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MODELING OF MICROSCALE VARIATIONS IN METHANE FLUXES

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Abstract: The current study analyzes the different modes of variation in methane fluxes from different microsites of a boreal mire. The results emphasize the importance of microsite characteristics, water table and vegetation cover for methane fluxes. Water level affects the moisture and oxygen profiles in peat matrix which are reflected to methane production and oxidation rates and the corresponding microbial populations. Vascular plants promote methane production by providing substrates in the form of root exudates and fine root litter, enhance methane oxidation by transporting oxygen to water saturated peat layers and accelerate methane transport by liberating methane from peat to the atmosphere via the aerenchymous tissue. The model presented in this study connects the methane fluxes to the seasonal photosynthetic cycle of plants at the microsite level while the thermal and hydrological conditions in peat are used as an operational framework. Overall, the model dynamically combines the microbial processes in peat to changing environmental factors in the level of peatland ecosystem. Sensitivity analysis of the model reveals the importance of substrate supply to methane fluxes. Furthermore, the model outcome is sensitive to increased capability of the vascular plants to transport oxygen downwards. Lack of oxygen and partly methane keep methane oxidation at a very low level. Any changes in model parameters or environmental conditions that compensate for these lacks have a remarkable decreasing effect on simulated flux. Simulated methane flux decreases considerably if the duration of simulated dry period increases, threshold for a dramatic change lying between 4 and 6 weeks of drought. Increase in air temperature enhances methane flux especially if the effect of increased temperature on gross primary production is taken into account.

Keywords: boreal peatlands, microsites, vegetation cover, water table, photosynthetic carbon cycle, methane production and oxidation potentials, flux dynamics, correlation techniques, regression and process-based models.

Academic dissertation

Systems Analysis Laboratory
Helsinki University of Technology

Modeling of microscale variations in methane fluxes

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Publications

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[V] Kettunen, A. (2002). Connecting methane fluxes to vegetation cover and water table fluctuations at microsite level, *Systems Analysis Laboratory Research Reports*, E10, November 2002. (In press in Global Biogeochemical Cycles)

Contributions of the author

The author is responsible for developing the theoretical framework of the study, and for the modeling and data analyses presented in all papers. She is also responsible for the interpretation of the results and has written all the papers. The co-authors have contributed to experimental design and practical measurements.

Preface

The work for this thesis was started in the Systems Analysis Laboratory at Helsinki University of Technology during 1994-1995, continued in the Department of Forest Ecology at University of Helsinki during 1995-1999 and finished during 1999-2002 while I already full-time worked for the Health and Nutrition group in Danisco. I am grateful to Prof. Veijo Kaitala, my supervisor, Prof. Raimo P. Hämäläinen, the head of the Systems Analysis Laboratory, Prof. Juhani Päivänen, the professor of Peatland Ecology and Forestry, and Docent Jukka Laine, the project leader of the "Carbon Balance of Peatlands and Climate Change – SUOSILMU" for providing me with working facilities. I also appreciate the friendly and warm atmosphere I have had the chance to enjoy both in the Systems Analysis Laboratory, in the Department of Forest Ecology and in the Health and Nutrition group.

My work was funded by the Academy of Finland in the project "Systems Analysis, Mathematical Modelling and Decision Making" led by Prof. Veijo Kaitala during 1994-1996, by a scholarship for post graduate students awarded by Helsinki University of Technology during spring 1997 and spring 1998, by a scholarship from the Foundation for Reseach of Natural Resources in Finland in autumn 1997 and again by the Academy of Finland in the project "Modelling of Dynamics of Trace Gas Exchange in Wetlands" led by Prof. Veijo Kaitala during autumn 1998 and spring 1999. The work was also supported financially by Emil Aaltonen Foundation, Leo and Regina Wainstain Foundation and Fortum Foundation (former IVO Foundation).

My supervisor, Prof. Veijo Kaitala introduced me to the research field and provided me with working facilities and funding which I appreciate. However, his most important contribution for my future was to push me towards independent research work which I warmly thank him for.

Data for the analyses were produced in the subproject "The Carbon Balance of Peatlands and Climate Change – SUOSILMU" of the project "Finnish Programme on Climate change – SILMU" financed by the Academy of Finland during 1990-1995. I greatly appreciate the fruitful scientific cooperation and discussions with SILMU researchers, Dr. Jukka Laine, Dr. Harri Vasander, Dr. Raija Laiho, Dr. Kari Minkkinen and Dr. Eevastiina Tuittila from University of Helsinki, Dr. Jukka Alm, Dr. Jouko Silvola and Dr. Sanna Saarnio from University of Joensuu, and Hannu Nykänen, M.Sc. and Dr. Pertti Martikainen from the National Public Health Institute in Kuopio.

The time and effort by my preliminary examiners, Docent Harri Vasander and Docent Hannu Rita from University of Helsinki, helped me to improve the thesis which is greatly acknowledged.

In this preface, I lack the space to describe in full detail the importance of my family, my relatives, my god-children, my close and more distant friends to the quality of my life during the years I have more or less worked for this thesis. I count on the hope that in other occasions I have the opportunity to tell you all how much appreciate your support and love. In the limited space, I still want to thank my parents for introducing the world to me in such a way that the extraordinary phenomena raised my interest, my spouse Tuomas for sharing my view of life and my son Matias and my yet unborn child for carrying the valuable from the past to the future.

Espoo, November 2002.

1. Introduction

1.1 Carbon cycling and enhanced greenhouse phenomenon

Life, as we know it, is based on flow of energy from the Sun and cycling of elements on Earth. The cycling of elements and the energy flow are interlinked as the composition of atmosphere affects the amount of energy that remains on the Earth. The atmosphere and in particular the so called greenhouse gases in the atmosphere increase the surface temperature of Earth by some thirty degrees from the situation without atmosphere, a phenomenon known as natural greenhouse effect (IPCC Climate change 1990, 1995, 2001). The changes in concentrations of greenhouse gases shift the energy balance and, according to the icecore records, atmospheric concentrations of carbon dioxide and methane have actually varied in accordance with changing temperature (Lorius et al. 1990).

Human activities have, however, increased considerably the atmospheric concentrations of the greenhouse gases, carbon dioxide, methane, nitrous oxide and chlorofluorocarbons (CFCs). The higher atmospheric concentrations of these gases affect the climate that most probably would be warmer on average terms but might differ from the current in many aspects, like seasonal and regional weather patterns and the duration and frequency of extreme events (IPCC Climate change 1990, 1995, 2001). In this context, studies on carbon cycles have recently received increasing attention.

Methane is the second important radiatively active gas the contribution of which to enhanced greenhouse phenomenon lies in the same range as that of carbon dioxide (Lashof and Ajuha 1990, Rodhe 1990, Crutzen 1991). Currently, atmospheric methane concentration increases by 0.5-1 % per year (Rasmussen and Khalil 1984, Crutzen 1991, Khalil and Rasmussen 1994, Quay *et al*. 1999) even though in the future, the increase has been speculated to cease, resulting in a stabile methane concentration (Kheshgi *et al.* 1999).

1.2 Methane sources and sinks

Methane is formed in strictly anaerobic conditions that prevail in water saturated ecosystems, land fills and in the gastrointestinal tracts of certain animals. Total methane source is estimated to lie between 500 and 550 Tg y^{-1} (Khalil and Rasmussen 1983, 1990, Cicerone and Oremland 1988, Fung *et al.* 1991, Hein *et al*. 1997, Quay *et al*. 1999, Lassey *et al.* 2000). Wetlands are the most important natural methane source contributing between 20-30 % of total methane emissions (Khalil and Rasmussen 1983, 1990, Matthews and Fung 1987, Cicerone and Oremland 1988, Bartlett and Harriss 1993, Hein *et al*. 1997, Lassey *et al.* 2000) while lakes, tundra and wild animals including termites act as minor natural sources (Khalil and Rasmussen 1983, 1990, Cicerone and Oremland 1988, Fung *et al.* 1991, Hein *et al*. 1997, Lassey *et al.* 2000). In anthropogenic methane sources, rice paddies and ruminants are most important while landfills, hydroeletric reservoirs and fluxes related to fossil fuel usage are of minor importance (Khalil and Rasmussen 1983, 1990, Crutzen 1991, Fung *et al.* 1991, Cicerone and Oremland 1988, Bartlett and Harriss 1993, Hein *et al*. 1997, Lassey *et al*. 2000).

