Storage	8.0	10.8
Spring Porewater Storage	1.6	0.9
Winter Flux (Difference)	6.4	9.9
Total Annual Flux	36.5	24.1

Including winter emissions results in new estimates of annual flux. Estimated winter emissions comprise only 18% of total annual flux from open water sites, but comprise 41% of the flux from vegetated sites. Since low rates of CH_4 production, and particularly CH_4 oxidation, may continue over the winter, these figures provide only a rough estimate of the winter flux of CH_4 from the pond.

Weyhenmeyer (1992) estimated that winter net production comprised 23% of the annual CH_4 flux from a low boreal beaver pond, based on an increase in the concentration of CH_4 in surface waters below ice between November and February, and assuming that production rates were constant and that CH_4 oxidation and release were negligible. No other information about winter emissions from beaver ponds is available, but the available evidence indicates that the winter flux may be significant.

4.3 Environmental Controls of CH_4 Emissions

The flux of CH_4 from a beaver pond results from production, consumption and transport processes. It is the contention here that the primary controls on CH_4 flux are those that affect the availability of CH_4 (i.e.production and oxidation), and the secondary controls are those that affect the transport of CH_4 from the sediments to the atmosphere. Primary factors such as temperature will control rates of production and oxidation, and will therefore control the amount of CH_4 that is available for release. The amount of CH_4 available and the amount actually emitted are not equal, however, due to storage of CH_4 in the sediments and differential rates of oxidation as CH_4 is transported by different pathways (diffusion, bubbles, and plant-mediated transport).

4.3.1 Primary Controls on CH_4 Availability

The amount of CH_4 available for release depends on the rates of CH_4 production and oxidation, and also on the size of the storage reservoir in the sediments. Since temperature directly controls rates of CH_4 production and oxidation, flux patterns broadly followed trends in sediment temperature, with other factors influencing emissions at specific times. At the beginning of the field season, temperature, porewater CH_4 concentrations, and fluxes were all low, therefore production of CH_4 was probably low. As sediment temperature increased, the flux measured in floating chambers and porewater CH_4 concentrations increased. Sediment temperature continued to increase after porewater concentrations reached saturation, and rates of production exceeded the capacity for diffusive loss of CH_4; therefore, significant ebullition occurred (cf. Chanton and Dacey, 1991). By the end of the sampling programme, near-surface sediment temperature was decreasing and production may have declined because both flux and storage were declining.

CH_4 producers (methanogens) and CH_4 consumers (methanotrophs) respond differently to temperature (Dunfield et al., 1993). Diffusing CH_4 is subject to oxidation during transport, and emissions will be the result of both production and oxidation processes. The relationship between diffusive CH_4 flux and sediment temperature will therefore be complicated because two groups of organisms are involved. Bubble flux should be more directly related to the production of CH_4 because the potential for oxidation is greatly reduced during bubble transport. Indeed, sediment temperature was a stronger predictor of bubble flux ($r^2 = 0.45$ to 0.64) than the flux measured in floating chambers ($r^2 = 0$ to 0.11) (Sections 3.2.3 and 3.3.3).

The relationship between sediment temperature and floating chamber flux was strongest when temperature was increasing monotonically rather than decreasing. This may also be due to the different temperature responses of CH_4 producers and consumers.

Photosynthetically active radiation may enhance CH_4 flux as indicated by the positive relationship between PAR and sediment temperature. Smoke from forest fires reduced PAR between J.d. 182 and 187, causing a decline in sediment temperature and there was a corresponding decline in CH_4 flux. Plant transport of CH_4 may also be enhanced by PAR. Increasing PAR may attenuate flux, however, because higher rates of photosynthesis by aquatic plants and epiphytic algae increase the amount of oxygen available for use by CH_4-consumers in the sediments (King, 1990). A significant but weak negative relationship was found between PAR and open water chamber fluxes (Section 3.2.3). This might be due to enhancement of CH_4 oxidation fueled by O_2 production at the sediment-water interface.

Other factors besides temperature will affect the availability of CH_4 for emission from a beaver pond. Substrate characteristics such as pH, nutrients, and organic matter content and quality likely affect rates of CH_4 production and oxidation, but these characteristics were not tested in the field. There were positive relationships between both CH_4 production and consumption rates and organic matter content when measured in the laboratory, but these relationships were generally weak. Production and consumption were also strongly correlated with each other (r = -0.84; where consumption rates are negative). Therefore, sites with higher organic matter contents tend to both produce and consume more CH_4 because high organic content enhances methanogenesis, and populations of methanotrophs are greatest where CH_4 is abundantly available (Svensson and Sundh, 1992; Sundh et al., 1995).

The degree of anaerobism also affects the balance between CH_4 production and oxidation. In other types of wetlands, where the water table is below the wetland surface, a large aerobic zone is present, and oxidation can significantly reduce the CH_4 flux (e.g. Fechner and Hemond, 1992; Moore et al., 1994). Since the sediments in beaver ponds are continuously saturated, anaerobic conditions dominate, and oxidation is minimized compared to other wetlands. The strongest predictors of CH_4 flux from other wetlands are the position of the water table and temperature. In beaver ponds, small changes in pond level do not affect anaerobism. Sediment temperature is therefore the dominant factor controlling CH_4 availability.

4.3.2 Secondary Controls on CH_4 Release: Diffusion

The rate of CH_4 diffusion depends on the concentration gradient of CH_4, and the conductance (or resistance) of the system to its transport. Virtually all of the resistance to the water-air transfer of CH_4 has be shown to occur in the liquid phase (Denmead and Freney, 1992). Therefore, the rate-limiting step for release of CH_4 from aquatic systems is the supply of CH_4 to surface waters. Turbulent mixing of the water column effectively transports CH_4-rich water from deeper layers at rates greater than diffusion alone could achieve. Because convective mixing of water is a function of windshear, windspeed controls the transport of CH_4 to the surface. Mean daily windspeed was the strongest predictor of CH_4 flux measured in floating chambers, explaining up to 35% of the variance in flux (Section 3.2.3). Although atmospheric mixing by winds is eliminated within the floating chambers, in the water under the enclosure considerable wind-induced mixing continues due to momentum in the water column. If the rate-limiting step for diffusion of CH_4 is on the atmospheric side of the water-air interface, then no relationship between windspeed and flux would be expected because windspeed inside the floating chambers is zero. Clearly, the transport of CH_4 from deeper layers to the surface controls the flux across the water-air interface.

