

Methane and Carbon Dioxide Flux From
Ponds and Lakes of the
Hudson Bay Lowlands

By

James David Hamilton

A Thesis
Submitted to the Faculty of Graduate Studies
in Partial Fulfillment of the Requirements
for the Degree of

MASTERS OF SCIENCE

Department of Microbiology
University of Manitoba
Winnipeg, Manitoba

• January, 1992



National Library
of Canada

Acquisitions and
Bibliographic Services Branch

395 Wellington Street
Ottawa, Ontario
K1A 0N4

Bibliothèque nationale
du Canada

Direction des acquisitions et
des services bibliographiques

395, rue Wellington
Ottawa (Ontario)
K1A 0N4

Your file *Votre référence*

Our file *Notre référence*

The author has granted an irrevocable non-exclusive licence allowing the National Library of Canada to reproduce, loan, distribute or sell copies of his/her thesis by any means and in any form or format, making this thesis available to interested persons.

L'auteur a accordé une licence irrévocable et non exclusive permettant à la Bibliothèque nationale du Canada de reproduire, prêter, distribuer ou vendre des copies de sa thèse de quelque manière et sous quelque forme que ce soit pour mettre des exemplaires de cette thèse à la disposition des personnes intéressées.

The author retains ownership of the copyright in his/her thesis. Neither the thesis nor substantial extracts from it may be printed or otherwise reproduced without his/her permission.

L'auteur conserve la propriété du droit d'auteur qui protège sa thèse. Ni la thèse ni des extraits substantiels de celle-ci ne doivent être imprimés ou autrement reproduits sans son autorisation.

ISBN 0-315-77918-7

METHANE AND CARBON DIXOIDE FLUX FROM PONDS

AND LAKES OF THE HUDSON BAY LOWLANDS

BY

JAMES DAVID HAMILTON

A thesis submitted to the Faculty of Graduate Studies of the University of Manitoba in partial fulfillment of the requirements for the degree of

MASTER OF SCIENCE

© 1992

Permission has been granted to the LIBRARY OF THE UNIVERSITY OF MANITOBA to lend or sell copies of this thesis to the NATIONAL LIBRARY OF CANADA to microfilm this thesis and to lend or sell copies of the film, and UNIVERSITY MICROFILMS to publish an abstract of this thesis.

The author reserves other publication rights, and neither the thesis nor extensive extracts from it may be printed or otherwise reproduced without the author's written permission.

Abstract

Methane and carbon dioxide fluxes ponds and lakes in the Hudson Bay Lowland to the atmosphere from were measured from June to October 1990. The study area was located near the town of Moosonee, Ontario (51° 29' N; 80° 27' W). The study area was divided into four different sites; the Coastal Marsh, Coastal Fen, Interior Fen and the Kinosheo Lake Bog. The Kinosheo Lake bog was the furthest inland (114 km inland from the Coastal Marsh).

In early July, the average daily rate of methane flux from the ponds in the Kinosheo Lake area was 20 mg CH₄/m²/day, increasing to 50 mg CH₄/m²/day by the end of the month. The average daily flux of carbon dioxide was 900 mg CO₂/m²/day. The Coastal Fen and Interior Fen Ponds exhibited much higher fluxes of both CH₄ (averaging 160 mg CH₄/m²/day) and CO₂ (averaging 9000 mg CO₂/m²/day) than were measured at the Kinosheo Lake Bog. At all the sites the flux of CH₄ and CO₂ were highest in September.

Differences between ponds were much greater than the differences on different dates, i.e., ponds with higher rates tended to remain higher and vice versa. All 24 ponds and lakes sampled had concentrations of CH₄ and CO₂ which were consistently above atmospheric equilibrium and thus were sites of net carbon loss from the Hudson Bay Lowland.

Computer modelling suggests that CH₄ concentration is controlled by the combination of wind driven gas exchange and CH₄ oxidation. Carbon dioxide concentrations appear to be controlled by the combined effects of wind driven gas exchange and algal photosynthesis/respiration.