The total sink of methane is estimated to range from 400 to 500 Tg y^{-1}, of which reaction with hydroxyl radical in trophosphere accounts for 85-90 % (Khalil and Rasmussen 1983, 1990, Crutzen 1991, Fung *et al.* 1991, Hein *et al*. 1997). Stratospheric sink and biological methane oxidation in dry soils and possibly in seas account for less than 10 % of the sink (Khalil and Rasmussen 1983, 1990, Crutzen 1991, Fung *et al.* 1991, Hein *et al*. 1997).

1.3 Wetlands as contributors of the global carbon cycle

Northern peatlands are important contributors to the global carbon cycle. In the cold and moist climatic conditions, boreal peatlands have sequestered large amounts of atmospheric carbon during the past few thousand years (Aselmann and Crutzen 1989, Gorham 1991). In the long term, the development of peatlands contributes as a mediator or even as a positive feedback to atmospheric trace gas concentrations and consequent change in climate (Prinn 1994, Gajewski *et al.* 2001). In the short term, the carbon balance in mires depends on the rates of photosynthesis and respiration which are affected by the short-term variations in environmental factors. During one year, a mire may show a positive carbon balance while during the next year, the carbon balance may turn negative (Alm *et al*. 1997, 1999b, Griffis *et al*. 2000).

Even though wetlands on average act as carbon sinks, they simultaneously are the most important single methane source. Especially, high latitude northern peatlands, most of which belong to the boreal zone, are suggested to contribute 34-60% of the wetland methane emissions (Matthews and Fung 1987, Cicerone and Oremland 1988, Aselman and Crutzen 1989, Bartlett and Harriss 1993).

1.4 Aims of this study and development of the research problem

In the context of global climate change, it is crucial to understand the dynamics of methane fluxes from wetland ecosystems and the processes affecting fluxes in relation to environmental factors. The overall aim of the current study was to understand and describe the different modes of variations in methane fluxes from boreal peatlands in current conditions and to predict the fluxes also in the future conditions.

The work started by analyzing the connection between abiotic factors, temperature and hydrological conditions, and methane fluxes using correlation techniques. In II, lagged cross-correlation analysis was applied to temperature, precipitation, water table and methane flux data to enlighten the possible control mechanisms between the abiotic environmental variables and methane emissions and, in particular, the time lags in the system. In III, frequently measured data from a boreal fen was used to evaluate the different modes of spatial and temporal variations in methane fluxes and to test how regression models capture these variations. II and III do not explicitly analyze processes, methane production, oxidation and transport in peat profile even though the effects of these processes on methane fluxes are discussed. In II, the relationship between vegetation and methane is mentioned but not discussed in detail. The results of III confirmed the earlier literature results that there are differences between microsites in relation to overall methane levels, diurnal patterns and predictive power of the regression models. In fact, III already attempted to explain the observed differences between microsites by microsite vegetation. Lateron in V, an explicit connection between microsite vegetation and methane fluxes was presented.

The processes of methane production and oxidation in peat profile were the subject of IV. Seasonal patterns in water table and methane production and oxidation potentials were considered and the effects of short-term changes in water tables on the potentials were studied in IV. The results of IV motivated the idea of describing the effects of water table fluctuations on methane fluxes by using dynamics of microbial populations as presented in V.

In order to describe the effects of microsite vegetation on methane fluxes and to analyze the relationship between green plant photosynthesis and methane emissions, there was a need to model the short-term dynamics of carbon dioxide exchange in I. The photosynthesis model from I was then used in V.

The process-based model presented in V summarized and further developed the work presented in I-IV and also gathered together the information from the literature in order to meet the overall aim of the thesis. Photosynthesis in different microsites was described in the process-based model as in I. The connection between vegetation and water level at microsite scale was modeled using ideas raising from the work presented in III while the effects of peat processes on methane fluxes during periods of fluctuating water tables were modeled as motivated by the results in IV. Abiotic factors were taken into account in the model in accordance with literature, II and III. Overall, V presents a model that is validated against measurements and hence, is capable of simulating methane fluxes from different microsites of a boreal fen.

2. Processes affecting methane flux from wet ecosystems

2.1 Substrate supply

Substrate availability is a crucial factor for methanogenesis in wetland ecosystems. Even though peat itself is a large reservoir of carbon, the carbon in peat matrix is very resistant to decomposition in the anaerobic conditions that prevail in peat profile and therefore, peat carbon can provide only limited amounts of substrate for methanogenesis (Kuder and Kruge 2001). In fact, it has long been known that recent carbon bound by vegetation can promote methanogenesis by providing root exudates and easily decomposable litter, which contain carbohydrates, organic and amino acids and phenolic compounds (Rovira 1969).

Still, only during the latest decade, the scientific community started to realize the importance of plants to methane fluxes. In the early 1990's, a book describing the effects of plants on trace gases devoted two chapters to the relationship between vegetation and methane fluxes (Chanton and Dacey 1991, Schütz *et al.* 1991). As the majority of plant biomass is situated below-ground (Wallen 1986, Saarinen 1996) where methane production also take place, it is not surprising that methane fluxes were first found to correlate to root biomass (Sass *et al*. 1990). Furtheron, supported by experimental evidence, methane flux was suggested to increase with the photosynthetic activity of plants (Whiting *et al.* 1991, Whiting and Chanton 1992, 1993). Indirect evidence for the importance of plants to the substrate supply provided the significantly lower methane fluxes from unvegetated surfaces compared to vegetated (Chanton *et al.* 1992a, Happell *et al.* 1993, Torn and Chapin 1993, Smith *et al*. 2000). Furthermore, methane fluxes were found to correlate to plant biomass (Ding *et al*. 1999) and more specifically, to sedge cover both across microsites within a single mire (Bubier *et al*. 1995a, 1995b, Schimel 1995, Bellisario *et al.* 1999) and across different mires (Nilsson and Bohlin 1993, Bubier 1995, Granberg *et al*. 2001b, Nilsson *et al*. 2001). Also in a restoration study, methane flux was observed to increase with increasing sedge cover (Tuittila *et al.* 2000). Studies where clipping of vascular plants decreased the flux considerable further supported the importance of plant related carbon to methanogenesis (Kelker and Chanton 1997, King *et al.* 1998, Verville *et al.* 1998, Frenzel and Karofeld 2000). Also the pore water concentrations were found to increase from unvegetated to vegetated surfaces (Whiting and Chanton 1992, Byrd *et al*. 2000).

Use of stable and radio isotopes of carbon has proven that photosynthetic carbon actually promotes methanogenesis both in rice paddies (Dannenberg and Conrad 1999) and in natural wetlands (Megonigal *et al.* 1996, King and Reeburgh 2002). The estimates for contribution of recent photosynthates to methane production vary a lot between different studies: in some cases the recent photosynthates are found to be the predominant substrate for methane production (Minoda *et al.* 1996, van den Pol-van Dasselaar and Oenema 1998, Chasar *et al.* 2000) while in others, their contribution is considered much lower (Minoda *et al.* 1996, Dannenberg and Conrad 1999, King and Reeburgh 2002). The large range is understandable as allocation of carbon to above- and below-ground parts of the plants and to exudation is known to be affected by plant species, plant age, tillering stage, root damage, light intensity, soil temperature, soil water stress, nutrient availability/deficiency and soil microorganisms (Rovira 1969, Shaver and Cutler 1979, Kummerow and Ellis 1984, Schütz *et al.* 1991). On average, about 15% of the photosynthetically fixed carbon is estimated to be released from the roots, mainly in microbial and plant respiration (see Saarnio *et al.* 1998, Saarnio and Silvola 1999).

2.2 Acetate and hydrogen pathways in high latitude wetlands

In freshwater systems, methane is formed either from acetate dissimilation (acetate pathway) or bicarbonate reduction (hydrogen pathway) (Kelley *et al.* 1992, Westermann 1993). Acetate and hydrogen pathways differ in relation to temperature dependence and substrate availability (Ferguson and Mah 1983, Svensson 1984, Westermann 1993, Conrad *et al.* 1987). At low temperatures (between 10 and 15 °C), the acetate pathway was found to contribute 85-90 % of methane produced and the contribution of the hydrogen pathway increased with increasing temperature (Avery *et al.* 1999, Fey and Conrad 2000). In addition to temperature control, the vegetation affects the pathways so that in vegetated sites where fresh organic matter is available due to high plant productivity, the acetate pathway dominates while in unvegetated sites the hydrogen pathway becomes important (see Bellisalio *et al.* 1999, Popp *et al.* 1999, Chasar *et al.* 2000). In fact, recent studies using carbon isotope methods (Chanton *et al.* 1995, Avery *et al.* 1999, Bellisario *et al.* 1999, Popp *et al.* 1999, Chasar *et al.* 2000) have observed that the acetate pathway clearly dominates in northern mires during the summer time.