One would expect higher fluxes from shallow sites because wind-induced mixing penetrates water layers with higher CH_4 concentrations at these sites. Flux may also decrease as the depth of water increases if diffusing CH_4 is oxidized in the water column (Rudd and Taylor, 1980). However, water depth was not a significant predictor of chamber fluxes here. Most sites sampled by chambers (85%) were deeper than 0.4 m. Since profiles of CH_4 concentrations in the upper 40 cm of the water column were similar between sites (see Fig. 3.25), intersite depth differences should not explain flux variability. Additionally, as explained below, open water oxidation is likely negligible in this pond.

4.3.3 Secondary Controls on CH_4 Release: Bubbles

Rates of CH_4 production exceeded rates of removal by diffusion and oxidation since porewaters became supersaturated with respect to CH_4. Bubbles, consisting of CH_4 and other gases (presumably N_2, Ar and small amounts of O_2; Chanton et al., 1989) were formed in the sediments. Assuming that these bubbles maintain equilibrium with hydrostatic pressure, changes in pressure may cause some bubbles to be released (Mattson and Likens, 1990). If the overlying pressure, which is exerted by the atmosphere and the water column, decreases below the internal bubble pressure, bubbles will be released into the water column, where they will rise to the surface and burst upon contact with the atmosphere.

Atmospheric pressure controlled bubble flux once the primary control of sediment temperature on production was considered. Atmospheric pressure was a weak predictor of bubble flux overall, explaining only 4% and 11% of variance in open water and vegetated site mean daily flux, respectively. However, during the middle of the season (J.d. 182-216) when sediment temperature was highest and least variable, atmospheric pressure explained 26% ($p<0.05$) and 61 % ($p<0.001$) of the variance in open water and vegetated site mean daily bubble flux, respectively.

Other investigators have found that pressure changes influence bubbling in inundated wetlands. Weyhenmeyer (1992) found atmospheric pressure changes explained 40% of the variance in bubble flux from a low boreal beaver pond, and Mattson and Likens (1990) reported a significant correlation between bubble flux and atmospheric pressure at Mirror Lake, New Hampshire. Hydrostatic pressure caused by tidal cycles has been identified as the primary control of bubbling in a freshwater subtidal wetland (Chanton et al., 1989) and in coastal marine sediments (Martens and Klump, 1980).

Water level was not a significant predictor of flux although the sudden drop in water level caused by dam failure on June 22 (J.d. 174) was associated with an increase in bubble flux. The maximum 24-hour change in water level (-8.8 cm) is equivalent to a decrease in atmospheric pressure of 0.86 kPa. Based on the mid-season regression equation of atmospheric pressure vs. open water bubble flux, this change should cause an increase in bubble flux of 109.5 mg CH_4 m^{-2} d^{-1}. The observed changes were lower: the 24-hour changes in mean bubble flux from open water sites ranged from 8 to 101 mg CH_4 m^{-2} d^{-1} in the 3 days following dam failure. The smaller change in flux is likely due to the lower sediment temperatures and less antecedent CH_4 storage since the dam failure occurred early in the season. The drop in water level was also concurrent with an increase in sediment temperature and was accompanied by a decrease in atmospheric pressure; therefore it is difficult to determine to what degree the changes in temperature and pressure each affected flux.

Wind velocity was not related to bubble fluxes but on one extremely windy day (J.d. 236), high fluxes of CH_4 were observed due to wind-driven turbulence in the water column that likely disturbed the sediments and caused bubble release.

4.3.4 Secondary Controls on CH_4 Release: Plant Transport

There was no evidence of plant-enhanced transport of CH_4 by most plant species at the beaver pond, but the chamber flux measurements were prone to the same problem as described earlier for *Carex* sites. Certain species of aquatic emergent plants have been found to ventilate CH_4 from the sediments to the atmosphere, although the mechanism involved probably differs between plant species (see Chanton and Dacey, 1991). Although very few floating chamber measurements were taken over *Typha* (n=4), the leaf areas enclosed were relatively large, and these fluxes were much higher than adjacent open water fluxes. High CH_4 fluxes from *Typha sp.* have been documented in other studies (Sebacher et al., 1985.). Plant enhanced CH_4 transport has also been shown for *Nymphaea sp.* (Sebacher et al., 1985), but was not found here, probably because the plants were small and only 1 plant was enclosed in each chamber.

Plant-enhanced transport might explain the observed differences in bubble flux and CH_4 concentrations in bubbles between open water and vegetated sites. If emergent macrophytes relieve the pressure of CH_4 in sediments, then less CH_4 will accumulate and lower bubble emissions will result at vegetated sites. Furthermore, if bubbles strip N_2 from the sediments, then areas with intense bubbling rates will release bubbles with less N_2 and relatively more CH_4. Studies in other flooded wetlands have illustrated these points. In estuarine North Carolina sediments (Chanton et al., 1989), and Alaskan tundra wetlands (Martens et al., 1992), open water sites sustained higher bubble fluxes and released bubbles with higher CH_4 concentrations than vegetated sites. At high bubbling rates, more N_2 was stripped from the sediments and this rate of removal exceeded the rate of N_2 resupply by molecular diffusion from the atmosphere. At sites vegetated by emergent macrophytes, the bubble flux was lower because the plants acted as conduits for CH_4 transport, less stripping of N_2 occured, and diffusive resupply maintained N_2 concentrations in bubbles. Bubbles from vegetated sites therefore contained more N_2 and less CH_4 than open water sites.