Aknowledgements

I wish to thank my thesis co-supervisors Dr. Carol Kelly (Dept. of Microbiology) and Dr. John W.M. Rudd (Dept. of Fisheries and Oceans) for their unfailing support and enthusiasm for my research. I would also like to thank them for making their facilities available to me and for their efforts to take the time to review my thesis along with the many other jobs that they had to do. I wish to thank Dr. Ray Hesslein (Dept. of Fisheries and Oceans) for his review of this thesis and the constructive input that he provided.

I would also like to thank Dr. Kelly, Dr. Hesslein and Akira Furutani (Dept. of Fisheries and Oceans) for all their patience while helping me to understand the gas flux equations.

Thanks also to the Water Chemistry Unit, Dept. of Fisheries and Oceans, Freshwater Institute, for their efforts in analyzing all the water chemistry samples I brought back. As well I wish to thank Ms. Hedi Kling (Dept. of Fisheries and Oceans) for here efforts in counting the algal samples. Many thanks also go to Ms. Susan Kasian (Dept. of Fisheries and Oceans) for her assistance with some of the more complicated statistical treatments conducted with SAS Stat and SAS Graph.

I also wish to thank Dr. Nigel Roulet (York University) for suppling the wind speed and light data. As well for his assistance with some of the sampling.

I would like to thank the Canadian Institute for Research in Atmospheric Chemistry for financial support and for the logistical support (lab space, helicopter time, etc.) necessary to conduct this research, funded in part by a Collaborative Grant from NSERC, Atmospheric

Environment Service, Environment Canada, and the NASA Global Tropospheric Experiment. I would also like to thank National Science and Engineering Council for their financial support (NSERC Operating Grant OGP GP 009 and a joint NSERC-AES Subvention Grant CRDPJ UGP).

Finally I would like to thank my father, Dr. Robert D. Hamilton and my wife, Kathleen, for their infinite patience in putting up with me while I wrote my thesis and for their reviews and input.

List of Figures

	Page
Figure 1	5
Figure 2	19
Figure 3	22
Figure 4	44
Figure 5	76
Figure 6a	83
Figure 6b	84
Figure 6c	85
Figure 7	86
Figure 8	91
Figure 9a	97
Figure 9b	98
Figure 9c	99
Figure 10	100
Figure 11	104
Figure 12	105
Figure 13	106
Figure 14	107
Figure 15	108
Figure 16	109
Figure 17	110
Figure 18	111
Figure 19	113
Figure 20	114
Figure 21	118
Figure 22	119
Figure 23a	120
Figure 23b	121
Figure 23c	122
Figure 24a	123
Figure 24b	124
Figure 24c	125
Figure 25	131
Figure 26	132
Figure 27	133
Figure 28	134
Figure 29	135
Figure 30	136
Figure 31	137
Figure 32	145