2.3 Methane production

Methane is formed as a terminal step of a very complicated anaerobic degradation chain (Cicerone and Oremland 1988) by methanogenic bacteria (e.g. Garcia *et al*. 2000). Strictly anaerobic conditions and a suitable carbon source are needed for methanogenesis to occur. The reactions leading to methane formation are understood relatively well. Different kinetic models including bacterial populations involved in different reactions and organic acids as intermediate products have been constructed to decribe methane formation in batch fermentation systems. Some models restrict to a specific substrate type, like acetate (Bhadra *et al.* 1983, Ferguson and Mah 1983, Fukuzaki *et al.* 1990, Kalyuznuy *et al.* 1991) while others consider a more heterogeneous substrate like whey permeate (Yang and Guo 1990), some organic waste (Beba and Atalay 1986, Sales *et al.* 1989, Lee *et al.* 1993) or unspecified substrate type (Kleinstreuer and Poweigha 1982, Havlik *et al.* 1986, Barthakur *et al.* 1991, Segers and Kengen 1998).

In wetlands, changes in substrate availability and redox conditions are suggested to control the methane production rate and growth and death of methanogenic bacteria (Conrad 1989, 1996, Morrissey and Livingston 1992, Valentine *et al.* 1994). In addition, in principle methane production is enhanced with an increase in temperature but *in situ* conditions substrate availability strongly affects the temperature response (Dunfield *et al.* 1993, Valentine *et al.* 1994, Bergman *et al.* 1998). Deeper in peat oxygen concentrations are smaller but the fresh organic carbon is mainly supplied to uppermost layers where plant roots survive (Schütz *et al.* 1991, Schimel 1995). In fact, maximal methane production has been observed at about 20 centimeters below the water table (Sundh *et al.* 1994).

2.4 Methane oxidation

Methane oxidation, opposite reaction for methane production, converts methane to carbon dioxide (Cicerone and Oremland 1988). Similarly to methane formation models in closed systems, kinetics of methane oxidation have been described in a continuous flow reactor system (Spivak and Rokem 1994, 1995). Methane oxidation can be carried out by high-affinity methane oxidizers in aerobic soils, like forest and agricultural soils, and by low-affinity methane oxidizers in anaerobic soils where methane is simultaneously produced. As high-affinity methane oxidation is conceptually different from low-affinity methane oxidation (Bender and Conrad 1992, 1993, 1994, 1995, Striegl 1993, Ridgwell *et al*. 1998, Del Grosso *et al*. 2000, Jäckel *et al*. 2000, Phillips *et al*. 2001, Reay *et al*. 2001), this summary restricts to low affinity methane oxidation that is relevant to wetland ecosystem and high-affinity methane oxidation is not considered.

In wetlands, methane oxidation rates depend on methane and oxygen availability which is connected to peat moisture conditions, temperature, and the activity of methane oxidizing bacteria in the peat matrix. As methane oxidation requires methane as substrate and oxic conditions, population of methane-oxidizers develops where methane and oxygen overlap in the peat profile (Conrad 1989, 1996, Sundh *et al.* 1995, Segers 1998). Temperature control has been suggested to be less important for methane oxidation than for methane production (Dunfield *et al.* 1993). Changes in methane and oxygen concentrations during the growing season affect the population dynamics of methanotrophic bacteria (Svensson and Rosswall 1984*,* Whiting and Chanton 1993) and are reflected in the net flux of methane.

Estimates of the methane fraction that becomes reoxidated before it reaches atmosphere vary from 0 to 100 % (Yavitt *et al.* 1988, 1990, Schütz *et al.* 1989, King *et al.* 1990, Fechner and Hammond 1992, Sass *et al.* 1992, Moosavi and Crill 1998, Frenzel and Karofeld 2000, Pearce and Clymo 2000, Popp et al. 2000). Also the modeled contribution of oxidation varies from wetlands to rice paddies and landfills (Bogner *et al.* 2000).

2.5 Methane transport

Methane is liberated from peat via three routes: diffusion, ebullition, and passage through plants (e.g., Conrad 1989*,* Chanton *et al.* 1992b). In unvegetated surfaces, ebullition mainly dominates (van det Nat and Middelburg 1998, Van der Nat *et al.* 1998). In vegetated surfaces, bubble flux may become important during wintertime when plant biomass is low (Schütz *et al.* 1989, Byrnes *et al.* 1995, van det Nat and Middelburg 1998). However, whenever vascular plants are present, bubbling is rare and flux via plants tends to dominate the diffusive flux, both in rice paddies (Schütz *et al.* 1989, Nouchi *et al.* 1990, Byrnes *et al.* 1995) and in wetlands (Sebacher *et al*. 1985, Chanton and Dacey 1991, Morrissey and Livingston 1992, Whiting and Chanton 1992, Schimel 1995, van der Nat *et al.* 1998, Frenzel and Karofeld 2000).

Plants have two possible ways of transporting methane from peat to atmosphere, active gas transport due to pressure differences and passive diffusion (Dacey 1981). Some plants, like *Phragmites* and *Typha,* show active gas transport while others, like *Carex* sp. only have passive diffusion (Konçalovà *et al.* 1988, Chanton *et al.* 1992a, 1993, Happel *et al.* 1993, van der Nat and Middelburg 1998, van der Nat *et al.* 1998, Popp *et al.* 1999). Active gas transport leads to a strong diurnal pattern in methane fluxes and consequently, if no diurnal pattern is observed, plants that use active gas tranport are not present (Morrissey *et al*. 1993, van der Nat and Middelburg 1998, van der Nat *et al.* 1998). The within-plant diffusion rate has also been found to be higher for *Eriophorum angustifolium* than for *Carex aquatilis* (Schimel 1995). Also temperature has been proven to have an effect on the within-plant diffusion rate (Thomas et al. 1996). In rice paddies, a linear relationship between plant-mediated methane flux rates through plants and pore water methane concentrations has been established (Nouchi and Mariko 1993). In spite of many examples for a plant-associated methane oxidation (Frenzel 2000, Heilman and Carlton 2001), there is growing evidence that a few plants including *Eriophorum* sp. do not support methane oxidation (King *et al.* 1990, Chanton *et al.* 1992b, Kelker and Chanton 1997, Frenzel and Rudolph 1998), possibly due to differences in the quality and type of root exudates between those plant species that support plant-associated methane oxidation and those who do not (Frenzel and Rudolph 1998).

3. Link between environmental factors and methane flux

3.1 Existing modes of variations

The dynamic balance between methane production and oxidation rates in peat profile and the transport rate from peat to atmosphere control methane fluxes from wetlands (Conrad 1989, 1996, Bubier and Moore 1994). The fluxes show high spatial and temporal variations (Moore *et al.* 1990, Whalen and Reeburgh 1988, 1992, Dise 1993). The spatial variations are due to the fact that the basic processes (methane production, oxidation, and transport from peat to atmosphere) are affected by site specific factors such as average hydrological conditions (Svensson and Rosswall 1984, Sebacher *et al.* 1986, Roulet *et al.* 1992, 1993, Moore *et al.* 1994, Fiedler *et al*. 2000), soil nutrient contents (Svensson and Rosswall 1984, Dise 1993), substrate concentration and quality (Morrissey and Livingston 1992, Whiting and Chanton 1992, Valentine *et al.* 1994, Fiedler *et al*. 2000) and vegetation type (Torn and Chapin 1993, Shannon and White 1994, Bubier 1995, Bubier *et al.* 1995). The temporal variations, namely interannual variations (Mattson and Likens 1990, Whalen and Reeburgh 1992, Frolking and Crill 1994, Shurpali and Verma 1998), seasonal variations (Dise *et al.* 1993, Shurpali *et al.* 1993, Frolking and Crill 1994, Alm *et al.* 1999a, Mast *et al.* 1998, Panikov and Dedysh 2000), diurnal cycles (Chanton *et al*. 1993, Mikkelä *et al.* 1995, Thomas *et al.* 1996, Van der Nat *et al.* 1998) and episodic fluxes (Mattson and Likens 1990, Windsor *et al.* 1992, Christensen 1993, Frolking and Crill 1994), are due to effects of temporally changing environmental factors, like weather conditions, on the basic processes affecting methane fluxes (Conrad 1989).