Holtzapfel-Pshorn and Seiler (1986) illustrated how the emergence of vegetation can shift the dominant mode of CH_4 transport within a site from ebullition to ventilation by plants. CH_4 transport was predominantly by ebullition when the rice plants were below the water surface, but after emerging, the transport was primarily through their stems. Plant transport reduced porewater CH_4 concentrations and ebullition ceased.

The relationship between bubbling rate and the ratio of N_2:CH_4 in bubbles is supported here. Although N_2 in bubbles was not measured, a positive relationship was observed between bubbling rate and bubble CH_4 concentration (Fig. 4.8). Plant transport may not be responsible for this relationship, however, since stripping of N_2 by bubbles may occur universally. Moreover, the plant transport hypothesis is not supported by CH_4 storage inventories in the pond. Storage of dissolved CH_4 was similar at the three piezometer nests, and bubble storage (determined once) was similar at a deep open water site and a shallow vegetated site. Bubble and dissolved storages were not determined at the same site, but have been shown to be maintain equilibrium (Chanton et al., 1989). If plant transport releases CH_4 in sediments, then both lower

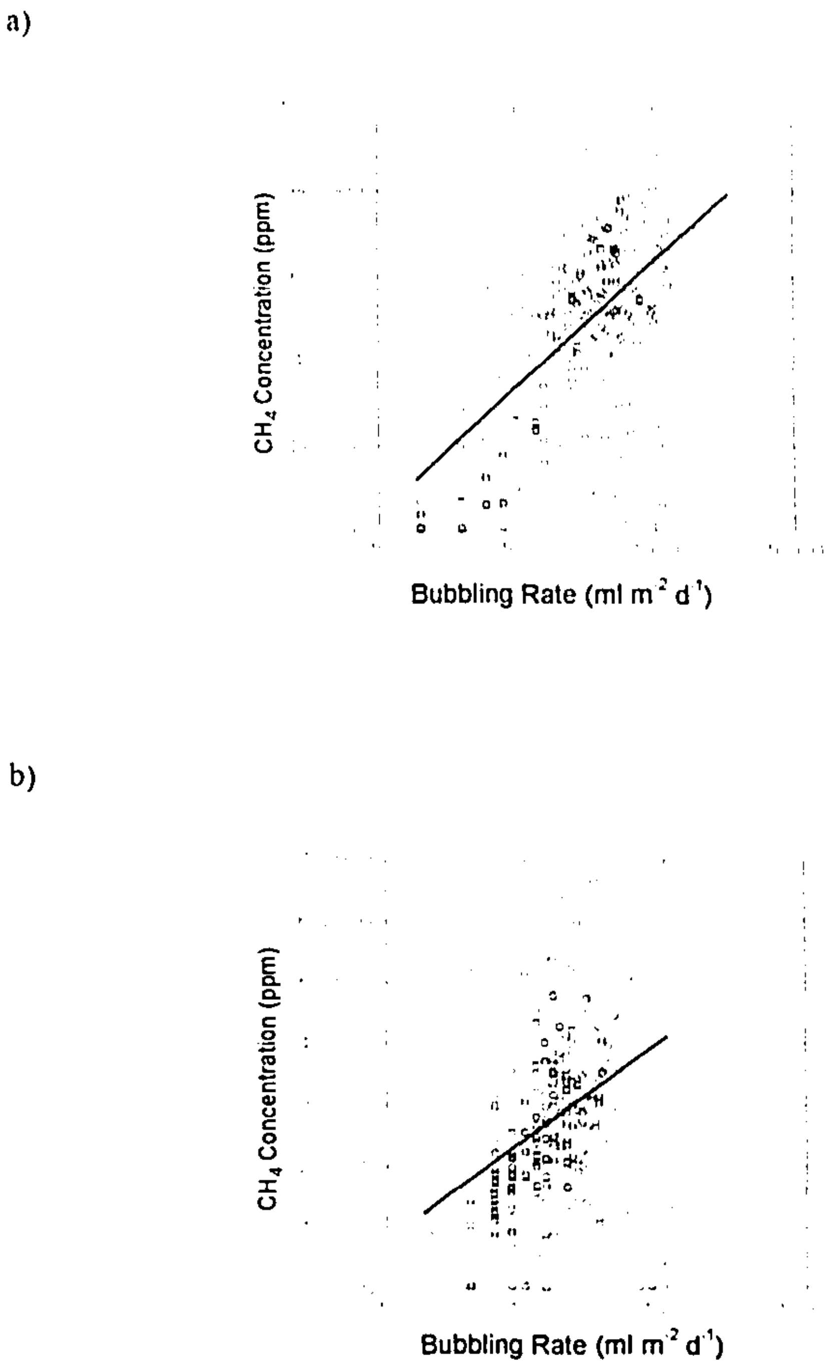


Fig. 4.8: Bubbling Rate vs. CH$_4$ Concentration at a) Open Water and b) Vegetated Sites

dissolved and bubble storage should be evident at vegetated sites. Although plant-transport is suspected in this pond, further investigation is required to determine the importance of this mechanism. It should be emphasized that since most beaver ponds are largely unvegetated, the CH_4 flux through plants will be less important than the flux transported by bubbles and diffusion on a regional scale.

4.4 CH_4 Dynamics in the Beaver Pond

In the previous section, the factors controlling CH_4 availability and release were identified. These factors explain some of the flux variability, but do not explain intersite flux differences. In this section, the processes of CH_4 production, oxidation and storage are addressed. The evidence for the relative importance of each is examined, and quantified where possible. Differences in these processes appear to control the differences in CH_4 flux from vegetated and open water areas of the pond.