Figure 33	Predicted CO ₂ Concentrations	147
Figure 34	Time weighted CH ₄ Flux	150
Figure 35	Time Weighted CO ₂ Flux	151
Figure 36	Geographical Pattern of CH ₄ and CO ₂ Concentrations	154
Figure A1	Methane Concentration vs time of day. Coastal Fen (pond 11-14), July 9-10, 1990	190
Figure A2	Methane Concentration vs time of day. Coastal Fen (pond 15-14), July 9-10, 1990	191
Figure A3	Methane Concentration vs time of day. Coastal Fen (pond 11-14), July 24, 1990	192
Figure A4	Methane Concentration vs time of day. Coastal Fen (pond 15-14), July 24, 1990	193
Figure A5	Methane Concentration vs time of day. Coastal Fen, August 14-15, 1990	194
Figure A6	Methane Concentration vs time of day. Coastal Fen, September 10-11, 1990	195
Figure A7	Methane Concentration vs time of day. Coastal Fen (pond 11-14), October 10-11, 1990	196
Figure A8	Methane Concentration vs time of day. Coastal Fen (pond 15-14), October 10-11, 1990	197
Figure A9	Methane Concentration vs time of day. Interior Fen, July 9-10, 1990	198
Figure A10	Methane Concentration vs time of day. Interior Fen, July 24, 1990	199
Figure A11	Methane Concentration vs time of day. Interior Fen, August 14-15, 1990	200
Figure A12	Methane Concentration vs time of day. Interior Fen, September 10-11, 1990	201
Figure A13	Methane Concentration vs time of day. Interior Fen, October 10-11, 1990	202
Figure A14	Methane Concentration vs time of day. Kinosheo Lake Bog, July 05-06, 1990.	203
Figure A15	Methane Concentration vs time of day. Kinosheo Lake Bog, July 13-14, 1990.	204
Figure A16	Methane Concentration vs time of day. Kinosheo Lake Bog, July 17, 1990.	205
Figure A17	Methane Concentration vs time of day. Kinosheo Lake Bog, July 25, 1990.	206
Figure A18	Methane Concentration vs time of day. Kinosheo Lake Bog, August 15-16, 1990.	207
Figure A19	Methane Concentration vs time of day. Kinosheo Lake Bog, September 12-13, 1990.	208
Figure A20	Methane Concentration vs time of day. Kinosheo Lake Bog (Ponds 1-5), October 12, 1990.	209
Figure A21	Methane Concentration vs time of day. Kinosheo Lake Bog (Ponds 6-10), October 12, 1990.	210
Figure A22	Carbon Dioxide Concentration vs time of day. Coastal Fen (pond 11-14), July 9-10, 1990	211
Figure A23	Carbon Dioxide Concentration vs time of day. Coastal Fen (pond 15-14), July 9-10,	

	1990	212
Figure A24	Carbon Dioxide Concentration vs time of day. Coastal Fen (pond 11-14), July 24, 1990	213
Figure A25	Carbon Dioxide Concentration vs time of day. Coastal Fen (pond 15-14), July 24, 1990	214
Figure A26	Carbon Dioxide Concentration vs time of day. Coastal Fen, August 14-15, 1990	215
Figure A27	Carbon Dioxide Concentration vs time of day. Coastal Fen, September 10-11, 1990	216
Figure A28	Carbon Dioxide Concentration vs time of day. Coastal Fen (pond 11-14), October 10-11, 1990	217
Figure A29	Carbon Dioxide Concentration vs time of day. Coastal Fen (pond 15-14), October 10-11, 1990	218
Figure A30	Carbon Dioxide Concentration vs time of day. Interior Fen, July 9-10, 1990	219
Figure A31	Carbon Dioxide Concentration vs time of day. Interior Fen, July 24, 1990	220
Figure A32	Carbon Dioxide Concentration vs time of day. Interior Fen, August 14-15, 1990	221
Figure A33	Carbon Dioxide Concentration vs time of day. Interior Fen, September 10-11, 1990	222
Figure A34	Carbon Dioxide Concentration vs time of day. Interior Fen, October 10-11, 1990	223
Figure A35	Carbon Dioxide Concentration vs time of day. Kinosheo Lake Bog, July 05-06, 1990.	224
Figure A36	Carbon Dioxide Concentration vs time of day. Kinosheo Lake Bog, July 13-14, 1990.	225
Figure A37	Carbon Dioxide Concentration vs time of day. Kinosheo Lake Bog, July 17, 1990.	226
Figure A38	Carbon Dioxide Concentration vs time of day. Kinosheo Lake Bog, July 25, 1990.	227
Figure A39	Carbon Dioxide Concentration vs time of day. Kinosheo Lake Bog, August 15-16, 1990.	228
Figure A40	Carbon Dioxide Concentration vs time of day. Kinosheo Lake Bog, September 12-13, 1990.	229
Figure A41	Carbon Dioxide Concentration vs time of day. Kinosheo Lake Bog (Ponds 1-5), October 12, 1990.	230
Figure A42	Carbon Dioxide Concentration vs time of day. Kinosheo Lake Bog (Ponds 6-10), October 12, 1990.	231