3.2 Correlation techniques

Very complex interactions occur between abiotic and biotic environmental factors and the actual processes affecting methane flux. The use of correlation techniques started from relating methane fluxes to abiotic environmental factors, such as temperature and soil hydrology (Moore and Knowles 1987, 1989, 1990, Crill *et al.* 1988, Moore *et al.* 1990). Some studies emphasize the effect of temperature on methane fluxes (Moore and Knowles 1987, 1990, Crill *et al.* 1988, Whalen and Reeburgh 1992, Dise *et al.* 1993, Shurpali *et al.* 1993, Shannon and White 1994, Moosavi *et al.* 1996, Syuker *et al.* 1996) while others have considered the depth of the water table to be a more important control (Sebacher *et al.* 1986, Bubier *et al*. 1993b, 1995b, Moore and Roulet 1993, Funk *et al*. 1994, Nykänen *et al.* 1998).

Regression techniques have proven useful in predicting average seasonal fluxes among microsites but it has turned out to be much more difficult to predict the temporal variations in methane fluxes using regressions with temperatures and water tables as independent variables (Moore *et al.* 1990, 1994, Whalen and Reeburgh 1992, Bubier *et al.* 1993a, 1993b, Roulet *et al.* 1992, 1993, Torn and Chapin 1993, Vourlitis *et al.* 1993). Models that use correlation techniques to connect methane fluxes to abiotic environmental factors have been applied also recently (Christensen and Cox 1995, Martikainen *et al.* 1995, Granberg *et al.* 1997, Nykänen *et al.* 1998, Bellisario *et al.* 1999, van den Pol-Van Dasselaar *et al.* 1999a, Wickland *et al.* 2001) even they have achieved only limited success in describing or predicting variations in methane fluxes. Models that include also biotic factors, such as microsite vegetation cover (Bubier et al. 1995b, Saarnio *et al.* 1997, van den Pol-van Dasselaar *et al.* 1999b, Granberg *et al.* 2001b, Nilsson *et al.* 2001) or net ecosystem production (Christensen *et al.* 1996, Bellisario *et al.* 1999, Friborg *et al.* 2000) can show better predictive power within the site. Still, statistical relationships depend on the spatial scale and temporal frequency of the measurements and it is not possible to reliably extrapolate the results of any model based on correlations at a specific situation to cover the interactions in a wide variaty of cases.

3.3 Process-based models

The processes affecting methane fluxes in wet ecosystems were first modeled using kinetic relationships (Lovley and Klug 1983, 1986, James 1993). During recent years, process-based models for methane fluxes from rice paddies (Cao *et al.* 1995, Cai and Yan 1999, van Bogedom and Stams 1999, van Bogedom *et al.* 2000, van Bogedom and Scholten 2001, van Bogedom *et al.* 2001a, 2001b, 2001c, 2001d) and natural wetlands (Cao *et al.* 1996, Walter *et al.* 1996, Potter 1997, Arah and Stephen 1998, Grant 1998, Walter and Heimann 2000, Granberg *et al.* 2001a, Segers and Leffelaar 2001a, 2001b, Segers *et al.* 2001, Walter *et al.* 2001a, 2001b) with different level of details have started to accumulate. Some models connect methane cycle directly to gross primary production and overall carbon cycle without modeling the soil gradient at all (Cao *et al.* 1996, Potter 1997, Grant 1998) while in others the processes in peat profile and transport from peat to atmosphere have been taken into account (Walter *et al.* 1996, Arah and Stephen 1998, Walter and Heimann 2000, Granberg *et al.* 2001a, Segers and Leffelaar 2001a, 2001b, Segers *et al.* 2001,Walter *et al.* 2001a, 2001b).

Most models (Cao *et al.* 1996, Walter *et al.* 1996, Potter 1997, Arah and Stephen 1998, Grant 1998, Granberg *et al.* 2001, Walter *et al.* 1996, Walter and Heimann 2000, Walter *et al.* 2001a, 2001b) neither include oxygen concentration as a state variable nor consider the dynamic effects of water table fluctuations which may become extremely important in future climate. These models assume that the oxygen concentration in vertical peat profile depends on water table position and peat moisture profile (Weiss *et al.* 1998) so strictly that low enough oxygen concentration in water saturated peat does not limit anaerobic processes, like methane production and high enough oxygen concentration in unsaturated peat does not limit aerobic processes, like methane oxidation. With these assumptions, a model where methane production takes place in certain zone below water table and methane oxidation in another zone around water table can be constructed without describing oxygen dynamics (Walter *et al.* 1996, Walter and Heimann 2000, Walter *et al.* 2001a, 2001b, Granberg *et al.* 2001a). Furthermore, if conditions in peat profile are assumed so stable that populations of methane producing and oxidizing microorganisms remain practically constant, the model can be further simplified by leaving out the population dynamics of these microbes (Walter *et al.* 1996, Walter and Heimann 2000, Walter *et al.* 2001a, 2001b, Granberg *et al.* 2001a, Segers and Leffelaar 2001a, 2001b, Segers *et al.* 2001). The validitys of the assumptions of stable methane producing and oxidizing zones is not easy to evaluate as conditions in rice paddies, where bacterial populations have been studied, differ from those in pristine wetlands. Furthermore, there are methodological difficulties in quantifying microbes in environmental samples. Nevertheless, rice field data indicate that models assuming stable methane producing and oxidizing zones capture relevant factors affecting methane fluxes as long as water table and other environmental conditions remain constant as relatively stable populations of methane producing (Schütz *et al.* 1989, Mayer and Conrad 1990, Sass *et al.* 1990, Boon *et al*. 1996, Asakawa *et al*. 1998, Bosse and Frenzel 1998) and methane oxidizing microbes (Gilbert and Frenzel 1995, Bosse and Frenzel 1998, Frenzel and Gilbert 1998) are observed in stable environmental conditions. However, such models apparently fail to correctly predict the consequences of changes in substrate supply or water table fluctuations as changes in environmental conditions (substrate supply, nutritional status or water table level) are observed to be reflected to microbe populations (King 1994, Eller and Frenzel 2001, Bodelier *et al.* 2000a, 2000b, van Bogedom *et al.* 2001c).

In addition to the model presented in V, only an extremely complex model in a three-paper series (Segers and Leffelaar 2001a, 2001b, Segers *et al.* 2001) is developed to describe the dynamic effects of water table patterns on methane fluxes unsaturation using a concept of alternative electron acceptors that remain in reduced form and do not affect methane fluxes as long as the environment is water saturated. According to their assumptions, during a dry period with a lowering water table and consequent unsaturation, alternative electron acceptors become re-oxidized very rapidly, during the first day of unsaturation. A rise in water table induces the reduction of alternative electron acceptors that prevents methane formation by substrate competition until all alternative electron acceptors are reduced which typically takes from one week to one month. The lag before methane production starts after a rise in water level is the most powerful argument for modeling alternative electron acceptor cycle, as it is not possible to measure the concentrations of either reduced or oxidized form of alternative electron acceptors. However, no lag in methane production in peat samples that had been unsaturated from two days to several weeks was observed in IV but a constant methane production rate prevailed during the first 10 days of incubation. Therefore, alternative electron acceptors apparently are not an important control for methane production from northern mires. Furthermore, the lag before methane production starts in Segers' model is not affected by the length of the dry period, but a single day low water level results in as long a lag than a period of low water level for several weeks. Data in IV, however, indicate the length of the drought period affects the rapidness of recovery in methane fluxes after an increase in water level. Hence, in V the effects of water table fluctuations on methane fluxes are modeled describing the oxygen dynamics and the population dynamics of methane producing and oxidizing bacteria. The approach taken in V has also the advantage that it is possible to validate the model simulations against measured peat oxygen concentrations and microbes if these are to be measured in future. Altogether, Segers' model was calibrated in temperate zone and apparently, in boreal zone, the response of methane fluxes to water table fluctuations does not seem to follow model assumptions. In addition, Segers' model did not show a very good predictive power in relation to measurements. In contrast, the model in V simulates methane fluxes in accordance to both literature data and measurements and substrate, methane and oxygen concentrations as well as microbial populations which were not measured in accordance to literature data.