4.4.1 Storage

Storage of CH_4 in the sediments may conceal the relationships between production, oxidation, and flux. Storage can delay the release of CH_4, but if release from storage is triggered (by external factors), very large emissions may result because the sediment CH_4 reservoir is large. However, in mid-season (J.d. 170- 252), the amount of CH_4 stored remained relatively constant; 24-hour changes in porewater CH_4 storage were rarely greater than 10%. The observed bubble flux comprised only a small portion of the sediment CH_4 reservoir (4-6%), therefore even large bubble emissions resulted only in small decreases in the amount of CH_4 stored (Section 3.3.4). Since storage was at steady-state, changes in flux should be directly related to changes in CH_4 production and oxidation processes. Furthermore, there was no significant difference in the mass of CH_4 stored between vegetated and open water areas of the pond (Section 3.7). Therefore, differences in the CH_4 flux between vegetated and open water areas should also be related to differences in the CH_4 production and oxidation processes between sites.

4.4.2 CH_4 Production

CH_4 production had to be greater than oxidation because the beaver pond was a net source of CH_4 to the atmosphere. This beaver pond was found to be a relatively large source of CH_4 compared to other wetlands in the same region, probably because conditions in the pond promoted CH_4 production and minimized CH_4 oxidation. Although absolute *in situ* rates of production and oxidation were not determined, the relative importance of each can be estimated.

As described above (Section 3.4.1), the *in situ* oxidation-inhibition experiments were used to estimate CH_4 production rates, but these results may not be reliable because of the small sample size and large standard error. Maximum rates of production for the beaver pond may be estimated, however, as the midseason net flux from open water sites. Open water sites sustained high bubble fluxes, and midseason porewater storage was constant. Peeper CH_4 profiles, dissolved O_2 profiles, and open water productivity measurements indicate that the potential for CH_4 oxidation was low at these sites (see Section 4.4.3); therefore, production rates likely equalled the flux from these sites. Similarly, in productive unvegetated sediments at Cape Lookout Bight, North Carolina, Crill and Martens (1983) determined that CH_4 storage was saturated and ebullition rates were equal to CH_4 production in the sediments. Rates of CH_4 production from these deep open water sites can, therefore, be estimated as the midseason (J.d. 194 to 220) mean net flux of 452 ± 130 mg CH_4 m^{-2} d^{-1}.

The large and consistent difference in bubble flux between open water and vegetated sites, despite similar storage reservoirs, suggests that differences in CH_4 production and/or oxidation occur between these two types of sites. Differences were found in the isotopic composition of CH_4 in bubbles between vegetated and open water areas of the pond. Differences in carbon (C) and hydrogen (H) isotopes in emitted CH_4 may result from different processes (i.e. chemical pathways) by which CH_4 is produced, and by oxidative processes. Fractionation of both C and H isotopes occurs during methanogenesis, but the degree of fractionation differs according to the pathway involved (Whiticar et al., 1986; Burke et al., 1988; Happell et al., 1993). Isotopic fractionation also occurs during oxidation, but is distinguishable from the fractionation caused by CH_4 production (Coleman et al., 1981). No fractionation occurs during bubble transport itself (Martens et al., 1986; Chanton and Martens, 1988).

During acetate fermentation, in which CH_4 is derived from methyl groups, CH_4 becomes enriched in ^{13}C and depleted in D (deuterium). During CO_2 reduction, in which hydrogen is used as the electron source, CH_4 becomes relatively depleted in ^{13}C

and enriched in D. During CH_4 oxidation, however, methanotrophs preferentially consume the lighter isotopes of both C and H, and the remaining CH_4 will be enriched in ^{13}C and D . Plots of the relative abundance of the light vs. heavy isotopes in emitted or stored CH_4 can illustrate trends in the importance of these processes between different areas (see Fig. 3.21).

The graph of the isotopic composition of CH_4 released in bubbles shows that CH_4 emitted from open water sites is isotopically heavier in H, but lighter in C, compared to CH_4 emitted from sites vegetated with emergent macrophytes. This difference is consistent with a difference in CH_4 production pathway. At open water sites, the released CH_4 resembles that produced by CO_2 fermentation, while the CH_4 in bubbles from vegetated areas is produced more by acetate reduction. Therefore, the dominant substrate used by methanogens differs between sites. This difference may account for the difference in total emissions. In open water areas, CO_2 is produced during decomposition of organic matter, and is abundantly available since the beaver pond was determined to be a large source of CO_2 to the atmosphere (N. Roulet, unpubl. data). In vegetated areas, acetate is the main substrate for CH_4 production. Acetate may also be available in smaller quantities than CO_2 due to competition from other methanogens and limited supply by plants (J. Chanton, personal communication). Therefore CH_4 production rates may be lower in vegetated areas than open water areas.

The difference in flux due to production is supported by two measurements of ^{14}C signatures in sediment samples from open water and vegetated areas of the pond

(S. Trumbore, unpubl. data). Measurements are reported as ratios relative to 1950 oxalic acid (ratio = 1; $\delta^{14}C$ = 0 ‰) (S. Trumbore, personal communication). Negative $\delta^{14}C$ values result where significant decay of ^{14}C has occurred (ratio < 1; $\delta^{14}C$ < 0 ‰), but positive values of $\delta^{14}C$ will only result when a more recent source of ^{14}C is present (ratio > 1; $\delta^{14}C$ > 0 ‰). This new source is bomb ^{14}C, produced by weapons testing. Since most bomb ^{14}C was released in the 1960s, a $\delta^{14}C$ > 0 ‰ value indicates that a significant amount of ^{14}C in the sample has been derived from carbon fixed from the atmosphere by plants during the past 30 years.

Both measurements of ^{14}C indicated that the carbon in beaver pond sediments have been fixed since the 1960s. However, the sediments from a vegetated area of the beaver pond contained newer carbon (del^{14}C = 6.49 ‰) than sediments from an open water area (del^{14}C = 7.37 ‰). This result is consistent with the hypothesis that more new carbon compounds produced by plants (e.g. acetate) support the populations of methanogens at vegetated sites, and that older peat materials (containing CO_2) supply substrates for methanogenesis at open water sites.