List of Tables

		Page
Table 1a	Summary of Literature Values for CH ₄ Flux from the Vegetated Surfaces of Wetland Environments	26
Table 1b	Summary of Literature Values for CH ₄ Flux from Pools or Lakes within Wetland Environments	26
Table 2a	Summary of Literature Values for CO ₂ Flux from the Vegetated Surfaces of Wetland Environments	29
Table 2b	Summary of Literature Values for CO ₂ Flux from Pools or Lakes within Wetland Environments	29
Table 3	Summary of Water Chemistry	69
Table 4	Comparison of Duplicate Samples	75
Table 5	Mean and Median CH ₄ Concentration Sum of Differences	78
Table 6	Kinosheo Lake Bog Time Weighted Mean Pond CH ₄ Concentration	80
Table 7	Coastal Fen Time Weighted Mean Pond CH ₄ Concentration	81
Table 8	Interior Fen Time Weighted Mean Pond CH ₄ Concentration	82
Table 9	Monthly Methane Concentrations in the Hudson Bay Lowland	87
Table 10	Mean CH ₄ and CO ₂ Concentrations in the Hudson Bay Lowland, September 13, 1989	89
Table 11	Mean and Median CO ₂ Concentration Sum of Differences	92
Table 12	Kinosheo Lake Bog Time Weighted Mean Pond CO ₂ Concentration	93
Table 13	Coastal Fen Time Weighted Mean Pond CO ₂ Concentration	94
Table 14	Interior Fen Time Weighted Mean Pond CO ₂ Concentration	96
Table 15	Monthly Carbon Dioxide Concentrations in the Hudson Bay Lowland	101
Table 16	Mean Dissolved Inorganic Carbon in the the Hudson Bay Lowland (June-October, 1990)	116
Table 17	Daily Methane Flux in the Hudson Bay Lowland (July-October, 1990)	126
Table 18	Daily Carbon Dioxide Flux in the Hudson Bay Lowland (July-October, 1990)	127
Table 19	Kinosheo Lake Bog Mean Pond Instantaneous CH ₄ Flux on Diel Sampling Days	138
Table 20	Coastal Fen Mean Pond Instantaneous CH ₄ Flux on Diel Sampling Days	139
Table 21	Interior Fen Mean Pond Instantaneous CH ₄ Flux on Diel Sampling Days	140
Table 22	Kinosheo Lake Bog Mean Pond Instantaneous CO ₂ Flux on Diel Sampling Days	141
Table 23	Coastal Fen Mean Pond Instantaneous CO ₂ Flux on Diel Sampling Days	142
Table 24	Interior Fen Mean Pond Instantaneous CO ₂ Flux on Diel Sampling Days	143

Table A1	Hudson Bay Lowland Water Chemistry Results	232
Table A2	Coastal Fen, June 07, 1990	235
Table A3	Coastal Fen, June 15, 1990	237
Table A4	Coastal Fen, June 24, 1990	238
Table A5	Coastal Fen, June 30, 1990	239
Table A6	Coastal Fen, July 09-10, 1990	240
Table A7	Coastal Fen, July 24, 1990	242
Table A8	Coastal Fen, July 31, August 4 and 12, 1990	244
Table A9	Coastal Fen, August 14-15, 1990	245
Table A10	Coastal Fen, September 10-11, 1990	246
Table A11	Coastal fen, October 10-11, 1990	248
Table A12	Interior Fen, June 07, 1990	250
Table A13	Interior Fen, June 16, 1990	251
Table A14	Interior Fen, June 30, 1990	252
Table A15	Interior Fen, July 03-04, 1990	253
Table A16	Interior Fen, July 09-10, 1990	254
Table A17	Interior Fen, July 19, 1990	255
Table A18	Interior Fen, July 24, 1990	256
Table A19	Interior Fen, July 31 and August 06, 1990	258
Table A20	Interior Fen, August 14-15, 1990	259
Table A21	Interior Fen, August 16, 1990	261
Table A22	Interior Fen, September 10-11, 1990	262
Table A23	Interior Fen, October 10-11, 1990	263
Table A24	Kinosheo Lake Area Bog, June 05, 1990	265
Table A25	Kinosheo Lake Area Bog, June 19 and 28, 1990	266
Table A26	Kinosheo Lake Area Bog, July 05-06, 1990	267
Table A27	Kinosheo Lake Area Bog, July 13-14, 1990	269
Table A28	Kinosheo Lake Area Bog, July 17, 1990	271
Table A29	Kinosheo Lake Area Bog, July 25, 1990	272
Table A30	Kinosheo Lake Area Bog, August 02 and 10, 1990	273
Table A31	Kinosheo Lake Area Bog, August 15-16, 1990	274
Table A32	Kinosheo Lake Area Bog, September 12-13, 1990	276
Table A33	Kinosheo Lake Area Bog, October 12, 1990	278
Table A34	Pond Physical Dimensions	281