Another difference between the previous models and the model presented in V is the connection of methane fluxes to site specific factors at microscale level. The manyfold differences in methane emission levels from microsites within a few meters distance from each other are well documented in the literature (Svensson and Rosswall 1984, Morrissey and Livingston 1992, Whalen and Reeburgh 1992, Funk *et al.* 1994, Moore *et al.* 1994, Waddington and Roulet 1996, Saarnio *et al.* 1997, van den Pol-van Dasselaar *et al.* 1999b, Fiedler and Sommer 2000, Frenzel and Karofeld 2000, Kettunen *et al.* 2000, Wickland *et al.* 2001). Hence it is surprising that none of the existing process-based models (Cao *et al.* 1996, Walter *et al.* 1996, Potter 1997, Arah and Stephen 1998, Grant 1998, Walter and Heimann 2000, Granberg *et al.* 2001a, Segers and Leffelaar 2001a, 2001b, Segers *et al.* 2001, Walter *et al.* 2001a, 2001b) consider microsite variation. In fact, the idea that water level and vegetation cover, especially abundance of sedges account for differences in methane flux levels in microsite scale was presented almost twenty years ago (Svensson and Rosswall 1984, Sebacher *et al.* 1986). Since then, the connection between methane fluxes and microsite hydrology and vegetation at microsite scale has been established in numerous studies (Bubier *et al.* 1993a, b, Christensen 1993, Roulet *et al.* 1992, 1993, Torn and Chapin 1993, Vourlitis *et al.* 1993, Moore *et al.* 1994, Shannon and White 1994, Bubier 1995, Bubier *et al.* 1995, Schimel 1995, Bellisario *et al.* 1999, van den Pol-van Dasselaar *et al.* 1999b, Tuittila *et al.* 2000, Granberg *et al.* 2001b, Nilsson *et al.* 2001). Still, none of the recent process-based models explicitly considers site specific factors while the model in V connects the methane fluxes to vegetation cover and water level.

4. Study approach

4.1 Mire, microsites and measurements

All articles I-V analyze data measured during summer 1993 from a minerotrophic low-sedge *Sphagnum papillosum* pine fen lagg of the mire complex Salmisuo (62° 47' N, 30° 56' E) which is an eccentric bog in eastern Finland (Tolonen 1967). In I, photosynthetically active radiation, temperature, water table, the net carbon dioxide exchange and the total dark respiration were measured throughout the summer season in 17 microsites representing different microsites with characteristic vegetation and moisture conditions (for details of measurements see Alm *et al.* 1997). Microsites were classified to 3 microsite types: dry microsites (containing hummocks, *Carex* lawns and dry *Eriophorum* lawns), wet *Eriophorum* lawns and flarks (minerotrophic hollows) of which *Eriophorum* lawns were the dominant microsite type.

In II, III and V, methane fluxes, temperatures, water tables were measured from six microsites with different vegetation and increasing water level (hummocks, lawns and flarks) that situated within a few tens of meters apart from each other. Hummocks A and B in II, III and V were high hummocks with low water tables (hummocks A and B in II, III and V). One collar was situated in a lawn surface which contained a low hummock with a typical hummock vegetation (lawn/low hummock B). One collar was located on a *Sphagnum* lawn surface with a high sedge cover (referred to as lawn A in II and III and as *Eriophorum* lawn A in V and furtheron in this summary). The microsite referred to as flark A in II and III and as *Carex* lawn A in V and furtheron in this summary showed high abundance of *Carex* rostrata. Flark B had a low field layer coverage and a high water table. An automatic flux chamber system installed on the permanent 60 by 60 cm collars detected methane fluxes every 5 to 6 hours (for details of the method see Silvola *et al.* 1992). The depth of the water table was measured immediately before the methane flux at each microsite. Water table in hummock B was, however, omitted from the analyses due to measurement problems in II and III and in V, a water table reconstructed from measurements in other microsites were used. The peat temperature profile at different depths (0-2, 10, 20 and 50 cm) was measured for one additional selected site a few meters away from the collars. In II and V, all data were converted to equally spaced time series using daily averages of the measurements while in III actual measurements were used. Virgin data from hummock B, lawn/low hummock B and flark B covered the period from the early May to the middle of October and from hummock A, *Eriophorum* lawn A and *Carex* lawn A from early May to the end of July as water tables and other factors were manipulated in the latter microsites during the late summer months.

In IV, methane production and oxidation potentials in peat profiles from two Finnish mires during two summer seasons were measured. During summer 1993, 3-4 peat profiles from 0-45 cm below peat surface were taken from different microsites of the same Salmisuo mire as data in I, II, III and V. During summer 1994, 5 peat profiles from 0-100 cm below peat surface from different microsites of an ombrotrophic, treeless *Sphagnum fuscum* bog in the mire complex of Ahvensalo (65° 51' N, 30° 53' E) were taken. Microsites again represented different moisture conditions with different vegetation. The dry microsites were *Sphagnum fuscum* hummocks and *Eriophorum vaginatum - S. balticum* lawns both at the fen and at the bog. The wet microsites at the fen were *S. balticum - S. majus* flarks and those at the bog *S. balticum - S. lindbergii* hollows. The vegetation in the microsites is described in detail by Saarnio *et al.* (1997) for the fen and by Alm *et al.* (1999) for the bog. The temporal changes in production and oxidation potentials were then studied in relation to water table fluctuations and manipulations.

4.2 Time series analysis and mathematical modeling

In I and III, regression techniques are used to relate carbon dioxide and methane fluxes to variations in environmental factors. Photosynthesis, respiration rates and consequently net carbon dioxide exchange depended on photosynthetically active radiation, temperature time series and water tables and the parameters of dependence were calculated separately for each microsite class in I. In III, both the linear and exponential regression models were estimated separately for each microsite as microscale differences in depth of water table and vegetation are related to methane flux (Svensson and Rosswall 1984, Sebacher *et al.* 1986, Morrissey and Livingston 1992, Christensen 1993, Bubier and Moore 1994).

In II, lagged cross-correlation analysis is applied to temperature, precipitation, water table and methane flux data to enlighten the possible control mechanisms between the abiotic environmental variables and methane emissions and, in particular, the time lags in the system.

In III, diurnal rhythms were analyzed using ANOVA and episodic values were detected by comparing the measured values to a calculated moving average flux.

In IV, significant difference between two reaction rates and the significance of a specific rate were tested with a t-test for the regression slopes.

In V, a one-dimensional (peat depth) partial differential equation soil model describing methane dynamics in different microsites of boreal peatlands is introduced. The model simulates temporal evaluations of chemical compounds (substrate for methanogenesis, methane and oxygen) and microbes (methane producers and methane oxidizers) in peat profile and methane fluxes from peat to athmosphere for the growing period using photosynthetically active radiation, peat temperature profile and water table as forcing inputs. Model describes the dependence of process rates on substrate and oxygen concentrations via Michaelis-Menten dynamics and temperature dependencies via Q10 values. In the computations, the partial-differential equations were transformed to ordinary differential equations by dividing the peat to 5 cm layers that are assumed homogenous.

4.3 Model describing methane flux dynamics

The model described mathematically in V and presented graphically in Figure 1 connects the supply of recent carbon to root exudation and root litter decomposition which depend on gross primary production (see section 2.1 Substrate supply for the basis of these assumptions). During late season, the contribution of dying plant roots and root litter to carbon supply is assumed to increase which is taken into account by doubling the corresponding parameter value for the late season. In flark with scarce field layer vegetation the overall photosynthesis level is assumed smaller than in the other microsites resulting in lower carbon supply to peat profile which is reflected to methane flux. In high hummocks with low water table and relatively low abundance of sedges, most of the photosynthetically fixed carbon is supplied to the uppermost unsaturated layers where it is subject to aerobic decomposition and does not promote methanogenesis. As a result, the methane flux from high hummock remains low. In the intermediately moist lawn surfaces, the abundance of sedges affects the substrate supply. Low sedge abundance results in a low methane flux due to lack of substrate and consequently, methane flux increases with an increase in sedge cover until at some point, the increased oxygen supply to peat profile starts to decrease methane flux.

Oxygen concentrations determine the proportion of substrate to aerobic decomposition and methane production. Aerobic decomposition consumes oxygen, resulting in a negative feedback in the model. The amount of substrate available for methanogenesis also depends on substrate production rate (affected by photosynthesis level and root profile in peat) and substrate consumption rate (affected by methanogens and substrate concentrations) Methane oxidation rate increases with increasing population of methane oxidizers and increasing methane and oxygen concentrations. The population dynamics, i.e. biomass gain and dying of methane producers and methane oxidizers is accounted for and play an important role when water table shows short- and long-term fluctuations.