Studies of other ebullition-dominated systems found similar CH_4 production differences between vegetated and open water areas (Martens et al., 1986; Burke et al., 1988; Chanton and Martens, 1988). Acetate reduction was found to be relatively more important in summer months, suggesting that temperature or substrate availability connected with plant activity may control the relative rates of the two production pathways.

This explanation for the observed bubble flux difference differs from that provided above (Section 4.3.4), in which it was explained that the lower bubble flux in vegetated areas may be due to ventilation of CH_4 in sediments by plants. These two explanations are not exclusive, however, and may act in combination to produce the observed flux. Since vegetative transport of CH_4 was not demonstrated, the relative contributions of the two mechanisms remain unclear.

The isotopic evidence that production pathways differed also does not preclude a difference in CH_4 oxidation rates between vegetated and non-vegetated sites. Oxidation of CH_4 may also occur, and rates may differ between areas of the pond. However, the dominant fractionation effect appears to be caused by differences in the CH_4 production pathways, and any isotopic effects of oxidation are obscured by this difference. If the difference in bubble CH_4 flux between vegetated and open water sites were predominantly due to greater oxidation of CH_4 at vegetated sites, however, the fitted line through the isotope data would have a positive slope (see Fig. 3.21).

4.4.3 CH_4 Oxidation

Evidence exists to indicate that some oxidation occurs in the beaver pond. CH_4 consumers (methanotrophs) are obligate aerobes, and will be present in greatest numbers at the anaerobic-aerobic interface where both CH_4 and O_2 are present in optimal quantities (King, 1990; Knowles, 1993). The availability of sufficient CH_4 in this beaver pond has been well established (e.g. see sediment profiles, Section 3.5), but the location of the anaerobic-aerobic interface is not known. Three lines of evidence may be used to indicate the importance of CH_4 oxidation in the sediments and water column: (1) low open water productivity indicates that little oxidation occurs in the water column; (2) profiles of dissolved oxygen show that O_2 is available at the sediment-water interface, but may be rapidly consumed by the competing processes of CO_2 production and CH_4 oxidation; and (3) peeper profiles, incubations and oxidation-inhibition experiments indicate that some CH_4 oxidation occurs, especially in surficial sediments at vegetated sites, but *in situ* rates are probably low.

Differences between benthic chamber fluxes and floating chamber fluxes (Section 3.4.1) indicated that oxidation of CH_4 in the water column depletes the flux at a mean rate of 43.5 mg CH_4 m^{-2} d^{-1}. While this provides indirect evidence for oxidation, intersite variability and differences between benthic and floating chamber measurement techniques (including disturbance of sediments during benthic sampling) may account for the flux difference. Furthermore, open water productivity was low, indicating that CH_4 oxidation in the water column is likely insignificant in the pond.

46 samples of water from 13 NSA beaver ponds were collected for chlorophyll a analysis (R. Bourbonniere, unpubl. data). From June through August, all values of chlorophyll a (corrected for the biodegradation product phaeophytin) were low (range <1 to 2 μg chlorophyll a L^{-1} water). In late August and early September, concentrations had increased to much higher levels (range 6-24 μg L^{-1}), presumably because macrophyte fragments in the waters contributed to the chlorophyll a content (R. Bourbonniere, personal communication). The concentration of chlorophyll a was only tested once in the beaver pond examined in this study (Sept. 12), and the

concentration was low (3.0 μg L^{-1}), indicating that little open water photosynthesis occurs in the pond. Since little O_2 is produced, CH_4 oxidation in the water column is likely negligible.

Profiles of temperature indicate that the pond was not stratified, but dissolved oxygen concentrations decreased markedly with depth (Fig. 4.9) (R. Bourbonniere, unpubl. data). The O_2 profile resembles the clinograde profile found in productive lakes (Wetzel, 1983), and indicates there is a large sink for O_2 at depth. O_2 is most depleted near the sediment-water interface, where bacterial decomposition of sedimenting organic matter is greatest. The CO_2 flux from this beaver pond is high and is probably due to heterotrophic respiration in the sediments (N. Roulet, unpubl. data). Since respiration also requires O_2, oxygen availability will be limited by the competing demands of decomposers and methanotrophs. CH_4 oxidation may in turn be limited by O_2 availability.

Although dissolved O_2 concentrations were low or below detectable limits in bottom waters, the presence of sediment algal mats, even in the deepest areas of the pond, indicates that O_2 is produced at the sediment surface. Calculations of PAR attenuation in the water column indicated that optimal photosynthetic activity for algae (at 1% incident PAR; Wetzel, 1983) occurs at an average depth of 1.2 m. Since most of the pond is shallower than 1.2 m, the majority of the pond sediments receive sufficient light to sustain algal production throughout the season. However, the amount of O_2 that is produced by epiphytic algae is probably small compared to that transported from the atmosphere by convective mixing, and it will also be consumed