Table of Contents

	Page
Abstract	i
Acknowledgements	ii
List of Figures	iv
List of Tables	vii
1	1
Historical and Introduction	6
I Microbial Production of CH ₄ and CO ₂	8
II Methane Production from Lake Sediments	11
III Methane Oxidation	13
IV Natural Freshwater Wetlands	17
V Measurement of Gas Flux from Aqueous Wetland Surfaces	24
VI Ebullition	25
VII Gas Transport by Aquatic Macrophytes	27
VIII Methane Flux from Wetlands	30
IX Carbon Dioxide Flux from Wetlands	31
X The Northern Wetland Study	34
2	34
Methods	35
I Study Area	37
II Sample Location	40
III Sampling Procedure	46
IV Water Chemistry Collection and Analysis	47
V Sample Analysis	50
VI Calculations	64
VII Computer Simulations	68
3	68
Results	73
I Water Chemistry	77
II Concentration of Dissolved Gases	103
III Observed Patterns of CH ₄ and CO ₂ Concentration	115
IV Influence of Wind History on CH ₄ and CO ₂ Concentration	117
V Dissolved Inorganic Carbon Concentrations	128
VI Flux of Methane and Carbon Dioxide to the Atmosphere	146
VII Computer Modelling	149
VIII Ebullitive Flux	152
IX Geographic Trend	156
4	156
Discussion	157
I Dissolved Gas Concentration	158
II Diel Variations in Flux	161
III Computer Modelling	163
IV Seasonal Flux	166
V Effects of Ponds on the Total Gas Flux from the Hudson Bay Lowland	168
VI Ebullition	169
VII Degradation of Peat Within the Ponds	169

	VIII Potential Impact of Global Warming on the Hudson Bay Lowland Gas Flux	171
5	Conclusions	173
6	Literature Cited	175
7	Appendix	189

Historical and Introduction

Atmospheric concentrations of both methane (CH_4) and carbon dioxide (CO_2) have been increasing since the Industrial Revolution (i.e 1700 A.D.) (see Chappellaz et al. 1990 for the most recent 160,000 year record of atmospheric CO_2 and CH_4 concentrations). Prior to the that time tropospheric concentrations of CH_4 averaged 0.75 p.p.m.v. (parts per million by volume) (Rasmussen and Khalil 1984). By 1990 the concentration reached 1.70 p.p.m.v. (Chappellaz et al. 1990) and is increasing at a rate of approximately 1.3%/year or 0.02 p.p.m.v./year (Rasmussen and Khalil 1984).

Pre-industrial tropospheric CO_2 concentrations averaged 260 p.p.m.v. (Raynaud and Barnola 1985). The concentration has now risen to 350 p.p.m.v. and continues to increase at 0.4% or 1.5 p.p.m.v., per year (Gammon et al. 1986).

The increasing concentrations of CH_4 and CO_2 are a growing concern as both of these gases have the property of being radiatively reflective or greenhouse gases. Greenhouse gases are gases that have the property of being transparent to incoming short-wave solar radiation but re-radiate much of the out going long-wave heat energy. Thus, an increase in their concentrations may have the effect of increasing the Earths temperature (Revkin 1988). Moreover the consumption of hydroxyl radicals (OH) by reaction with CH_4 results in a depletion of atmospheric OH and the increase of other greenhouse gases. Hydroxyl radicals are derived from the breakdown of ozone (O_3). Therefore the depletion of the OH

pool in the atmosphere will affect the tropospheric chemistry by depleting O_3 (Cicerone and Oremland 1988). Approximately 85% of the CH_4 input to the troposphere is consumed by this reaction. The end products of this process is CO_2 , H_2O , CO (which are all greenhouse gases) and H_2 (Cicerone and Oremland 1988).