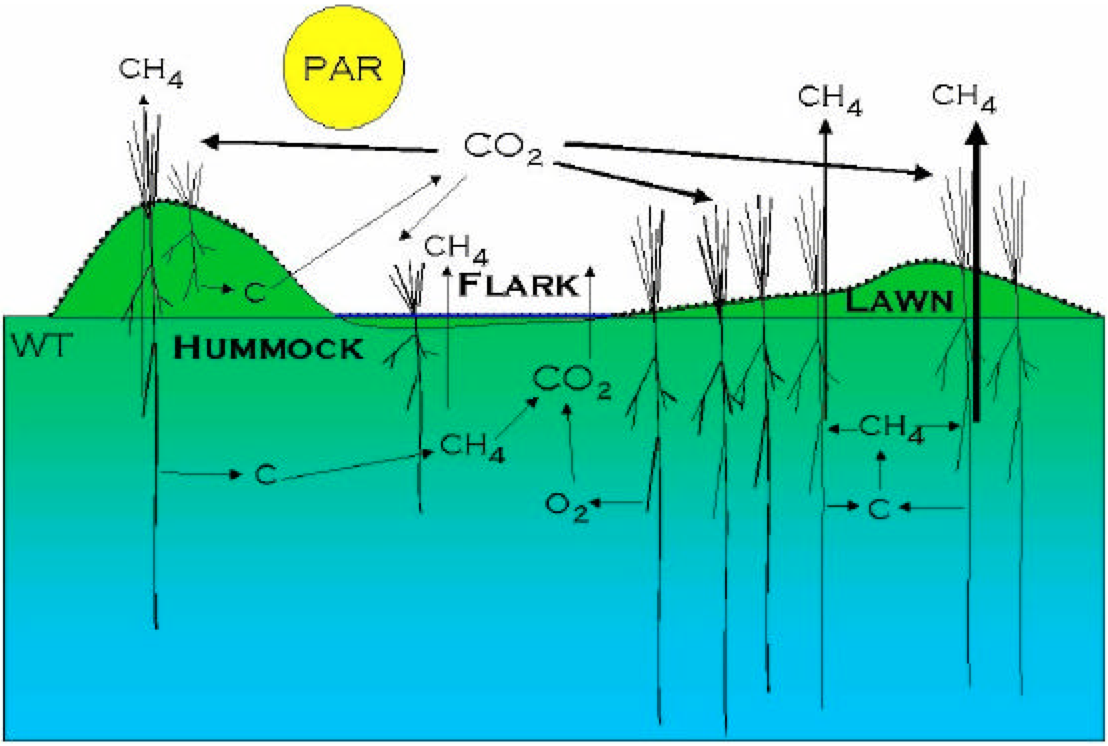

Figure 1. Schematic representation of the key interactions in carbon cycling and methane flux dynamics in different microsites (hummock, flark and lawn surfaces) of a boreal mire. Plants take atmospheric carbon in photosynthesis and supply part of the carbon to peat matrix. In flark with scarce field layer vegetation the carbon supply is lower. In high hummocks, the carbon is mainly supplied to the unsaturated layers where it is aerobically degraded. In lawn surfaces, low sedge abundance results in low methane flux due to lack of substrate and consequently, methane flux increases with an increase in sedge cover until at some point, the increased oxygen supply to peat profile starts to decrease methane flux. Plants also supply the peat matrix with oxygen which enhances methane oxidation and inhibits methane production. Methane is transported upwards by plants and diffusion.

Bacteria are assumed to be attached to peat particles while the chemical compounds are assumed to diffuse in the peat profile. Transporting non-sedges and sedges are assumed capable of transporting methane and oxygen. The oxygen consumption of the plant itself is accounted for, while methane transport and oxidation within the plant are not explicitly modeled. Ebullition, which was negligible in our vegetated microsites (see III) where methane concentrations remained below the limit for bubble formation was not modeled. Methane fluxes from our microsites do not show diurnal pattern and hence, active gas transport is not modeled. For simplicity, within plant diffusion were assumed to be similar for all plants. Within plant oxidation is not modeled as current species probably do not support methane oxidation (see section 2.5 Methane transport for the basis of the assumptions presented in this paragraph).

5. Main results and discussion

5.1 Carbon dioxide dynamics in current climate

The multiplicative model in I described well the short-term dynamics in carbon dioxide exchange. All microsites showed similar diurnal rhythm, acting carbon sinks during the day when photosynthesis rate exceeded respiration and carbon sources during the night when photosynthesis ceased but respiration continued. Dry sites were found to bind more carbon during the daytime than wet sites which is in line with the reported differences in carbon dioxide exchange across hydrological and vegetation gradients in other studies (Bubier *et al*. 1998, 1999, Frolking *et al*. 1998, Christensen *et al*. 2000) Respiration rates remained relatively low as water table stayed close to peat surface and consequently, daily carbon balance was clearly positive for all microsites for most of the season, indicating that during the study period the mire accumulated carbon at a higher rate than the long term average of Finnish mires (Tolonen and Turunen 1996). The results in I emphasize that carbon dioxide exchange is extremely sensitive to variations in environmental factors on short-term time scale and consequently, the annual carbon exchange estimates are also affected by short-term variations in accordance with earlier studies on carbon dioxide exchange in mires (Bubier *et al*. 1998, 1999, Griffis *et al*. 2000, Soegaard *et al*. 2000).

5.2 The capability of models to describe methane dynamics in current climate

5.2.1 Spatial variations

In the spatial microscale, methane fluxes were lower from hummocks with low water table and flark with high water table but low sedge cover than from the intermediately moist lawns with a high sedge cover. Differences in methane fluxes result from differences in substrate, methane and oxygen concentrations and consequent differences in methane producing and methane oxidizing populations in peat profile between the microsites. In hummocks with low water table, most of the easily degradable carbon is supplied to unsaturated layers above the water table where it is aerobically degraded and not converted to methane resulting in a low flux. In wet microsites, carbon supplied to peat profile by the plants meets anaerobic conditions and promotes methane production resulting in high methane emissions. Among the microsites, water table was an important distinguishing factor and improved the explanatory power of the regression models in III. The substrate supply apparently limited methane production in the flark with low sedge cover while in the lawns, sedges provided methanogenesis with substrate. The lower methane flux from *Carex* lawn compared to that from *Eriophorum* lawn was apparently related to enhanced oxygen transport to peat matrix by the sedges.

Regression models with separately estimated parameters for each microsite reproduced the annual fluxes in spatial scale in III. The process-based model in V was able to reproduce the microscale differences without any parameter adjustments as microscale differences were explicitly taken into account in the model.

5.2.2 Diurnal variations and episodic fluxes

Diurnal variations in methane fluxes were very weak. Interestingly, in the microsites with higher sedge abundance no diurnal pattern was seen while in the microsites with a diurnal pattern field layer species capable of transporting methane did not dominate. This clearly implies that current segde species do not apply active gas transport (Konçalovà *et al*. 1988, Chanton *et al*. 1992a, 1993, Happel *et al*. 1993, Morrissey *et al*. 1993, van der Nat and Middelburg 1998, van der Nat *et al*. 1998, Popp *et al*. 1999). In our data, diurnal fluctuations in methane emissions tended to occur when the difference between the air temperature and the peat temperature was large, i.e. during the warm days in the early season when deep peat layers had not warmed up. The large diurnal variations in peat temperatures were apparently reflected to the diffusion rate of methane in peat (Jähne et al. 1987) and possibly also to methane production (e.g. Dunfield et al. 1993, Westerman 1993) causing diurnal variations in methane flux. The result that diurnal fluctuations in the microsites, where they occurred, could be correlated to peat surface temperatures only for short time periods indicates that the control mechanisms for methane fluxes change over the growing season. The weak diurnal patterns were not considered in V that dealt with daily data.

The importance of fluxes, that were classified to episodic in III, somewhat increased with decreasing water table level, i.e. from the flarks to the hummocks during the early season. Neither the regression model in III nor the process-based model in V was not able to capture all the episodic fluxes and consequently, thorough understanding of the control of these fluxes remains a challenge for future research.

5.2.3 Water table dynamics

The water table in mires typically shows a seasonal pattern with lowest water levels during the period of high evaporation in midsummer. In addition, there are short-term fluctuations in water table due to drought periods and rain showers. However, the wet summer 1993 resulted in persistently high water tables with extremely low variations in water tables throughout the growing period and consequently, the data set probably did not reveal the dynamic effects of water table fluctuations on methane fluxes very clearly in the cross-corraletion analysis carried out in II. Neither in III, temporal variations in methane fluxes could not be related to the nearly non-existing temporal variations in water levels in III.