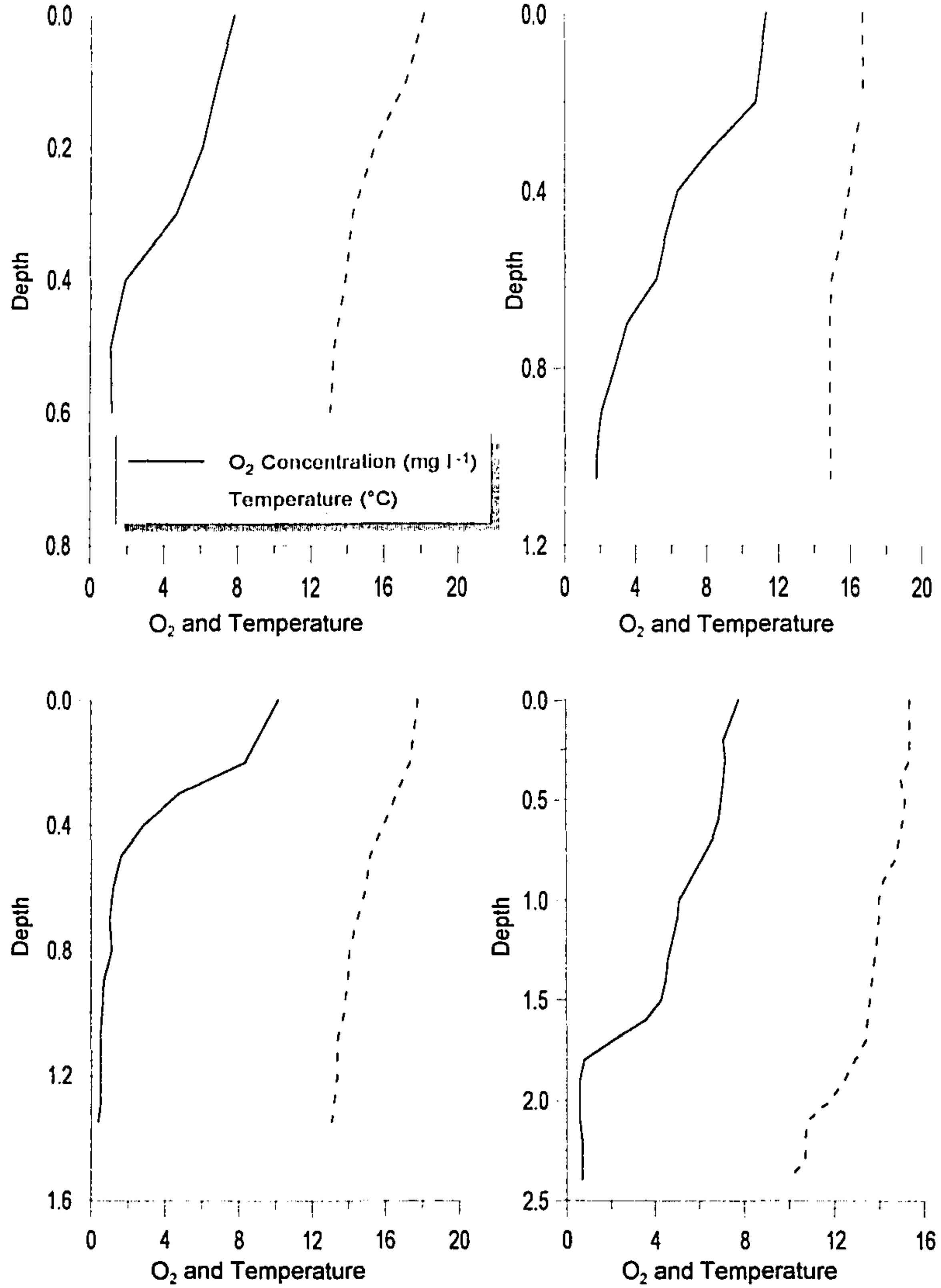


Fig. 4.9: Water Column Profiles of O_2 and Temperature from the Beaver Pond, Late August, 1994 (R. Bourbonniere, unpubl. data) Legend applies to all figures

by competing processes of CO_2 production and CH_4 oxidation. Even low concentrations of O_2 may be sufficient for CH_4 oxidation (King, 1992), however, and some CH_4 oxidation likely occurs although *in situ* rates remain uncertain.

Profiles of sediment CH_4 concentrations indicated that significant consumption of CH_4 occurs within the upper layers of the beaver pond sediments (cf. Yavitt et al., 1992). CH_4 concentrations in surface layers were commonly 20% of concentrations in deeper sediments, but CH_4 production potentials determined under anaerobic conditions in the laboratory were similar with depth. Since the surface sediments are equally capable of producing CH_4, the reduction of CH_4 concentrations near the sediment-water interface is likely due to oxidation of CH_4, and not merely due to bulk flow of CH_4 from the sediments. Consumption potentials were also greatest in surface sediments, indicating that the greatest numbers of methanotrophs inhabit these layers (cf. Sundh et al., 1995).

The oxidation zone appeared to be extend deeper at shallow water sites than deep water sites (Section 3.5). O_2 concentrations were slightly higher in bottom waters at shallow sites (R. Bourbonniere, unpubl. data), probably because atmospheric O_2 can be effectively transported by convection to shallow depths, and because O_2 is transported to the sediments by aquatic plants growing at shallow sites in the pond. Incubation experiments yielded the highest potential oxidation rates from a vegetated floating mat. Therefore, higher rates of CH_4 consumption likely occur in shallow, vegetated areas of the beaver pond.

Other researchers (Yavitt et al., 1992) have used benthic chambers to measure fluxes of CH_4 across the sediment-water interface, and compared these with CH_4 production rates measured in the laboratory to calculate oxidation rates. However, incubation experiments do not accurately simulate field conditions; instead they indicate potential rates of CH_4 production (cf. Sundh et al., 1995). *In situ* rates of CH_4 oxidation are extremely difficult to obtain. Separation of production and oxidation components of flux requires the use of oxidation inhibitors, all of which may have side effects. For example, picnolinic acid may be toxic to plants and methanogens (Bédard and Knowles, 1989; Epp and Chanton, 1993). Methyl fluoride (MF) was used here to inhibit populations of methanotrophs in benthic chambers because it is reportedly non-toxic to plants and does not interfere with methanogenesis at low MF concentrations (Oremland and Culbertson, 1992; Epp and Chanton, 1993). Oxidation was calculated by difference between fluxes measured in benthic chambers where MF was used, and fluxes measured without the inhibitor.

The results indicated that oxidation reduced the flux of CH_4 across the sediment-water interface. The results are tenuous due to small sample sizes and large standard deviations, but they indicate that CH_4 oxidation was occuring, at least at the sites (depth < 1 m) where the sampling was performed. Quantitative interpretation of the results is not possible because complete inhibition of oxidation was probably not achieved. Successful inhibition of methanotrophs with MF may have occurred within the benthic chamber, but MF was likely restricted from diffusing far into the sediments because the fluxes were measured immediately after chamber and MF deployment.