At present CO_2 is causing the most concern because of it's greater concentration. However, CH_4 is a growing concern even though it is found in significantly smaller concentrations than CO_2 . It has 30x the radiative capacity of CO_2 on a mass basis (Revkin 1988). To illustrate this point Cicerone and Oremland (1988) have demonstrated that the radiative heating effect of increasing CH_4 from 0.7 ppm (pre-industrial revolution) to 1.7 ppm (1988 concentration) is half as large as that caused by the simultaneous increase of CO_2 concentrations from 275 ppm to the 1988 concentration of 345 ppm. The half life of CH_4 in the atmosphere of 8-10 years (Prinn et.al 1987) and is different from CO_2 which makes comparisons complicated.

Paleoclimatological studies have suggested that there is a strong relationship between CH_4 and CO_2 concentrations and climatic warming (Kuhn and Kasting 1983; Raynaud and Barnola 1985; Lindstrom and MacAyeal 1989; Broecker and Denton 1989). Ice core data suggests that the lowest concentrations of both CH_4 (.35 p.p.m.) and CO_2 (200 p.p.m.) occurred during the periods of maximum glaciation. When the earth's temperature

increased during the inter-glacial periods the pre-industrial maximums of both gases were observed (Chappellaz *et al.* 1990).

Hypotheses regarding past CO₂ changes usually involve how chemical processes in the world's oceans influence the atmospheric CO₂ concentrations and subsequently the glacial cycles (Broecker and Peng 1987; Broecker and Denton 1989). Raynaud *et al.* (1988) have hypothesized that the increase in CH₄ during interglacial periods comes from CH₄ production from wetlands, which increase in size during the glacial retreats. Thus CH₄ further contributes to the warming during the interglacial period.

At present, anthropogenic sources of both CO₂ and CH₄ are added to natural sources. With the data now available it is predicted that at the present emission rates the atmospheric CO₂ concentration will double the preindustrial concentration some time early in the next century. With this doubling there may be an increase in the earth's average atmospheric temperature of 1.5°C to 4.5°C (Understanding CO₂ and Climate, AES Report 1985). This would bring about many far reaching physical and socio-economic changes.

Both CO₂ and CH₄ are produced biologically, by the combustion of materials such as wood or fossil fuels, and by volcanic eruptions. Of the biological sources, production from northern wetlands may be the most sensitive to anthropogenic environmental impacts. These ecosystems have not been well studied and it is not known how these systems will respond to

anthropogenic influences.

The following is a review of the literature pertaining to the biogenic production of CH_4 and CO_2 from wetlands and the transport pathways that these gases follow to reach the atmosphere. A discussion of the methods by which gas exchange between water surfaces and the atmosphere may be determined is included.

I Microbial Production of CH_4 and CO_2

Biogenic CH_4 and CO_2 production result from anaerobic decomposition of organic material. CO_2 may also be produced from aerobic decomposition of organic carbon and CH_4 oxidation. Many environments provide conditions for both aerobic and anaerobic decomposition such as natural wetlands, lake sediments, rice paddies, and enteric fermentation of ruminants.

The primary pathway of CH_4 and CO_2 production in anaerobic sediments is the degradation of acetate into CH_4 and CO_2 (Hobson *et al.* 1974 and Lovely and Klug 1982). Another pathway is the reduction of CO_2 by H_2 to form CH_4 (Bryant *et al.* 1967).

Because organic matter is primarily in the form of large complex molecules such as carbohydrates, proteins and lipids, the methanogens must rely on other organisms to convert the organic material to a acetate, H_2 and CO_2 (Figure 1). The classic example of this association of methanogens with other

organisms is the association of *Methanobacterium bryantii* and the S-organism. In this case the chemoheterotrophic S-organism oxidizes ethanol to acetate and H_2 . *M. bryantii* then utilizes the excess H_2 to reduce CO_2 to CH_4 (Bryant et al. 1967). Another example is the fermentation of cellulose in the rumen. In the rumen, *Ruminococcus flavefaciens* ferments cellulose to acetate, formate, H_2 and CO_2 . *Methanobacterium ruminantium* can grow by using the H_2 and CO_2 directly to form CH_4 or by the breakdown of formate to H_2 and CO_2 (Latham and Wolin 1977).