In IV, the water table in the bog showed a seasonal pattern with lower midsummer values and in the fen, the water table was artificially modified in a lawn surface making it possible to analyze the effects of water table changes on methane fluxes. When water level showed a downwards shift, production and oxidation potentials in the layers that no longer were water saturated very slowly decreased towards rates in permanently unsaturated layers. The decrease was faster in wet microsites where a two-week period of unsaturation eliminated the potentials while in dry microsites, significant methane production and oxidation potentials were found after 6 weeks of unsaturation. Hence, the findings in IV imply that methanogenic and methanotrophic bacteria are well adapted to natural conditions where water table shows both seasonal cycle and short-term fluctuations. In fact, under laboratory conditions, both methanogenic (Huser *et al.* 1982, Mayer and Conrad 1990, Wagner *et al.* 1999) and methanotrophic (Roslev and King 1994) bacteria have been shown to retain their viability also during periods of unsaturation and nutritional starvation. The results in IV also indicate that methanogenic and methanotrophic bacteria are attached to peat particles and not transported by vertical water movements in accordance with results in van den Pol-van Dasselaar and Oenema (1999). The reactivation of potentials in IV and V and simulated methane flux in V depended on the length of the period of unsaturation being slow after a rise in water level if the populations of methane producing and oxidizing bacteria had considerably decreased during the period of unsaturation (see Freeman *et al*. 1993).

In addition to the direct effect on moisture and oxygen concentrations in peat profile, the changes in water level may affect the substrate levels. After a decrease in water level drawdown, increased aerobic degradation in the unsaturated layers consumes the carbon compounds that in anoxic conditions would promote methane production. The reduction in substrates then decreases the methane production potential. Methane oxidation potential may also be reduced by a decrease in methane concentration in unsaturated peat layers. On the other hand, a temporary rise followed by a downward shift in the water level may liberate methane in deep layers (Moore *et al.* 1993) so that methane oxidation may be reactivated by the substrate peak as the lawn and hummock data from the bog in IV indicate.

5.2.4 Substrate availability and temperature dynamics

Both in II and III, methane emissions in the microsites correlated positively to peat temperatures. However, as other environmental variables, like the photosynthetic activity of plants, follow a similar seasonal cycle as temperature, the observed correlation does not necessarily imply that temperature controls methane fluxes in wetlands but rather may reflect the dynamic interactions between development of vegetation, consequent substrate supply and temperature (Schütz *et al.* 1991, Chanton and Dacey 1991, Whiting and Chanton 1993, Valentine *et al*. 1994, Bergman et al. 1998, Verville *et al.*

1998). Similar interactions prevail also in rice paddies where methane fluxes are also affected by the development of vegetation (Cicerone *et al*. 1992, Kaku *et al*. 2000, Watanabe *et al*. 1999, 2001), substrates supplied by rice plants (Cicerone *et al*. 1992, van der Gon 2000) and addition of organic matter (Bossio *et al*. 1999, van der Gon 1999, Watanabe *et al*. 1999, Lu et al. 2000) interacting with temperature control. Furthermore, the extremely low variations in water tables in II and III may affect the relationship between temperature and methane fluxes especially in flarks and lawns where practically the whole peat profile remained water saturated throughout the season. In fact, the regression models in III tended to overestimate the fluxes in the spring when temperatures have already risen but lack of suitable substrate due to low photosynthesis level apparently inhibited methane production indicating that the availability and quality of substrate are more important controls than temperature. In addition, the pore water methane concentration builds up only gradually and causes a lag before the methane formed in the soil is released to the atmosphere (Christensen 1993, Shurpali *et al.* 1993). The result in II that methane fluxes did not correlate to differentiated temperature series during the early season further strengthens the hypothesis that during early season, substrate availability is a dominant control for methane fluxes. Later during the season, the correlation between differentiated temperature series and methane fluxes in II and the higher production potentials towards late summer in IV indicated that the higher photosynthetic activity of plants had supplied methanogenesis with substrates so that temperature effects became more evident. The methanogenic activity that is found to be strongly temperature dependent (Dunfield *et al.* 1993, Segers 1998) is argued to decrease at low autumn temperature so that excess substrate may accumulate to peat (see Saarnio *et al.* 1997). In laboratory, the production potential measured at a higher than the *in situ* temperature activates the methane producing bacteria resulting in high production potential (see Yavitt *et al.* 1988, Valentine *et al.* 1994). The population dynamics of methanogenic population in response to substrate supply may also contribute to the observed increase in production potentials in late season in IV (Svensson and Rosswall 1984, Dunfield *et al.* 1993, Westerman 1993, Whiting and Chanton 1993, Valentine *et al.* 1994).

The observation in III that the seasonal pattern in methane fluxes is quite satisfactorily related to peat temperatures for flarks, lawns and low hummocks but less satisfactorily for high hummocks again emphasizes the substrate-temperature interactions as in hummocks, most of the photosynthetic substrate is subject to aerobic decomposition in unsaturated peat. Furthermore, the goodness of fit values for independent data sets were usually low in III. As the model predictions in III for data from the same microsites and the same mire for a relatively short time period are not accurate, the models definitely cannot be generalized to predict emissions from different microsites, different mires or for longer time periods. In contrast, the process-based model in V was able to simulate the methane flux patterns for the different microsites throughout the growing season without any parameter adjustment.

The process-based model in V turned out to be extremely sensitive to substrate availability. According to model simulations, an increase in air temperature resulted in much more significant increase in methane fluxes gross primary production is recalculated to correspond to the new air temperature than if only the direct temperature effects are accounted for. This is due to the fact that recalculated gross primary production results in higher amount of substrate for methane production. The model simulations are hence in accordance with the idea that temperature and substrate availability interact so strongly that in fact, it is hard to reveal their independent effects.

5.2.3 Oxygen dynamics

Measured methane production and oxidation potentials in IV and simulated oxygen concentrations in V indicate that the water table quite strongly distinguishes the anaerobic peat from aerobic. As long as changes in water table did not affect the potentials, peat below water level showed significant potentials while peat above water level showed only low, even non-significant potentials in III.

The capability of sedges to transport oxygen to water saturated peat layers turned out to be an important factor for methane fluxes in V and in fact, an increase in sedge coverage may result in a decrease in methane flux due to this reason.

The lack of oxygen in peat profile limited methane oxidation rates and prevented the existence of stable methane oxidizing populations in most microsites in V. As a consequence, the contribution of oxidation in V remained very low in five of our six microsites in accordance with Bellisario *et al.* (1999). Only in flark B with a scarce field layer vegetation where all in surface layers, oxidation clearly decreased the flux. So, any change in parameter set or environmental conditions that would compensate the lack of oxygen will result in increased simulated oxidation and decreased simulated flux. One explanation for the low oxidation rate is the relative high abundance of *Eriophorum* species in the majority of our microsites. In volumetric terms, large proportion of peat belongs to the rhizosphere of *Eriophorum* where methane oxidation apparently does not take place (King *et al.* 1990, Chanton *et al.* 1992b, Kelker and Chanton 1997, Frenzel and Rudolph 1998). Frenzel and Rudolph (1998) present a hypothesis that type and quality of root exudates differ between plants species that do not support plant-associated methane oxidation and plants that support plant-associated methane oxidation which then would explain the observed difference in methane oxidation rates.

5.3 Responses of methane fluxes to changing conditions

5.3.1 Changes in hydrology

Even though an increase in the overall precipitation of +2 % per decade in anticipated for northern Europe, it is also considered very likely that frequencies and intensities of summer heat waves will also increase, resulting in longer dry periods in the future (IPCC Climate Change, 2001). The effects of simultaneous increase in the precipitation and the increased likelihood for drought periods on water table patterns in northern peatlands are hard to anticipate, especially if one considers the complex interactions in hydrological and thermal cycles. An example of the complexity of the interactions is presented by Rouse (1998) who found that in increase in air temperature by +4^{o}C and an +20 % increase in the precipitation in fact resulted in a lower water table in a fen site due to the fact that increased evaporation dominated the effects of the increased precipitation. It is also interesting to note that the summer season during which the methane fluxes and environmental conditions were measured was very wet and warm. Consequently, the fluxes during the current summer with extreme climate may already represent average future conditions. In fact, the simulated effects of wet periods were not very dramatic in V as water table persistently remained relatively high. The longer the wet period prevailed, the closer the methane flux came to the situation where water table remained at the peat surface throughout the growing season.

However, dry periods were found to affect methane fluxes more than wet periods in V. Therefore, the duration of the anticipated more frequent summer droughts is decisive for methane release rates in peatlands. If the drought prevails for a period shorter than one month, methane production potential are not severily declined and the production and also the flux is rapidly reactivated after water level rises. However, if the duration of a drought period approaches two months, methanogens decrease to so low a level that flux may not recover during the remaining growing season which would reduce the potential climatic feedback of boreal peatlands.