MF is extremely soluble (≈ 1.7 ml MF ml^{-1} H_2O; Oremland and Culbertson, 1992) and probably remained in the water within the benthic chamber. Because some portion of the methanotrophs was probably not inhibited, a significant but unknown amount of oxidation may still have occurred.

Production potentials determined in anaerobic incubations were similar to CH_4 production potentials determined in a wide range of peat samples from saturated wetlands in the Hudson Bay lowlands (Moore et al., 1994). Oxidation potentials from the floating mat site were also similar or greater than the oxidation potentials from these peats, but the open water sites displayed much lower consumption potentials, especially in core 3 which was obtained from a deep water, high flux, site. Unfortunately, oxidation potentials are not directly comparable across studies since they depend on the initial concentration of CH_4 available in the sediment slurry. These results indicate, however, that since production rates were similar, the high flux of CH_4 from the beaver pond probably resulted from low potential to oxidize the produced CH_4, especially *in situ* where oxidation is limited by anaerobic conditions.

4.5 Summary and Conclusions

The mean net flux of CH_4 from this beaver pond (320 mg m^{-2} d^{-1} and 155 mg m^{-2} d^{-1}, for open water and vegetated sites, respectively) was greater than the flux from most other northern study area wetland sites. Confidence in the measured flux is high because large sample sizes were obtained, and because the net CH_4 flux is confirmed by independent measurements by a different method at the same site. A large proportion of the total CH_4 flux was released by ebullition, and future studies in flooded wetlands should measure bubbles separately if floating chambers are employed.

It was initially hypothesized that the beaver pond would sustain high CH_4 emissions because factors in the pond maximize CH_4 production and minimize oxidation. Indeed, high sediment temperatures promoted CH_4 production, and inundation restricted oxidation. Oxidation of CH_4 occured at the sediment water interface, but was limited by O_2 availability. Oxidation in the water column was determined to be negligible.

The differences in CH_4 availability and transport between open water and vegetated sites, and the factors which controlled these processes, are shown in Fig. 4.10. The diffusive flux was similar at open water and vegetated sites. The factors that controlled the diffusive flux were sediment temperature (by controlling CH_4 availability) and windspeed (by controlling transport). Bubble flux from open water sites was twice that from vegetated sites, because CH_4 availability was greater in open water areas. The dominant pathway for CH_4 production was CO_2 fermentation at open water sites, and acetate reduction at vegetated sites. The lower flux observed from vegetated sites may have resulted from limited acetate availability, and greater oxidation. In addition, plants may have enhanced CH_4 transport, thus reducing porewater CH_4 concentrations, although porewater storage was similar between sites. The role of emergent plants in transporting CH_4 remains unclear, but since most beaver ponds probably comprise open water, plant transport may be insignificant at a regional scale.