The presence of methanogens in a culture influences the types of fermentation end products that are formed. In co-cultures of chemoheterotrophs and methanogens, methanogens can utilize the H_2 produced by the chemoheterotroph. This symbiotic relationship is known as interspecies H_2 transfer. Interspecies hydrogen transfer was first reported by Bryant et al (1967) and the first systematic verification was conducted by Iannotti et al. (1973). When interspecies H_2 transfer occurs there is a shift of the fermentation end products from volatile fatty acids to CH_4 and CO_2 (Mah 1982).

When chemoheterotrophs are grown in the absence of methanogens the fermentation end products that are produced are volatile organic compounds such as acetate, butyrate, propionate and neutral end products such as acetone, butanol and propanol. A small quantity of H_2 and CO_2 is also produced (Figure 1). In the presence of H_2 oxidizing methanogens, H_2 production becomes the major electron sink for the

chemoheterotrophs. Acetate becomes the major organic end product which can be further reduced to CH_4 and CO_2 (Figure 1)(Mah 1982). The relationship is a symbiotic one as the chemoheterotrophs benefit by the removal of inhibitory H_2 and other fermentation products by the methanogens while the methanogens benefit from a readily available supply of substrates produced by the chemoheterotrophs. All the organisms benefit from increased overall energy release (Iversen et al. 1987).

In anaerobic lake sediments and peat organic matter is also hydrolysed to the reduced fermentative end products acetate, H_2 , CO_2 (Yavitt et al. 1987). To a lesser degree proprionate, butyrate, valerate and formate are produced as products of incomplete decomposition and are eventually converted to acetate (Lovely and Klug 1982). Of these products acetate is the major precursor of CH_4 and CO_2 (Yavitt et al. 1987, Lovely and Klug 1982) by methanogenic bacteria. In anaerobic lake sediments CH_4 and CO_2 from non-respiratory pathways are produced in approximately equal quantities (Kelly et al. 1988)

II Methane Production from Lake Sediments

Most of the information available on natural populations of methanogens is from studies on aquatic systems. The major zone of CH_4 production in freshwater lakes is the sediment

(Strayer and Tiedje 1978, Lindstrom and Sommers 1984).

The amount of CH_4 produced varies with location within the lake as well as seasonally and geographically. Rudd and Hamilton (1978) showed that for a small eutrophic lake, the CH_4 production rates for well oxygenated epilimnetic sediments was $0.8 \text{ mmol/m}^2/\text{day}$ and $10.8 \text{ mmol/m}^2/\text{day}$ for anaerobic hypolimnetic sediments during summer stratification. During fall turnover the average CH_4 production rate for the total lake sediments was $4.8 \text{ mmol/m}^2/\text{day}$. During the winter the hypolimnetic sediments produced CH_4 at a rate of $12.1 \text{ mmol/m}^2/\text{day}$ after the hypolimnion became anoxic. Ellis-Evans (1984) found a similar pattern of methane production from lake sediments in freshwater maritime lakes in the Falkland Islands although not at the same magnitude as those found by Rudd and Hamilton (1978) for a north temperate lake. In these Antarctic lakes CH_4 was produced at a rate of only $0.11 \text{ mmol/m}^2/\text{day}$ for profundal sediments and $0.04 \text{ mmol/m}^2/\text{day}$ for littoral sediments during the winter. Rates decreased during the summer to $0.08 \text{ mmol/m}^2/\text{day}$ for profundal sediments and $0.03 \text{ mmol/m}^2/\text{day}$ for littoral sediments.