5.3.2 Changes in temperature

The increase in the temperature for the European boreal zone is estimated to be +0.4 ^{o}C per decade resulting in +2 ^{o}C higher average air temperature in 50 years (IPCC Climate Change, 2001). According to model simulations, an increase in air temperature results in a consequent increase in the methane flux even in the case when the effect of temperature on gross primary production in the microsite is not taken into account. However, when gross primary production is recalculated to correspond to the new air temperature which results in a higher amount of substrate for methane production, the order of change increases again, emphasizing the fact that substrate availability limits the methane production in the current situation. Despite some speculations that methane production in high latitudes might be temperature limited (Sorrell *et al.* 1997, Worthy *et al*. 2000), our model simulations indicate that substrate availability limits the temperature effects with complex interactions as has been suggested also before (Westermann 1993, Bergman *et al.* 1998). Interaction between substrate availability and temperature control became evident also in the modeling study by Granberg *et al.* (2001) where methane flux increased with interaction term T*sedge cover. Temperature may first increase methane production directly via Q10 values enchancing the actual processes. Another possible mechanism is a shift in carbon allocation from shoots to roots due to an increase in temperature (Kummerow and Ellis 1984), that would most likely promote root litter, root exudation and finally methane flux. Third mechanism would be increased gross primary production due to increased air temperature as photosynthesis in northern conditions is temperature limited. In fact, Verville *et al.* (1998) observed that the increasing effect of increase in temperature to methane flux was due to an increase in gross primary production.

5.3.3 Changes in carbon dioxide level

Different plants may respond differently to an increase in atmospheric carbon dioxide level. Some may maintain the same photosynthesis level and via stomatal control decrease transpiration resulting in a positive feedback for surface warming while others may benefit from increased carbon dioxide level by increasing gross primary production and increase transpiration which would then result in a negative feedback for warming (Douville *et al.* 2000). In cases where gross primary production and plant biomass would increase with increasing atmospheric carbon dioxide level, carbon allocation would be shifted from shoots to root (increase in root/shoot ratio) (Cotrufo and Gorissen 1997) which would probably enhance root litter and root exudation increasing substrate supply for methanogenesis and finally methane flux. In experiments carried out in temperate conditions, methane fluxes have been found to respond positively to increase in carbon dioxide level (Dacey *et al.* 1994, Hutchin *et al.* 1995, Megonigal and Schelsinger 1997) but the experiments in boreal conditions have resulted in a much weaker response (Saarnio *et al.* 1998, Saarnio and Silvola 1999, Saarnio *et al.* 2000, Saarnio *et al.* 2002). The normalization of the flux to a constant shoot number, however, might have eliminated the increase in methane flux as also the number of shoots increased by 10-20 % (Saarnio and Silvola 1999). The model simulations in V, anyhow, suggested that if both temperature and carbon dioxide level increase in the future climate that methane fluxes increase considerably if gross primary production is enhanced.

In addition to physiological changes, structural changes in vegetation are also likely to occur due to increase in carbon dioxide level (Douville *et al.* 2000). According to model simulations, the effect of a change in coverage % of either non-transporting or transporting non-sedges is negligible. A decrease in segde cover, however, implies a clear decrease in methane flux. The surprising simulation result that methane flux slightly decreases if the sedge cover increases is due to the enchanced oxygen supply to deep peat layers when more sedges are present. In practise, a less than 10 % decrease in methane flux would probably lack notice. Thus, the observation that sedge cover in *Eriophorum* lawn A is close to optimum value (that maximizes methane flux) raises mainly academic interest. However, the fact that also measured methane fluxes are higher from *Carex* lawn A than from *Eriophorum* lawn A even though the sedge cover is higher in *Carex* lawn A than in *Eriophorum* lawn A supports the idea that methane fluxes do not automatically increase with increasing segde cover.

Overall, the short-term carbon balance under high carbon dioxide levels would most likely depend on short-term weather conditions just like in the present climate (Saarnio *et al.* 2002) and changes in hydrology to drier direction may compensate the effects of increases in temperature and carbon dioxide levels (Laine *et al*. 1996, Douville *et al.* 2000).

5.3.4 Effects of nutrients

The availability of nutrients also affects methane flux dynamics. The effects of an increase in nitrogen availability are relatively well understood. On one hand, increased nitrogen supply might increase methane flux via different mechanisms. Firstly, increase in nitrogen availability can inhibit methane oxidation (Christensen *et al*. 1999, Cai and Mosier 2000). Secondly, sedge cover might increase by increased nitrogen supply (Vasander *et al*. 1996). Thirdly, increased nitrogen availability may directly enchance root exudation (Cotrufo and Gorissen 1997). Fourth possible increasing mechanism is the higher decomposition rate of an organic matter with a low C/N ratio (Aerts *et al*. 1992). On the other hand, increase in nitrogen could decrease the decomposition rate in peat soil (Aerts and Toet 1997) and shift the carbon allocation from roots to shoots (decrease in root/shoot ratio) (Gebauer *et al*. 1995, Cotrufo and Gorissen 1997, Saarinen 1998a, 1998b) that would decrease methane flux by decreasing root litter. Methane production can be inhibited by nitrate (Boon and Mitchell 1995, Yao *et al*. 1999). Furthermore, methane oxidation might also be nitrogen limited (Bodelier et al. 2000a, 2000b) in which case increase in nitrogen level would decrease the flux. In fact, both a decrease (Granberg *et al.* 2001b) or a small increase (Dise and Verry 2001, Saarnio and Silvola 1999, Saarnio *et al.* 2000, Saarnio *et al.* 2002) in methane fluxes have been observed in recent studies with increased nitrogen supply. When both carbon dioxide and nitrogen availability were higher, methane flux showed no clear response or even decreased (Saarnio and Silvola 1999) again emphasizing the complex interactions that affect the different processes behind methane fluxes from northern peatlands.

In addition to nitrogen, also other nutrients affect methane cycling. Lu *et al.* (1999) describe a chain of responses to phosporus related stress that finally leads to higher methane fluxes. High concentrations of sulfate reduce methane fluxes as documented both in natural wetlands (Nedwell and Watson 1995, Van der Nat and Middelburg 1998, Dise and Verry 2001) and in rice paddies (Kimura *et al*. 1992, Yao and Conrad 1999, Yao *et al*. 1999, Lueders and Friedrich 2002) due to the fact that sulfate can act as alternative electron acceptors limiting or even inhibiting methane production. Metal ions, like ferric ions can have similar effect as sulfate due to the same reason (Boon and Mitchell 1995, Frenzel *et al.* 1999, Jäckel and Schnell 2000, Van der Nat and Middelburg 1998, Yao and Conrad 1999, Yao *et al.* 1999, Lueders and Friedrich 2002). One possible mitigation stragegy to reduce methane emissons from rice paddies would actually be the introduction of nitrogen/phosporus supply in combination with e.g. sulfate that has been demonstrated to decrease methane flux rate (Yao and Chen 1994, Adhya *et al*. 1998). Furthermore, recent findings state that methanogens may be limited by metals and natrium to greater extent than other bacteria (Basiliko and Yavitt 2001), a piece of information that might show useful in designing new mitigation strategies to reduce methane fluxes in a global scale.

6. Concluding remarks and future research

The current study describes methane flux dynamics in different microsites of a boreal peatland. The spatial differences in methane fluxes result from site specific factors, vegetation cover and water table in the microsites while the seasonal pattern is due to seasonal temperature and photosynthetic cycle. The current study emphasizes the importance of vegetation cover and water table pattern to methane fluxes. The extreme sensitivity of the modeled methane fluxes to changes in substrate availability provides future research with challenges. The model presented in this study might be improved if the controls for plant related substrate supply and the complex interactions between environmental factors and the processes involved were understood more deeply. In the concept of climate change, increases in air temperature and carbon dioxide levels would, according to the model simulations, result in remarkable increases in methane fluxes if they enhanced gross primary production and substrate supply for methanogenesis. Even more dramatic changes in methane flux may occur if the vegetation experiences structural changes due to increases in carbon dioxide level and/or changes in thermal and hydrological conditions. Even if vegetation and gross primary production remained the same, drought periods would decrease the methane fluxes remarkably if the duration of drought exceeded 6 weeks due to dynamic effects of a decline in the methanogenic population. The simulations also suggest that any change that would enhance methane oxidation would result in a considerable decrease in methane flux. Overall, the current study provides new information on the relative importance of environmental controls that affect the dynamics of methane fluxes in current and future conditions.

7. References

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