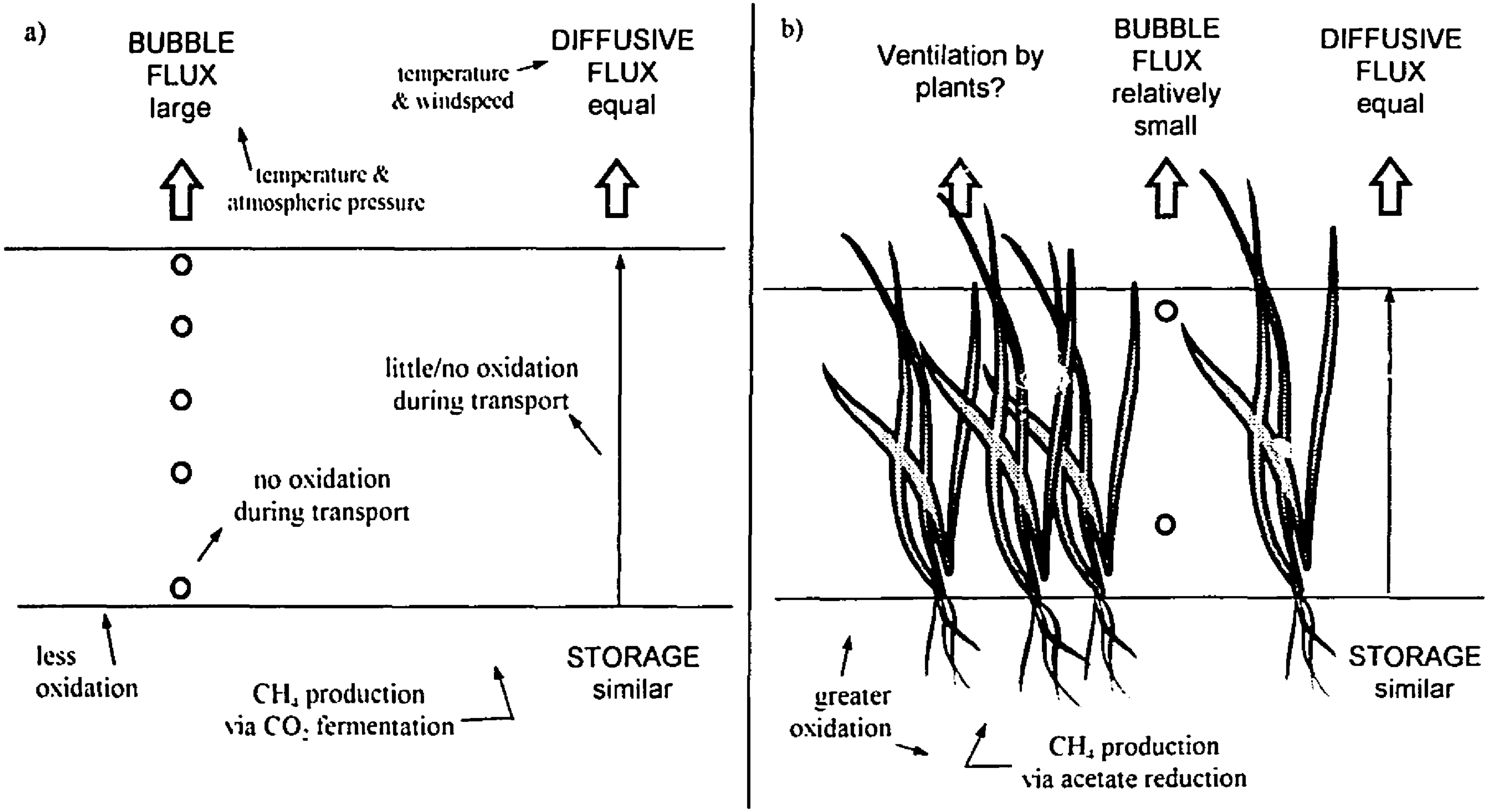


Fig. 4.10: Methane Dynamics in a Northern Boreal Beaver Pond at a) open water sites and b) sites vegetated with emergent aquatic plants

Ebullition of CH_4 was found to be a significant transport mechanism, comprising 20 and 52% of the total flux, depending on site. The amount of CH_4 available for ebullition was controlled by sediment temperature, and bubble release was controlled by atmospheric pressure. Large water level changes also affected bubble transport. Bubble flux was not related to the loss of CH_4 stored in the sediments, probably because fluxes were small relative to the stored reservoir of CH_4.

Most regional and global CH_4 budgets have neglected beaver ponds. The results from this study, however, indicate that beaver ponds are disproportionately high emitters of CH_4. The budget presented above (Section 4.1.2) illustrates the large effect that beaver ponds play in determining the net regional flux of CH_4. With increasing knowledge about the flux of CH_4 and its variability from beaver ponds, the areal extent of ponds will be the greatest potential error in determining their contribution to regional flux.

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Appendix I: Data Available through BORIS (BOREAS Information Systems)

Data are available, with special permission, from BOREAS Information Systems (BORIS). Contact: J. Newcomber, NASA Goddard Space Flight Center, Greenbelt, Md., U.S.A.

Data	Particulars	Sample Size
Chamber Flux Data	Individual Fluxes, date, time, site characteristics (vegetation and depth of water)	260
	Daily mean flux for 2 vegetation categories	37-41
Surface Water CH_4 Concentrations	Surface water CH_4 concentrations, date, time, windspeed, concurrent chamber flux, site characteristics	141
Bubble Flux Data	Individual fluxes for each site, site characteristics, volume of bubbles, CH_4 concentration, time accumulated	771
	Daily mean flux for 2 vegetation categories	51
Gross Bubble Storage and Production	Volume and concentration of bubbles released by prodding from 2 sites	2
	Volume and concentration of bubbles accumulated since first prodding, and released by further prodding	2
Dissolved CH_4 Storage	Porewater CH_4 concentrations from 15 piezometers	286
	Mass of dissolved CH_4 stored in porewaters	64
Water Column CH_4 Profiles	Concentrations of CH_4 dissolved in the water column	21 profiles
Sediment-Water Interface CH_4 Profiles	High resolution profiles of dissolved CH_4 concentrations across the sediment-water interface	10 profiles
Sediment-Water Chamber Fluxes	Individual fluxes measured in benthic chambers, time and site characteristics (vegetation water depth)	39
	Daily mean benthic chamber flux	12
	Individual benthic chamber fluxes with MF inhibition	10
	Daily mean MF-inhibited benthic chamber flux	2
Sediment Incubations	Individual sample CH_4 production potentials, dry weight, organic matter content (loss on ignition)	51
	mean CH_4 production potential for each depth	17
	Individual sample CH_4 consumption potentials, dry weight, organic matter content (loss on ignition)	34
	mean CH_4 consumption potential for each depth	17
C and H isotopes	$\delta^{13}C$ and δD of CH_4 in naturally released bubbles	30
	$\delta^{13}C$ and δD of CH_4 in prodded bubbles	2
	$\delta^{13}C$ and δD of CH_4 dissolved in porewater	12
	$\delta^{13}C$ and δD of CH_4 in the water column	2

Appendix II: Julian Day - Calendar Day Conversion Table

	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30	31
JAN	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30	31
FEB	32	33	34	35	36	37	38	39	40	41	42	43	44	45	46	47	48	49	50	51	52	53	54	55	56	57	58	59			
MAR	60	61	62	63	64	65	66	67	68	69	70	71	72	73	74	75	76	77	78	79	80	81	82	83	84	85	86	87	88	89	90
APR	91	92	93	94	95	96	97	99	99	100	101	102	103	104	105	106	107	108	109	110	111	112	113	114	115	116	117	118	119	120	
MAY	121	122	123	124	125	126	127	128	129	130	131	132	133	134	135	136	137	138	139	140	141	142	143	144	145	146	147	148	149	150	151
JUN	152	153	154	155	156	157	158	159	160	161	162	163	164	165	166	167	168	169	170	171	172	173	174	175	176	177	178	179	180	181	
JUL	182	183	184	185	186	187	188	189	190	191	192	193	194	195	196	197	198	199	200	201	202	203	204	205	206	207	208	209	210	211	212
AUG	213	214	215	216	217	218	219	220	221	222	223	224	225	226	227	228	229	230	231	232	233	234	235	236	237	238	239	240	241	252	253
SEP	244	245	246	247	248	249	250	251	252	253	254	255	256	257	258	259	260	261	262	263	264	265	266	267	268	269	270	271	272	273	
OCT	274	275	276	277	278	279	280	281	282	283	284	285	286	287	288	289	290	291	292	293	294	295	296	297	298	299	300	301	302	303	304
NOV	305	306	307	308	309	310	311	312	313	314	315	316	317	318	319	320	321	322	323	324	325	326	327	328	329	330	331	332	333	334	
DEC	335	336	337	338	339	340	341	342	343	344	345	346	347	348	349	350	351	354	353	354	355	356	357	358	359	360	361	362	363	364	365