Kelly and Chynoweth (1981) have shown that CH_4 production from sediments is correlated with short-term temperature changes in laboratory core incubations. More importantly they have shown CH_4 production *in situ* correlates best to the rate of input of organic material and suggest that activity proceeds at a maximum rate even under long-term cold

conditions. CH_4 production decreases during summer stratification as the input of new organic material into the hypolimnion is slowed by the strong thermal gradient of the thermocline. The rate increases again in the fall as algal sedimentation increases during fall turn over and winter when there is a large amount of new organic material in the anoxic sediments.

A significant amount of the new carbon fixed by primary productivity is recycled as CH_4 in anaerobic sediments. Strayer and Tiedje (1978) found that 24-37% of the summer productivity was released from the sediments as CH_4 . Kelly and Chynoweth (1981) also found that approximately 40% of the organic input into the sediments was returned as CH_4 . Rudd and Hamilton (1978) found that 55% of carbon input into the lake was regenerated as CH_4 . This variation in the amount of CH_4 released probably reflects the difference in the contribution of respiratory processes to total decomposition in each of the lakes studied.

Another controlling factor in the rate of CH_4 production from sediments involves competitive interactions with other groups of bacteria. There is a large body of literature that shows that methanogens can be inhibited by all aerobic processes and by other anaerobes such as sulfate reducers (ex. *Desulfovibrio spp.*), through competition for the main sources for terminal electron donors such as CO_2 , H_2 and acetate (Abram and Nedwell 1978 and Smith and Klug 1981 and Lovely and Klug

1983). Oremland *et al.* (1982b) and Lovely *et al.* (1982) have shown that methanogenesis can occur simultaneously with sulfate reduction when the methanogens utilize other organic carbon substrates such as methanol or methionine. Naguib (1984) has also demonstrated this effect with incubations of cores from a eutrophic lake. Naguib amended sulfate reducing cores with acetate, H_2/CO_2 and methanol. Only the methanol enhanced CH_4 production.

III Methane Oxidation

CH_4 oxidation is a major form of loss of CH_4 within lakes. Rudd and Hamilton (1978) found that 60% of the CH_4 produced in lake sediments was oxidized before it could escape to the atmosphere, with most of the oxidation occurring during spring and fall lake turnover.

In freshwater systems during summer stratification CH_4 oxidation usually occurs near the aerobic/anaerobic interface as CH_4 oxidizers must fix N_2 and the N_2 fixation process is very sensitive to the presence of O_2 (Rudd *et al.* 1976, Rudd and Hamilton 1978 and Lindstrom and Somers 1984). However when the fall turnover occurs, ammonia (NH_3), which had been trapped below the thermocline, is mixed throughout the lake and the CH_4 oxidizers are no longer restricted to the aerobic/anaerobic interface as there is no longer a need to fix N_2 (Rudd *et al.* 1976). In laboratory incubation experiment

Rudd et al. (1976) demonstrated that CH_4 oxidation could be turned on or off with the presence or absence of N_2 fixation. When the dissolved inorganic nitrogen concentration in the culture was increased to 7 mM, CH_4 oxidation could proceed without N_2 fixation.

The amount of CH_4 oxidized varies seasonally as well as with changing lake characteristics between different lakes. Very little CH_4 oxidation occurs throughout the period of summer stratification as very little CH_4 diffuses across the highly stable thermocline. Rudd et al. (1976) and Rudd and Hamilton (1978) have shown that >95% of CH_4 oxidation occurs during the period of fall overturn and winter when the lake is uniformly mixed.

Of the CH_4 that is oxidized, approximately 50% is taken in by the cell for incorporation as new cell material and 50% is converted to CO_2 (Rudd and Hamilton 1978). Since the majority of CH_4 oxidation occurs during fall overturn, approximately 90% of the CO_2 produced escapes into the atmosphere as there is very little algal activity at this time in northern temperate lakes (Rudd and Hamilton 1978). Therefore CH_4 oxidation can significantly increase the export of CO_2 from the lake to the atmosphere.

In freshwater systems species such as *Pseudomonas methanitrificans*, *Methylomonas methanica*, *Methanomonas methanooxidans* have been implicated in CH_4 oxidation (Rudd and Taylor 1980).